

Effect of accelerators and stabilizers on the formation and characteristics of electroless Ni–P deposits

I. Baskaran^a, T.S.N. Sankara Narayanan^{b,*}, A. Stephen^a

^a Materials Science Division, Department of Nuclear Physics, University of Madras, Guindy Campus, Chennai 600 025, India

^b National Metallurgical Laboratory, Madras Centre, CSIR Complex, Taramani, Chennai 600 113, India

Received 31 May 2005; received in revised form 7 September 2005; accepted 4 October 2005

Abstract

The effect of thiourea, succinic acid and lead acetate on the formation and characteristics of electroless Ni–P deposits obtained from an acidic hypophosphite reduced electroless nickel bath is addressed in this paper. The rate of deposition of electroless Ni–P coating is found to be a function of concentration of these additives. Thiourea accelerates the rate of deposition up to 0.8 ppm and started to inhibit at a concentration of 1 ppm. Similarly, succinic acid increases the plating rate up to 12 g l⁻¹ and exhibit an inhibiting effect at higher concentrations of the order of 15 g l⁻¹. Addition of lead acetate inhibits the rate of deposition even at a concentration of 0.5 ppm and the extent of inhibition is increased when the concentration is higher than 1 ppm. Addition of these additives also caused a change in phosphorus content of the deposits; lead acetate (1 ppm) tends to increase the phosphorus content whereas thiourea (0.8 ppm) and succinic acid (12 g l⁻¹) tends to decrease the phosphorus content. The X-ray diffraction patterns of electroless Ni–P coatings obtained in the absence of additives and in presence of 1 ppm of lead acetate exhibit a single broad peak centered at 44.5° 2θ, indicating the amorphous nature of these coatings. The peak broadening suggests a greater tendency to form amorphous structure when lead acetate is used as the additive. In contrast, for electroless Ni–P coatings obtained from thiourea and succinic acid containing baths, besides the reflection from Ni (1 1 1) plane, a weak reflection from Ni (2 0 0) plane is also observed. The X-ray diffraction patterns of electroless Ni–P coatings after annealing at 400 °C for 1 h exhibit the formation of fcc nickel and bct nickel phosphide (Ni₃P) phases in all the cases with Ni₃P (2 3 1) as the most intense reflection. Electroless Ni–P coatings obtained in presence of thiourea and succinic acid exhibit a nodular feature with a typical cauliflower like structure. The size of the nodules is relatively less in the latter case. In contrast, the electroless Ni–P coating obtained in the absence of additives and in presence of 1 ppm of lead acetate is relatively smooth. However, the deposit obtained in the absence of additives reveals the presence of fine particulates, attributed to the precipitation of Ni₃P phases in the absence of stabilizers. The DSC traces of electroless Ni–P coatings exhibit a single well-defined exothermic peak in the temperature range studied in all the cases, which could be attributed to the precipitation of metallic nickel phase and formation of nickel phosphide (Ni₃P) phase. The variation in the peak temperature and the energy evolved during the phase transition is due to the slight variation in the phosphorus content caused by the addition of thiourea, succinic acid and lead acetate. The study recommends that the choice of accelerators and stabilizers should be made only after a careful study.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Electroless plating; Electroless Ni–P deposits; Accelerators; Stabilizers; Structure; Phase transformation behaviour

1. Introduction

Electroless nickel coatings have gained widespread acceptance since their discovery by Brenner and Riddel [1] in the middle of the 20th century. Due to their ability to provide improved hardness, wear and abrasion resistance and, corrosion resistance, electroless nickel coatings are widely used in chemical, aerospace, automobile and textile industries [2–4].

Electroless Ni–P coatings are classified into three types, viz., low (1–3 wt.% P), medium (4–7 wt.% P) and high (7 wt.% and above) phosphorus coatings [5]. The phosphorus content of the deposit is a function of the pH of the plating bath, the concentration of hypophosphite in the bath and the deposition temperature. In general, electroless Ni–P deposits having >7 wt.% phosphorus is amorphous in nature and exhibit good corrosion resistance and solderability. They are normally prepared from acidic baths at high temperatures of the order of 90 °C. At such high temperatures, nickel phosphite, formed due to the oxidation of hypophosphite, will precipitate in the bath [6,7]. Since electroless nickel baths are highly sensitive to impurities, maintaining the stability of the bath is very critical and this warrants

* Corresponding author.

E-mail addresses: tsnsn@rediffmail.com (T.S.N.S. Narayanan), steve.arum@yahoo.co.in (A. Stephen).

the addition of stabilizers to avoid decomposition of the plating bath. Stabilizers are chemical agents that are deliberately added in electroless plating baths to prevent the homogeneous reaction that triggers the spontaneous decomposition of an entire plating operation [8,9].

A variety of compounds have been identified as effective stabilizers for electroless nickel deposition [10–12]. These include: (i) compounds of group IV elements (i.e., Se, Te, thiourea, MBT, thiocyanate, etc.); (ii) unsaturated organic acids (i.e., maleic, itaconic, etc.); (iii) heavy metal cations (i.e., Sn^{2+} , Pb^{2+} , Cu^{2+} , etc.); (iv) oxygen containing anions (i.e. AsO_4^{2-} , MoO_4^{2-} , etc.); (v) some classes of surfactants, dispersants of various charges and emulsifying agents (i.e. potassium perfluoroalkyl sulphonates, lauryl trimethyl ammonium chloride, *N*-oleyl betaine, etc.) [12].

The stabilizing action of these compounds can generally be divided into two categories: one is a substitution type mechanism [6], in which heavy metal ions such as Pb^{2+} , Cd^{2+} , Hg^{2+} , Sn^{2+} and Fe^{2+} when added to the plating bath, deposits on the active metal surface through displacement reaction and thus inhibits the occurrence of the random reduction of nickel. The other category is the adsorption-poisoning type mechanism [2,13], whereby some anodic ion stabilizers, namely, hydrogen sulphide, sulphide, arsenide and iodide ions can inhibit the nickel deposition via adsorption on the catalytic sites of the metal surface. It was expected that these stabilizers would also adsorb onto the deposit. Too much adsorption of the stabilizer on the substrate or deposit certainly would also poison the deposition reaction and decrease the plating rate [14]. In addition, the stabilizers could influence the electroless plating process in many ways: (i) they can lead to co-deposition of sulphur (in case of sulphur containing compounds such as mercapto benzothiazole) and lead (in case of lead acetate) [15–17]; (ii) they can act as brighteners and/or leveling agents [18]; (iii) they might influence the phosphorus content of the electroless Ni–P coatings [16]; (iv) they can increase the porosity of the electroless Ni–P coatings; (v) affect the corrosion resistance of the electroless Ni–P coating (due to co-deposition of elements like sulphur as well as the decrease in porosity).

