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Effects of Surfactants in an Electroless Nickel-Plating Bath on the Properties of Ni–P Alloy Deposits

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Effects of added surfactants in the acidic hypophosphite plating baths on the properties of the resulting electroless nickel–phosphorus (Ni–P) deposits on the brass substrates were studied. The surface appearance and microstructures were examined under a reflective optical microscope and a scanning electron microscope equipped with an in situ energy-dispersive X-ray spectroscopy with which the phosphorus contents were measured. The deposition rate and the corrosion rate of the Ni–P deposits were estimated respectively from the weight gains and losses after a period of time. It is found that the addition of suitable amounts of surfactants can increase the deposition rate up to 25% and reduce the formation of the pores on the surface of Ni–P alloys, as well as enhance the corrosion resistance of the deposits. The corrosion rate of the Ni–P alloys in 10 wt % HCl was determined. The corresponding corrosion rate fits well as an empirical power function having an order of near $1/3$ in the amount of dissolved Ni–P deposits, equivalent to the concentration of nickel ions present in the acidic corrosive solution. The corrosion mechanism is discussed in line with the experimental discoveries.

1. Introduction

Electroless nickel coatings have been widely used in many applications,^{1,2} such as the aerospace industry, automotive productions, applications in the chemical processing industry as well as oil and gas production, medical and dental devices, military applications, and other applications where it is expected to provide good resistance to corrosion, oxidation, and wear.^{1,3} Nowadays electroless nickel plating has also even been attempted in nanofabrications in optics⁴ and in decoration on carbon nanotubes.⁵ Among various nickel alloys, the nickel–phosphorus (Ni–P) alloys containing high phosphorus content near 12% show very good fatigue resistance and near-zero tensile stress.¹ Despite the many studies that have been conducted to understand this technology, there are still some concerns affecting the performance of Ni–P.

One of the problems concerning end users of electroless Ni–P plating⁶ is micropitting on the nickel surface as a result of hydrogen evolution during the plating, while the other concern is the corrosion resistance, especially in the acidic corrosive environments.¹ Stirring the plating solution or rotating objects being plated can lessen the problem but cannot provide a satisfactory resolution for the problem. Incorporation of the surface-active compounds with suitable structures into a plating bath appears to be a promising remedy to diminish surface pinholes. This is because the hydrogen formed via coupling of the adsorbed hydrogen atoms has little chance, in the presence of surfactant molecules, to grow into bubbles on the plating frontier. The adsorption of tiny H_2 bubbles at the surface of a plated Ni–P deposit

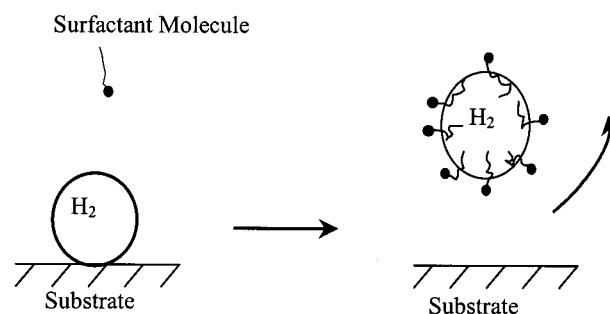


Figure 1. Schematic diagram showing the adsorption of surfactant molecules on the hydrogen bubble.

is regarded as the root cause of pinholes or pits. Because the electroless nickel-plating system involves a very complicated combination of several types of chemical reactions, the introduction of a surfactant into the plating system may affect these reactions in certain ways and lead to the pit-free nickel deposits.^{3,7,8} In principle, the surfactant molecules play a role in the removal of tiny hydrogen bubbles from the surface of the substrate through adsorption at the H_2 –liquid interface as illustrated in Figure 1. Hence, for those water-soluble surfactants that have relatively lower hydrophilic–lipophilic balance (HLB) values, a stronger capability of cleaning up H_2 bubbles from the Ni–P deposition frontier is anticipated.

Uniform and pit-free nickel deposits were achieved by adding 150 ppm of sodium dodecyl sulfate to the electroless nickel bath.³ Likewise, a very brief and similar conclusion was drawn by Hagiwara et al.⁷ as well, who studied the effect of three different surfactants added in the Ni–P electroless bath on the morphology of the resulting Ni–P particles. Still, no quantitative and systematically qualitative data on the effect of added surfactants on the deposition rates and the corrosion resistance of the electroless Ni–P deposits are available in the literature. Therefore, a systematic study

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on the effect of surfactants bound with the plating process is of great importance because it will help us gain an in-depth understanding of the special roles of surfactant molecules in the electroless nickel-plating system.

This paper attempts to establish a quantitative and qualitative relationship between the effect of surfactants and the surface properties of the Ni-P-plating layer obtained as well as the corrosion resistance of the resulting Ni-P deposits. The effect of surfactant is to be governed by the structure of the surfactant, the dosage of surfactant in an electroless nickel bath, and the combination of surfactant with other constituents of the plating solution. The rationale behind this study lies in the following two aspects: first, surfactant molecules affect the deposition rate of the Ni-P alloy because of their influence on the availability of the reductive hydrogen atoms adsorbed on the plating frontier; second, the identity of the surfactant plays a role in shaping the surface morphology as well as the porous structure of the deposit due to various interfacial behaviors. Furthermore, a porous surface greatly reduces the corrosion resistance of a plated Ni-P coating.⁸⁻¹² On the whole, the study in the surface properties of the Ni-P deposit is an appropriate way to embody the surfactant effect.

2. Experimental Section

2.1. Reagents. Brass of 0.45 mm thickness used as the substrate is supplied by Hiap Guan Electroplating Materials (Singapore). Prior to Ni-P deposition the brass substrate with dimensions of 30 × 15 mm was first immersed in acetone for 5 min followed by dipping in a Na₂CO₃ solution and a 60 g·L⁻¹ Plaschem PSC 1139 cleansing solution for 10 min, repeatedly, and then rinsed with deionized water.

Nickel sulfate (NiSO₄·6H₂O) and sodium hypophosphite (NaH₂PO₂·H₂O) were purchased from Nacal Tesque, Inc. (Tokyo, Japan), while lactic acid (COOH-CHOH-CH₃) and lead acetate [Pb(CH₃COO)₂·3H₂O], used as stabilizers, as well as sodium acetate (CH₃-COONa), were obtained from Merck (St. Louis, MO). DL-Malic acid (COOH-CHOH-CH₃-COOH) and ammonium hydroxide (NH₄OH) were acquired from Aldrich (Milwaukee, WI). The chemicals employed in the experiments of corrosion resistance, HCl and NaCl, were purchased from Merck, while NaOH was obtained from Mallinkrodt Baker (Phillipsburg, NJ). All chemicals were of reagent grade and were used as received.

