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Hydrogen evolution reaction on electroless Ni-P coatings deposited at different pH values

V. Chakarova, M. Monev

Rostislaw Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria

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Electroless Ni-P coatings are deposited on a steel substrate at pH of the solution from 2.8 to 5.3. Under these conditions, the P content of the Ni-P coatings varies from 10.5 to 18.1 mass %. It is found by electrochemical methods that the electrochemical activity of the amorphous Ni-P alloys in regard to the hydrogen evolution reaction in 1M KOH is comparable to that of electrodeposited Ni at current density close to the real values for hydrogen production. The structure, morphology and elemental composition of Ni-P coatings are characterized by XRD, SEM and EDS.

Key words: Electroless deposition, Ni-P coatings, Hydrogen evolution reaction, SEM, XRD

INTRODUCTION

Ni-based electrodes are usually employed in industrial electrolytic cells for electrochemical production of hydrogen from KOH solution. Their application is a result of the specific properties of Ni, as good corrosion resistance and high electrocatalytic activity in respect to hydrogen evolution reaction (HER) [1].

Ni-P_x alloys have been considered as potential candidates for HER electrocatalysis [2]. Articles, devoted to the regularities of HER on electroless Ni-P_x coatings, are significantly less than those referring to electrodeposited coatings and moreover, there is a contradiction between the experimental results. The activity of the electrodes depends on the experimental conditions of their preparation, as well as on the P content. According to [3, 4], the catalytic activity of electroless Ni-P coatings decreases with the increase of the P content in the alloy. However, it is reported in [5] that the catalytic activity is high at a high content of P upon annealing. Some authors point out an optimal value of P content of 3.8 mass % P [6], while other authors claim that this value is 10 mass % P [7]. The P content into the coating can be controlled by the deposition conditions, for example the acidity of the solution and the concentration of the reducing agent (NaH_2PO_2). The increase of pH leads to a decrease of the P content in the coating [8, 9], while the increase of NaH_2PO_2 concentration increases the P content [5, 7]. However, the conditions which cause changes in the P content of the alloys also change other properties of the coatings, for example structure [10], real surface [11] and corrosion resistance [12].

The aim of the present study was to obtain Ni-P coatings with different content of P by alteration of the acidity (pH) of the solution for electroless Ni deposition, as well as to investigate their activity with respect to HER in alkaline solution by electrochemical methods.

EXPERIMENTAL

The composition of the Ni-P bath is presented in Table 1.

Table 1. Composition and operating conditions of the Ni-P plating bath.

Components of the solution	Concentration
$NiSO_4.7H_2O$, g L^{-1}	25
$NaH_2PO_2.2H_2O$, g L^{-1}	22
CH_3COONa, g L^{-1}	20
Lactic acid /80 %/, g L^{-1}	20
Operating conditions	
pH	2.8 – 5.3
Temperature, °C	82
Deposition time, min	30

The coatings were deposited onto mild steel substrates with dimensions 50 × 35 mm. For further analyses, samples of appropriate size were cut out. To determine the elemental chemical composition of the coatings, energy dispersive spectroscopy (EDS) was used (JEOL JSM 733, Japan). The thickness of the coatings was measured on-line with a cross-section by X-ray microanalysis with the help of a combined scanning electron microscope (focused ion beam system LYRA I XMU (Tescan) equipped with EDX microanalyzer (Quantax, Bruker) (Fig. 1). Before preparing the cross-section,

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* To whom all correspondence should be sent:
E-mail: vchakarova@ipc.bas.bg

the samples were covered with a protective layer of Cu by electroplating.