Thiourea and lead acetate are the commonly used stabilizers in electroless plating baths [14,19–22]. The effect of thiourea and lead acetate as stabilizers in electroless nickel plating bath was studied by de Minjer and Brenner [20] and Lin and Hwang [14]. Since the toxicity of lead is not desirable, thiourea was used as a substitute for lead acetate. However, lead acetate and thiourea behave distinctly in electroless nickel deposition process. At low concentrations of the order of 1 ppm, thiourea enhances the rate of deposition and crystallinity of the Ni–P coating yielding a coarse nodular morphology whereas addition of lead acetate at a similar concentration lowers the deposition rate and decrease the crystallinity yielding a relatively smooth and fine textured morphology. Hence the use of thiourea in place of lead acetate requires a careful study on the effect of these compounds on the plating rate, structural characteristics and corrosion resistance.

Many organic and inorganic compounds were used in trace amounts to accelerate the electroless deposition process. According to Gutzeit [23], sodium or potassium salts of mono-

and dibasic organic acids, which were originally used as buffers in electroless nickel baths, is also capable of enhancing the deposition rate of electroless Ni–P coating. Fang [24] suggests the utility of a mixed ligand complex, which increases the rate of deposition of electroless Ni–P coating. Heterocyclic organic compounds, such as mercapto benzothiazole (MBT), are widely used as accelerators in electroless plating processes [25]. In addition, phenyl thiourea, fluoride, glycine, cysteine and thioglycolic acid have also been found to exhibit an accelerating effect [26–28]. These accelerators are thought to function by loosening the bond between hydrogen and phosphorus atoms in the hypophosphite molecule, allowing it to be more easily removed and adsorbed on to the substrate surface. The delocalization of electrons possible in these molecules makes them suitable to use as accelerators in electroless plating processes. Succinic acid, a dibasic organic acid having much lower volatility than acetic and propionic acids, is found to be capable of acting as both a buffer and a complexing agent effectively. It can also exert an accelerating or inhibiting effect depending on its concentration [26,29].

The ability of various additives added to the electroless plating bath to stabilize the bath or to accelerate the rate of deposition is influenced by several parameters such as their concentration, pH, temperature, solution fluid dynamics, the concentration of reducing agents and the presence of foreign bodies [30]. Of these, concentration of the additives is considered to be the most critical parameter [31] since these additives can act as accelerators [15,18] or inhibitors of the deposition depending on their concentration in the plating bath [1,2,15,16,22]. Consequently, it is important to determine the effective concentration of these additives for specific bath chemistry.

Hence it is evident that the right choice of stabilizers and accelerators for electroless nickel plating baths has to be made only after a careful study of the effect of these compounds on the plating rate and the coating characteristics. In this perspective, the present paper aims to study the effect of thiourea, succinic acid and lead acetate on the formation and characteristics of electroless Ni–P deposits.

2. Experimental details

Nickel sulphate hexahydrate was used as the source of nickel. Sodium hypophosphite was used as the reducing agent, which also serves as the source of phosphorus in the coating. Lactic acid and propionic acid were used as the complexing agents to control the rate of release of free metal ions for the reduction reaction. Succinic acid, thiourea and lead acetate were used as additives in the plating bath. Among them, succinic acid is added to accelerate the rate of deposition of the coating whereas thiourea and lead acetate were used as stabilizers to prevent the decomposition of the plating bath. The chemical composition of the plating baths and their operating conditions are given in Table 1. During plating, the temperature of the bath was maintained at 90 ± 1 °C using a constant temperature bath and the pH of the bath was maintained at 4.50 with the addition of sodium hydroxide.

Electrolytic grade copper (40 mm × 30 mm × 1 mm) was used as the substrate material for determining the plating thickness of electroless Ni–P deposits. The copper substrate was cleaned with dilute nitric acid, washed thoroughly with de-ionized water, rinsed with acetone and dried. A nickel strike was immediately given to the cleaned copper plates to prevent them from tarnishing. Besides, the deposited nickel provides a catalytic surface for the deposition of the electroless Ni–P deposits. The plating rate is determined by gravimetric method

Table 1
Bath composition and operating conditions of the baths used

Bath composition and operating conditions	Bath A	Bath B	Bath C	Bath D
Nickel sulphate hexahydrate (g l^{-1})	21.2	21.2	21.2	21.2
Sodium hypophosphite monohydrate (g l^{-1})	24	24	24	24
Lactic acid (g l^{-1})	28	28	28	28
Propionic acid (g l^{-1})	2.2	2.2	2.2	2.2
Succinic acid (g l^{-1})	–	–	12.0	–
Thiourea (ppm)	–	0.8	–	–
Lead acetate (ppm)	–	–	–	1.0
pH	4.50	4.50	4.50	4.50
Temperature ($^{\circ}\text{C}$)	90 ± 1	90 ± 1	90 ± 1	90 ± 1
Plating rate ($\mu\text{m h}^{-1}$)	15 ± 1	25 ± 1	19 ± 1	13 ± 1
Nickel (wt.%)	88.77	89.53	89.29	88.04
Phosphorus (wt.%)	11.23	10.47	10.71	11.96

[22]. For structural characterization and phase transformation behaviour, thin foils of electroless Ni–P deposits were used. The thin foils of electroless Ni–P deposits were prepared after depositing them on stainless steel (AISI 304 grade; 60 mm \times 30 mm \times 1 mm) substrates and subsequently peeled off from the substrate.

The nickel and phosphorus content of the deposits were analyzed using energy dispersive spectrometry (EDS). The structure of electroless Ni–P deposits, both in as-plated and heat-treated conditions was assessed by X-ray diffraction (Rich Siefert; Model 3000) using a Cu K α ($\lambda = 1.540598 \text{ \AA}$) radiation. The surface morphology of the deposits was assessed by scanning electron microscopy (SEM). The phase transformation behaviour was studied by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7). The lattice parameter was determined by the XRD peak fit (Using XRDA software) and the average crystallite size was determined using Scherrer formula. The volume fraction of the Ni₃P phase present in the coating was estimated using the formula:

$$\text{Ni}_3\text{P}(231)\% = \frac{\text{Ni}_3\text{P}(231)}{\text{Ni}_3\text{P}(231) + \text{Ni}(111)} \times 100$$

3. Results and discussion

The thickness of deposition of electroless Ni–P coatings obtained using baths A–D, as a function of time, is given in Fig. 1. It is evident from Fig. 1 that addition of lead acetate (1 ppm) (bath D) decreases the plating rate whereas addition of thiourea (0.8 ppm) (bath B) and succinic acid (12 g l^{-1}) (bath C) helps to increase the plating rate. When analyzing the variation in the plating rate as a function of concentration of these additives (Fig. 2(a–c)) it is clear that addition of thiourea accelerates the rate of deposition up to 0.8 ppm and started to inhibit at a concentration of 1 ppm (Fig. 2(a)). Similar observation is also observed when succinic acid is used as the additive; increase in plating rate up to 12 g l^{-1} and inhibition at higher concentrations of the order of 15 g l^{-1} (Fig. 2(b)). Addition of lead acetate inhibits the rate of deposition even at a concentration of 0.5 ppm and the extent of inhibition is increased when the concentration is higher than 1 ppm (Fig. 2(c)).

