

Investigation of electroless nickel plating from Ni(II)-citrate solutions containing adipate and Cu(II) as additives

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The accelerating action of adipate alone and used together with stabilizer Cu(II) ions has been studied in acidic citric electroless nickel plating solutions by kinetic and electrochemical measurements. The coatings deposited with hypophosphite in the presence of 70 mM adipate and 0.2 mM Cu(II) at pH 4.5 contain about 9 wt.% P and 1 wt.% Cu. Electrochemical modelation has shown that citrate and adipate diminish the current of hypophosphite anodic oxidation and increase the current of NiP electrode oxidation. Adipate to some extent increases the rate of cathodic reactions in Ni(II)-citrate solutions. Electrochemical behavior of NiP and NiPCu electrodes in corresponding electroless plating solutions shows differences: the NiPCu electrode oxidation in solutions containing Cu(II) ions is shifted when compared with that of the NiP electrode about 0.2 V to the negative potential values and anodic H_2PO_2^- ions oxidation on the NiPCu electrode takes no place in the reverse potential sweeping.

Key words: electroless nickel, Ni(II)-citrate, hypophosphite, anodic oxidation, adipate

INTRODUCTION

Electroless nickel (EN) alloys have widely been investigated and used in the surface treatment of electronic and other industries because of their excellent corrosion and wear resistance, hardness and non-magnetism [1-3]. These properties, changing with nickel and phosphorus levels in the deposit, depend on the composition and pH of the plating bath used [4-10]. However, the advanced EN baths must meet not only plating rate and coatings composition standards. The baths should be sufficiently stable for a long-term use by continuous replenishment with the components required. A possibility to regenerate them and easily decontaminate is an indispensable condition for the advanced EN baths [11-14]. This is one of the reasons why EN process has still been extensively studied.

The use of citrate as a ligand for Ni(II) ions to a certain degree meets these requirements [15-17]. However, the main disadvantage of citrate containing baths is a low EN deposition rate in both acidic and alkaline solutions [18] and their insufficient stability. Therefore, the basic challenge is to choose

the proper accelerants and stabilizing agents. Promising results in this field were achieved by using adipic acid as an accelerant and Cu(II) ions as a stabilizer in acidic Ni(II)-citrate EN solutions [19]. Since the EN deposition process is assumed to consist of partial electrochemical reactions, anodic oxidation of hypophosphite and cathodic discharge of Ni and P [20], the electrochemical investigation is highly important for gaining a complete understanding of this system. In spite of some contradictions with mixed potential theory [21], electrochemical investigations have been assumed as a basis for elucidation of the EN plating mechanism [22-24].

The aim of the current study was to investigate by using the electrochemical model the influence of the additives adipate and Cu(II), which together improve EN deposition from acidic citric solutions.

EXPERIMENTAL

NiP coatings were plated at a temperature of 85 °C from solutions containing (M): NiSO_4 - 0.1, Na citrate - 0.1, NaH_2PO_2 - 0.25 and additives (mM): adipic acid 0-70 and CuSO_4 0-0.2. The solutions' pH was adjusted to 4.5 with NaOH solution. NiP coatings were deposited onto copper (to determine

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the plating rate) and onto roughhewed glass (to determine their composition). The P and Cu contents in the deposits were found photometrically with ammonium molybdate and diethyldithiocarbamate, respectively, and the concentration of hypophosphite in EN plating solution was determined by titration with ammonium vanadate [25].

Electrochemical measurements were carried out using a PI-50-1 potentiostat, a PR-8 programmer and two digital B7-43 voltmeters for automatic registration of voltammetric characteristics at a potential scan rate of 50 mV/s. The working electrode was a NiP or NiPCu coating deposited onto a 2 cm² Cu plate prior to measurements from the baths corresponding to the investigated solutions, the reference electrode – Ag / AgCl / KCL_{sat} and the counter electrode – platinum (potential values are given vs. SHE). The NaH₂PO₂ concentration in its anodic oxidation investigations was of 0.25 M and the NiSO₄ concentration in cathodic reduction investigations 0.1M. The pH of all solutions was adjusted to 4.5 at room temperature.

The cell was thermostated at 85 °C. Solutions were deoxygenated with argon before each experiment.