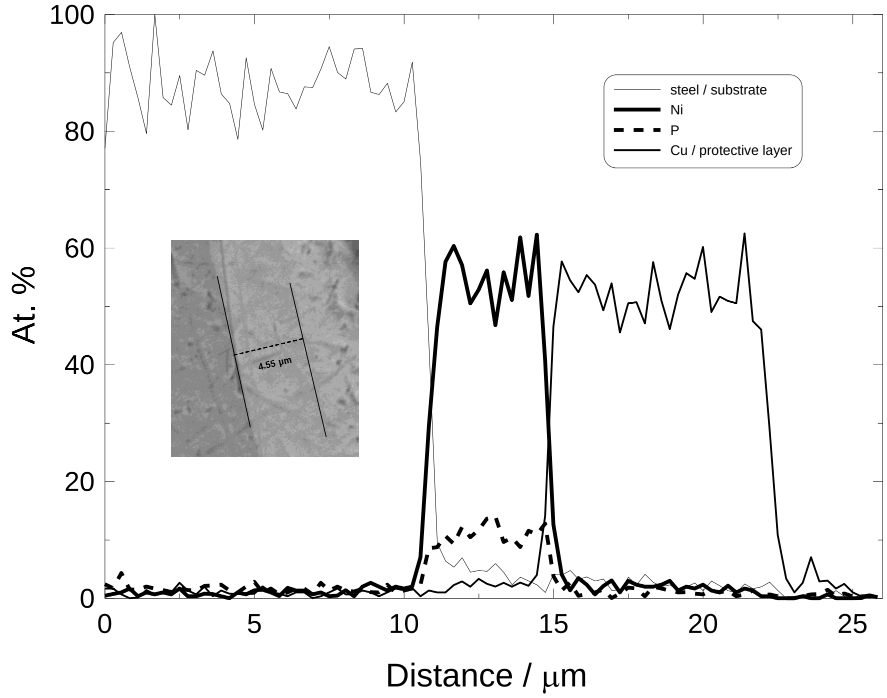


Fig. 1. EDX line-scan over the coating thickness. Inset: SEM of the measuring area with markers outlining the Ni-P layer.

The electrochemical investigations were performed in 1 M aqueous KOH solution (analytical reagent grade) at 20 ºC. A three-electrode cell, supplied with a Pt-counter electrode, Hg/HgO reference electrode and working electrode with surface area of 0.2 cm^2 was used. The measurements were fulfilled by using a potentiostat/galvanosat model 263A (EG&G Princeton Applied Research, USA). The voltammetric dependences were obtained by scanning the potential from the open circuit potential to the vertex potential in the cathodic direction and *vice versa* at a scan rate of 25 mV s^{-1}. The electrokinetic properties of the Ni-P coatings in respect to HER were compared with those of electroplated Ni coatings deposited in Watt's electrolyte. For greater clarity, in some figures only the dependences of Ni-P coatings obtained at two pH values are presented.

X-ray powder diffraction patterns were recorded in the angle interval of 10-90^o (2θ), on a Philips PW 1050 diffractometer, equipped with CuKα tube and scintillation detector.

The morphology of the coatings was examined by scanning electron microscopy (SEM) (JEOL JSM 733, Japan).

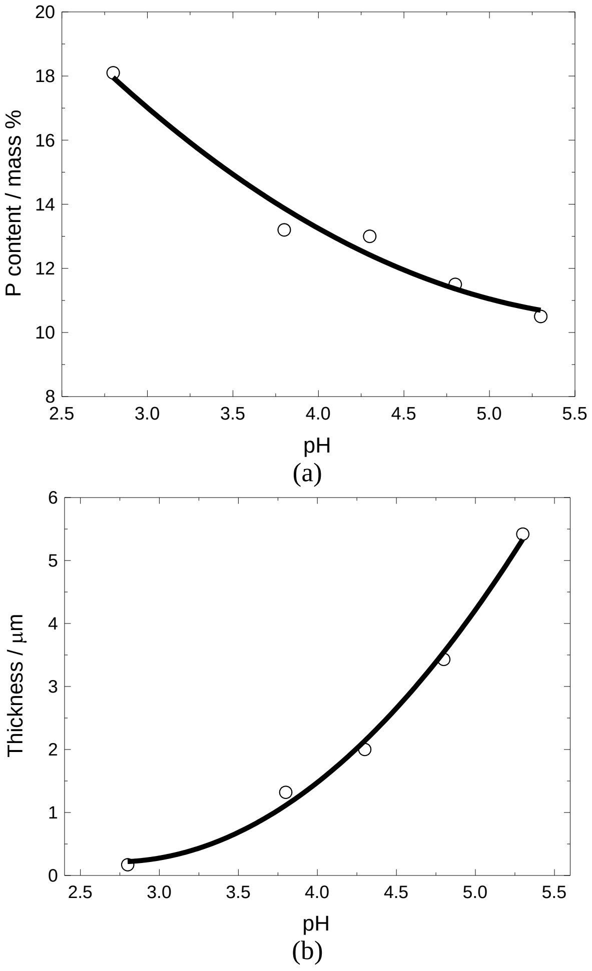


Fig. 2. Influence of pH of the solution on the content of P in the coating (a) and on the thickness of the Ni-P coating (b).