It has long been suggested that thiourea can exert an accelerating or inhibiting effect on the plating rate, depending on the thiourea concentration [32,33]. Radiochemical studies of thiourea in the electroless nickel deposition process have been conducted by Sallo et al. [34] and Kivel and Sallo [15]. It has already been reported [35] that thiourea can lower the activation energy of the electroless nickel deposition reaction. Hence,

the increase in deposition rate when the thiourea concentration is less than 1 ppm is due to the enhancement in the reaction rate. At concentrations greater than 1 ppm, addition of thiourea becomes poisonous to the deposition due to surface coverage of the deposit by thiourea. The lowering in activation energy of the deposition reaction is overwhelmed by the poisoning effect of surface adsorption at high thiourea concentration.

Xu et al. [21] have proposed the mechanistic pathway by which thiourea accelerates and inhibits the deposition of electroless Ni–P coating. According to them, thiourea was first oxidized into a reactive intermediate radical by a two-step mechanism; in the first step, the tautomeric form of thiourea is oxidized to a thiourea free radical (thiourea*) through a charge transfer process [36] and in the second step, the thiourea* reacts with another radical to form the reactive intermediate, formamidine disulphide. The radical formation is a reasonable intermediate for a single electron oxidation process because the end product is a disulphide [36]. The presence of the radical formation from thiourea has been confirmed by chemical oxidation by hydrogen peroxide using electron spin resonance [37]. The

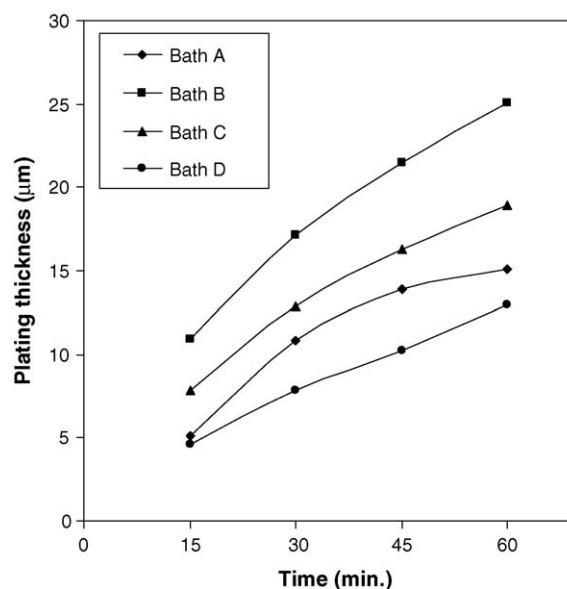


Fig. 1. The plating thickness of electroless Ni–P coatings obtained using baths A–D, as a function of time.

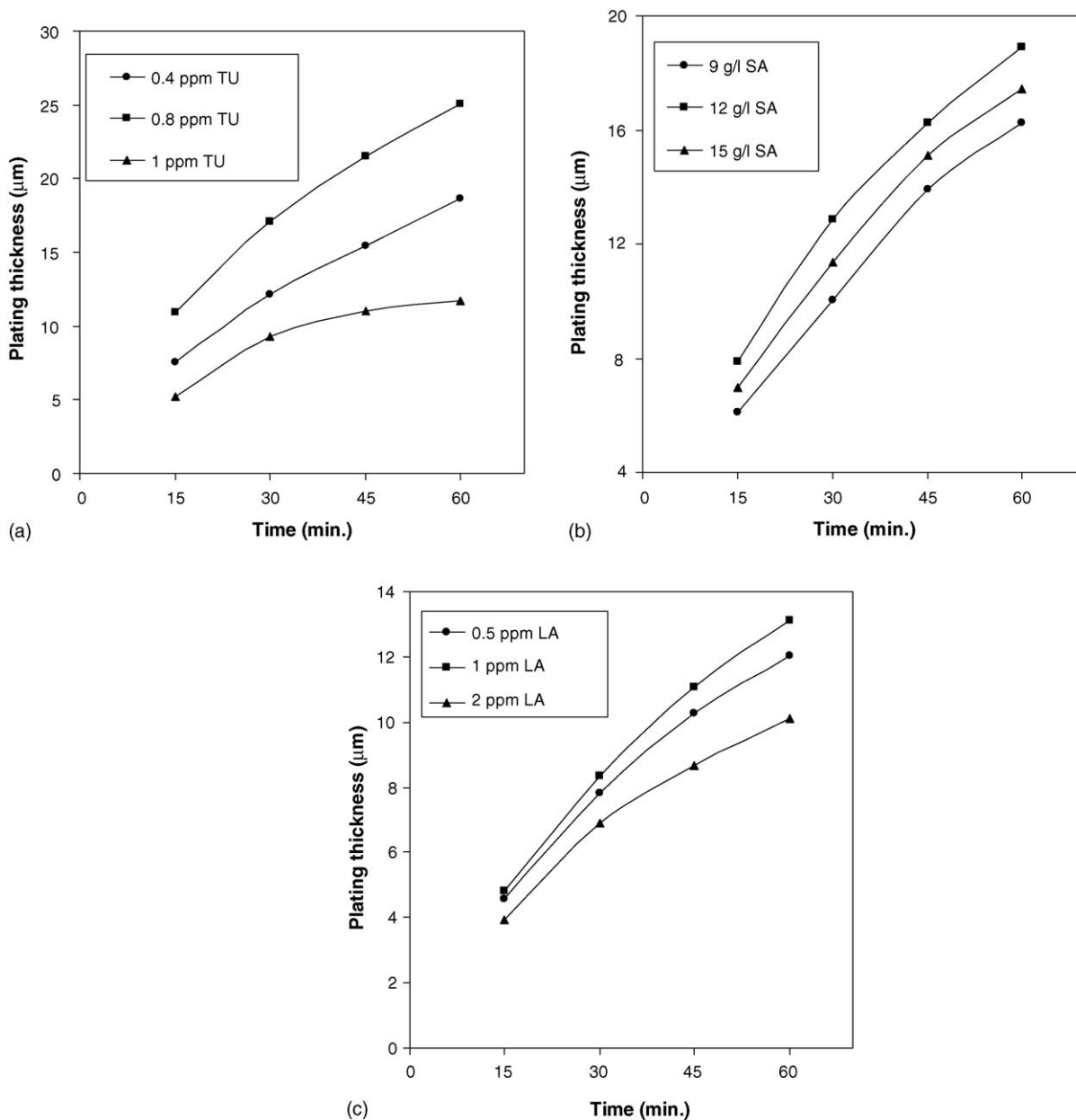


Fig. 2. Variation in plating thickness as a function of the concentration of the additives, (a) thiourea; (b) succinic acid; (c) lead acetate.