Various types of commercially available surfactants with different kinds of charges are chosen for this work. Nonionic surfactants, Triton X-100 and Tergitol 15-S-12, were supplied by Union Carbide (Danbury, CT), while other nonionic surfactants, Tergitol NP-9, Tween 20, Tween 80, and Tween 85, were purchased from Sigma (Milwaukee, WI). Some of these surfactants carry the molecular similarity among them. For example, Tergitol NP-9 is from the nonylphenol (Nonoxynol) family with 9 ethylene oxide (EO) units on its hydrophilic part, while Triton X-100 comes from the octylphenol (Octoxynol) family with the same, ca. 9 to 10, EO units on its hydrophilic portion. Tween 20 and Tween 80 as well as Tween 85 share the same hydrophilic moiety consisting of a sorbitan backbone having 20 EO units, but differ in the hydrophobic tail. Tween 20 has a laurate chain on the aforementioned hydrophilic part, while Tween 80 and Tween 85, instead, have one and

three oleate chains, respectively. Their selected properties are listed as the following:

surfactant	CAS no.	HLB value
Tergitol 15-S-12	68131-40-8	14.7
Tergitol NP-9	9016-45-9	12.9
Triton X-100	9002-93-1	13.5
Tween 20	9005-64-5	16.7
Tween 80	9005-65-6	15.0
Tween 85	9005-70-3	11.1

Two kinds of cationic surfactants, dodecyltrimethylammonium bromide (DTAB) and dodecyltrimethylammonium chloride (DTAC), were obtained from Aldrich and Fluka, respectively. Although DTAB and DTAC give the same surface-active portion in aqua, i.e., dodecyltrimethylammonium (DTA) cation, they possess different properties. For example, the critical micelle concentration of DTAB is found at 0.016 M at 25 °C, compared to 0.02 M for that of DTAC at the same temperature. The anionic surfactant, sodium dodecylbenzenesulfonate (SDBS), was acquired from Sigma. These surfactants are deliberately chosen so that the specific effect associated with either their hydrophobic or hydrophilic moieties on the properties of the Ni-P deposits could be investigated. All surfactants were used as received.

Deionized water, having a resistivity greater than 18.2 MΩ·cm, obtained from a Milli-Q purification system (Millipore, Bedford, MA) was used in sample preparation and in rinsing of the glassware as well as the experimental setup.

Deposition of electroless Ni-P on the brass substrates was performed by immersing the brass substrates in the acidic hypophosphite bath of the following compositions:

nickel sulfate	22.4 g/L
sodium hypophosphite	25 g/L
lactic acid	21 mL/L
DL-malic acid	4 g/L
stabilizer	2 mg/L
sodium acetate	8.5 g/L
ammonium hydroxide	the amount needed to main the desirable pH value, <i>circa</i> 4.7 ~ 4.8

No agitation was employed to the bath during the plating process. The surfactant was added continuously to the plating bath in order to maintain the desirable concentration for studying its effect on the properties of the Ni-P deposits.

2.2. Apparatus and Experimental Procedures. Four Pyrex glass beakers containing plating solutions for electroless Ni-P deposition were mounted in a temperature-regulated water bath. The temperature of the water bath was monitored with a Heidolph EKT temperature controller connected to a Heidolph MR 3001K heating magnetic stirrer (Schwabach, Germany). The variation of temperature was less than 1 °C from the set point. The plating conditions were set as the following:

pH	4.7 ~ 4.8
temperature	89 ± 1 °C
bath load	2 dm ² /L
plating time	1.5 hr

The pH value of the plating solution was adjusted to that between 4.7 and 4.8 with addition of NH₄OH followed by heating of the plating solution to 89 °C. The pretreated brass substrate was then immersed in the plating solution followed by initiation of the plating process using a clean iron wire. After 1.5 h the metal piece was taken out and rinsed with deionized water

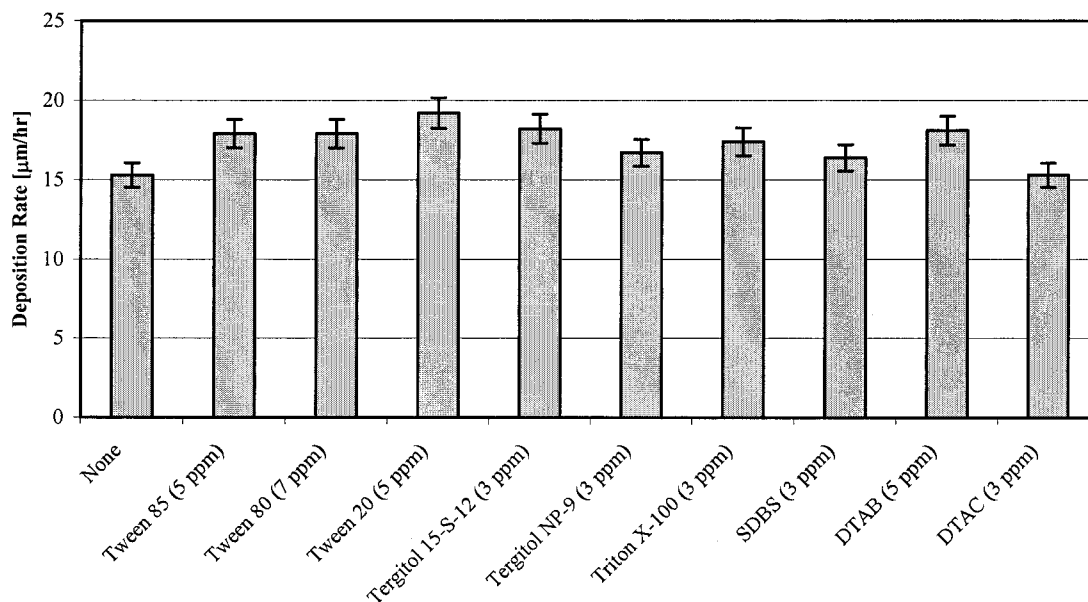


Figure 2. Effect of added surfactant at its optimal concentration on the rate of the electroless Ni-P deposition. The concentration of surfactant is indicated in parentheses.

before drying by blowing air. The as-deposited brass was weighed and was then subjected to all property tests.

2.3. Characterization of Ni-P Deposits and Its Deposition Rate. The deposition rate R of the electroless Ni-P alloy is expressed in terms of the weight gain during the deposition process.^{10,13} An analytical balance A&D GR-200 (Goldbell, Singapore) with a precision to 10 μg was employed to weigh the as-deposited samples. The as-deposited brass was dried and weighed repeatedly until no further change in the reading to ensure complete drying of the Ni-P alloy. Accordingly, the deposition rate can be expressed as the following equation:

$$R = \frac{\omega \times 10^4}{dAt} \quad (1)$$

where R is the deposition rate ($\mu\text{m}\cdot\text{h}^{-1}$), ω is the weight gain (g), d is the density of the deposit ($7.8\text{ g}\cdot\text{cm}^{-3}$), A is the surface area of deposition (cm^2), and t is the deposition time (h). Strictly speaking, d is an envelope density because the deposit layer is not fully dense. In addition, it also varies with the phosphorus content in the deposit.^{8,13} In this work, the phosphorus content in the deposits was found to be nearly 10 wt %. Thus, the corresponding value of the density is taken at $7.8\text{ g}\cdot\text{cm}^{-3}$.^{8,13} The experimental results reported in this work are the average values of several runs, at least the quadruplicate experiments, which are reproducible within about 5% from the average values.