RESULTS

Influence of pH of the solution on the thickness and P content of the coatings

The decrease in pH of the solution leads to a decrease in the reduction activity of NaH_2PO_2 and at pH lower than 3, the reaction slows down [8]. The deposition rate of Ni increases with increase of pH, however, at pH higher than 5.5 the stability of the solution decreases. For that reason, the deposition rate and the elemental composition of the Ni-P coatings were determined at five selected values of pH in the range of pH 2.8-5.3. The dependences of the deposition rate and the content of P in the coating on pH of the solution are shown in Fig. 2. As seen, the increase of pH leads to an increase of the thickness of the N-P coating, while the content of P in the coating decreases. This conclusion is in agreement with the literature data [8, 9], as well as with our previous studies [13]. Generally, the values of the P content in the coating at the selected experimental conditions are in the range of high-P coatings [14]. This feature determines the amorphous structure of the coatings (Fig. 3).

Figure 4 presents the alteration of the surface morphology of the Ni-P coatings. For comparison, a picture showing the surface morphology of electrodeposited Ni coating is also given (Fig. 4a). As the Ni-P coating deposited at pH 2.8 for 30 min is very thin (an average thickness < 0.5 μm), it is possible to draw some conclusions for the initial stages of crystallization of the electroless coating (Fig. 4b). The iron has no catalytic properties, but as it is more negative than Ni, crystalline nuclei of Ni are formed through exchange onto the iron surface during its immersion into the solution for electroless deposition. The Ni nuclei initiate the subsequent process of deposition [8]. After formation of a thin Ni-P layer which covers the steel surface, the process of growing is followed by formation of spherical aggregates. With increase of pH, the deposition rate also increases and at one and the same time of deposition, thicker coatings are formed with a spherical nodular structure (Fig. 4c-e). With increase of pH, the size of the formations also increases and at pH 5.3, new nanosized spherical formations are observed on them (Fig. 4f). According to the X-ray microanalysis, the new formations are characterized by about 3 % higher content of P as compared with the remaining surface. The cited value is approximate, as the method can not exclude the contribution of the remaining surface.

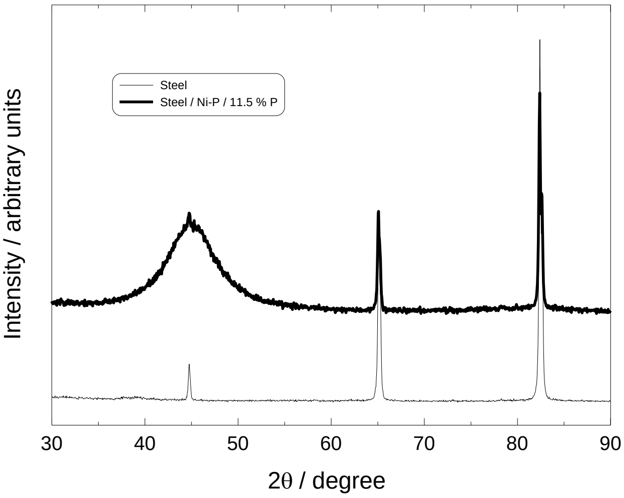
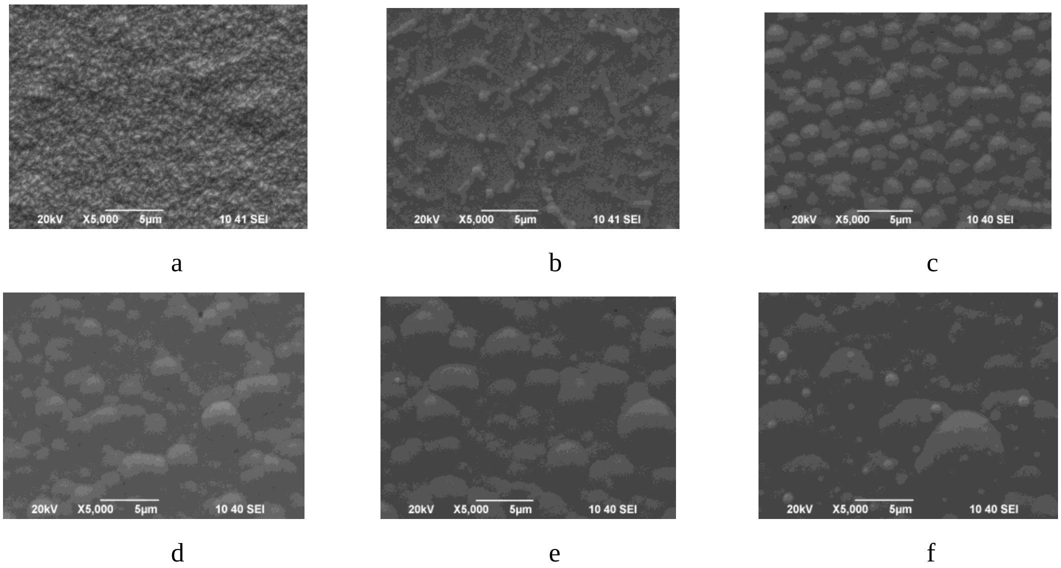


