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Contributed Paper

# Influence of Bath Formulations on Low-Temperature Electroless Deposition of Ni-P Alloys

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## ABSTRACT

The influence of the concentrations of a metal source, a reducing agent, and hydrogen ions on the electroless deposition of Ni-P alloys is investigated at a relatively low deposition temperature of 65$^{o}$C. Hypophosphite and pH are determined to be the main controllers of the deposition rate. Decent bath stability and a fair deposition rate of ~20 ìm/hr, comparable to that obtained under the typical deposition temperature of ~85$^{o}$C, are achievable by maintaining the nickel sulfate/sodium hypophosphite concentration ratio at ~0.4. A moderately high sodium hypophosphite concentration of 0.38 M and a high pH of 9 and above are required. The empirical kinetics equations of the electroless nickel deposition are discussed and developed.

**Keywords:** electroless plating, nickel-phosphorus alloys, bath formulation, deposition characteristic

## 1. INTRODUCTION

Electroless deposition has been widely employed for productions of metallic coatings, as the technique provides high coating uniformity, even for intricate parts. For deposition, surface-cleaned articles can simply be submerged into a temperature-controlled electrolytic bath, where redox reactions take place, for some specified durations. With their high hardness and excellent thermal conductivity, electrolessly-deposited nickel alloys, including Ni-P and Ni-B, receive relatively high attentions for use in both the electronic and tooling applications [1-3]. Furthermore, these Ni-based coatings exhibit relatively high corrosion resistance [4-7], and their mechanical and corrosion properties can be further enhanced by subsequent heat treatment processes [5-6, 8-9].

Nevertheless, the electroless deposition of Ni-based alloys, which is typically performed at a temperature of ~85$^{o}$C, suffers from relatively low deposition rates, low chemical stability, and high energy cost. Compared to the typical rate of deposition of Ni of ~30 mm/hr obtained from a 60$^{o}$C electrodeposition Watt's bath [10] and the deposition rate of 50 mm/hr of electrodeposited Ni-B from a 50$^{o}$C sulphamate bath [11], the relatively slow deposition rate of electrolessly-deposited Ni-P of below 20 mm/hr [6, 12-14] results in somewhat long processing time and hence contributes to higher production cost. Attempts have been made in the recent past to develop a suitable approach to improve the kinetics of the electroless deposition. For example, as demonstrated by I. Baskaran et al., the high deposition rate of ~90°C coupled with an accelerator and a stabilizer in a bath can boost electroless-deposition rate to about 25 mm/hr [14]. Similarly, W. L. Liu et al. show that the high deposition temperature of ~90°C can enhance the deposition rate of Ni-P to as much as 30 mm/hr [15]. This however may prompt bath stability to quickly downgrade, owing to rapid precipitation of nickel compound particles, such as nickel phosphide or nickel boride [16]. Often, the turnover rate, defined as the number of achievable deposition rounds above which the electroless solution become unstable, could be as low as 4-8 [16-17]. On the other hand, K.M. Shartal and G.J. Kipouros investigated the electroless deposition of Ni-based alloys at relatively low temperatures in the range of 35-75°C, where bath stability and energy cost reduction can be well-achieved [13]. However, these were compromised by low deposition rates of 4-16 mm/hr.

Therefore, it is critical to achieve a high deposition rate while maintaining decent bath stability. In the present work, we extend the prior studies in this subject and systematically investigate the influence of process variables of the alkaline Ni-P electroless deposition, including bath compositions and pH levels, at a relatively low bath temperature of 65°C. The deposition rates of the materials are analyzed in relation to the deposits' microstructure and bath stability. From the investigation, the understanding on the relationships between the process variables and the deposition rate is obtained, and thus provides important basis for the improvement of low-temperature electroless nickel alloy depositions.