two-step oxidation reaction of thiourea facilitates the transfer of electrons to the nickel ions and enables acceleration of the plating rate. The formamidine disulphide is subsequently reduced by hypophosphite and regenerates thiourea. This mechanism explains the increase in plating rate at lower concentrations of thiourea (0.4–0.8 ppm) but could not explain the decrease in plating rate at higher concentrations of thiourea (≥ 1 ppm). Hence it is evident that other competing mechanisms might also influence the deposition of electroless Ni–P coatings in presence of thiourea. The possibility of complex formation between thiourea and nickel ion, which leads to the reduction of free nickel ion concentration and a decrease in plating rate is ruled out because the partial cathodic polarization curves show that thiourea has no effect on the reduction of nickel in the absence of hypophosphite [38]. However, the partial anodic polarization curves show

that thiourea inhibits the oxidation of hypophosphite. Hence a mechanism based on the adsorption of thiourea might be operative. Accordingly, adsorption of thiourea on the catalytic sites of the metal surface hinders the access of the hypophosphite ions, thus inhibiting the oxidation of hypophosphite or the production of atomic hydrogen, which would affect the hydrogen evolution and nickel deposition reactions simultaneously. Being a soft base [39], thiourea can exert a strong interaction with the metal surface (a soft acid) leading to a strong adsorption of thiourea on the catalytic metal surface via the sulphur atom, which is the most polarizable atom and has the lowest electronegativity. When the concentration of thiourea exceeds a critical level, its adsorption tends to impede the deposition of electroless Ni–P coating. Hence the enhancement of the nickel deposition at low thiourea concentration of the order of 0.4–0.8 ppm is due to the

participation of thiourea in the formation of the reactive intermediate that facilitates the oxidation of hypophosphite anion, thus accelerating the deposition of Ni–P coating [35]. The decrease in deposition rate at higher concentrations (≥ 1 ppm), is due to reduction in the number of catalytic sites on the metal surface due to the formation of a thin film of adsorbed thiourea on the top of the catalytic surface [38]. While both opposing factors contribute to the deposition rate throughout the entire concentration range, the experimental results suggest that the oxidation of hypophosphite ion is dominant at a lower thiourea concentration while the reduction in the catalytic sites becomes dominant when the concentration exceeds 1 ppm.

Addition of succinic acid increases the plating rate up to 12 g l^{-1} , beyond which there is a decrease in the plating rate. Succinic acid, a dibasic organic acid having much lower volatility than acetic and propionic acids, performs the role of a buffer and a complexing agent in the electroless nickel-plating bath. Besides it also exerts an accelerating or inhibitive effect depending on concentration [26,29]. According to the atomic hydrogen theory of electroless nickel-plating [40], tetrahedral hypophosphite is adsorbed on the catalytic metal surface, and, because catalytic metal has strong adsorption ability for hydrogen, the hydrogen atom of P–H bond locates on the metal surface. Due to the higher electronegativity of the oxygen atom, the phosphorus atom is positively charged. Consequently, under the direct attack of hydroxide ions, the cleavage of the P–H bond happened to produce a hydrogen atom at the catalytic sites, which results in the subsequent hydrogen evolution and nickel deposition. Succinic acid enables loosening of the bond between hydrogen and phosphorus atoms in the hypophosphite molecule, allowing it to be more easily removed and adsorbed on to the substrate surface. The decrease in plating rate at concentration higher than 12 g l^{-1} is due to the complexing nature of succinic acid, which decreases the free nickel ions.

Addition of lead acetate is found to inhibit the deposition of electroless Ni–P coatings at all concentrations in the range of 0.5 and 2.0 ppm; the extent of inhibition is high at concentrations higher than 1 ppm. Further increase in concentration of lead acetate, beyond 3 ppm, practically results in strong inhibition and eventual cession of the plating process. It has been established by electrochemical measurements that the anodic polarization curve was not affected by the addition of lead ions whereas they cause a shift in cathodic polarization curve towards the negative potential, suggesting that lead ions stabilize the bath by inhibiting the reduction reaction of nickel ions [16].

Though the effect of thiourea, lead acetate and succinic acid on the deposition of electroless Ni–P coatings have been studied earlier [14,16,19,21,26], the critical concentration at which these additives exhibit an accelerating or inhibiting effect vary much. It is understandable that the influence of these additives on the rate of deposition, coating composition and the characteristic properties of the coating is a function of the other constituents of the plating bath. Since the critical concentration of these additives is bath specific, it has to be evaluated carefully during bath formulation. Besides, the effect of these additives on the composition and characteristic properties also has to be evaluated.

The composition of the electroless Ni–P deposits obtained using baths A–D, evaluated by energy dispersive spectroscopy is given in Table 1. It is evident that the addition of lead acetate (bath D) due to its inhibiting effect on the cathodic reduction of nickel ions causes a relative increase in the phosphorus content of the coating, compared to that of bath A. In contrast, addition of thiourea (bath B) and succinic acid (bath C), due to their ability to increase the rate of deposition causes a decrease in the phosphorus content compared to that of bath A. Since the structure of electroless Ni–P coatings is dependent on the phosphorus content, it will be of interest to know how the variation in composition obtained in presence of these additives is going to influence the structure of the Ni–P coatings.

The X-ray diffraction patterns of electroless Ni–P coatings obtained from baths A–D in their as-plated conditions are depicted in Fig. 3(a–d). The diffraction pattern of electroless Ni–P coating obtained from bath ‘A’ exhibits a single broad peak centered at $44.5^\circ 2\theta$, indicating the amorphous nature of the coating. Amorphous nature precludes in electroless Ni–P when the phosphorus content of the deposits is higher than 7 wt.% [2]. Energy dispersive spectroscopic analysis of the phosphorus content of the electroless Ni–P coatings obtained from bath A confirms such a possibility (Table 1). The X-ray diffraction pattern of the Ni–P coating obtained from bath D (1 ppm lead acetate), though resembles the one obtained from bath A (no additive), the peak broadening suggests a greater tendency to form amorphous structure when lead acetate is used as the stabilizer. The increase in phosphorus content also supports this view (Table 1). However, for deposits obtained from thiourea and succinic acid containing baths (baths B and C), besides the reflection from Ni (1 1 1) plane, a weak reflection from Ni (2 0 0) plane is also observed. Hence it is evident that among the three types of additives, succinic acid and thiourea tend to promote the rate of reduction of nickel ions whereas lead acetate reduces the rate of reduction of nickel ions and hence results in deposits which are relatively more amorphous compared to those obtained from the other three baths. Lin and Hwang [14] have observed that increasing concentration of lead acetate from 0.25 to 3 ppm promotes amorphous nature of the coating whereas thiourea in the same concentration range enhances the crystallization of the electroless Ni–P coating. A single sharp Ni (1 1 1) peak is observed at 0.25 ppm of thiourea whereas both Ni (1 1 1) and Ni (2 0 0) peaks are observed when the concentration of thiourea is increased to 3 ppm.

The X-ray diffraction patterns of electroless Ni–P deposits obtained using baths A–D, after annealing at 400°C for 1 h, are shown in Fig. 4(a–d). In all the cases, the formation of fcc nickel and bct nickel phosphide (Ni_3P) phases is evident. The lattice parameter, cell volume, average crystallite size and the volume fraction of Ni_3P (2 3 1 plane) are given in Table 2. It is evident from Fig. 4(a–d) that Ni_3P (2 3 1) is the most intense reflection in all the four deposits, which is further supported by the volume fraction of Ni_3P (2 3 1) (Table 2).