Fig. 3. XRD spectra of samples of steel and Ni-P coating containing 11.5 mass % P.



a b c

d e f

Fig. 4. Surface morphology of electrodeposited Ni (a) and alteration of the morphology of electroless Ni-P coatings *vs* pH of the solution: (b) pH 2.8, (c) pH 3.8, (d) pH 4.3, (e) pH 4.8, (f) pH 5.3.

Open circuit potential/time (OCP) measurements

Two types of Ni-P coatings with different content of P (Ni-11.5 mass % P and Ni-18.1 mass % P), as well as electrodeposited Ni coating were subjected to potential/time measurements at OCP in a solution of 1 M KOH (Fig. 5). Both samples of electroless Ni-P coatings show more negative potential as compared to that of electrodeposited Ni. The Ni-P coating with the lower P content of 11.5 mass % is more positive. This behavior could be explained not only by the lower P content, but also with the contribution of the smaller thickness of the coating.

Cyclic voltammetry

The activity of the electroless Ni-P coatings in respect to HER was investigated by cyclic voltammetry (Fig. 6). For comparison, samples of steel and electrodeposited Ni coating were also tested. In the investigated potential range, both types of electroless Ni-P coatings show lower activity in respect to HER as compared to electrodeposited Ni. The Ni-P coating with 11.5 mass % P shows higher activity and HER starts at a more positive potential as compared to the Ni-P coating with 18.1 mass % P.

The curve of the steel sample displays a cathodic maximum at about -1.2 V which can be explained by the reduction of the oxide layer. Similar maxima (but significantly smaller) are also registered on the corresponding curves of the Ni-P samples at a more positive potential. The maxima of the steel and Ni-P coating containing 18.1 mass % P are compared in the inset of Fig. 6.

Polarization measurements

At low polarization, the rate of HER is different for the different samples (Fig. 6). However, with increase of the current density to values of 10-20 A dm^{-2}, close to the real values for hydrogen production [1], the potentials of the Ni and Ni-P coatings overlap. Figure 7 presents the alteration of the polarization with time at 10 A dm^{-2}.

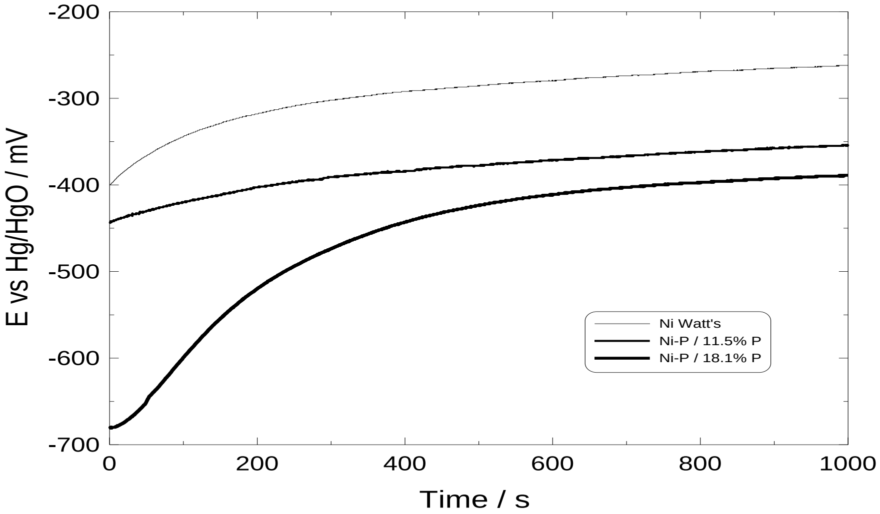


Fig. 5. OCP *vs*. time relations for samples of Ni, Ni-11.5 mass % P and Ni-18.1 mass % P in 1 M KOH.