## 2. MATERIALS AND METHODS

A series of Ni-P electroless depositions were conducted with different concentrations of a metal source, a reducing agent, and pH levels in the electrolytes. For all cases, an AISI SS400 steel plate (C 0.151%wt, Si 0.00502%wt, Mn 0.452%wt, P 0.00463%wt, Cr 0.0652% wt, balance Fe) of the size 4 x 2 x 0.2 $cm^3$ was used as a substrate. Prior to deposition, the surfaces of the steel articles were cleaned and prepared by a typical procedure [18-19]. This included polishing with 180-grit SiC paper, ultrasonic cleanning, degreasing in 10 wt.% NaOH at 60°C for 10 mins, and acid pickling in 14 wt.% HCl for another 20 mins. Subsequently, to proceed with deposition, the steel articles were immersed in an electroless bath, following the common procedure [20]. Table 1 shows the formulations of the Ni-P electroless bath (300 cc) under study. Nickel sulfate ($NiSO_4.6H_2O$) and sodium hypophosphite ($NaH_2PO_2.H_2O$)'s concentrations were varied from 0.08-0.60 M and 0.08-0.76M, respectively using a bath pH of 9. Additionally, pH, as adjusted by NaOH, was varied from 8-11 for the electrolytes with 0.15 M $NiSO_4.6H_2O$ and 0.38 M $NaH_2PO_2.H_2O$. In each case, the deposition was conducted at the low temperature of 65 °C for 20 mins. On a separate study, the stability test was performed by conducting the electroless deposition using some selected bath formulations for a longer period up to 24 hours. The formation of precipitations in the baths was closely observed.

The microstructure and compositions of the electroless deposits was then characterized by a scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS) (Hitachi S-3400, 20 kV). These two techniques provide the microstructure and the composition of the deposits, respectively. All specimens were etched with 1% Nital prior to the examination. For each specimen, the EDS measurements were conducted at 3 regions across the deposits' surface, and the average contents of phosphorus were reported. The deposition rates were determined from the average coating thickness divided by the deposition duration. The former was determined from the specimens cross-sections captured by a polarized optical microscope, and 30 measurements were made in each specimen. The obtained deposition rates were then analyzed in relation to the deposition mechanism and process variables.

## 3. RESULTS AND DISCUSSION

### 3.1 The Deposits' Characteristics

A uniform coating was obtained for all sets of the electroless deposition under investigation. The microscopy reveals that the microstructure of the deposits is generally comprised of arrays of nodular cauliflower like structure, as shown by representative micrographs in Figures. 1 a-b and Figures 2 a-b. Larger coverage along with wider and smoother arrays of the nodular structure are generally observed in deposits with relatively high deposition rates (Figure. 1b and 2b), as to be further discussed in the subsequent section. In contrast, those with relatively low deposition rates exhibit small arrays of nodular structure (Figure. 1a and 1b). Figure 3 shows that there are some small variations of the relative Ni and P contents among the deposits. Specifically, the relative P content was found to increase slightly with the metal source and reducing agent's concentrations. Increasing of

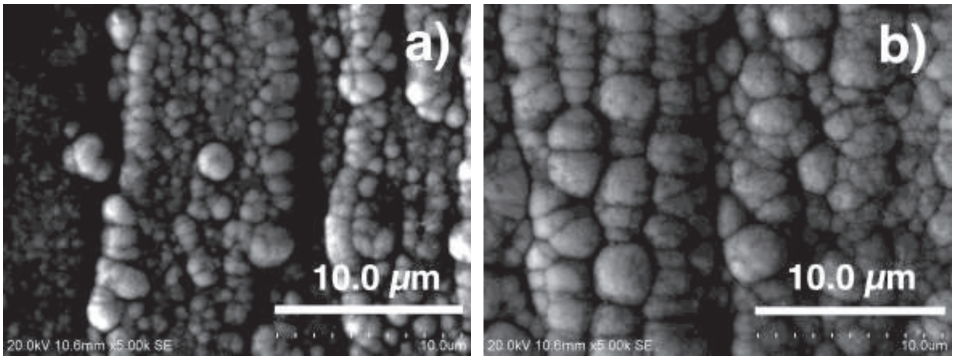

**Figure 1.** Micrographs showing surface morphology of Ni-P coatings deposited from baths containing 0.15 M $NiSO_4.6H_2O$ and pH 9 with $NaH_2PO_2.H_2O$ a) 0.08 mol. and b) 0.19 mol.