Selected as-deposited samples were further investigated for their corrosion resistance by immersing these samples in three different corrosive solutions containing 10 wt % HCl, 5 wt % NaCl, and 10 wt % NaOH at ambient temperature (about 22 $^{\circ}\text{C}$). The volume of these corrosive solutions used in the experiments of the corrosion test was maintained constant. The corrosion rate of the electroless Ni-P deposits was then obtained from the specific weight loss of the Ni-P deposits over the period of exposure time. It can be written as the following:

$$R_c(t) = \frac{d\omega_c(t)}{dt} = \frac{d}{dt} \left(\frac{\omega_T(t)}{A_T} \right) \quad (2)$$

where $R_c(t)$ is the corrosion rate ($\text{mg}\cdot\text{dm}^{-2}\cdot\text{day}^{-1}$ or mdd), $\omega_c(t)$ is the specific weight loss ($\text{mg}\cdot\text{dm}^{-2}$) and defined as the overall weight loss, ω_T (mg), divided by the total area of exposure, A_T (dm^2), and t is the exposure time (days). Another common expression of the corrosion rate is expressed in the rate of penetration, such as mils per year (mpy). In this work, 1 mdd is equal to (1.437/7.8) mpy, i.e., 1 mdd = 0.1842 mpy.¹⁰ It has to be pointed out that the complete or incomplete removal of corrosion products is directly reflected in the corrosion rate.¹⁰ To reduce the error of the corrosion rate measurement due to incomplete removal of corrosion products, these samples were vigorously scrubbed on the surfaces with an abrasive cloth under a stream of deionized water before weighing.

The surface quality of the electroless Ni-P deposits was first examined by visual inspection¹³ and/or under an optical microscope at low magnitude ($\times 200$) in reflected mode. The brightness and appearance on the surface of the Ni-P deposit is the primary indicator of the surface quality.^{10,13} A more detailed surface morphology of the as-deposited samples was observed with a JEOL JSM 5600 scanning electron microscope (SEM) equipped with an in situ energy-dispersive X-ray spectroscopy (EDX) facility, with which the phosphorus contents were measured.

3. Results

3.1. Deposition Rate and Surface Morphology of Electroless Ni-P Deposits. Figure 2 displays the effect of added surfactant on the rate of electroless Ni-P deposition. The concentration of the surfactant was maintained at optimal levels between 3 and 7 $\text{mg}\cdot\text{L}^{-1}$, i.e., from 3 to 7 ppm. The optimal condition was established through the concentration variation of a particular surfactant so as to achieve the maximum deposition rate on the ground that a minimum extent of pitting in the Ni-P deposits should be guaranteed. It clearly shows that the addition of a surfactant, except

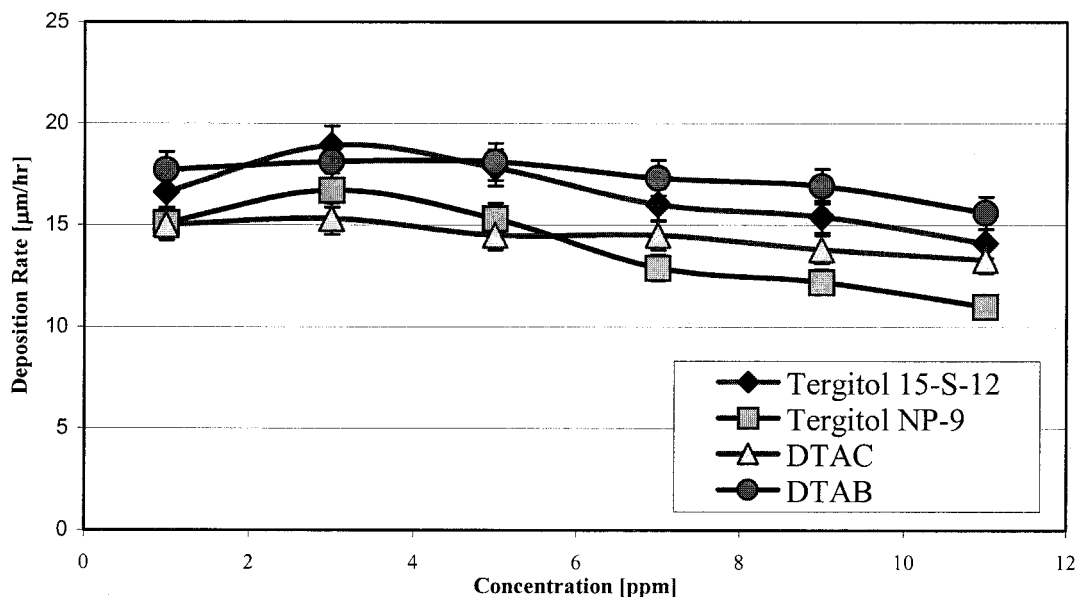


Figure 3. Rate of the electroless Ni-P deposition as a function of the additive concentration.

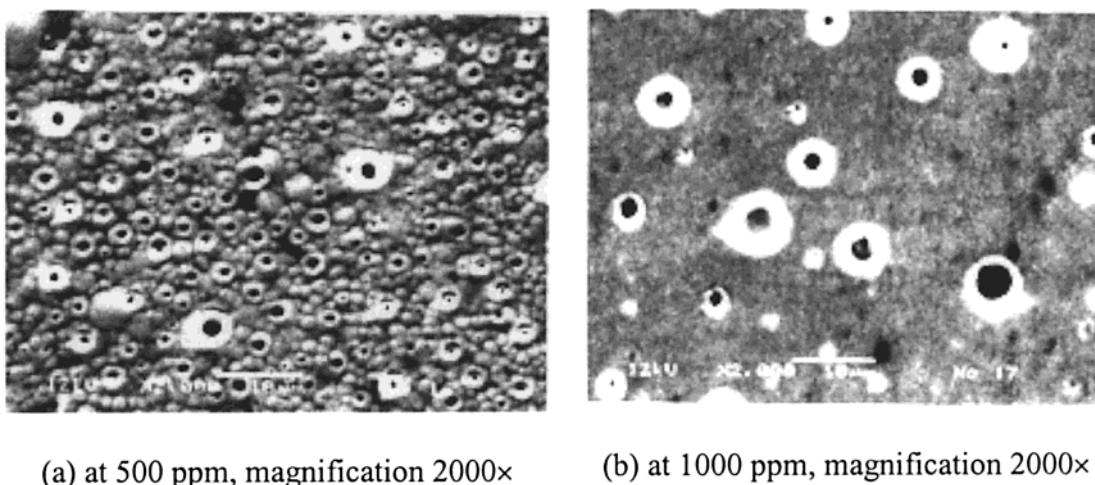


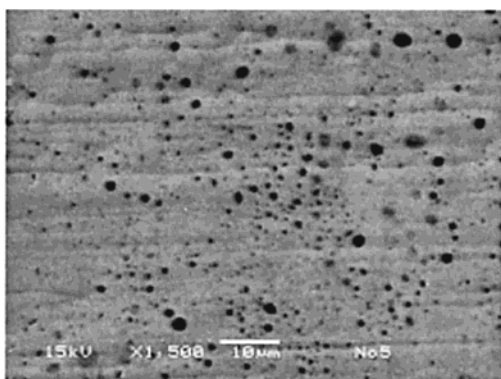
Figure 4. SEM micrographs showing the pits on the surface of the electroless Ni-P deposits from the plating solutions containing Triton X-100 with initial concentrations at (a) 500 and (b) 1000 ppm. Both micrographs have the same magnification factor of 2000 \times .

