

Electrochemical investigations of Ni–P electroless deposition in solutions containing amino acetic acid

Ona Gylienė*,
Algirdas Vaškelis,
Rima Tarozaite and
Aldona Jagminienė

*Institute of Chemistry,
A. Goštauto 9,
LT-01108 Vilnius, Lithuania*

The complexity of the anodic process taking place during electroless nickel plating in a solution containing hypophosphite as a reducing agent and amino acetic acid as a ligand has been verified by the results of electrochemical investigations. In the case of low nickel deposition rate, $v_{\text{Ni-P}}$, c.a. $2\text{--}4\ \mu\text{m}\cdot\text{h}^{-1}$, an electrochemical reaction played the main role in the autocatalytic process. With an increase in the intensity of the plating process, the difference between $v_{\text{Ni-P}}$ and the maximal anodic current intensity i_a increased due to the difficulties in estimating the i_a value (coupled cathodic Ni deposition reaction has a retarding effect on the anodic process) as well as due to the participation of chemical reactions in the catalytic process. Voltammetric measurements carried out at potentials more positive than the mixed potential showed the increase in Ni–P electrode activity with an increase in anodic polarization.

The rate of catalytic hypophosphite oxidation by H_2O estimated as the difference between the volumes of H_2 evolved in the anodic process and in Ni–P deposition process was independent of the potential applied. These results as well as the results obtained for hypophosphite solutions, when Ni–P deposition does not proceed, indicate the pure chemical nature of the catalytic oxidation of hypophosphite by H_2O .

The stability of the solutions had no relation to the values of neither $v_{\text{Ni-P}}$ nor i_a .

Key words: Ni–P deposition, hypophosphite, anodic oxidation, voltammograms, surface activation

INTRODUCTION

Electroless (autocatalytic) metal deposition is rather complicated and incomprehensible investigating process. For example, it is supposed that the catalytic behavior of surfaces has both chemical, throughout the formation of intermediate active products, and electrochemical nature [1–4]. In the latter case, the metal surface serves as an electron transmitter from the reducing agent to metal ions since the oxidation of the reducing agent and the reduction of the metal ion reactions proceed separately on the surface. Recent investigations have shown also the relevancy of electrochemical reactions to the reactions proceeding during the electroless copper plating when Co(II) salt is used as a reducing agent [5, 6]. The authors of these works have shown that the rate of copper deposition depends strongly on the mixed potential and obeys the mixed potential equation for systems containing both reducing and oxidizing agents independent of the chemical composition of the solutions.

In the case of hydrogen containing reducing agents, the coincidence of chemical reactions with the electrochemical ones is not so evident. However, the relations between electroless nickel deposition rate and the rate of

partial electrochemical reactions taking place during the oxidation of the reducing agent and the reduction of the metal ions has been observed in all the investigated cases. Evidently, the main reason of the discrepancy between the processes in electrochemical modeling solutions and electroless plating solutions is the interactions of the coupled electrochemical reactions during electroless plating. Such interactions are evident in the case of electroless nickel plating when hypophosphite is used as a reducing agent [7]. Though the oxidation of hypophosphite is rather complicated process, it has been shown earlier [8] that there exists a correlation between the maximal anodic current density of hypophosphite oxidation and electroless nickel deposition rate. These maximal anodic current intensities are considerably lower than the rate of nickel deposition. They make up from 30 to 40% only implying that the electrochemical reactions are not exclusive in the autocatalytic process. Direct interactions of hypophosphite with Ni^{2+} are also possible.

The aim of this work was to evaluate the role of the maximal anodic current density in the autocatalytic process of electroless nickel deposition. In this study, a solution containing hypophosphite as a reducing agent and amino acetic acid as a ligand for Ni^{2+} ions was used for the electrochemical investigations. Noteworthy, this solution is characterized by a high deposition rate

* Corresponding author. E-mail: gyliene@ktl.mii.lt

and the possibility to obtain Ni–P coatings with various content of phosphorus in a wide range of pH.

EXPERIMENTAL

The main investigations were carried out in a solution containing (in mol·l⁻¹): 0.1 NiCl₂, 0.3 NaH₂PO₂, 0.33 NH₂CH₂COOH (amino acetic acid), 0.06 CH₂(COONa)₂ (sodium malonate) at pH 6 (adjusted with NaOH solution and measured at room temperature) and 90 °C. The depositions were obtained on Pt plates and the thickness of Ni–P coatings was determined by weight gain of the plate.

Voltammetric measurements were performed using a potentiostat PI-50-1 and a three-camera thermostated electrochemical cell at a potential sweep rate 2 mV·s⁻¹. In this set-up, a Pt plate coated with Ni–P (or Pd–P) was used as the working electrode, a Pt wire as a counter, and Ag/AgCl/KCl_{sat} as the reference electrode. All potentials are given vs the normal hydrogen electrode.