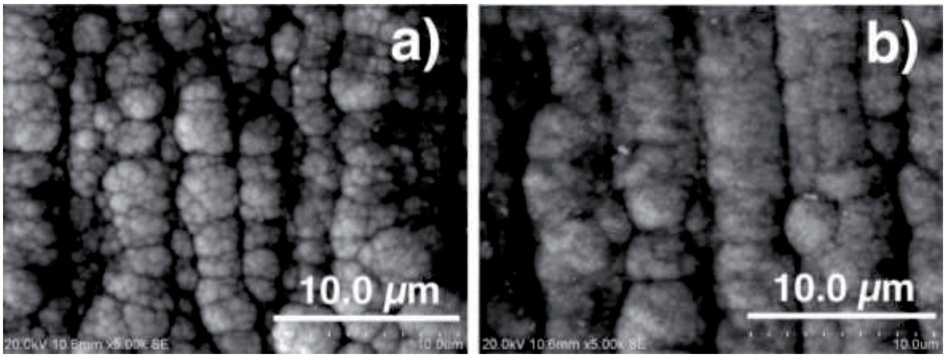

**Figure 2.** Micrographs showing surface morphology of Ni-P coatings deposited from baths containing 0.15 M $NiSO_4.6H_2O$ and 0.38 M $NaH_2PO_2.H_2O$ with a) pH 8 and b) pH 9.

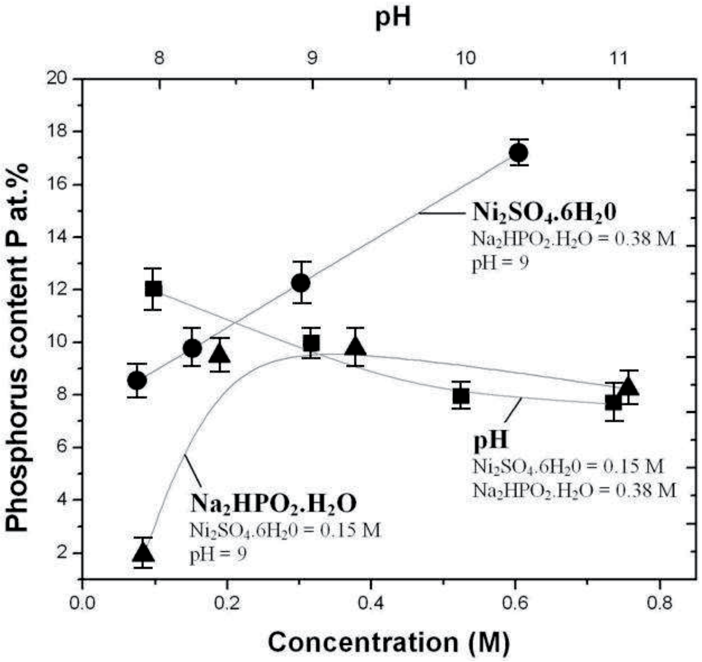

**Figure 3.** Relative phosphorus contents of the Ni-P electroless deposits with respect to the concentrations of nickel sulfate and sodium hypophosphite, and pH.

pH however resulted in a reduction of the P relative content, and also a small increased of nodular size, in parallel to prior observations [21-23] the results shown in Figure 2. Overall, the P content varies in the approximate range of 2 to 17 at.%.

### 3.2 Rate of Deposition

The deposition rate of Ni-P electroless deposition was measured as a function of the concentrations of sodium hypophosphite and nickel sulfate and pH levels of the baths, as shown in Figure 4. With an increase of the reducing agent's content, the deposition rate monotonically increases. On the other hand, the deposition rate increases with the nickel sulfate's concentration up to about 0.15 M, above which, the rate slightly reduces. When the deposition rate is plotted as a function of the ratio between sodium hypophosphite and nickel sulfate's concentrations (Figure 5), it is observed that the two curves, which respectively correspond to fixed concentrations of sodium hypophosphite and nickel sulfate, do not unite. This signifies that the deposition rate does not directly depend on the ratio between the two bath components. Furthermore, Figure 4 shows that the pH levels also critically affect the deposition rate. The more alkalinity the bath is, the higher the deposition rate. A drastic influence is observed when the pH is increased from 8 to 9.

