Influence of Cu²⁺ and dicarboxylic acid additives on electroless nickel plating

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Electroless nickel plating in solutions containing acetate, lactate, citrate and glycine as ligands has been studied at pH 4.5 and a temperature of 85 °C. A decrease in nickel plating rate and an increase in P amount incorporated into the coatings have been found to be proportional to the increase in stability of Ni²⁺ ions complexes with organic acid ions and are related to their steric and adsorption hindrance on the nickel surface. This is distinctly expressed at higher concentrations of glycine and citate bound with nickel in a more complicated manner, if compared to acetate and lactate.

0.2 mM CuSO₄ stabilize all the electroless plating solutions studied and increase the nickel plating rate. The Cu content in the coatings varies in the range 0.8 to 1.3 wt.%. The presence of dicarboxylic acid (malonic, succinic or adipic) along with Cu²⁺ ions in the plating solutions increases the NiP plating rate even more, due to the increased buffering capacity of solutions. An increase in nickel plating rate always is related to a decrease in P content in the coating and to an increase in the hypophosphite utilization efficiency. These effects are more pronounced if dicarboxylic acid of higher molecular weight is used as an additive.

Key words: electroless nickel, Cu²⁺ stabilizer, dicarboxylic acid

INTRODUCTION

Electroless nickel coatings have gained a good deal of popularity and acceptance in recent years as they provide considerable improvement of desirable properties. The plating process enables to deposit a uniform coating regardless of the shape of surface irregularities. Electroless nickel plating has been conducted in different baths to find optimum conditions for desirable properties, such as good corrosion and wear resistance, hardness and others [1–7]. The amount of phosphorus codeposited with nickel can affect the strength and wear properties of coatings. The P content can be changed under certain conditions of plating, such as composition and pH of the plating bath used.

An addition of some inhibitors may improve the stability of the plating bath, surface roughness of coatings, however, they frequently lower the NiP deposition rate. It has been established that a certain quantity of Cu²⁺ ions sufficiently stabilizes electroless nickel plating solution containing glycine as a ligand for Ni²⁺ ions, increases the NiP plating rate, improves coating appearance and ensures non-ferromagnetic stability [8]. Experiments of using Cu²⁺ in an acetate–citrate bath allowed proposing a model to explain the stabilizing role of Cu²⁺ ions by a partial reduction of them to the Cu⁺ state [9]. A positive action of the combination of Cu²⁺ with adipate was observed in an acidic citrate nickel plating solution [10]. It has been established that the deposition of smooth and bright nickel coatings in this case is determined by a stronger adipate interaction with NiPCu surface than with that of NiP [11].

The aim of the present work was to study peculiarities of electroless nickel plating in acidic solutions containing different ligands for Ni²⁺ ions and to elucidate the influence of adipic and other dicarboxylic acids present in these solutions along with Cu²⁺ ions.