DTAC, increases the deposition rate by about a factor of up to 25%. Addition of DTAC at 3 ppm neither increases nor decreases the deposition rate in comparison with that containing no surfactant. The highest deposition rate occurs in the system added with Tween 20 at the 5 ppm level. Interestingly, the system added with DTAB gives a higher deposition rate than that added with DTAC. In general, the addition of ionic surfactants studied in this work gives a smaller increase in the deposition rate than that with the addition of a nonionic surfactant. This difference might be related to the possibility that DTA cations and hypophosphite anions form ion pairs at the interfacial region between the substrate and plating solution.

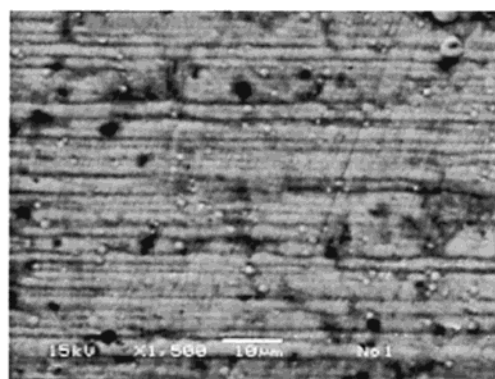
Increasing the concentration of the surfactant present in the plating baths has a mixed effect on the deposition rate of the Ni-P alloy (shown as Figure 3). When concentrations of nonionic surfactants Tergitol 15-S-12 and NP-9 as well as cationic surfactants DTAB and DTAC are increased, the deposition rate increases initially and then drops upon a further increase in the surfactant concentration. Deposition rates from the plating solutions containing DTAB or DTAC were less influenced than those with nonionic surfactants Tergitol

15-S-12 and Tergitol NP-9. In contrast, nonionic surfactants of the Tween series and Triton X-100 as well as ionic surfactant SDBS have an insignificant effect on the Ni-P deposition rate within the range up to 15 ppm. Therefore, the plating rate can be increased when an appropriate amount of a suitable surfactant is added into the plating solution.

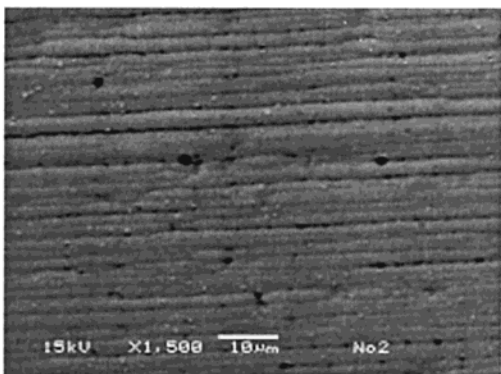
It is noteworthy of mentioning that the investigation of the effect of the additive concentration on the deposition rate has also been studied at a higher concentration range from a few tens to 1000 ppm as well, despite not being shown in the figure. Interestingly, the ionic surfactants including DTAC and DTAB as well as SDBS yield almost constant deposition rates. For example, an addition of SDBS at 1000 ppm to the plating solution gave a deposition rate of about $15.6 \mu\text{m}\cdot\text{h}^{-1}$, slightly smaller than the aforementioned value of $16.4 \mu\text{m}\cdot\text{h}^{-1}$ with 3 ppm initially present in the plating solution. Similarly, an addition of DTAB with an initial concentration of 500 ppm to the plating solution yields a deposition rate near $16.0 \mu\text{m}\cdot\text{h}^{-1}$, slightly larger than the value of $15.6 \mu\text{m}\cdot\text{h}^{-1}$ for that deposited from the bath having 11 ppm of DTAB initially present in the plating solution. However, the surface quality of the Ni-P



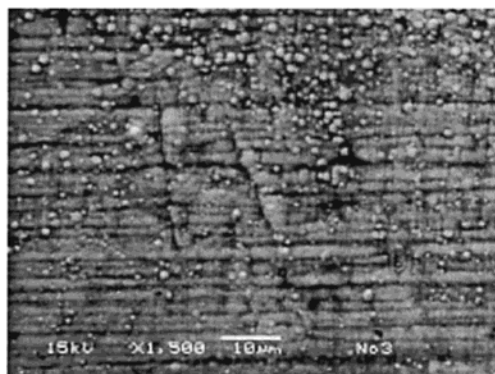
(a) No additive



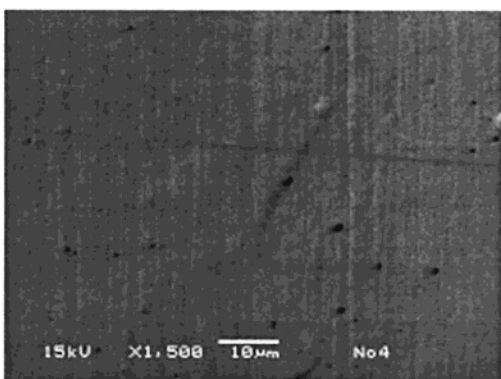
(b) Tween 85 (5 ppm)



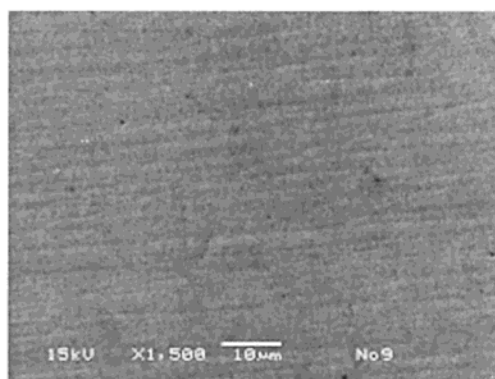
(c) Tween 80 (7 ppm)



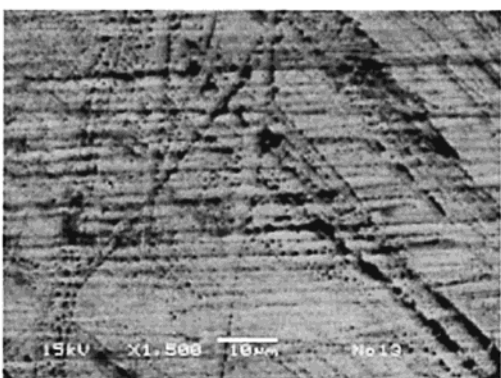
(d) Tween 20 (5 ppm)



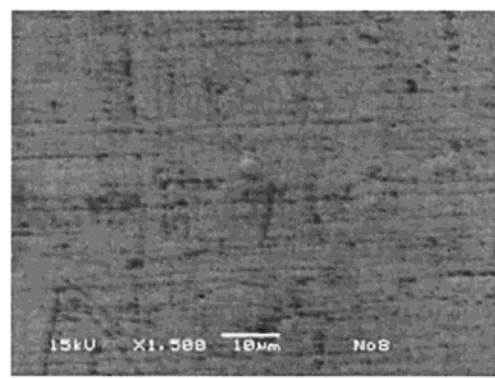
(e) Tergitol 15-S-12 (3 ppm)