The electroless deposition of Ni-P involves an oxidation reaction of hypophosphite ($H_2PO^{2-}$) and reductions of nickel, phosphorus, and hydrogen ions, according to Eqns. (1)-(3) [24].

$H_2PO^{2-} + H_2O$ à $H_2PO^{3-} + 2H$ (1)

$Ni^{2+} + 2H$ à $Ni + 2H^+$ (2)

$H_2PO^{2-} + H$ à $P + OH^- + H_2O$ (3)

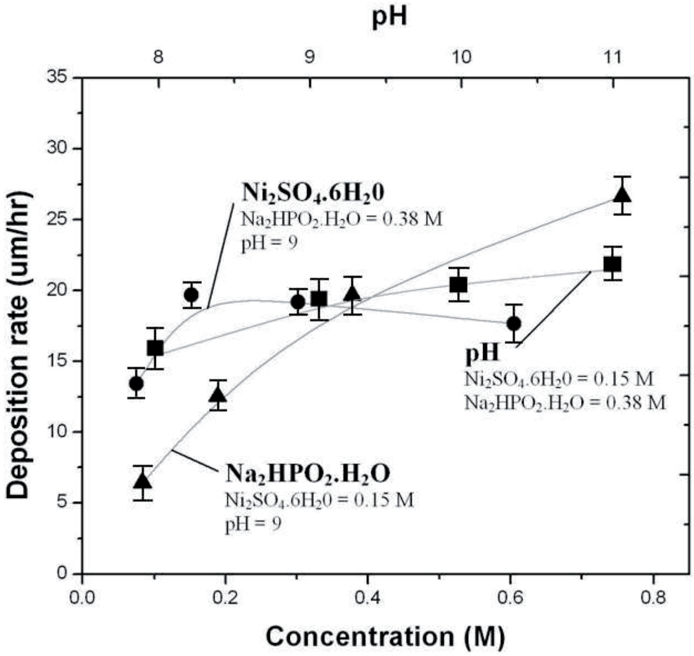

**Figure 4.** Deposition rates of the Ni-P electroless coatings with respect to the concentrations of nickel sulfate and sodium hypophosphite, and pH.

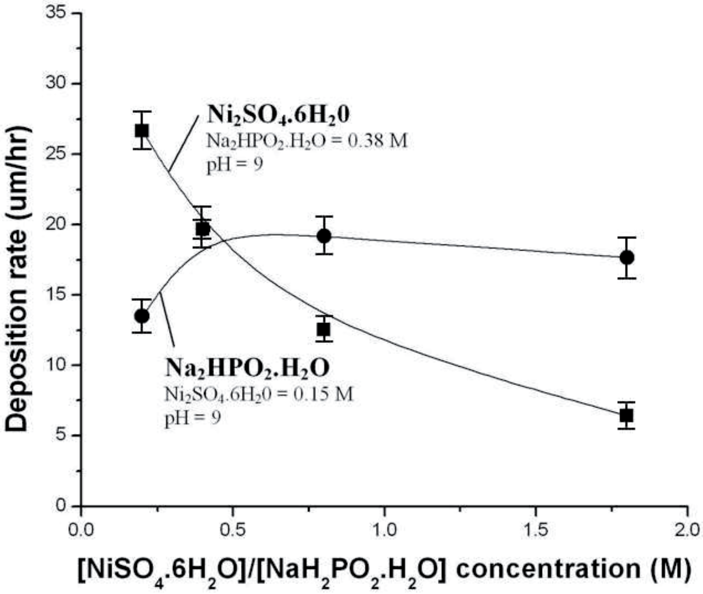

**Figure 5.** Deposition rates of the Ni-P electroless coatings with respect to the ratio of the concentrations of nickel sulfate and sodium hypophosphite..

According to the Mixed-Potential Theory [25] , the electroless deposition process occurs at the mixed potential ($E_{mp}$) with a respective current density that is influenced by the partial reactions, e.g., Eqns. (1)-(3). With no net accumulation of electric charge during an electrochemical reaction, the deposition current density, which directly dictates the rate of deposition, corresponds to the point at which current density of the anodic reaction equates that of the cathodic one. It is therefore comprehensible that the variables that affect the current-potential response of the partial reactions influence the rate of the electroless deposition.