The instability of electroless nickel plating solutions was ascertained by determining the Ni–P powder content formed during 1 h in 100 ml of the plating solution at a load of 20 cm². For this purpose, after the plating, the solution was filtered and after rinsing with water, the precipitate was dissolved in a dilute HNO₃ (1:1) solution. The obtained solution was evaporated to ~2 ml after the addition of H₂SO₄, the content of Ni was determined colorimetrically using dimethylglyoxime.

The content of hydrogen evolved during the deposition was measured volumetrically using a microburette. The reliability of such measurements was checked by the determination of the concentrations of hypophosphite and Ni²⁺ after plating in parallel experiments.

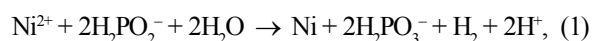
The content of phosphorus was determined colorimetrically using molybdate [9] after the dissolution of the coating in a dilute HNO₃ (1:1) solution, while the content of hypophosphite was according to [10].

All the data presented are averaged between the data obtained in 2–3 parallel experiments.

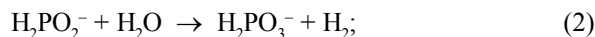
The rate of all the electrochemical reactions investigated was expressed as ν (mol·s⁻¹·cm⁻²), using the equation $\nu = i/nF$, where i is the current density in A·cm⁻², n is a number of electrons sharing during reaction (for Ni(II) reduction it is equal to 2, for the oxidation of hypophosphite $n = 1$, and for H₂ evolution $n = 2$). Thus, for the Ni deposition at 1 mA·cm⁻², ν is equal to 1.23 μm·h⁻¹.

RESULTS AND DISCUSSION

Electroless deposition of nickel coatings using hypophosphite is a rather complicated process. In this process, hypophosphite takes part in at least three different reactions [11–13]: Ni(II) ion reduction according to the reaction



the catalytic oxidation in the reaction with water



and the reaction resulting in phosphorus co-deposition:



As is well known, Ni(II) reduction is a pH-dependent reaction; the rate of hypophosphite oxidation increases with an increase in pH. Experiments carried out at different pH values (Fig. 1) showed its crucial influence on nickel deposition rate ($\nu_{\text{Ni-P}}$), maximal anodic current density (i_a) and the stability of electroless nickel plating solutions. The highest rate of the deposition and the highest value of i_a are achieved at pH 7. However, at this pH value the solution is most unstable.

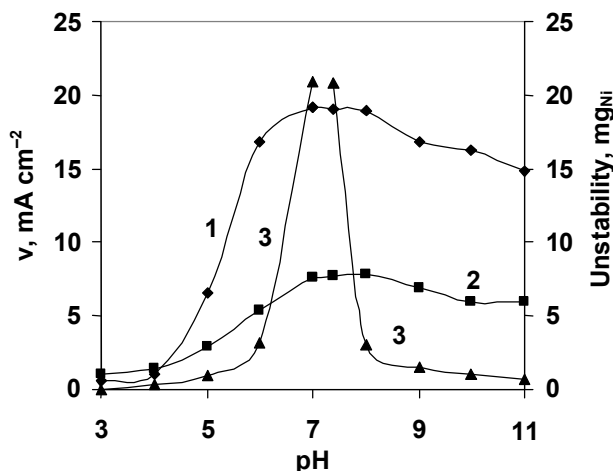


Fig. 1. Influence of pH on Ni–P deposition rate (1), intensity of maximal anodic current (2) and unstability of solutions (3) containing, mol·l⁻¹: 0.1 NiCl₂, 0.3 NaH₂PO₂, 0.33 NH₂CH₂COOH, 0.06 CH₂(COONa)₂ at pH 6 (measured at room temperature) and 90 °C

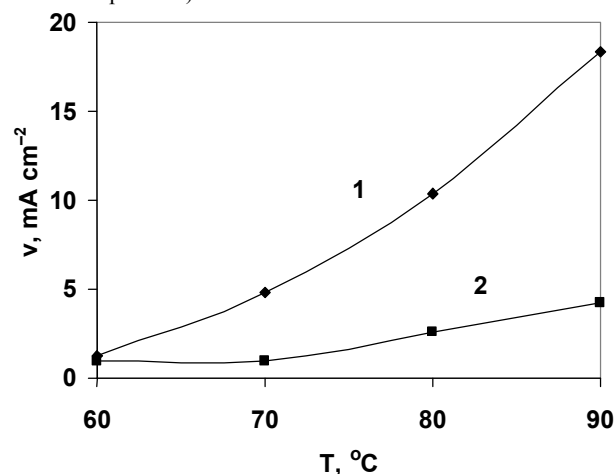


Fig. 2. Influence of temperature on electroless nickel plating rate (1) and maximal anodic current intensity (2) containing, mol·l⁻¹: 0.1 NiCl₂, 0.3 NaH₂PO₂, 0.33 NH₂CH₂COOH, 0.06 CH₂(COONa)₂ at pH 6 (measured at room temperature)