RESULTS AND DISCUSSION

1. Plating rate and coating composition

In accordance with Ni(II)–citric acid complex distribution in aqueous solution at pH 4.5 when the ratio Ni(II) : citric acid = 1:1, about 80% of Ni(II) ions are bound to NiL⁻ complex and only 10% remain in the form of Ni(II) [25]. As is shown in Table, the NiP deposition rate from citric EN plating solution under these conditions is not high if compared with widely used acetic solution which cannot be adjusted after deposition of 3 g nickel in 1 l EN plating solution. It may be increased to 30% by adding adipic acid to EN solution. When adipate is used, the change in pH is slighter after the same NiP amount deposition. This fact indicates that adipate acts in EN solutions as a buffering agent. Although the EN solution is rather stable at pH 4.5, during a long-term use by replenishing with the components required, some nickel content settles on a bottom of the bath. The use of a certain amount of Cu(II) ions as a stabilizer makes it possible not only to realize the plating process from a sufficiently stable bath, but also accelerates the plating rate just as in glycine as a ligand-containing solution [27]. Addition of Cu(II) together with adipic acid improves the quality of coatings, they become ve-

ry smooth and glossy. This may be due to adsorption of Cu(II) (or reduced by H₂PO₂⁻ to Cu(I) ions) onto the most quickly growing NiP centers, which stimulates a rise in the number of new centers and thus the deposition of smooth coatings. About 1 wt.% of Cu is incorporated into the NiP coating (Table). The amount of P in the coatings plated without additives is close to 10 wt.%. When adipate is added, P content in the coatings slightly decreases due to improved buffering properties of the EN plating solution (the P content in NiP coatings increases with a decrease in solution pH). Some decrease in P content is also observed with Cu incorporation to the coatings.

2. Electrochemical studies

The NiP electrode potential in hypophosphite solution is approximately -0.46 V. With an increase in citrate or adipate concentration in hypophosphite solution the NiP electrode potential shifts to more positive values. The current of anodic oxidation of hypophosphite on NiP electrode passes through the maximum at -0.2 V. Even small amounts of these organic additives downregulate the anodic H₂PO₂⁻ oxidation current to a considerable degree (Figs. 1 and 2). An increase in citrate concentration up to 0.1 M shifts the maximal values of the anodic H₂PO₂⁻ oxidation current to a more negative range of potentials (from -0.19 V without additives to -0.35 V) (Fig. 1). When adipate is added to H₂PO₂⁻ solution, the maxima of its oxidation current are also observed at potentials close to -0.3 V (Fig. 2). A decrease in the anodic H₂PO₂⁻ oxidation current in the presence of these additives may be attributed to the passivity of active NiP electrode surface due to their adsorption. The adsorption may facilitate the nickel electrode oxidation, since a rather straight rise of anodic current in the presence of these organic additives is observed at potentials more positive than -0.15 V. The anodic H₂PO₂⁻ oxidation on NiPCu electrode is rather similar to that on NiP electrode, but the current of NiPCu electrode oxidation is lower than that of NiP electrode oxidation

Table. Parameters of electroless nickel plating from citrate solution at pH 4.5 and the composition of coatings

Additive, mM	Plating rate, μm/h	pH after plating 1h	ΔpH for 1 mg NiP	Coating composition, wt.%		
				Ni	P	Cu
-	4.1	4.35	0.015	90.4	9.6	-
Cu(II) 0.2	4.3	4.35	0.014	89.8	9.1	1.1
Adipate 70	5.3	4.4	0.008	91.0	9.0	-
Adipate 70 Cu(II) 0.2	5.9	4.4	0.007	89.9	8.9	1.2

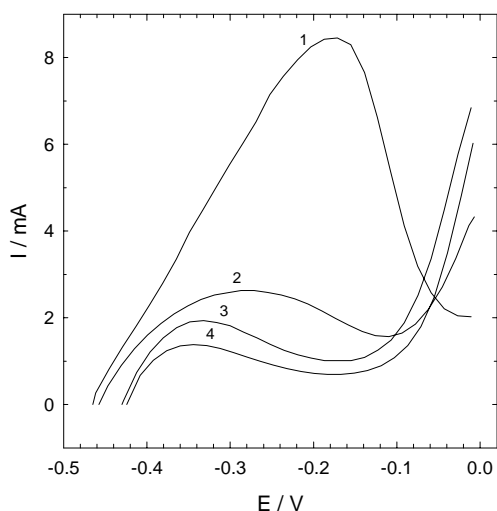


Fig. 1. Anodic hypophosphite oxidation on NiP electrode: 1 – without additives; with citrate (M): 2 – 0.01; 3 – 0.05; 4 – 0.1. NaH_2PO_2 – 0.25 M