The surface morphology of the electroless Ni–P coatings obtained using baths A–D is given in Fig. 5(a–d). Coatings obtained using bath B and bath C exhibit a nodular feature with a typical cauliflower like structure (shown at the inset of

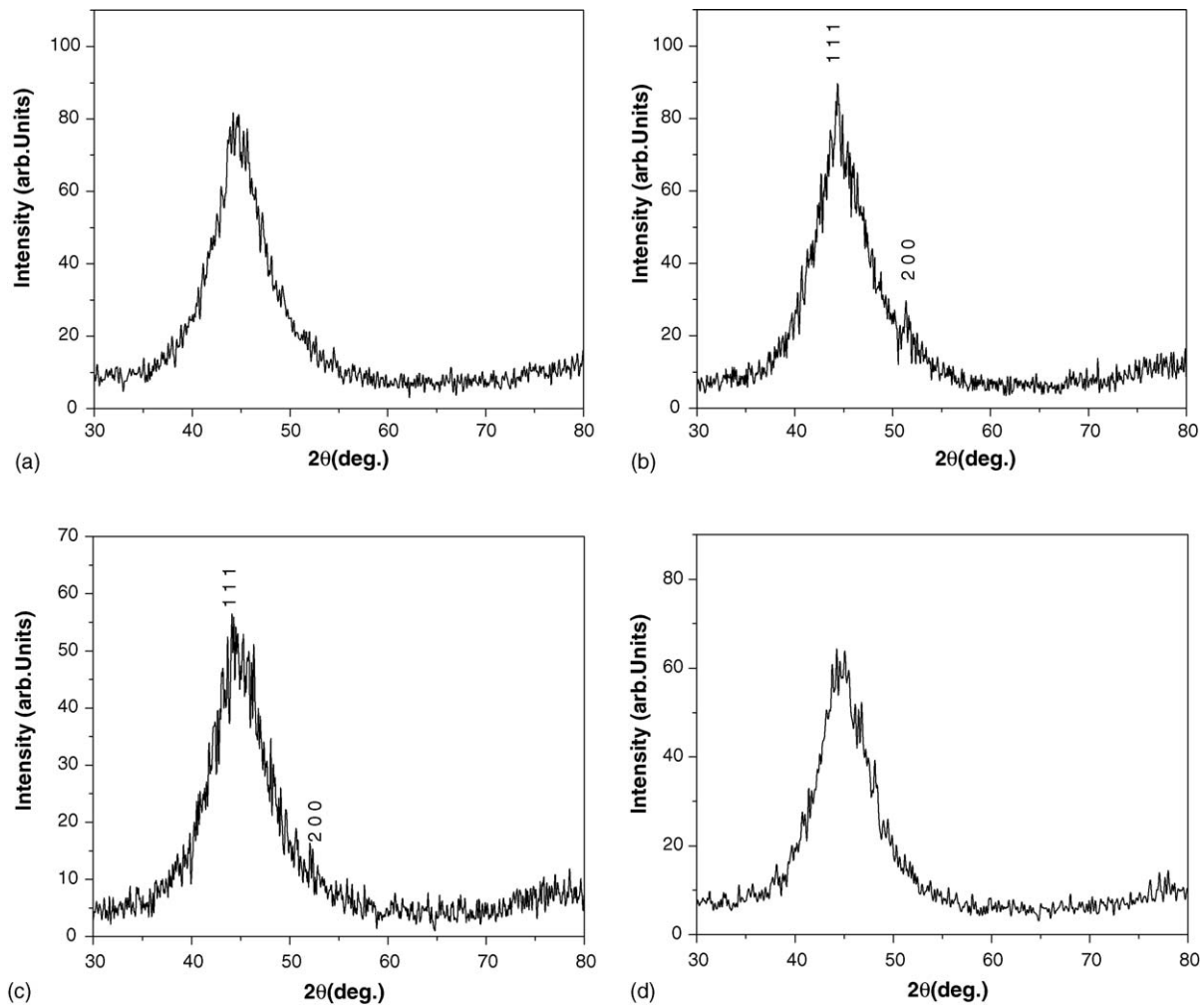


Fig. 3. X-ray diffraction pattern of electroless Ni–P coatings obtained using baths A–D in as-plated condition, bath A (no additive); bath B (0.8 ppm thiourea); bath C (12 g l^{-1} succinic acid); bath D (1 ppm lead acetate).

Fig. 5(b)); the size of the nodules is relatively less in the latter case. Although nodule formation is a common feature of electroless Ni–P coating, the rapid formation of nuclei and subsequent growth of the Ni–P deposit promotes the nodular feature in coatings obtained in presence of thiourea and succinic acid. The plating rate obtained in presence of these additives also supports this view. The nodules grew preferentially in the Z-direction than the X and Y directions due to the fast supply atoms. The surface diffusion of adatoms could also be inhibited to a certain extent by the rapidly arriving atoms. In contrast, the electroless Ni–P coating obtained using baths A and D are relatively smooth. However, the deposits obtained using bath ‘A’

reveal the presence of fine particulates, which could be attributed to the precipitation of Ni_3P phases in the absence of stabilizers. Das and Chin [16] have suggested that the electroless Ni–P coatings had a spherical nodular structure both in presence and absence of stabilizers viz., Pb^{2+} , IO_3^- , maleic acid and mercapto benzothiazole and, the nodule size is relatively less when lead and iodate ions were used as stabilizers. Lin and Hwang [14] and Chenong et al. [19] have also confirmed that the electroless Ni–P coatings obtained in presence of lead acetate as additive are very smooth. The precipitation of Ni_3P particulates along with the Ni–P deposit is also reported earlier by Chenong et al. [19].

Table 2

Grain size, lattice constant, cell volume and volume fraction of metastable tetragonal Ni_3P phase of electroless Ni–P deposits annealed at 400°C for 1 h

Bath Used	Grain size (nm)		Lattice parameter (\AA)		Cell volume (\AA^3)		Volume fraction of Ni_3P phase (%)
	Ni	Ni_3P	Ni (fcc) $a=b=c$	Ni_3P (bct) c/a	Ni	Ni_3P	
Bath A	24	27	3.526(3)	0.581(2)	43.84	377.16	64.1
Bath B	27	43	3.517(4)	0.574(3)	43.53	370.29	70.4
Bath C	33	44	3.529(6)	0.578(3)	43.96	376.65	71.3
Bath D	42	19	3.542(2)	0.587(3)	44.07	378.68	72.2