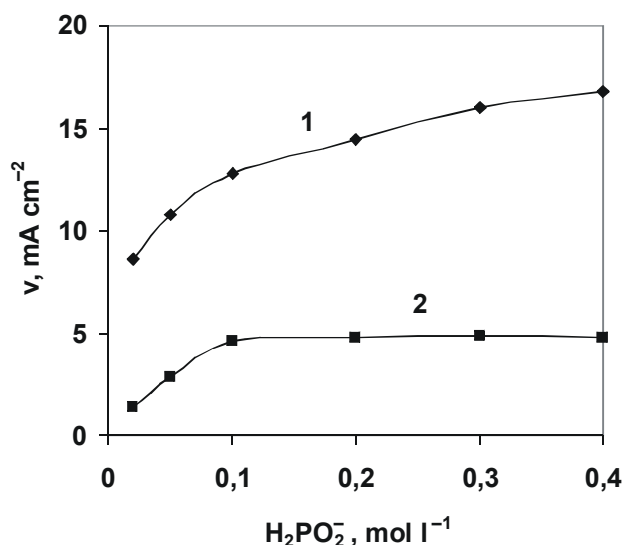


Fig. 3. Influence of hypophosphite concentration on electroless nickel plating rate (1) and maximal anodic current intensity (2) in solutions containing, mol l^{-1} : 0.1 NiCl_2 , 0.33 $\text{NH}_2\text{CH}_2\text{COOH}$, 0.06 $\text{CH}_2(\text{COONa})_2$ at pH 6 (measured at room temperature) and 90 °C

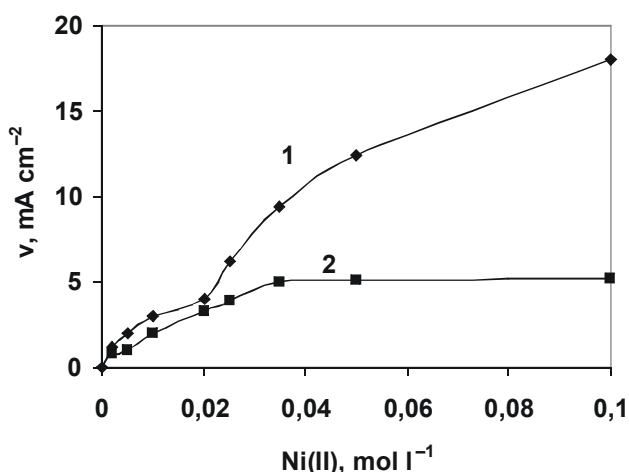


Fig. 4. Influence of Ni(II) concentration on electroless nickel plating rate (1) and maximal anodic current intensity (2) in solutions containing, mol l^{-1} : 0.3 NaH_2PO_2 , 0.33 $\text{NH}_2\text{CH}_2\text{COOH}$, 0.06 $\text{CH}_2(\text{COONa})_2$ at pH 6 (measured at room temperature) and 90 °C

It was found that the deposition rate increased with an increase in the bath temperature (Fig. 2), hypophosphite concentration (Fig. 3) and Ni(II) concentration (Fig. 4). The plating rate in most cases investigated was higher than i_a . However, some exceptions were observed in a slightly acidic solution at pH close to 3–4 or in the cases of low concentration of Ni^{2+} c.a. 3 to 20 mM. In these cases, $v_{\text{Ni-P}}$ was also low (less than $5 \mu\text{m}\cdot\text{h}^{-1}$). However, the low plating rate does not always indicate the approach of i_a to $v_{\text{Ni-P}}$ value. This was evidenced in the case of low temperatures. On the other hand, when $v_{\text{Ni-P}}$ exceeded $5 \mu\text{m}\cdot\text{h}^{-1}$ it was always higher than i_a . Moreover, higher values of $v_{\text{Ni-P}}$ resulted in the increase of the disparity between $v_{\text{Ni-P}}$ and i_a , $\Delta v_{\text{Ni-P}}$.