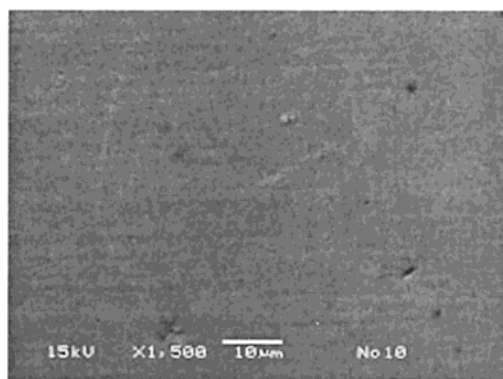
(f) Tergitol NP-9 (3 ppm)



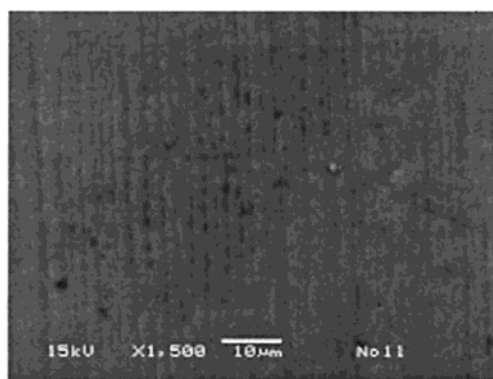
(g) Triton X-100 (3 ppm)



(h) SDBS (3 ppm)



(i) DTAB (5 ppm)



(j) DTAC (3 ppm)

Figure 5. SEM micrographs of the electroless Ni–P deposits from the plating solution with different additives at optimal concentration shown in Figure 2: (a) no additive; (b) Tween 85 (5 ppm); (c) Tween 80 (7 ppm); (d) Tween 20 (5 ppm); (e) Tergitol 15-S-12 (3 ppm); (f) Tergitol NP-9 (3 ppm); (g) Triton X-100 (3 ppm); (h) SDBS (3 ppm); (i) DTAB (5 ppm); (j) DTAC (3 ppm). All of these micrographs have the same magnification factor of 1500 \times .

deposits is affected to different extents. The surface of the electroless Ni–P deposits from the plating solutions with various initial concentrations of SDBS was not influenced in this study, while that of those Ni–P deposits from the plating solutions with concentrations of DTAB or DTAC larger than 100 ppm was deteriorated.

Similarly, the addition of nonionic surfactants Tergitol 15-S-12 or Triton X-100 with initial concentrations larger than 50 ppm did not alter the rate much. However, the surface quality of the deposits was sacrificed (shown as Figure 4). Figure 4 displays the formation of large holes on the surfaces of the Ni–P deposits from the plating solutions containing Triton X-100 with two different initial concentrations of 500 and 1000 ppm. Porous surfaces are clearly observed on both SEM micrographs. The dimensions of the largest pits on the surfaces of the corresponding Ni–P deposits from the plating solutions with initial concentrations of Triton X-100 at 500 and 1000 ppm are found around 2.3 and 4.5 μm , respectively, while the latter has a smaller number density of pits. In contrast, this porous surface was not seen on the deposit made from the plating solution containing an initial concentration of 3 ppm of Triton X-100, as shown in Figure 5g. As a result, these porous deposits will have larger specific areas to be exposed to the corrosive environments, which are not favorable for the engineering applications of electroless Ni–P alloys.

In contrast to Figure 4, Figure 5 presents the SEM micrographs on the surface morphology of the electroless Ni–P deposits from the plating solutions having surfactants added at optimal concentrations as shown in Figure 2. The white bar in each micrograph represents 10 μm . The performance of the electroless Ni–P deposits is, to a large extent, determined by the structure of the material. It clearly demonstrates that pits with dimensions of a few microns are seen in the sample deposited from the additive-free plating solution, as well as on those plated from the bath solutions with added nonionic surfactants except Tergitol NP-9. Only a very few pits were observed in the Ni–P deposit plated from the bath containing Tergitol NP-9. Its presence in the plating solution successfully prevents the formation of pits and gives a very smooth surface. However, an overdose of Tergitol NP-9, viz. greater than 9 ppm, to the plating solutions, instead, would give the deposits a very rough surface.

Table 1. Effect of Surfactant on the Phosphorus Content in Ni–P Deposits Measured by In Situ EDX

	surfactant	concn (ppm)	P content (wt %)
(1)	none		10.4
(2)	Tween 20	5	9.2
(3)	Tergitol 15-S-12	3	9.8
(4)	SDBS	3	10.1
(5)	DTAB	5	10.1
(6)	DTAC	3	10.4

Addition of Tween or Triton X-100 surfactants to the plating solutions produces quite a ragged surface on the Ni–P deposits. Its terrain observed by SEM appears like ripples, where pits exist randomly. Likewise, the effect of adding a large concentration of Tergitol 15-S-12, greater than ca. 50 ppm, to the plating bath on the surface morphology of the resulting Ni–P alloys is quite similar to that resulting from adding a large concentration of Tergitol NP-9.

On the contrary, the initial presence of ionic surfactants in the plating baths, in general, produces the Ni–P deposits with smoother morphology. Pits are not so obvious, and the terrains are more flat on the resulting deposits. As aforementioned, the surface quality of these Ni–P deposits is affected to different extents by the concentrations of ionic surfactants present initially in the plating baths. The surface quality of these deposits, in general, is better than that of those deposited from bath solutions containing nonionic surfactants with the same concentration but larger than 10 ppm.

Table 1 lists the phosphorus contents in the Ni–P deposits, with the values being obtained from EDX surface elemental analysis. On average, the phosphorus contents are near 10 wt %. Therefore, the Ni–P deposits are considered as high phosphorus deposits. Their structures are reported as rather amorphous and comparably smoother.^{14,15}

3.2. Corrosion Resistance. The corrosion resistance of the as-deposited sample was evaluated by the specific weight loss after submerging the samples into the acidic, basic, or saline solutions over a period of 16 days.¹⁰ Table 2 lists the average corrosion rates of the Ni–P deposits, plated from the baths with surfactants shown in the Figure 2, in various corrosive environments. The outcomes clearly demonstrated that the different surfactants initially present in the plating baths resulted in different corrosion resistance. Compared to those submerged in the acidic corrosive environment (10 wt

Table 2. Effects of Additives Initially Present in the Plating Solutions on the Average Weight Loss of Electroless Ni–P Deposits over a Period of 16 days in Various Corrosive Environments (Units: $\text{mg}\cdot\text{dm}^{-2}\cdot\text{day}^{-1}$ or mdd)

	additive	concn (ppm)	10 wt % HCl	10 wt % NaOH	5 wt % NaCl
(1)	none		35.5	2.40	1.46
(2)	Tween 85	5	18.4	1.15	0.84
(3)	Tween 80	7	24.5	1.70	0.73
(4)	Tween 20	5	13.1	0.42	1.15
(5)	Tergitol 15-S-12	3	25.6	0.41	0.31
(6)	Tergitol NP-9	3	23.2	1.02	1.04
(6)	Triton X-100	3	11.3	0.73	0.63
(7)	SDBS	3	14.6	1.10	0.21
(8)	DTAB	5	32.1	0.31	0.41
(9)	DTAC	3	14.2	0.63	0.63