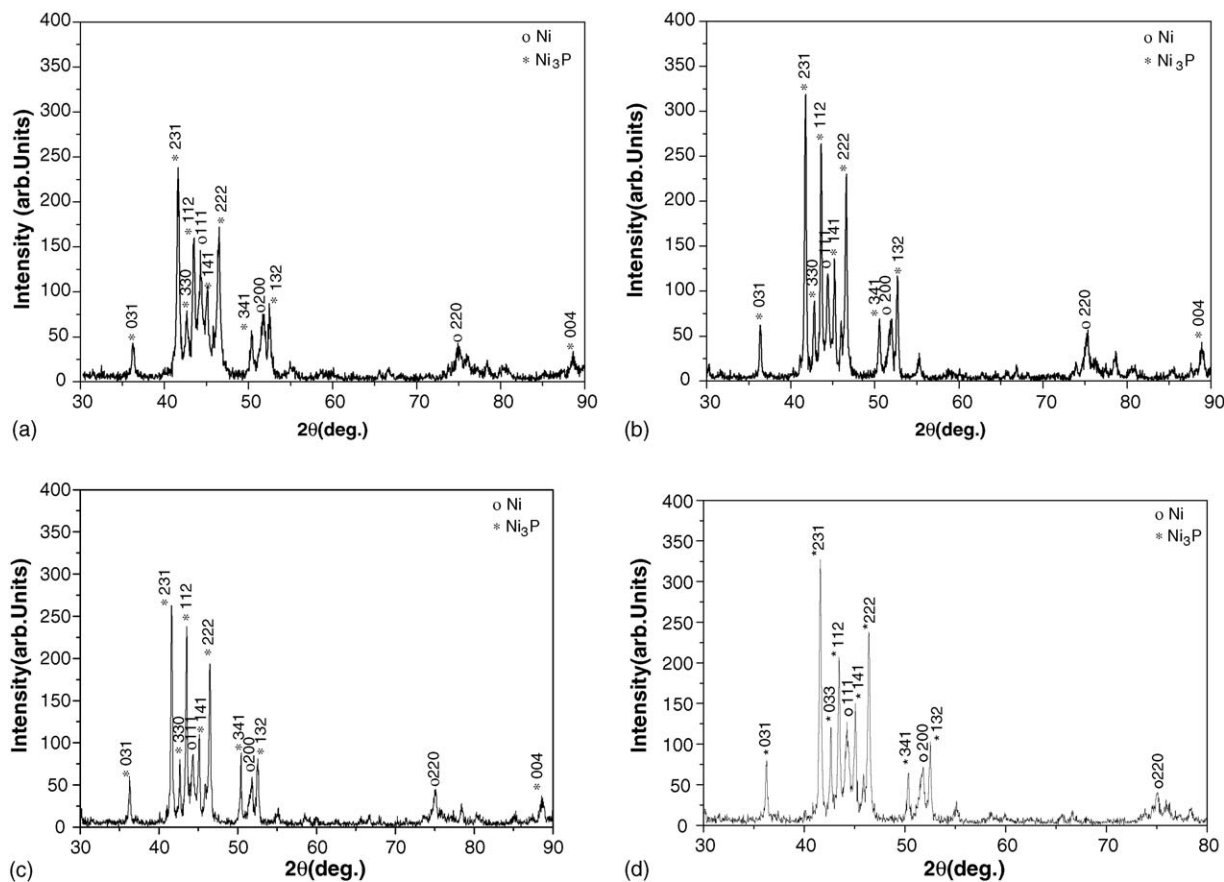


Fig. 4. X-ray diffraction pattern of electroless Ni–P coatings obtained using baths A–D after heat-treatment at 400 °C for 1 h bath A (no additive); bath B (0.8 ppm thiourea); bath C (12 g l⁻¹ succinic acid); bath D (1 ppm lead acetate).

The other possible effects that could influence the surface morphology of the electroless Ni–P coating is the adsorption of certain ions on the growing crystal faces [41] and the laterally limited Ni–P layer growth due to such adsorption phenomenon [42]. Macheras et al. [41] have claimed that the hydrogenolysis of the C–S and S=O bonds produces sulphur anions, which inhibit the crystal growth in a particular direction. They have attributed the predominance of the [1 0 0] texture in their electroless nickel deposit to the specific adsorption of the sulphur anions on the [1 1 0] crystallographic direction leading to a suppression of growth in this plane [41]. Hence when thiourea is used as the stabilizer in electroless nickel-plating bath, the sulphur anions might influence an orientation-specific adsorption that favors the crystal growth of a particular orientation and results in an increased formation of larger crystals. Salvago et al. [43] have reported that the thio-derived stabilizer, MBTA, promotes a columnar cauliflower like morphology instead of stratified layer type morphology. Cheong et al. [19] have also observed a similar columnar cauliflower like morphology when thiourea was used as the stabilizer at concentrations higher than 2 ppm. This is due to the fact that the Ni–P layer growth is laterally limited due to the presence of stabilizers, resulting in a columnar form of Ni–P deposit.

Electroless Ni–P coatings undergo phase transformation upon heat-treatment, which is best characterized by differential

scanning calorimetry. It has been established that the number of exothermic peaks and the temperature range at which they occur is sensitive to the phosphorus content of the electroless Ni–P coating. Since the phosphorus content of the electroless Ni–P coatings obtained using baths A–D varies slightly, it will be of interest to know how far this will influence the phase transformation behaviour of the coating. Fig. 6 depicts the DSC trace of electroless Ni–P coating obtained using bath A (no additive) in the temperature range from 200 to 500 °C at heating rate of 10 °C per minute. The DSC thermogram exhibit a single well-defined exothermic peak at a temperature of 344 ± 1 °C in the temperature range studied. This exothermic peak can be attributed to the precipitation of metallic nickel phase and formation of nickel phosphide (Ni₃P) phase. XRD patterns of Ni–P coatings heat-treated at 400 °C for 1 hour ascertain the formation of nickel and nickel phosphide phases (Fig. 4(a)). The exothermic peak gives a measure of the heat liberated during the transition from an amorphous to crystalline structure. The crystallization occurs over a narrow temperature range of 329–356 °C and the energy evolved during the exothermic transition, which is comparable to the values obtained for similar deposits reported elsewhere [44–48].

The DSC traces of electroless Ni–P coatings obtained from baths B–D, under similar experimental conditions, also exhibit a single well-defined exothermic peak in the temperature range