We suggest that $\Delta v_{\text{Ni-P}}$ could be attributed to the reactions of electroless nickel plating proceeding according to direct chemical interactions between Ni^{2+} ions and hypophosphite. If so, it can be assumed that the direct interactions caused the formation of Ni-P particles in the bulk and instability of the solution. Actually, the stability of electroless plating solutions decreased with an increase in temperature and hypophosphite concentration. The data presented in Figs. 2 and 3 also showed the increase of $\Delta v_{\text{Ni-P}}$ with the increase in hypophosphite concentration and the temperature of the solution. However, this relation was not seen in the case of electroless nickel plating in neutral and alkaline solutions (Fig. 1), since the extremely high instability of the solutions at pH 6–8 was not related to $\Delta v_{\text{Ni-P}}$, which practically was invariable in the range of pH from 6 to 11. The influence of Ni(II) salt concentration on the stability of electroless plating solutions was also ambiguous. When the concentration of hypophosphite was sufficiently high, the decrease in Ni(II) concentration led to the decrease of the deposition rate and solution stability (Table 1), meanwhile the value of $\Delta v_{\text{Ni-P}}$ decreased as well. Thus, the overall relation between the measured $v_{\text{Ni-P}}$ and i_a in modeling experiments does not exist. Actually, the stability of electroless nickel plating solutions containing amino acetic acid as a ligand depends on the ratio between hypophosphite and Ni(II) concentrations in the solution. The higher is this ratio, the lower is the stability of solutions (Table 1). So, the stability of the solution cannot be connected with the deposition rate; it may be high in the cases of both low and high deposition rates.

Table 1. The influence of Ni(II) and H_2PO_2^- concentrations on the stability of electroless plating solutions at 90 °C at ratio Ni(II) : $\text{NH}_2\text{CH}_2\text{COOH}$: $\text{CH}_2(\text{COONa})_2$ 1 : 3.3 : 0.6

Concentration, mol l^{-1}		Unstability, mg_{Ni}	Deposition rate $v_{\text{Ni-P}}$, $\mu\text{m h}^{-1}$
H_2PO_2^-	Ni(II)		
0.3	0.1	3.6	19.8
0.3	0.05	22	11.3
0.3	0.01	52	0.3
0.15	0.1	1	14.5
0.6	0.1	36	19.6

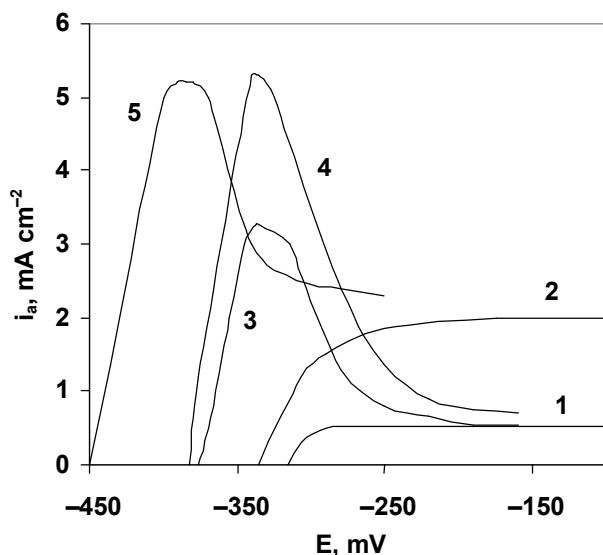


Fig. 5. Anodic voltammograms of Ni-P electrode in solutions containing, mol·l⁻¹: 0.1 NiCl₂, 0.33 NH₂CH₂COOH, 0.06 CH₂(COONa)₂ and NaH₂PO₂: 0.01 (1); 0.02 (2); 0.05 (3); 0.09 (4); 0.28 (5) at pH 6 (measured at room temperature) and 90 °C

Figs. 3 and 4 show that with the increase of $v_{\text{Ni-P}}$, owing to the increase in Ni(II) ions and hypophosphite concentrations, value i_a remained constant after its maximal value at about 5 mA·cm⁻² had been obtained. However, the shape of anodic voltammograms changed drastically with the increase in H₂PO₂⁻ concentration. At low concentrations, the current rapidly reached the limited value with an increase in the potential, meanwhile at high concentrations, the voltammetric curve had a pronounced peak. The similar relations in the anodic voltammograms were also observed when the concentration of Ni(II) ions was increased (Fig. 6). The distinct limited current density was observed only at low concentrations of Ni(II) when the plating process was slow enough. Again, the increase in pH had the same effect on the anodic process.

The investigations of the peculiarities of anodic H₂PO₂⁻ oxidation allowed to draw the following conclusions:

1. The distinct limited anodic current shows the possibility to run the autocatalytic Ni-P deposition process according to the electrochemical mechanism. It takes place at a low concentration of Ni(II) and low values of pH when the deposition rate is low. In all these cases $v_{\text{Ni-P}}$ is equal to the limited current density and can be described as resultant of two coupled reactions: anodic oxidation of H₂PO₂⁻ and cathodic reduction of Ni(II).