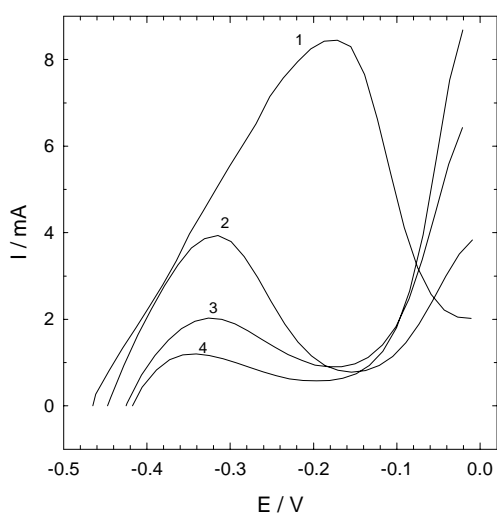


Fig. 2. Anodic hypophosphite oxidation on NiP electrode: 1 – without additives; with adipate (mM): 2 – 35; 3 – 70; 4 – 70 together with 0.1 M citrate. NaH_2PO_2 – 0.25 M

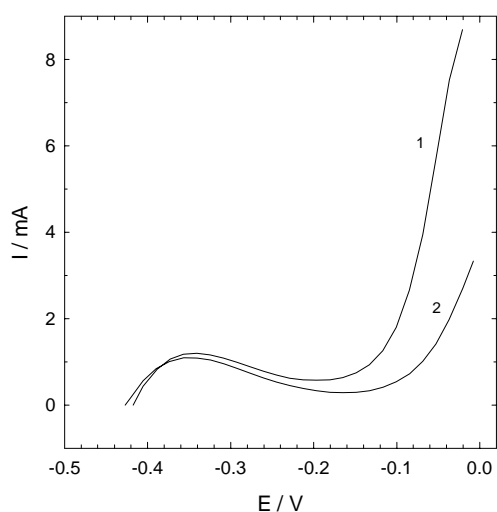


Fig. 3. Anodic hypophosphite (0.25 M) oxidation on NiP 1 and NiPCu 2 electrodes

(Fig. 3). This results in a smooth and more corrosion-resistant NiPCu electrode surface containing 1 wt.% of copper along with phosphorus.

Voltammetry studies of the EN plating system show a 4-fold higher catalytic activity of NiP electrode in hypophosphite oxidation in a complete electroless plating solution than in an analogous solution without Ni(II) ions (Fig. 4), which is in good agreement with electrochemical studies in other solutions [28, 29]. It is possible that when organic additives are bound with Ni(II) to a coordination compound, their blocking effect on the electrode surface is less expressed. In the reverse sweeping from 0 V to the negative potential values, a lower anodic H_2PO_2^- oxidation current is caused by a residual passive film on the NiP electrode surface.

In the case of cathodic NiP electrode polarization in Ni(II)-citrate solution a rise in the cathodic current is observed from a potential of -0.08 V (Fig. 5). It may be related to the reduction of a certain oxide film on the electrode surface. A distinct discharge of both Ni(II) and protons from water occurs at potentials more negative than -0.45 V. The addition of adipate to this system does not change noticeably the character of the cathodic current. The potential of the NiPCu electrode in both solutions (without and with adipate) additionally containing Cu(II) ions noticeably shifts to the positive

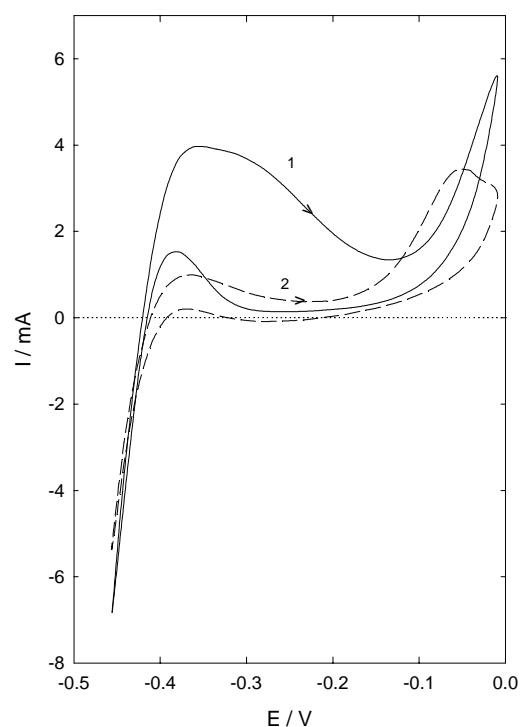


Fig. 4. NiP electrode cyclic voltammograms recorded in solutions containing (M): 1 – NiSO_4 – 0.1, NaH_2PO_2 – 0.25 citrate – 0.1 and adipate 0.07; 2 – as in 1 without Ni(II)