EXPERIMANTAL

The NiP coatings were plated at a temperature of 85 °C in solutions containing (M): NiSO₄ – 0.1, NaH₂PO₂ – 0.25 and one of the ligands: Na acetate, Na citrate, glycine or lactic acid. Their concentrations necessary to bound 0.1 M Ni²⁺ were established spectrometrically (FEK 2). The concentrations of the additives used in the indicated cases were: CuSO₄ – 0.2 mM, dicarboxylic acid (malonic, succinic or adipic) – 0.1 M. Solution pH was adjusted to 4.5 at room temperature with NaOH and H₂SO₄. NiP coatings were deposited during 1 h onto acti-
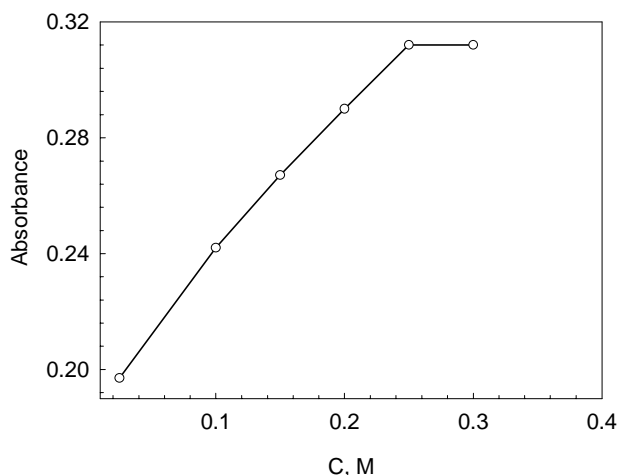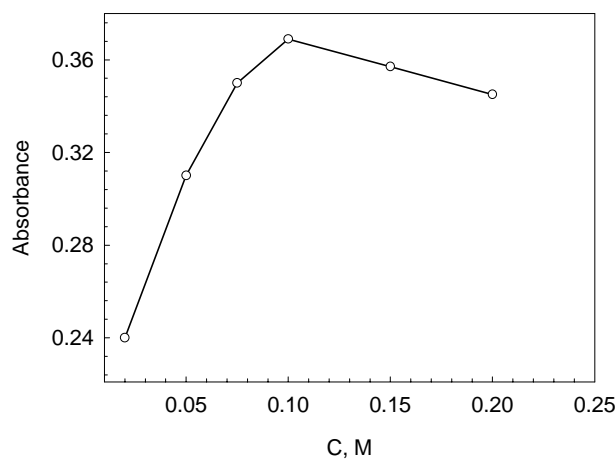
Fig. 1. Dependence of absorbance at λ 670 nm on the concentration of lactic acid in solution containing 0.1 M NiSO₄; pH 4.5
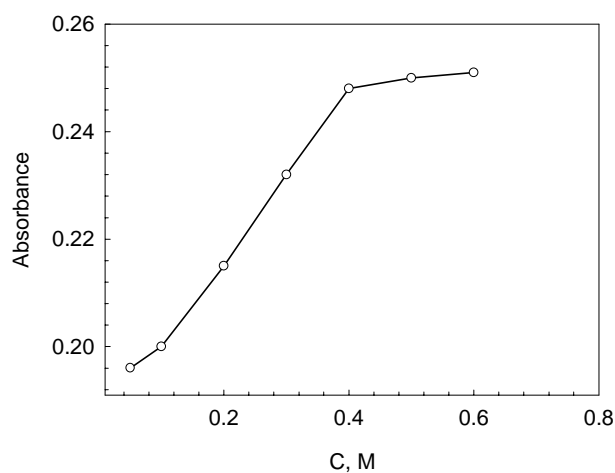
Fig 3. Dependence of absorbance λ 670 nm on the concentration of glycine in solution containing 0.1 M NiSO₄; pH 4.5
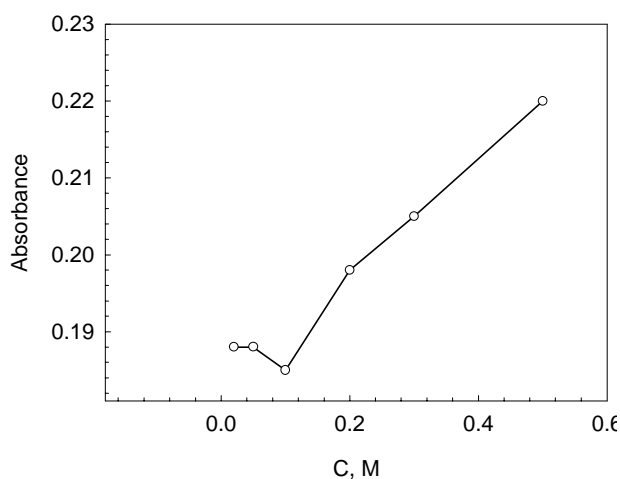
Fig. 2. Dependence of absorbance λ 670 nm on the concentration of Na acetate in solution containing 0.1 M NiSO₄; pH 4.5