Considering the oxidation reaction presented in Eqn. (1), by increasing the concentration of hypophosphite ions, the releasing amount of hydrogen, required for the reduction of nickel ions, is increased. This leads to the increment of the oxidation reaction's rate and hence of the rate of the overall reaction. Likewise, at a constant concentration of hypophosphite, an increase of free nickel ions available for reduction may induce an increase of the equilibrium potential of the partial reduction reaction. This leads to the increase of the rate of the reduction reaction and hence of the overall reaction. It appears that this influence only occurs up to a certain limit, after which the concentration of the hypophosphite ions may not be sufficiently supplied to interact with the nickel ions. According to Eqn. (2) of the partial reduction reaction, it can be expected that the concentration of H+, i.e., the pH level, plays a role in the deposition rate as well. Indeed, as observed from the experimental results, the deposition rate increases monotonically with a degree of alkalinity.

The empirical rate law for the electroless deposition under investigation may be expressed as follows:[13]

$$v = K_0[HPO_2^-]^{\alpha}[Ni^{2+}]^{\beta}[H^+]^{\gamma}\exp(-E_a/RT) =$$

$$K_1\,[HPO_2^-]^{\alpha}[Ni^{2+}]^{\beta}[H^+]^{\gamma}, \qquad (4)$$

where $v$ is the deposition rate (μm/hr); $K_0$ and $K_1$ are the rate constants; α, β and γ are the reaction orders; T is the temperature (K); $E_a$ is the activation energy. The reaction orders can be determined from the slopes of the log-log plots of the deposition rates versus the concentrations of nickel sulfate and sodium hypophosphite, and the solution's pH. Accordingly, α and γ are determined to be 0.65 and -0.04, respectively. β of 0.61 and -0.08 are found for conditions with relatively low and high concentrations of nickel sulfate, respectively (e.g., below and above 0.15 M $NiSO_4.6H_2O$, for 0.38 M $NaH_2PO_2.H_2O$). Finally, the rate constant $K_1$ can be calculated by extrapolating the lines in the plots described above to the point where the concentration of the bath components is unity. By reading the corresponding deposition rates from the coordinate and plugging in respective values of the concentrations shown in Table 1, the values of $K_1$ are determined to be 50.5 ìm/hr and 13.8 ìm/hr for the relatively low and high nickel sulfate concentrations, respectively. The empirical rate reactions of the electroless

**Table 1.** Formulation of the electroless Ni-P baths operated at $65^{o}$C.

| Chemical | Formula | Concentration |
|---|---|---|
| Nickel Sulfate | $NiSO_4.6H_2O$ | 0.08, 0.15, 0.30, 0.60 M |
| Sodium Hypophosphite | $NaH_2PO_2.H_2O$ | 0.08, 0.19, 0.38, 0.76 M |
| Tri-Sodium citrate | $Na_3C_6H_5O_7$ | 0.16 M |
| Ammonium Sulfate | $(NH_4)_2SO_4$ | 0.23 M |
| Thiourea | $SC(NH_2)_2$ | 0.8 ppm |
| pH | | 8, 9, 10, 11 |

deposition under study thus become:

$$v = 50.5\ [HPO_2^-]^{0.65}[Ni^{2+}]^{0.61}[H^+]^{-0.04} \quad \text{(relatively low } Ni^{2+} \text{ levels)} \qquad (5)$$

$$v = 13.8\ [HPO_2^-]^{0.65}[Ni^{2+}]^{-0.08}[H^+]^{-0.04} \quad \text{(relatively high } Ni^{2+} \text{ levels)} \qquad (6)$$

### 3.3 Baths' Stability

Three sets of bath formulations that yield relatively high deposition rates were investigated for bath stability at 65°C. These include electrolytes with moderate and high hypophosphite concentrations of 0.38M (electrolyte A) and 0.76M (electrolyte B) (both with 0.15 M $NiSO_4.6H_2O$, pH = 9), respectively, and that with high pH of 11 (electrolyte C) (0.15 M $NiSO_4.6H_2O$, 0.38 M $NaH_2PO_2.H_2O$).