% HCl), the corrosion of the Ni–P deposits in base (10 wt % NaOH solution) or in brine (5 wt % NaCl solution) is much less obvious. Nonetheless, the fastest average rate of corrosion in both environments was still found on the deposits made from the plating baths without any surfactant added. Their corresponding values are 2.40 mdd (0.44 mpy) in 10 wt % NaOH and 1.46 mdd (0.27 mpy) in 5 wt % NaCl. These values are comparable to those reported in the literature.^{16,17}

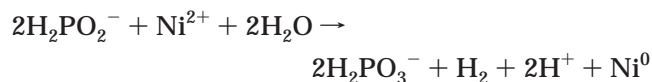
The average corrosion rate of the Ni–P deposits in 10 wt % HCl is about 1 or 2 orders of magnitude higher than those in the basic and saline corrosive environments. In general, the presence of surfactant in the plating bath enhances the corrosion resistance of the Ni–P deposits obtained.

Figure 6 exhibits the specific weight loss of the Ni–P deposits submerged in a 10 wt % HCl solution over a period of 16 days. The linear least-squares method is employed to fit the data of the specific weight loss due to corrosion with the exposure time on the log–log scale. The specific weight loss is found to be a power function of the exposure time with a power index near 1.5. The parameters of the best fits are tabulated in Table 3. Subsequently, the corrosion rate $R_c(t)$ can be expressed as a power function of the specific weight loss $\omega_c(t)$ itself (discussed in Appendix 1), which is equivalent to the concentrations of the dissolved Ni and P ions due to corrosion in 10 wt % HCl solution.

The power indices of the corrosion rates as a power function of the specific weight loss are also included in Table 3. Their values range from 0.3 to 0.4. It has to be emphasized that these rate equations are empirical.

4. Discussion

4.1. Effect of Surfactant on the Deposition Rate and Surface Morphology. The overall reaction of electroless Ni–P deposition in acidic hypophosphite baths can be broadly expressed as⁸



The detailed reaction mechanisms of electroless deposition processes have been studied extensively.^{8,18–22} However, no conclusive result has been obtained yet. In addition to the formation of metallic nickel on the as-deposited substrate, hydrogen gas is also produced in the electroless nickel-plating process. This hydrogen gas may, sometimes, be adsorbed on the surface of the as-deposited substrate to prevent further deposition of

nickel on sites where the bubbles occupy. The unwanted voids or pits in the deposits are thus formed accordingly.

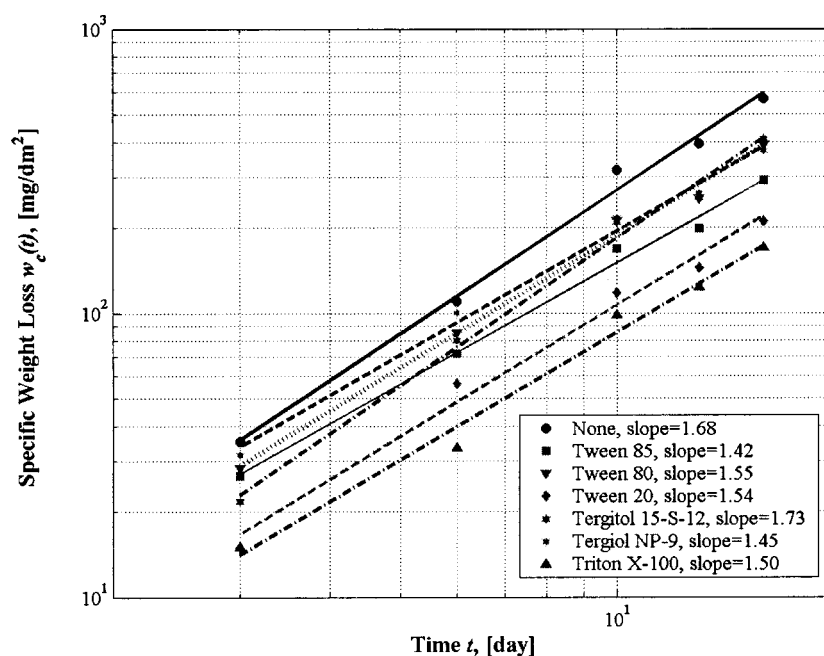
Many factors can affect the deposition rates of the electroless Ni–P alloys. For example, they could be the deposition temperature, pH of solution, tank loading, concentrations of nickel and the reducing agent, and the surface properties of the substrates. Wetting agents, such as ionic and nonionic surfactants, are often added to increase the wettability of surfaces to be coated.⁸ Despite the complicated nature of the deposition reactions and adsorption of surfactants to the as-deposited substrates, qualitative discussions on the effects of added surfactants to the plating solutions on the deposition rates and the surface morphology are attempted here.

Adsorption and desorption of surfactants at interfaces have been studied extensively with the adsorption isotherm. However, it was not until very recently that direct images showed the adsorption of surfactants on both hydrophobic and hydrophilic substrates to form stable linear cylindrical and half-cylindrical aggregates.^{23–26} Adsorbed surfactants can change the wettability of the as-deposited substrates and reduce the interfacial tensions between the generated hydrogen bubble and the as-deposited substrate or those between the bubble and the plating solution. Under these circumstances, trapped hydrogen gas on the as-deposited substrate would take place less frequently. Karuppusamy and Anantharam³ found that reducing the surface tension of the bath can enhance the removal of the hydrogen gas bubbles more quickly and thus form pit-free Ni–P deposits. It is true that a lower surface tension will give smaller hydrogen bubbles, as can be explained from the Young–Laplace equation. The gas bubbles will encounter the static pressure in the plating bath due to the gravity, usually a function of the liquid depth, that will be balanced by the Laplace pressure of the bubble. Moreover, the Laplace pressure of the bubble is proportional to the product of the interfacial tension along the liquid–gas interface as well as the curvature that is equal to 2 times the reciprocal of the bubble radius if the bubbles are spherical. Additionally, the adsorption of the ionic surfactants can affect the net charges on the as-deposited substrates. However, because of the incomplete understanding of the detailed mechanisms of the reaction mechanism of electroless deposition, it is difficult to draw any conclusive remark on the beneficial or detrimental effects of the charged surfactants on the deposition rate.

Because hydrogen is one of the products of the reactions, the quick removal of hydrogen gas may shift the deposition reactions to the direction in favor of the reduction of Ni^{2+} ions. Hence, the addition of surfactants can thus increase the deposition rate. These effects of added surfactants to the plating solutions are clearly demonstrated in this work as (1) the increase in the deposition rate and (2) the diminishment of pitting observed on the electroless Ni–P deposits.