Fig 4. Dependence of absorbance λ 670 nm on the concentration of Na citrate in solution containing 0.1 M NiSO₄; pH 4.5

vated copper foil to determine the plating rate and buffering properties of solutions (load 1dm²/l). Coatings of equal thickness (10 µm) were deposited onto roughened glass, to determine coatings composition and hypophosphite utilization efficiency.
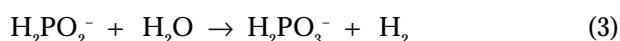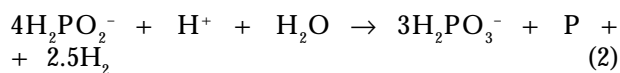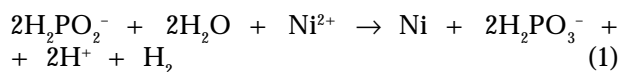
The quantities of P and Cu after dissolution of coatings were detected photometrically with ammonium molybdate and diethylditiocarbamate, respectively. The concentration of hypophoaphite in the plating solution was determined by titration with ammonium vanadate [12]. Hypophosphite utilization efficiency was estimated as a ratio of its theoretical quantity necessary for the discharge of the Ni, P and Cu quantities detected in the coatings to a total sum of hypophosphite consumed in the process. It has been accepted that the discharge of 1 M nickel or 1M copper requires 2M of hypophosphite while 1M phosphorus requires 4 M hypophosphite [13].

The data presented in Tables are the arithmetical mean of no less than three experiments.

RESULTS AND DISCUSSION

NiP plating without additives

Three reactions catalyzed by Ni and taking place simultaneously comprise the electroless plating process, which in a weak acidic solution may be described as follows [13]:

$$2H_2PO_2^- + 2H_2O + Ni^{2+} \rightarrow Ni + 2H_2PO_3^- + 2H^+ + H_2 \tag{1}$$

$$4H_2PO_2^- + H^+ + H_2O \rightarrow 3H_2PO_3^- + P + 2.5H_2 \tag{2}$$

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + H_2 \tag{3}$$

The amount of the hypophosphite consumed in each of these reactions (at constant Ni^{2+}, $H_2PO_2^-$ concentrations, pH and temperature) depends on the nature of the ligand which determines the stability of a complex with Ni^{2+}, the buffering properties of

Table 1. Nickel plating parameters and composition of coatings. Solution composition (M): NiSO$_4$ 0.1, NaH$_2$PO$_2$ 0.25; pH 4.5

Ligand, M	Additive, mM	Plating rate, μm/h	ΔpH for deposition of 1 mg NiP	Coating composition, wt. %			Hypophosphite utilization	
				Ni	P	Cu	for reaction (3) mol/mol Ni	efficiency
Na acetate 0.2	–	9.4	0.0068	91.7	8.3	–	0.35	0.88
	CuSO$_4$ 0.2	10.6	0.0095	93.0	6.2	0.79	0.35	0.88
	" malonic acid 100	12.8	0.0033	92.5	6.7	0.78	0.20	0.92
	" succinic acid 100	13.0	0.0029	93.4	5.9	0.73	0.25	0.91
	" adipic acid 100	12.5	0.0024	93.1	6.1	0.80	0.30	0.90
Lactic acid 0.25	–	7.4	0.112	91.5	8.5	–	0.35	0.88
	CuSO$_4$ 0.2	7.9	0.135	91.2	7.9	0.86	0.31	0.89
	" malonic acid 100	9.7	0.0059	92.1	7.1	0.76	0.18	0.94
	" succinic acid 100	10.1	0.0056	91.9	7.3	0.78	0.24	0.92
	" adipic acid 100	10.3	0.0048	92.3	6.9	0.81	0.12	0.96
Glycine 0.4	–	3.7	0.0071	90.2	9.8	–	0.54	0.84
	CuSO$_4$ 0.2	4.1	0.0079	88.8	10.0	1.21	0.37	0.88
	" malonic acid 100	6.2	0.0059	90.9	8.1	1.0	0.25	0.91
	" succinic acid 100	6.7	0.0033	89.8	9.2	0.98	0.27	0.91
	" adipic acid 100	7.5	0.0030	90.0	9.1	0.94	0.27	0.91
Na citrate 0.1	–	3.7	0.0065	89.3	10.7	–	0.86	0.77
	CuSO$_4$ 0.2	4.3	0.0082	89.1	9.8	1.13	0.61	0.82
	" malonic acid 100	4.8	0.0032	90.0	9.0	1.02	0.64	0.81
	" succinic acid 100	4.7	0.0034	89.3	9.6	1.10	0.58	0.82
	" adipic acid 100	5.2	0.0024	89.3	9.7	1.01	0.64	0.81