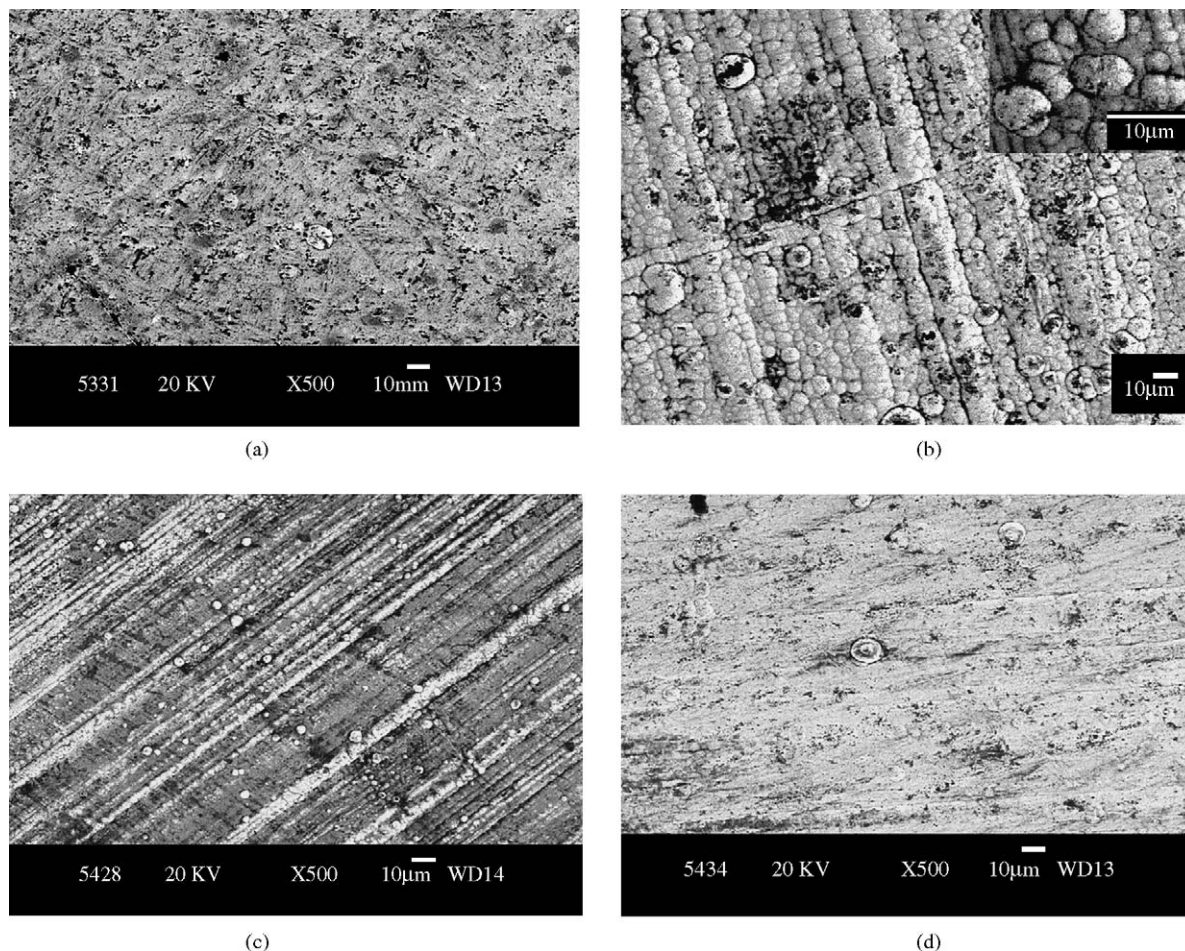


Fig. 5. Surface morphology of the electroless Ni–P coatings obtained using baths A–D after heat-treatment at 400 °C for 1 h bath A (no additive); bath B (0.8 ppm thiourea); (inset: morphology at higher magnification) bath C (12 g l⁻¹ succinic acid); bath D (1 ppm lead acetate).

studied, which could again be attributed to the precipitation of metallic nickel phase and formation of nickel phosphide (Ni₃P) phase, confirmed by XRD measurements (Fig. 4(b–d)). The peak temperatures and ΔH values calculated for these coatings are presented in Table 3. From Table 3, it is evident that there is a slight variation in the peak temperature and the energy

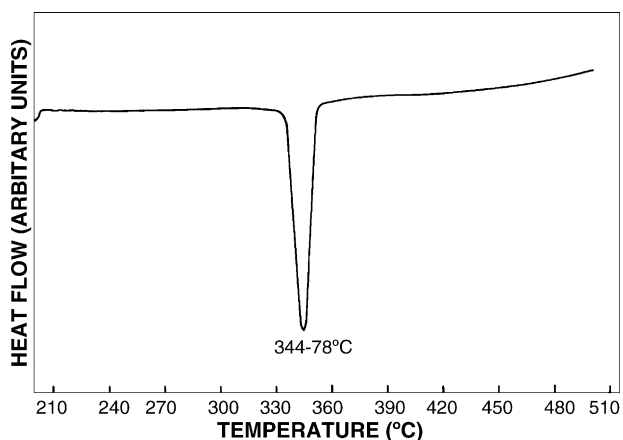


Fig. 6. DSC trace of electroless Ni–P coating obtained using bath A.

Table 3

Temperature range, onset temperature, peak temperatures and ΔH values of electroless Ni–P coatings obtained using baths A–D

Bath used	Peak temperature (°C)	ΔH (J g ⁻¹)
Bath A	344.78	-90.15
Bath B	350.57	-78.10
Bath C	349.27	-84.20
Bath D	343.07	-98.13

evolved during the phase transition compared to the Ni–P coating obtained using bath A. It has been reported earlier that the exact position of the exothermic peak and the energy evolved during phase transition are very sensitive to the phosphorus content of the electroless Ni–P coating. It is valid to conclude that the observed variation in peak temperature and the energy evolved during phase transition is due to the difference in the phosphorus content caused by the addition of thiourea, succinic acid and lead acetate.

4. Conclusions

The effect of thiourea, succinic acid and lead acetate on the formation and characteristics of electroless Ni–P deposits

obtained from an acidic hyposphosphite reduced electroless nickel bath is studied in this paper. The study reveals that the rate of deposition of electroless Ni–P coating is a function of concentration of these additives. Thiourea accelerates the rate of deposition up to 0.8 ppm and started to inhibit at a concentration of 1 ppm. Similar observation is also observed when succinic acid is used as the additive; increase in plating rate up to 12 g l^{-1} and inhibition at higher concentrations of the order of 15 g l^{-1} . Addition of lead acetate inhibits the rate of deposition even at a concentration of 0.5 ppm and the extent of inhibition is increased when the concentration is higher than 1 ppm. Addition of lead acetate (1 ppm) causes a relative increase in the phosphorus content of the coating whereas addition of thiourea (0.8 ppm) and succinic acid (12 g l^{-1}) causes a decrease in the phosphorus content, compared to that obtained from the bath without any additive. The X-ray diffraction patterns of electroless Ni–P coatings obtained from bath A (without additive) and bath D (1 ppm of lead acetate) exhibit a single broad peak centered at $44.5^\circ 2\theta$, indicating the amorphous nature of these coatings. The peak broadening suggests a greater tendency to form amorphous structure when lead acetate is used as the stabilizer. In contrast, for electroless Ni–P coatings obtained from thiourea and succinic acid containing baths (baths B and C), besides the reflection from Ni (1 1 1) plane, a weak reflection from Ni (2 0 0) plane is also observed. The X-ray diffraction patterns of electroless Ni–P coatings after annealing at 400°C for 1 h exhibit the formation of fcc nickel and bct nickel phosphide (Ni_3P) phases in all the cases with Ni_3P (2 3 1) as the most intense reflection. Electroless Ni–P coatings obtained in presence of thiourea (bath B) and succinic acid (bath C) exhibit a nodular feature with a typical cauliflower like structure due to the rapid formation of nuclei and subsequent growth of the Ni–P deposit. The size of the nodules is relatively less in the latter case. In contrast, the electroless Ni–P coating obtained using baths A and D are relatively smooth. However, the deposits obtained using bath ‘A’ reveal the presence of fine particulates, which could be attributed to the precipitation of Ni_3P phases in the absence of stabilizers. The DSC traces of electroless Ni–P coatings obtained from baths A–D, exhibit a single well-defined exothermic peak, which could again be attributed to the precipitation of metallic nickel phase and formation of nickel phosphide (Ni_3P) phase. The variation in the peak temperature and the energy evolved during the phase transition is due to the slight variation in the phosphorus content caused by the addition of thiourea, succinic acid and lead acetate. Since the addition of lead acetate/succinic acid/thiourea significantly influence the plating rate and surface morphology and to some extent the composition, structural and thermal characteristics, it is recommended that the choice of accelerators and stabilizers should be made only after a careful study.