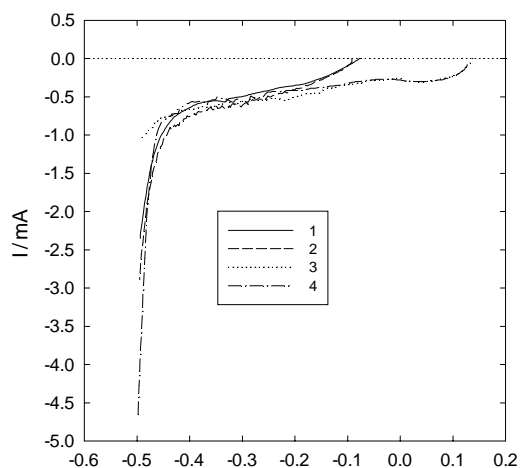


Fig. 5. NiP (1, 2) and NiPCu (3, 4) electrodes cathodic polarization recorded in solutions containing NiSO_4 and citrate – 0.1 M each: 1 – without additives; with additives (mM): 2 – adipate – 70; 3 – CuSO_4 – 0.2; 4 – adipate 70 and CuSO_4 – 0.2

potential range up to 0.13 V, and deposition of a Cu film on the electrode is observed. The discharge of Ni(II) ions on the electrode in the presence of Cu(II) ions in solutions occurs in a similar way as that without Cu(II). However, the cathodic current at a potential of -0.5 V in the presence of adipate in both solutions (without and with Cu(II) ions) is the highest. The fact that adipate accelerates cathodic reactions is in accordance with an enhanced EN plating rate, especially in the presence of Cu(II) ions (Fig. 5 and Table).

The cyclic voltammograms on NiP electrode in plating solution and in analogous solutions without hypophosphite or without Ni(II) ions are presented in Fig. 6. The value of the cathodic current of Ni(II) reduction is equal to that of the anodic current of hypophosphite oxidation at a potential of -0.41 V. This value practically conforms with the mixed potential in EN plating system. The higher cathodic current in the common solution as compared to Ni(II)–citrate solution is caused by the phosphorus and particularly by hydrogen discharge from hypophosphite and water occurring simultaneously with Ni(II) reduction. In the presence of adipate the general run of cyclic voltammograms is similar to those above. The values of plating rate calculated from the partial anodic and cathodic currents at this potential should be much higher (more than five times) if compared with the EN plating rate, which takes place in reality. This discrepancy of real EN plating with the results of electrochemical modeling indicates that the EN plating process is more complicated and cannot be described reasonably well by investigating only separate anodic and cathodic reac-

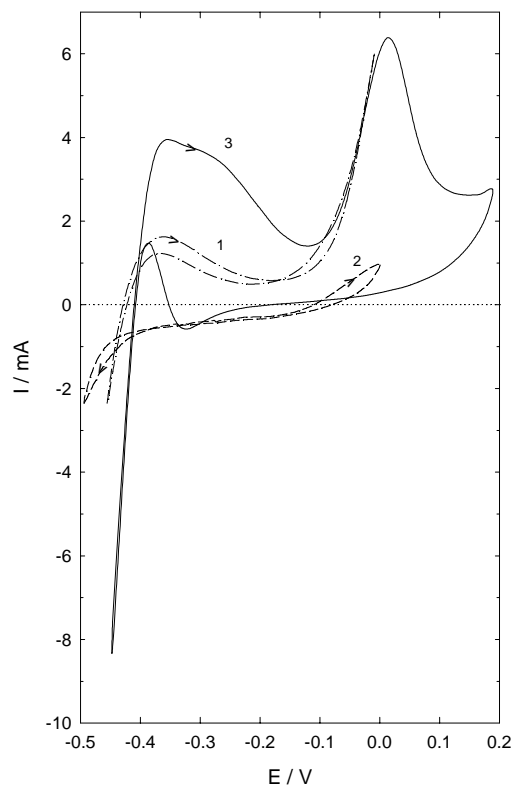


Fig. 6. NiP electrode cyclic voltammograms recorded in solutions containing (M): 1 – NaH_2PO_2 – 0.25 and citrate – 0.1; 2 – NiSO_4 – 0.1 and citrate – 0.1; 3 – NiSO_4 – 0.1, citrate – 0.1 and NaH_2PO_2 – 0.25

tions. Probably deviations of the results of electrochemical measurements arise due to a strong absorption of organic ligands or surface passivation of any kind, because electrochemical investigations cannot be carried out on the permanently renovated NiP or NiPCu surface. Cyclic voltammograms, when the hypophosphite oxidation and nickel reduction potential values are achieved in the reverse sweeping, also support this opinion. In spite of some discrepancies, electrochemical investigations give a considerable amount of information on these process.