and NaH$_2$PO$_2$ was carried out first. According to the stability of complexes with Ni^{2+} they may be aligned as follows: acetate < lactate < citrate < glycinate [14]. Ligand concentrations necessary to bind 1 M Ni^{2+} ions were established on the basis of spectrometric measurements. Taking into account the data presented in Figs. 1–4, ligand concentrations for further investigations were chosen as follows (M): lactic acid 0.25, acetate 0.2, citrate 0.1, glycine 0.4.

As is shown in Table 1, the NiP plating rate from acetate solution was the highest and tended to diminish with an increase in the stability of the complex Ni^{2+}–acid ions. It decreases drastically when glycine or citrate are used as ligands. It should be noted that citrate nickel plating solution is unstable under the studied conditions (as is also acetate plating solution) and may be used in practice only after its stabilization. Taking into account this circumstance, NiP coating deposition in citrate nickel plating solution could be somewhat easier. It is likely that the low NiP plating rate in the case of more complicated glycinate and citrate complexes is caused by difficulties related to their steric hindrance in hypophosphite adsorption and nickel discharge onto an active surface. A particularly strong adsorption of citrate onto the NiP surface, observed in our previous work [11], may support this presumption. According to the literature data, the hindering action of some additives on Ni^{2+} ions discharge from acetate nickel plating solution was arranged as follows: lactate < malonate < citrate < EDTA [15]. The fact that these additives may be aligned in the same manner according to their steric complexity is another point in favour of the steric hindrance. Strong adsorption of ligand ions onto NiP

solution and other parameters. Therefore, a comparison of electroless nickel plating in solutions containing different types of organic acid (acetic, lactic, citric or glycine) ions as ligands along with NiSO$_4$

Table 2. **Nickel plating parameters and coating composition depending on ligand concentrations. Solution composition (M): NiSO₄ 0.1, NaH₂PO₂ 0.25, adipic acid 0.1 and CuSO₄ 0.2 mM; pH 4.5**

Ligand, M		Plating rate, μm/h	ΔpH for deposition of 1 mg NiP	Coating composition, wt. %			Hypophosphite utilization	
				Ni	P	Cu	for reaction (3) mol/mol Ni	efficiency
Na acetate	0.1	11.7	0.0035	93.1	6.1	0.96	0.32	0.89
	0.3	12.3	0.0020	93.7	5.5	0.84	0.20	0.92
	0.6	12.3	0.0012	93.4	5.8	0.79	0.10	0.96
Lactic acid	0.1	11.4	0.0053	93.5	5.8	0.69	0.12	0.96
	0.2	11.0	0.0049	92.5	6.8	0.71	0.11	0.96
	0.3	11.2	0.0046	92.5	6.8	0.71	0.11	0.96
Glycine	0.2	8.0	0.0043	91.5	7.6	0.92	0.27	0.91
	0.4	7.3	0.0030	90.5	8.8	0.98	0.31	0.89
	0.6	6.4	0.0027	90.7	8.3	0.96	0.55	0.84
Na citrate	0.05	7.5	0.0040	92.0	7.0	0.89	0.39	0.87
	0.1	5.1	0.0025	89.6	9.4	1.0	0.64	0.81
	0.15	2.6	0.0020	89.1	8.9	1.50	1.53	0.64