2. In the cases when the voltammograms have sharp anodic peaks, the measured values of the maximal current density i_a may be imprecise due to a shift of a mixed potential towards the direction of more negative values or due to the retarding effect of the reaction (1) taking place in the electroless plating solution (Fig. 5, curves 3–5 and Fig. 6, curves 4–6). On the other hand,

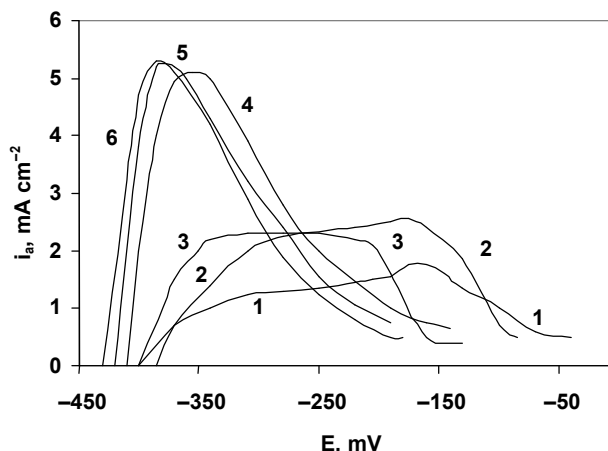


Fig. 6. Anodic voltammograms of Ni-P electrode in solutions containing, mol·l⁻¹: 0.3 NaH₂PO₂, 0.33 NH₂CH₂COOH, 0.06 CH₂(COONa)₂ and NiCl₂: 0.005 (1); 0.01 (2); 0.016 (3); 0.032 (4); 0.05 (5); 0.1 (6) at pH 6 (measured at room temperature) and 90 °C

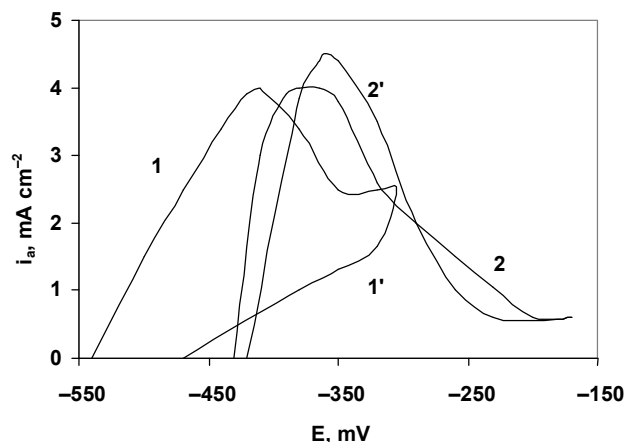


Fig. 7. Anodic voltammograms of Pd-P electrode (1 and 1') and Ni-P electrode (2, 2') in: solution containing, mol·l⁻¹: 0.011 PdCl₂, 0.1 NaH₂PO₂, 1.6 NH₄OH, 0.5 NH₄Cl at 60 °C (1,1') and solutions containing, mol·l⁻¹: 0.05 NiCl₂, 0.03 NaH₂PO₂, 0.16 NH₂CH₂COOH, 0.03 CH₂(COONa)₂ at pH 6 (measured at room temperature) and 90 °C (2, 2'). The potential sweep in direction of positive values (1 and 2), in reverse order (1' and 2')

the Ni-P coating deposition rate was twice and more higher than i_a . It hardly can be explained by the retarding effect of the nickel deposition process. Therefore, it can be assumed that at high deposition rate the autocatalytic process proceeds according to the two parallel mechanisms – electrochemical and chemical.

The retardation of the anodic process at more negative values of the potential may be attributed to the Ni-P electrode surface state as well. The data presented in Figs. 5 and 6 pointed not to the oxidation on the surface (the passivation proceeds at more negative potentials), but, probably, to the retarding effect of intermediate products forming on the surface during the electroless plating process. It could be the hydrogen formed

in catalytic oxidation of hypophosphite and sorbed on the surface.

To check this assumption, further studies were carried out for electrochemical oxidation of H_2PO_2^- on Pd-P and Ni-P electrodes in the corresponding electroless plating solutions (Fig. 7). The results obtained showed that Pd activity in the hypophosphite anodic oxidation reaction is lost more easily than that of Ni-P electrode. In the latter case, the shape of voltammograms is similar in both directions of the potential sweep. It is worth noting that the passivation of Ni-P electrode in plating solutions under anodic polarization was not observed independent of pH, Ni(II) and H_2PO_2^- concentrations, meanwhile the passivation of Pd-P proceeded in all the cases investigated. The different character o electrochemical of H_2PO_2^- oxidation on different electrodes denotes the significance of the chemical interactions.