The cyclic voltammometry studies of NiP and NiPCu plating systems presented in Fig. 7 show some differences. In the case of anodic polarization the current of hypophosphite oxidation on the NiPCu electrode is lower than that on the NiP electrode, while the real EN plating rate is higher in the presence of Cu(II), indicating that the NiPCu surface is more sensitive to passivation than NiP. The peak of the NiP surface oxidation current at about 0 V in the NiPCu plating system is not observed, and a rather sharp jump of the anodic current at potentials more positive than 0.1 V is close to the nickel electrode dissolution current in the system without Cu(II) ions. In the reverse potential

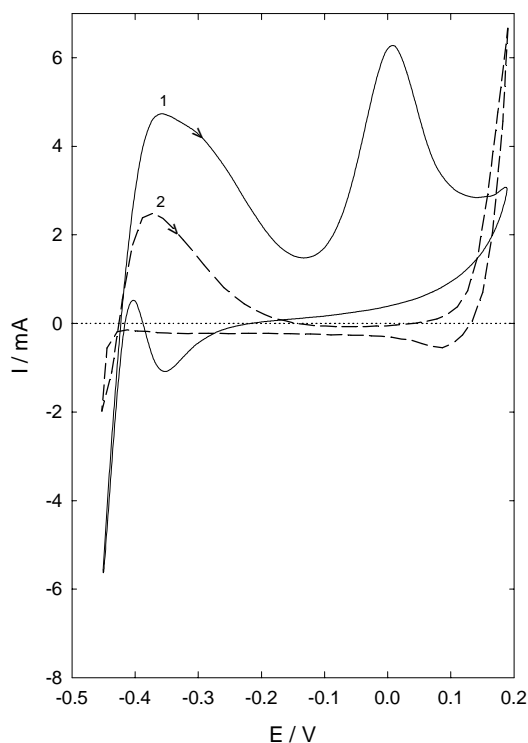


Fig. 7. Cyclic voltammograms of NiP 1 and NiPCu 2 electrodes recorded in solutions containing (M): 1 – NiSO₄ – 0.1, citrate – 0.1, NaH₂PO₂ – 0.25 and adipate – 0.07; 2 as in 1 with 0.2 mM CuSO₄

sweeping from positive potentials, copper is deposited onto the NiPCu electrode and oxidation of hypophosphite does not occur. A similar inhibiting action of Cu(II) ions on H₂PO₂⁻ oxidation might occur on the nickel crystallization nucleus due to the different potential of nickel germs and a useful plating surface. This may be one of the reasons for an increased stability of EN plating solution containing Cu(II) ions.

CONCLUSIONS

1. Nickel coatings deposited from citric EN plating solution with adipate and Cu(II) ions as additives at pH 4.5 contain about 9 wt.% P and 1 wt.% Cu.
2. The accelerating effect of adipate on EN plating rate is related to its buffering action.
3. Adipate similarly to citrate diminishes the anodic current of hypophosphite oxidation on NiP electrode and to some extent accelerates cathodic reactions in the Ni(II)-citrate system.
4. NiPCu electrode anodic oxidation is shifted to the range of more positive potentials at about 0.2 V.

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**CHEMINIO NIKELIAVIMO Ni(II)-CITRATO
TIRPALUOSE SU ADIPATO IR Cu(II) PRIEDAIS
TYRIMAS**

S a n t r a u k a

Cheminio nikelio dangos nusodinimą hipofosfitu Ni(II)-citrato tirpaluose pagreitinanti vieno adipato poveikis, taip pat su stabilizatoriumi Cu(II) jonais, buvo tiriamas naudojant kinetinius ir elektrocheminius matavimus. Á ni-

kelio dangas, nusodinamas hipofosfitu esant tirpalø pH 4,5, patenka apie 9 sv.% P ir 1 sv.% Cu. Elektrocheminiais tyrimais nustatyta, kad citratas ir adipatas sumažina anodinės hipofosfito oksidacijos srovę bei greitina NiP elektrodo oksidaciją. Adipatas tam tikru laipsniu greitina katodines reakcijas Ni(II)-citrato tirpale. Elektrocheminė NiP ir NiPCu elektrodo elgsena jø nusodinimo tirpaluose skiriasi: NiPCu elektrodo oksidacija yra pastumta per 0,2 V link neigiamesniø potencialo verëiø, palyginti su NiP elektrodo oksidacija, o grąžinant á neigiamø potencialø pusę, $H_2PO_2^-$ oksidacija ant NiPCu elektrodo nebevyksta.