surface hinders $H_2PO_2^-$ adsorption and formation of a $\cdot PHO_2^-$ radical, which is considered as an intermediate in the following (1–3) reactions [16–18]. Probably acetate and lactate ions distinguished by simpler steric location do not create such troubles in hypophosphite adsorption, Ni^{2+} discharge, and are easier to remove from the NiP surface.
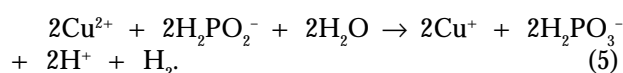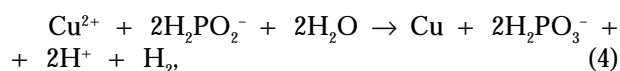
NiP coatings plated in acidic solutions usually contain 8–12 wt.% of phosphorus, depending on the deposition conditions. The catalytic reactions of P reduction (2) and oxidation of hypophosphite by the proton from a water molecule (3) also need active hypophosphite ions adsorbed on the NiP surface, so both these reactions compete with the reaction of Ni^{2+} discharge (1). A comparatively higher P quantity found in the coatings whose deposition occurs at a low rate (in glycinate and citric solutions) and a higher consumption of the hypophosphite observed in these cases (Table 1) is probably conditioned by difficulties in Ni^{2+} ions access to the surface because of the steric factors of glycinate and citrate complexes. Thus, the conditions stimulating the plating rate lead to a higher hypophosphite utilization efficiency but, unfortunately, to a low quantity of P incorporated into a nickel coating.

2. Action of additives in nickel plating

The presence of 0.2 mM Cu^{2+} ions essentially stabilizes all the nickel plating solutions studied and increases the plating rate by 7–15% (Table 1). An increase in nickel plating rate was attributed to the improved catalytic activity of the surface with Cu incorporated [19]. A similar increasing effect was also observed for Cd, Pb and S ions containing stabilizers at certain concentrations [20] and might be also attributed to qualitative changes in the nickel surface structure. The content of Cu in the coatings 10 μm thick varies from 0.8 to 1.3 wt.%, depending on the plating solution composition. A higher Cu

quantity, similarly to that of phosphorus, is found in the coatings deposited at a lower rate.

The alteration in plating solution pH after deposition of 1 mg NiP in the presence of Cu^{2+} ions is slightly higher as compared to that in the plating solutions without the additive (Table 1). A more pronounced decrease in solution pH after deposition of the same NiP quantity in the presence of Cu^{2+} ions may confirm the earlier proposed model [9], whereby the adsorbed Cu^{2+} ions are reduced equally into Cu^0 (codeposited in the alloy) and Cu^+ (acting as a stabilizer) by the following reactions:

$$Cu^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Cu + 2H_2PO_3^- + 2H^+ + H_2, \tag{4}$$

$$2Cu^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow 2Cu^+ + 2H_2PO_3^- + 2H^+ + H_2. \tag{5}$$

These reactions occur only in the presence of active nickel surface, because Cu does not catalyze hypophosphite oxidation.

The hypophosphite utilization efficiency in the presence of Cu^{2+} ions has a tendency to increase with an increase in the coating deposition rate and a decrease in the P content incorporated into the coating, since these reactions are interdependent, similarly to NiP deposition without additives (Table 1).

The NiP plating rate increases even more significantly when a dicarboxylic acid (malonic, succinic or adipic) takes part in the plating solution along with Cu^{2+} ions. This increase (at equal acid concentrations) is proportional to the length of a $-CH_2-$ chain in the dicarboxylic acid. The increase in plating rate is the highest when adipic acid is used, reaching 100% in the glycinate solution (in the other plating solutions – about 40%). An increase in

plating rate is related to an improvement of solution buffering capacity and is proportional to the molecular weight of the dicarboxylic acid used.

No distinct changes are evident in the composition of coatings plated in the presence of dicarboxylic acid as compared to the coatings plated only with a Cu^{2+} ion additive. Some tendencies in the decrease of P and Cu quantities, observed in the presence of dicarboxylic acids are probably related to the increase in the nickel plating rate.