The influence of the surface state was confirmed also by the data presented in Fig. 8. It has been known [7] that anodic current is considerably lower in the hypophosphite solutions without Ni(II) ions, when electroless nickel plating in not proceeding. We found that the rate of anodic oxidation can be increased by the anodic pre-treatment of the Ni-P electrode in the same hypophosphite solution. Slight anodic polarization had an inconsiderable influence on the anodic current density

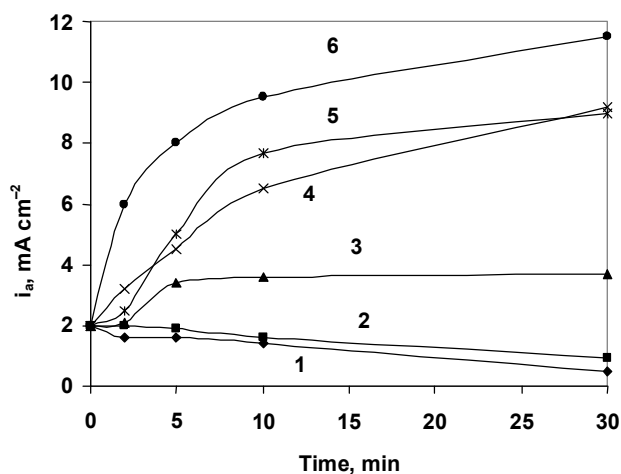


Fig. 8. Influence of duration of Ni-P electrode polarization at constant potential, mV: -500 (1); -450 (2); -350 (3); -300 (4); -250 (5) and -200 (6) on maximal anodic current density in solutions containing, $\text{mol}\cdot\text{l}^{-1}$: 0.1 NiCl_2 , 0.3 NaH_2PO_2 , 0.33 $\text{NH}_2\text{CH}_2\text{COOH}$, 0.06 $\text{CH}_2(\text{COONa})_2$ at pH 6 (measured at room temperature) and 90 °C

(Fig. 8, curves 1 and 2), while a long term polarization at higher potentials (from -300 to -200 mV) increased the anodic current by 5–6 times (Fig. 8, curves 4–6) reaching i_a values comparable to $v_{\text{Ni-P}}$.

It must be emphasized that the increase in Ni-P surface anodic polarization leads to the increase in i_a and also in remarkable changes of H_2PO_2^- anodic voltammograms (Fig. 9). After the further polarization, the passivation of Ni-P electrode decreased, and after a more prolonged polarization disappeared completely. The surface of Ni-P electrode even at high rates of anodic oxidation of hypophosphite remained active; actually, more active than that in the electroless nickel plating solutions. It is unlikely that the increase in the surface activity is related to the renewal of Ni-P surface due to its electrochemical oxidation and chemical reduction by hypophosphite as in the electroless plating solutions the surface renewal does not prevent the decrease in the current intensity with anodic polarization. It is also unlikely that the reason of the surface renewal could be the dissolution or oxidation of phosphorus as its quantity in the coatings is low and independent of the potential (Table 2). Again, the dissolution of Ni at these values of potentials is impossible.

The distinct activation of the surface was observed at the potentials more positive than these of the

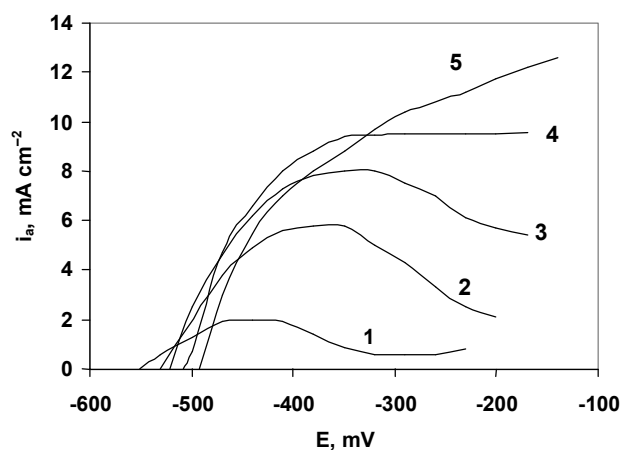


Fig. 9. Anodic voltammograms of Ni-P electrode in the solutions containing, $\text{mol}\cdot\text{l}^{-1}$: 0.1 NiCl_2 , 0.3 NaH_2PO_2 , 0.33 $\text{NH}_2\text{CH}_2\text{COOH}$, 0.06 $\text{CH}_2(\text{COONa})_2$ at a pH 6 (measured at room temperature) and 90 °C after polarization at -200 mV for 0 (1); 2 (2); 3; 10 (4) and 30 (5) min

Table 2. The influence of anodic potential on the average maximal anodic current i_a , volume of H_2 evolved, deposited Ni-P and content of P incorporated. Surface area 16 cm^2 ; deposition duration 15 min

E , mV	i_a , mA	H_2 , ml	Ni-P, mg	P, mg	P, mass. %
-440	0	51	77.2	6.5	8.4
-400	62	40	47.8	4	8.4
-375	82	30	25.5	2.2	8.7
-350	73	30	18.2	1.5	8.1
-325	70	16	6.2	0.53	8.5