At higher concentration of surfactant added in the bath solution (Figure 4), the morphology of the Ni–P deposits was, instead, horrible. As aforementioned, the surfactant molecules at a high enough concentration could form either stable cylindrical or half-cylindrical aggregates lying on the substrates,^{23–26} which will give nonuniform distribution of surfactant molecules in

(a) Effect of Addition of Nonionic Surfactants to Plating Baths



(b) Effect of Addition of Ionic Surfactants to Plating Solutions

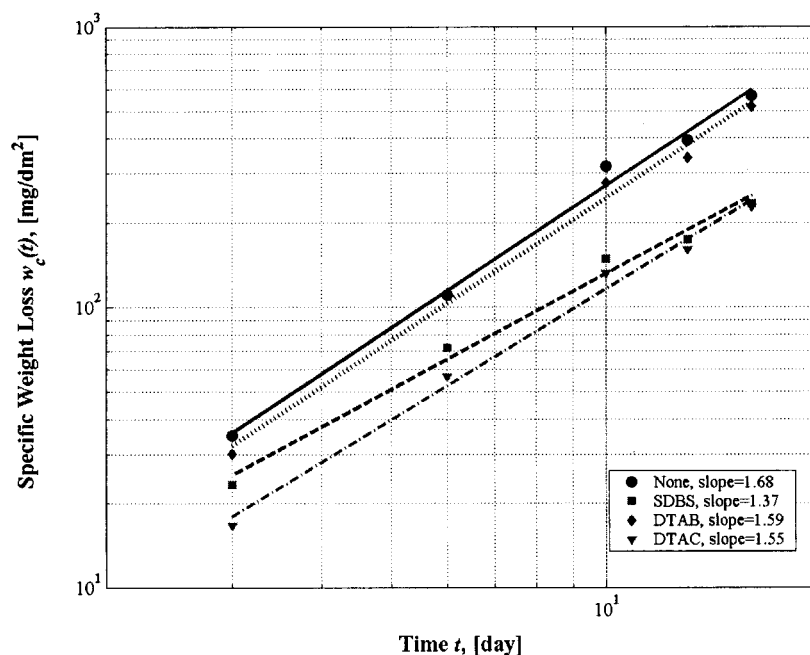


Figure 6. Specific weight loss $w_c(t)$ of the electroless Ni-P deposits plated from conditions shown in Figure 2 in 10 wt % HCl as a function of exposure time t .

substrates. That is, the regions covered by the surfactant aggregates would have a higher charge density or less surface tension. As a result, the nonuniform deposition of electroless Ni-P takes place and the resulting surface morphology would be deteriorated. In addition, the formation of ripplelike textures on the Ni-P deposits plated from the baths with the addition of nonionic surfactants (Figure 5) may be associated with the formation of these stable aggregates. More work is needed and has to be conducted to answer to the above question.

4.2. Corrosion Resistance. Corrosion resistance or corrosion rate is conventionally calculated from the

weight loss of the metal specimens during the corrosion test.¹⁰ Sometimes from an engineering point of view it is preferably expressed as the rate of penetration (mils per year). Alternatively, the corrosion rates could be continuously monitored and evaluated with the electrochemical techniques, such as Tafel extrapolation and linear polarization as well as electrochemical impedance spectroscopy.^{10,17} These electrochemical techniques could give rapid measurements on very low corrosion rates (less than 0.1 mpy) and could be used in some systems that are difficult to perform with conventional weight loss. However, there are numerous restrictions to be met

Table 3. Summary of Fitting Parameters Used in the Expressions of Corrosion Rates of the Ni–P Deposits in 10 wt % HCl from the Results Shown in Figure 6^a

additive	concn (ppm)	$\ln \omega_c(t) = m \ln(t) + n$ <i>m</i>	n	$R_c(t) \propto \omega_c(t)^p$ where <i>p</i> =
(1) none		1.68	1.73	0.41
(2) Tween 85	5	1.42	1.74	0.30
(3) Tween 80	7	1.55	1.66	0.36
(4) Tween 20	5	1.54	1.11	0.35
(5) Tergitol 15-S-12	3	1.73	1.23	0.42
(6) Tergitol NP-9	3	1.45	1.92	0.31
(6) Triton X-100	3	1.50	1.00	0.33
(7) SDBS	3	1.36	1.74	0.27
(8) DTAB	5	1.68	1.63	0.40
(9) DTAC	3	1.55	1.19	0.35

^a $R_c(t)$ is the corrosion rate and is expressed as $R_c(t) = d\omega_c(t)/dt$, and $\omega_c(t)$ is the specific weight loss and is defined as the overall weight loss divided by the exposure time t .

before these electrochemical methods can be used successfully.^{10,17}

The corrosion resistance of the electroless Ni–P alloys is known to be dependent on several factors.⁸ Porosity or surface morphology is one of them^{9–12} especially when the amorphous Ni–P deposit (with a high phosphorus content) is attained. Because all of the Ni–P specimens investigated in this work were prepared using the high phosphorous electroless plating solution, containing about the same level of phosphorus, the aforementioned two factors thus become critical. The SEM micrographs of the Ni–P deposits obtained from the baths with the addition of surfactants reveal a smaller number density of pores than could be found on the one plated from the bath solution without any added surfactant. The latter has the highest corrosion rate among all of the tested samples. Interestingly, the SEM micrographs from those deposited with the addition of Tergitol 15-S-12, Tergitol NP-9, SDBS, DTAB, or DTAC display very smooth surfaces on these deposits. However, the lowest corrosion rates do not always happen with the use of these surfactants. Instead, despite having a very smooth surface, the deposit particularly with the use of DTAB shows the highest corrosion rate among those samples plated from the addition of any surfactant. In contrast, its corresponding corrosion rates in 10 wt % NaOH or 5 wt % NaCl are, nonetheless, among the lowest.

Here too, the similar behavior of the corrosion resistance is observed on those deposits plated from the addition of Tergitol 15-S-12. Interestingly, a very flat texture on the surface is obtained, but it has a higher corrosion rate in the acidic environment as well as the lowest rates of corrosion in the basic or saline corrosive environments. It seems that the microstructures of the Ni–P deposits as well as the nature of the corrosive environments also have certain effects on the corrosion resistance. Indeed, the microstructure was found to affect significantly the anodic behavior, i.e., the corrosion or dissolution behavior, of Ni–P alloys. Królikowski²⁷ showed very different dissolution mechanisms of Ni–P deposits in 0.1 N NaCl and 0.1 N Na₂SO₄ solutions. Crystalline samples show active dissolution, while, on the contrary, amorphous alloys exhibit passivation.²⁷

Because the corrosion rates of our Ni–P deposits in 10 wt % NaOH and 5 wt % NaCl are not significant enough (less than 0.5 mpy), the discussions on the corrosion rates of the Ni–P deposits will be limited to those in the acidic corrosive environments (10 wt % HCl). The corrosion of the Ni–P deposits in the corrosive

environments can also be regarded as the dissolution processes of such deposits in such corrosive environments.