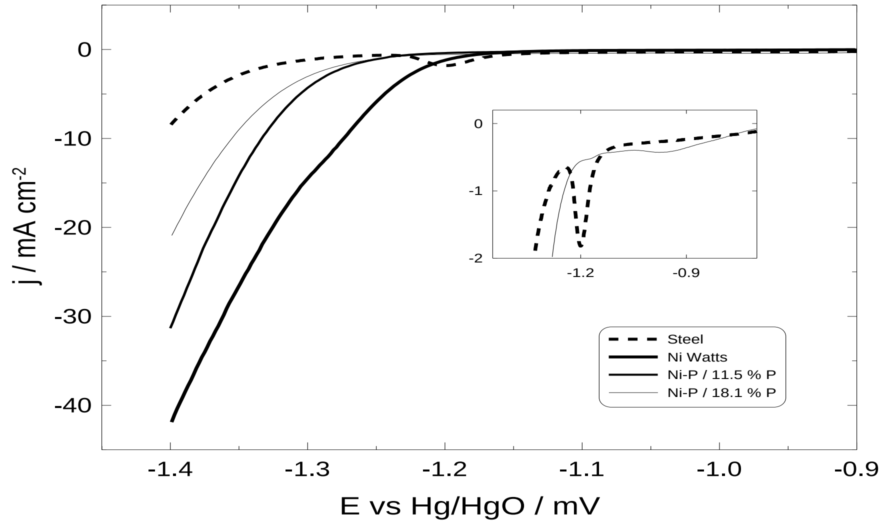


Fig. 6. Voltammograms of samples of steel, Ni, Ni-11.5 mass % P and Ni-18.1 mass % P in 1M KOH.

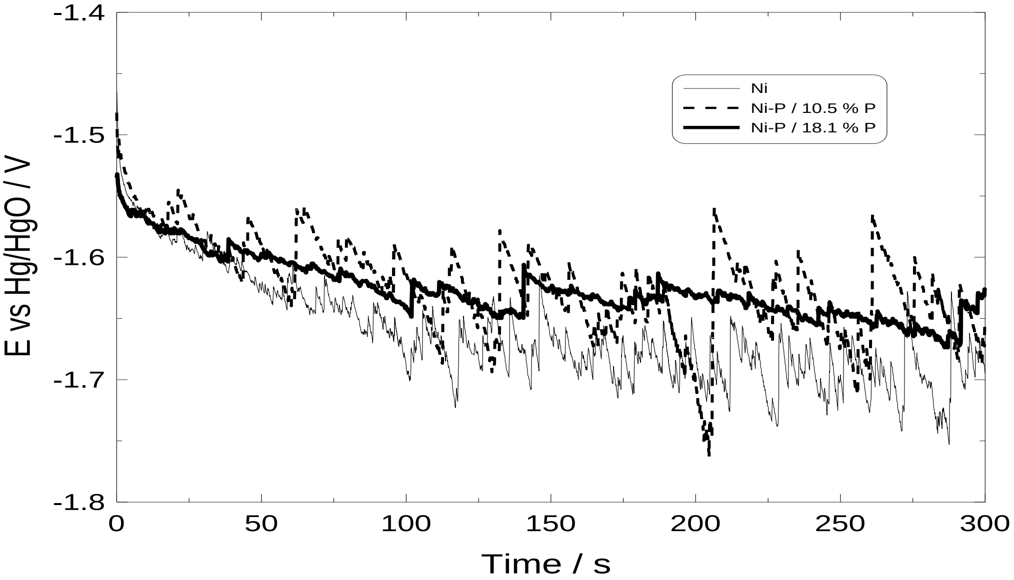


Fig. 7. Galvanostatic potential *vs*. time curves obtained with samples of Ni, Ni-10.5 mass % P and Ni-18.1 mass % P at 10 A dm^{-2} in 1M KOH.

CONCLUSIONS

Electroless Ni-P coatings with P content in the range from 10.5 to 18.1 mass % are deposited by alteration of pH of the solution from 2.8 to 5.3. The corresponding coatings display an amorphous structure. At sufficiently high current density (10-20 A dm^{-2}), the overpotential of HER on the Ni and Ni-P coatings is approximately the same. This feature of the Ni-P coatings allows the advantages of the electroless deposition as deposit uniformity and physical and chemical stability to be used, if necessary.

At lower polarization, different rates of HER are observed during the measurements with electrodeposited Ni and electroless Ni-P coatings. In addition to the content of P, the thickness of the coatings may also be a factor. Therefore, the next investigations should be directed to deposition of coatings with lower P content, probably by controlling the concentration of the reducing agent (NaH_2PO_2). It is also important to perform a more comprehensive study of HER on electroless Ni-P coatings obtained in the initial stages of the deposition.

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