With moderately high deposition rate of ~20 ìm/hr, electrolytes A and C were clear of precipitates following 24 hours of deposition. In contrast, after 7 hours, a trace of darkish precipitates, as shown in Figure 6, could be observed visually in electrolyte B which exhibits a high deposition rate of 27 ìm/hr. It has been noted that low bath stability is typically induced in the system with rapid deposition rate. During electroless deposition, orthophosphate ($HPO_3^{2-}$) and hydrogen ions accumulate in the solution and interfere with the reaction. These ultimately results in precipitation of nickel phosphide and nickel phosphate residues, which in turn may lead to spontaneous decomposition of the electrolyte [15, 21]. The bath stability study performed here therefore points to a limit of the hypophosphite concentration suitable for concurrently stable and high-rate deposition, and demonstrates that a somewhat stable bath with moderately fast deposition rate can be achieved at the low deposition temperature of 65°C.

## 4. CONCLUSIONS

Electroless deposition of Ni-P at the low temperature of 65°C was investigated with a focus on the influences of bath formulations on deposits' characteristics, deposition rates, and bath stability. Deposits with nodular cauliflower like surface morphology with relative phosphorus contents ranging from 2-17 at.% could be obtained at relatively low deposition temperature. In general, the morphology of the deposits with relatively high deposition rates exhibits relatively large and smooth arrays of the nodular structure. A relatively large content of phosphorus is usually associated with deposits of high deposition rates. Increasing the hypophosphite concentration and the pH in the electrolytes was found to strongly benefit the rate of deposition. The high deposition rate of almost 30 ìm/hr was achievable at a low $NiSO_4.6H_2O$ / $NaH_2PO_2.H_2O$ concentration

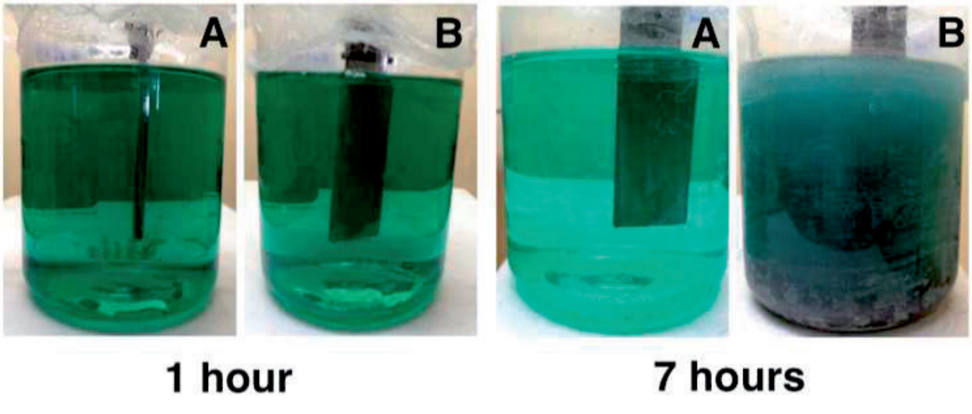

**Figure 6.** The results of baths' stability tests of electrolytes A and B following 1 and 7 hours.

ratio of 0.2 with a high $NaH_2PO_2.H_2O$ concentration of 0.76 M, although low bath stability was observed. The fair deposition rate of about 20 ìm/hr and decent bath stability could be obtained by maintaining the $NiSO_4.6H_2O$ / $NaH_2PO_2.H_2O$ concentration ratio at ~0.4 and using a moderately high $NaH_2PO_2.H_2O$ concentration of 0.38 M with pH of 9 and above. From the analysis of the empirical rate law, $NaH_2PO_2.H_2O$ was determined to be the main rate controller. Through a careful control of electroless bath formulations, the electroless deposition of Ni-P at 65$^o$C could therefore progress at the rates as high as that typically achieved under the normal operation temperature of ~85$^o$C. Nevertheless, it was evidenced that the high depositions rates could lead to baths' instability. In the following step of the research work, it is advised that an investigation of a method to control bath stability is pursued, so that the electroless deposition with relatively high deposition rates can be effectively employed.

## ACKNOWLEDGEMENT

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