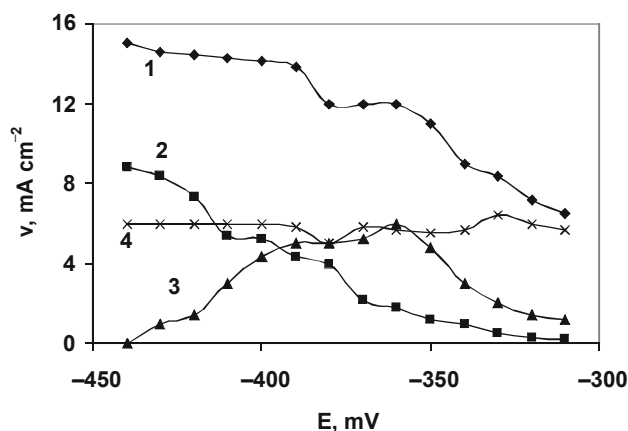


Fig. 10. Influence of potential on the hydrogen evolution rate (1), nickel deposition rate (2), anodic current intensity (3) and the calculated value of hydrogen evolving rate (4) in the solutions containing, mol·l⁻¹: 0.1 NiCl₂, 0.3 NaH₂PO₂, 0.33 NH₂CH₂COOH, 0.06 CH₂(COONa)₂ at pH 6 (measured at room temperature) and 90 °C. Duration of experiments – 10 min

equilibrium potential of hydrogen electrode in these solutions (~-360 mV). It is possible that the activation throughout the anodic polarization proceeded due to the oxidation of hydrogen or its compounds (hydride) present in the surface layer of Ni-P coating. Besides, the surface activity in the hypophosphite oxidation process changed rather slowly; the activation as well as the subsequent passivation without polarization proceeded during several minutes.

During the electroless nickel plating process, an intensive evolution of hydrogen gas proceeds. In order to evaluate its influence on the anodic hypophosphite oxidation, measurements of hydrogen volumes evolved at different potentials were carried out. The data given in Fig. 10 show that with the increase in the potential, the rates of hydrogen evolution (curve 1), Ni-P deposition (curve 2) and anodic current density (curve 3) decreased (at more positive potentials than -300 mV). Taking into account that during Ni-P deposition H₂ evolves in reactions (1) and (2), the difference between curves 1 and 2 (Fig. 10, curve 4) gives the part of H₂ falling to reaction (2), i. e. to the catalytic oxidation of hypophosphite with H₂O. In these calculations, the amount of H₂ formed in the reduction of phosphorus was not taken into account, since it does not exceed 10% of the whole hydrogen evolved. The rate of reaction (2) is independent of the potential indicating its chemical nature.

The feasible catalytic oxidation of hypophosphite with H₂O according to the chemical mechanism was confirmed also by the further electrochemical investigations in hypophosphite solutions without Ni(II), when the deposition of Ni-P did not proceed (Fig. 11). In this case the experiments were also carried out at potentials more positive than that equilibrium hydrogen potential in these solutions, when the cathodic reduction of H₂O is impossible. The calculated values of H₂ formation rate (Fig. 11, curve 3) did not depend also on the potential

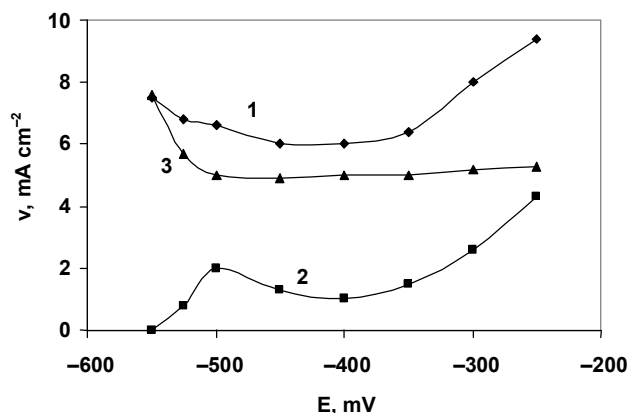


Fig. 11. Influence of potential on the hydrogen evolution rate (1), anodic current intensity (2) and hydrogen evolution rate in reaction of catalytic oxidation of H₂PO₂⁻ with H₂O (3) in solutions containing, mol·l⁻¹: 0.3 NaH₂PO₂, 0.1 NH₂CH₂COOH, 0.06 CH₂(COONa)₂ at pH 6 (measured at room temperature) and 90 °C. Duration of experiments – 10 min

in a very wide range. Therefore, the catalytic oxidation of hypophosphite with H₂O on Ni-P electrode is a chemical process and the electrochemical reactions do not play any role.