The consumption of hypophosphite in the catalytic reaction with water (3) is lower, thereby hypophosphite utilization efficiency is higher in the presence of dicarboxylic acid independently on its nature. One more advantage of using them (especially adipic acid) along with Cu^{2+} ions is an improvement in coatings' appearance, because they become brighter and smoother.

Table 2 shows that no distinct changes were observed in the nickel plating parameters either with an increase or decrease in acetate or lactate concentrations in the solutions containing Cu^{2+} ions and adipate. At the same time, an increase in glycine or citrate concentrations in corresponding solutions leads to a significant decrease in nickel plating rate, particularly in citrate solution. With the increase in glycine or citrate concentrations the P and Cu quantities in the coatings first increase to some extent, however, with a subsequent increase in ligand concentrations the composition of the coatings remains practically idential. A more considerable increase in Cu quantity is observed at a higher citrate concentration in the solution when the plating rate decreases drastically. The decrease in hypophosphite utilization efficiency with the increase in glycine and citrate concentrations in the nickel plating solutions is proportional to the decrease in nickel plating rate. Therefore, steric and absorption hindrances of ligand ions significantly affecting the Ni^{2+} ion discharge apparently less affect the other two reactions taking place simultaneously.

CONCLUSIONS

1. The reaction of nickel discharge from more complicated complexes is more significantly hindered by steric and adsorption factors than the other reactions catalyzed by nickel, that simultaneously take place in the electroless plating solution. Therefore, a decrease in nickel plating rate is related to a increase in the quantity of P incorporated into the coating and to a decrease in the hypophosphite utilization efficiency.

2. 0.2 mM Cu^{2+} sufficiently stabilizes all the electroless nickel plating solutions studied and to some extent increases the plating rate. The quantity of Cu incorporated into the coatings 10–15 μm thick varies in the range 0.8 to 1.3 wt.% depending on the plating conditions.

3. The ability of dicarboxylic acids (malonic, succinic, adipic) to increase the nickel plating rate is proportional to their molecular weight and is related to an improvement of the solution buffering capacity. The presence of dicarboxylic acid along with Cu^{2+} ions in the plating solution increases the hypophosphite utilization efficiency.

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Cu²⁺ IR DIKARBOKSIRÛGÐÈIØ ÁTAKA CHEMINIAM NIKELIO DANGØ NUSODINIMUI

S a n t r a u k a
Nikelio dangos buvo nusodinamos 85°C temperatûroje hipofosfitu tirpaluose, kuriuose Ni^{2+} jonams ligandais buvo

acetatas, citratas, pieno rûgðtis arba glicinas. Tirpalø pH iki 4,5 buvo reguliuojamas kambario temperatûroje. Nustatyta, kad dangø nusëdimo greitis tuo maþesnis, o fosforo kiekis jose tuo didesnis, kuo patvaresnis Ni²⁺ – organinës rûgðties jonø kompleksas. Ypaè lëtai nusodinamos dangos tirpaluose, kuriuose ligandais yra glicinas arba citratas. Manoma, kad Ni²⁺ jonø iðsikrovimà apsunkina ðiø kompleksø erdviniai faktoriai bei þenklesnë laisvø ligando jonø adsorbcija ant aktyvaus NiP pavirðiaus.

0,2 mM $CuSO_4$ pakankamai gerai stabilizuoja visus tirtus cheminio nikeliavimo tirpalus ir greitina dangø nusodinimà. Á dangas ásiterpia 0,8–1,3 sv.% Cu. Kartu su Cu²⁺ jonais pridëjus á nikeliavimo tirpalà dikarboksirûgðties (malono, gintaro arba adipino) dangø nusëdimas dar labiau pagreitëja, padidëjus tirpalø buferinei talpai. Nikelio dangø nusëdimo pagreitëjimas yra susijæs su fosforo kiekio jose sumaþëjimu bei efektyvesniu hipofosfito sunaudojimu. Ðie efektai ryðkesni, kai á tirpalà pridedama didesnio molekulinio svorio dikarboksirûgðties.