Acknowledgements

The authors express their sincere thanks to Prof. S.P. Meharotra, Director, National Metallurgical Laboratory, Jamshedpur and Dr. S. Srikanth, Scientist-in-Charge, NML Madras Centre, Chennai, for their constant support and encouragement to

carry out this research work. The authors also thank Prof. P.R. Subramanian, Head, Department of Nuclear Physics, University of Madras, Chennai-25, for his support and encouragement. This work is supported by UGC-SAP program of Department of Nuclear Physics, University of Madras, Chennai.

References

- [1] A. Brenner, G.E. Riddell, *J. Res. Natl. Bureau Standards* 37 (46) (1946) 31.
- [2] G.O. Mallory, J.B. Hajdu, *Electroless Plating*, American Electroplaters and Surface Finishing Society, Norwich, New York, 1996.
- [3] M. Schlesinger, *Electroless Deposition of Nickel*, John Wiley & Sons Inc., Canada, 2000, p. 667.
- [4] K. Parker, *Plat. Surf. Finish.* 79 (3) (1992) 31.
- [5] K.G. Keong, W. Sha, S. Malinov, *J. Alloys Compd.* 334 (2002) 192.
- [6] G. Salvago, P.L. Cavallotti, *Plating* 57 (1972) 665.
- [7] J.E.A.M. Van Den Meerakker, *J. Appl. Electrochem.* 11 (3) (1981) 395.
- [8] M. Schlesinger, in: M. Schlesinger, M. Paunovic (Eds.), *Modern Electroplating*, 4th ed., John Wiley & Sons, Inc., New York, 2000 (Chapter 18).
- [9] K. Chen, Y. Chen, *Plat. Surf. Finish.* 84 (1997) 80.
- [10] G.O. Mallory, J.B. Hajdu, *Electroless Plating*, American Electroplaters and Surface Finishing Society, Norwich, New York, 1996.
- [11] M. Schlesinger, *Electroless Deposition of Nickel*, John Wiley & Sons Inc., Canada, 2000, p. 667.
- [12] N. Feldstein, D.J. Lindsay, US Patent 5,863,616 (1999).
- [13] N. Feldstein, P.R. Amodio, *J. Electrochem. Soc.* 117 (1970) 1110.
- [14] K.L. Lin, J.-W. Hwang, *Mater. Chem. Phys.* 76 (2002) 204.
- [15] J. Kivel, J.S. Sallo, *J. Electrochem. Soc.* 112 (1965) 1201.
- [16] L. Das, D.T. Chin, *Plat. Surf. Finish.* 83 (8) (1996) 55.
- [17] I.V. Petukhov, M.G. Shcherban, *Prot. Met.* 35 (6) (1999) 566.
- [18] E. Lanzoni, C. Martini, R. Ruggeri, R. Bertonecello, A. Glisenti, *European Federation of Corrosion Publications*, 1997, p. 232.
- [19] W.J. Cheong, B.L. Luan, D.W. Shoosmith, *Appl. Surf. Sci.* 229 (2004) 282.
- [20] C.H. de Minjer, A. Brenner, US Patent 2,929,742 (1973).
- [21] H. Xu, J. Brito, O.A. Sadik, *J. Electrochem. Soc.* 150 (1) (2003) C816.
- [22] K.P. Han, J.L. Fang, *Met. Finish.* 95 (2) (1997) 73.
- [23] G. Gutzeit, *Plating* 47 (1960) 63.
- [24] J.L. Fang, *Chemistry* 4 (1978) 226.
- [25] R. Ambat, W. Zhou, *Surf. Coat.* 179 (2004) 124.
- [26] K.P. Han, W. Yong, Z. Min, W. Jianhong, *Trans. IMF* 74 (3) (1996) 91.
- [27] K.P. Han, J.L. Fang, *J. Appl. Electrochem.* 26 (1996) 1273.
- [28] J.F. Fang, Y. Wu, K.P. Han, *Plat. Surf. Finish.* 84 (1997) 91.
- [29] K. Parker, *Plat. Surf. Finish.* 74 (1987) 60.
- [30] P.N.N. Namboodiri, K.V. Prasad, P.B. Mathur, *Trans. SAEST* 7 (1972) 122.
- [31] G. Gabrielly, F. Raulin, *J. Appl. Electrochem.* 1 (1971) 167.
- [32] P. Talmey, G. Gutzeit, US Patent 2,762,723 (1956).
- [33] C.H. de Minjer, A. Brenner, *Plating* 44 (1957) 1297.
- [34] J.S. Sallo, J. Kivel, F.C. Alberts, *J. Electrochem. Soc.* 110 (1963) 890.
- [35] K.-P. Han, J.-L. Fang, *Int. J. Chem. Kinet.* 28 (4) (1996) 259.
- [36] S. Reddy, J. Krishnan, *J. Electroanal. Chem.* 27 (1970) 473.
- [37] S. Saka, D.J. Greenslade, *Bull. Chem. Soc. Jpn.* 65 (1992) 2720.
- [38] K.A. Holbrook, P.J. Twist, *Plating* 56 (1969) 523.
- [39] R.G. Pearson, *J. Chem. Edu.* 45 (1968) 581.
- [40] R.M. Lukes, *Plating* 51 (1964) 69.

- [41] J. Macheras, D. Vouros, C. Kollia, N. Spyrellis, *Trans. Inst. Met. Finish.* 74 (2) (1996) 55.
- [42] K. Azumi, T. Yugiri, T. Kurihara, M. Seo, H. Habazaki, S. Fujimoto, *J. Electrochem. Soc.* 150 (2003) C461.
- [43] G. Salvago, D. Sinigaglia, G. Fumagalli, D. Continenza, G. Taccani, *Proceedings of the INTERFINISH 80*, 1980.
- [44] M.W. Mahoney, P.J. Dynes, *Scripta Metallurg.* 19 (1985) 539.
- [45] J.N. Balaraju, T.S.N. Sankara Narayanan, S.K. Seshadri, *Mater Res. Bull.*, in press.
- [46] R.M. Allen, J.B. Vander Sande, *Scripta Metallurg.* 16 (1982) 1161.
- [47] K.-H. Hur, J.-H. Jeong, D.N. Lee, *J. Mater. Sci.* 25 (1990) 2573.
- [48] K.S. Rajam, S.R. Indira Rajagopal, B. Rajagopalan, Viswanathan, *Mater. Chem. Phys.* 33 (1993) 289.