CONCLUSIONS

When the electroless nickel deposition rate ($v_{\text{Ni-P}}$) is low (2–4 $\mu\text{m}\cdot\text{h}^{-1}$), the electrochemical reaction of hypophosphite oxidation plays the main role in the autocatalytic process. With an increase in the intensity of the process, the difference between $v_{\text{Ni-P}}$ and maximal anodic current intensity (i_a) increases due to difficulties in the estimation of the apparent value of i_a (coupled cathodic Ni deposition reaction has a retarding effect on the anodic process) as well as due to the participation of chemical reactions in the catalytic process. The increased activity of Ni-P electrode due to the positive polarization in the solutions containing hypophosphite indicates a significant role of intermediate products in the autocatalytic process.

The stability of the solutions is not related to the values $v_{\text{Ni-P}}$ or v_a , implying that the reactions having proceeded in the bulk of the solutions and on the surface are not related.

The catalytic oxidation of hypophosphite with H₂O on Ni-P surface does not depend on the potential, indicating a reaction of a purely chemical origin.

Received 9 February 2007

Accepted 26 February 2007

References

1. E. C. Perena and S. Wolyneć, *Met. Finish.*, **91**, 45 (1993).
2. Z. Jusys, J. Liaukonis and A. Vaškelis, *J. Electroanal. Chem.*, **30**, 787 (1991).

3. L. M. Abrantes and J. P. Corraera, *J. Electrochem. Soc.*, **141**, 2356 (1994).
4. Y. Zeng and Sh. Zhou, *Electroch. Comm.*, **1**, 217 (1999).
5. A. Jagminienė, I. Stankevičienė and A. Vaškelis, *Chemija*, **14**, 140 (2003).
6. A. Jagminienė, A. Vaškelis, I. Stankevičienė and L. Tamašauskaitė-Tamašiūnaitė, *Chemija*, **16**, 2, 33 (2005).
7. A. Vaškelis and G. Klimantavičiūtė, *Lietuvos TSR MA darbai. B serija*, **2**(81), 33 (1974); **3**(88), 3 (1975); **5**(96), 15 (1976) (in Russian).
8. O. Diemontaitė, J. Lenkaitienė and I. Genutienė, *Lietuvos TSR MA darbai. B serija*, **3**(142), 3 (1984) (in Russian).
9. A. M. Babko and I. V. Piatnickii, *Quantitative Analysis*, Moskva (1965) (in Russian).
10. P. K. Norkus and R. M. Markevičienė, *Zhurnal Analiticheskoi Khimii*, **22**, 1525 (1967) (in Russian).
11. A. A. Sutiagina, K. M. Gorbunova and M. P. Glazunov, *J. Physical Chemistry*, **37**, 1022 (1963) (in Russian).
12. J. H. Marshal, *J. Electrochem. Soc.*, **130**, 369 (1983).
13. Z. Jusys and J. Liaukonis, *J. Inorg. Chem.*, **34**, 337 (1989).

**Ona Gylienė, Algirdas Vaškelis, Rima Tarožaitė,
Aldona Jagminienė**

CHEMINIO NIKELIAVIMO TIRPALŲ, KURIUOSE YRA LIGANDAS AMINOACTO RŪGŠTIS, ELEKTROCHEMINIAI TYRIMAI

S a n t r a u k a

Elektrocheminių tyrimų rezultatai patvirtino anodinių procesų, vykstančių nusodinant cheminio nikelio dangas tirpaluose, kuriuose yra reduktorius hipofosfitas ir ligandas aminoacto rūgštis, sudėtingumą. Kai nikelio nusėdimo greitis ($v_{\text{Ni-P}}$) buvo nedidelis – apie $2\text{--}4\ \mu\text{m h}^{-1}$, elektrocheminė reakcija vaidino pagrindinę rolę autokataliziniame procese. Dangų nusėdimo procesui intensyvėjant skirtumas tarp $v_{\text{Ni-P}}$ ir išmatuotos maksimalios anodinės srovės dydžio i_a didėjo dėl i_a reikšmės nustatymo sudėtingumų (kartu vykstanti nikelio nusėdimo reakcija lėtinančiai veikia anodinį procesą) bei dėl cheminių reakcijų, tuo pat metu vykstančių katalizės procese. Voltamperometriniai matavimai, atlikti esant potencialams, teigiamesniems už mišrų potencialą, parodė Ni–P elektrodo aktyvumo didėjimą, didinant anodinę poliarizaciją.

Katalizinės hipofosfito oksidacijos vandeniu greitis, įvertintas skirtumu tarp vandenilio, išsiskyrusio anodiniame procese ir nusodinant Ni–P dangas, tūrių, nepriklausė nuo suteiktojo potencialo reikšmės. Šie rezultatai, taip pat duomenys, gautieji hipofosfito tirpaluose nesant Ni(II) (kai Ni–P dangų nusėdimas nevyksta), rodo tik cheminę hipofosfito katalizinės oksidacijos vandeniu prigimtį.

Tirpalų stabilumas nėra susijęs nei su v , nei su v_a reikšmėmis.