The corrosion of Ni–P deposits in the acidic environment is contributed from two simultaneous partial reactions: oxidation (anodic reaction) and reduction (cathodic reaction). The anodic reactions include two main parts: (1) oxidation of element P to a hypophosphite anion (H₂PO₂[−]) and the further oxidation of phosphorus (P⁺) in hypophosphite to phosphate (P⁵⁺); (2) oxidation of element Ni to Ni²⁺ or Ni³⁺. The cathodic reaction involves the reduction of H⁺ to hydrogen gas (H₂).^{28–33} It is important to mention that the rate of oxidation must equal the rate of reduction during metallic corrosion.¹⁰

The corrosion rates of Ni–P deposits in 10 wt % HCl were empirically determined to be proportional to ω_c^p , i.e., $R_c \propto \omega_c^p$, where the value of p is between 0.3 and 0.4 (see Appendix 1). It is interesting to note that ω_c stands for the specific weight loss of Ni–P due to corrosion, which is proportional to the total amount of Ni–P deposits dissolved in the corrosive solutions. Therefore, if the volume of the 10 wt % HCl solution is known or maintained constant in every batch, the bulk concentrations of nickel or phosphorus could be easily expressed in term of ω_c .

If the mechanism of such a corrosion process were governed by any interfacial factor, such as the formation and adsorption of a hypophosphite anion to the exposed area of the Ni–P deposits,^{29,30} the corrosion rate R_c would be a constant. Therefore, the specific weight loss of the Ni–P deposit would be a linear function of the exposure time t , and the corrosion rate R_c would be independent of ω_c , i.e., $p = 0$. Alternatively, if the corrosion were controlled by diffusion, such as the diffusion of H⁺ to the surface of Ni–P alloys through the possible electric double layer or the diffusion of the oxidized corrosion film away from the deposit surface, the corrosion rate would be proportional to the square root of the exposure time t or the reciprocal of ω_c (see Appendix 2). Clearly, this diffusion-controlled mechanism is not supported by our experimental data either.

As aforementioned, the corrosion of the Ni–P deposits in 10 wt % HCl can also be regarded as the dissolution process of such deposits in this 10 wt % HCl solution. This dissolution mechanism in H₂SO₄ and HCl electrolytes was reported as being kinetically controlled, i.e., interfacially or passively controlled, by Diegle et al.^{29,30} Diegle et al.^{29,30} proposed the chemically passive model accordingly to describe the dissolution process of “glassy” Ni–P alloys in H₂SO₄ and HCl electrolytes. Van der Kouwe³⁴ and Hofmann³⁵ also drew similar conclusions from their studies of amorphous Ni–P deposits in solutions containing 0.99 M Na₂SO₄ + 0.01 M H₂SO₄ or 3% NaCl + 0.7 M HCl, respectively. Hofmann³⁵ showed that the corrosion rate, expressed as a relative mass loss, is a linear function of the exposure time over a period of about 1 h. However, this was disputed by Zeller and Salvati^{16,17} and Splinter et al.²⁸ Zeller and Salvati^{16,17} did not observe any significant contribution from either diffusion or adsorption to the dissolution in their corrosion work of amorphous Ni–P deposits, containing from 10 to 11 wt % P, in 5% NaCl. Splinter et al.²⁸ reported no passivity exhibited in the corrosion of the nanocrystalline and amorphous Ni–P alloys, which have the phosphorus contents of 1.9 and 6.2 wt %, respectively, in 0.1 M H₂SO₄.²⁸ It is interesting to

note that Van der Kouwe³⁴ also found that the electroless nickel coatings protected the substrate by forming a protective layer at first, i.e., showing passivity, and the active dissolution would then be observed if the penetration of the coatings, namely, pitting, reaches the substrates. He also demonstrated that the porous Ni–P layers often resulted in the active dissolution.

Finally, based on our experimental data, it is clearly shown that the governing mechanism in the corrosion process in the acidic corrosive environment (10 wt % HCl) is controlled neither kinetically nor diffusionally. Indeed, the detailed governing mechanisms are complicated and require more work to be conducted accordingly for possibly complete understandings.

5. Conclusion

Nine different surfactants were assessed and employed in the plating processes of electroless Ni–P deposits. Their effects on the properties of the resulting electroless Ni–P deposits were examined.

An addition of small amounts of surfactants to the plating baths could increase the deposition rates by 25% compared to that from the surfactant-free bath. The formation of micropitting on the deposits can also be reduced, and the corresponding corrosion resistance is enhanced. However, the addition of an excessive amount of nonionic surfactants to the plating baths will, in general, yield the Ni–P deposits with inferior surface quality and slow the deposition rate. In contrast, the surface properties of the Ni–P deposits are less influenced by the concentration effect of ionic surfactants initially present in the plating baths. The phosphorus contents of the resulting Ni–P deposits in this study are found to be around 10 wt %.

The corrosion of the Ni–P deposit in basic or saline corrosive environments is less obvious, in contrast to the significant corrosion observed in the acidic corrosive environment. The consequent corrosion rate of the Ni–P deposit in such an acidic environment is determined empirically and found to be described well by a power function of the amount of the dissolved Ni–P alloys, equivalently the concentration of the nickel ions present in the corrosive solution. The corresponding power indices are between 0.3 and 0.4, which indicates that the corrosion process is controlled neither diffusionally nor interfacially.

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Appendix 1

The corrosion rate of the electroless Ni–P deposits can be expressed as the following:

$$R_c(t) = d\omega_c(t)/dt \quad (2)$$

where $R_c(t)$ is the corrosion rate ($\text{mg}\cdot\text{dm}^{-2}\cdot\text{day}^{-1}$ or mdd), $\omega_c(t)$ is the specific weight loss ($\text{mg}\cdot\text{dm}^{-2}$), and t is the exposure time (h). The specific weight loss $\omega_c(t)$ can be empirically determined as

$$\ln \omega_c(t) = m \ln(t) + n \quad (3)$$

That is,

$$\omega_c(t) = Kt^m \quad (4)$$

where K is a constant equal to e^n . Substituting eq 4 into eq 2, one will get

$$R_c(t) = \frac{d\omega_c(t)}{dt} = (mK)t^{m-1} = m \sqrt[m]{K} \omega_c^{(m-1)/m} = K_1 \omega_c^p \quad (5)$$

where $p = (m - 1)/m$. Equation 5 clearly demonstrated that the corrosion rate $R_c(t)$ is proportional to ω_c^p .

Appendix 2

The specific weight loss of the electroless Ni–P deposits in planar geometry can be expressed as the following:

$$\omega_c(t) = 2\rho\Delta h(t) \quad (6)$$

where ρ is the density of the Ni–P deposit and can be treated as a constant and $\Delta h(t)$ is the difference of the thickness of Ni–P deposits. The factor of 2 in eq 6 accounts for both sides of the deposits in which corrosion can take place. It is well-known that the characteristics of the diffusion-controlled mechanism give^{36,37}

$$\Delta h(t) \propto \sqrt{t} \quad (7)$$

That is, $\omega_c(t)$ is proportional to the square root of the exposure time t . The corrosion rate is, hence,

$$R_c(t) = \frac{d\omega_c(t)}{dt} \propto \frac{1}{\sqrt{t}} \propto \omega_c^{-1} \quad (8)$$

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