Kinetics of Electroless Ni-P-BAlloy Deposition

By S.S. Abd El-Rehim, N.N. El-Ibiari, M Shaffei & S. Abdel Halem

Using kinetics data, an empirical deposition rate was derived for electroless deposition of ternary alloys nickelphosphorus-boron on pretreated aluminum substrate: $r = 463.33 (H_2PO_2)^{0.46} (BH_4)^{0.3} (HCOOH)^{0.35} (H^+)^{0.15} exp (18.15[T-353]/T) where r is the rate of deposition (mg/cm²/hr) and T is the absolute temperature, from baths containing nickel ions, hypophosphite ions, borohydride ions and formic acid. This equation can be applied only in limited ranges of concentration of the bath components at 80 °C. The correlation coefficient between the experimental plating rates and those computed using the developed empirical rate equation is 96 percent.$

Within the past decade, electroless nickel plating has become commercially available on a broad scale. It has gained increasing importance as a coating material having several unique properties, such as uniform thickness, hardness, corrosion resistance and low porosity.¹⁻³ Because of all the merits of such properties, it has found extensive application in several industries, such as petroleum, chemical, plastic, printing, aerospace, nuclear, textile and food industries, as well as in the computer and optical hardware industries.

The aim of this study is to develop an empirical rate correlation that holds only in a limited range of operating conditions for electroless nickel baths, using sodium hypophosphite and sodium borohydride as reducing agents.

Experimental Procedure

The electroless nickel plating baths used in this study are listed in Table 1. The deposition was carried out on 0.3 mm thick aluminum foil (99.9% purity) having a total surface area of 20 cm². The aluminum substrate was subjected to treatment before plating by etching for three min in 12percent NaOH solution at room temperature. The weighed substrate was suspended in the plating bath at a fixed depth with the help of a glass rod for a given time. The ratio between the substrate area (a cm²) and the plating bath volume ($v \text{ cm}^3$) was constant throughout all experiments, (a/v = 1/5 cm⁻¹ to ensure complete immersion of the substrate in the solution. All experiments were performed under stagnant conditions. At the end of each experiment, the plated specimen was withdrawn, rinsed with distilled water, dried and finally weighed.

In such a solution, the concentration of the components changed little during deposition. The plating rate could therefore be determined gravimetrically and calculated as follows:

Plating rate = Weight gain/substrate area/ plating time = mg/cm²/hr.

Deposit Analysis

Nickel, boron and phosphorus percentages in the deposits were determined by analytical methods, after preparation of the samples for analysis, as follows:

1. The as-plated deposit was stripped from the substrate by immersion in 5 cc of 65-percent (v/v) nitric acid solution.



Fig. 1-Determination of reaction order for nickel ions.



Fig. 2—Determination of reaction order for hypophosphite ions.

- 2. The stripping solution was adjusted to 100 cc with distilled water. Analysis was as follows:
 - (a) Nickel percentage was determined by direct titration⁴ with EDTA, using murexide indicator.
 - (b) Boron percentage was determined by spectrophotometer for sample absorbance at 585 nm in a cell of 1-cm light path. The sample was prepared by the "carmine method," using carminic reagent.⁵
 - (c) Phosphorus percentages were determined by subtracting Ni and B percentages from 100 percent.

Results & Discussion

The main chemical reactions for electroless deposition of the ternary alloy (Ni-P-B) with hypophosphite and borohydride as reducing agents on etched Al substrate can be written as:^{6,7}

$$Ni^{+2} + 2H_2PO_2^{-} + 2H_2$$
 (in acidic medium) $\rightarrow Ni^0 + 2HPO_3^{-2} + 4H^+ + H_2$
 $2Ni^{+2} + BH_4^{-} + 4H_2O$ (in acidic medium) $\rightarrow 2Ni^0 + B(OH)_4^{-} + 4H^+ + 2H_2$

The empirical rate equation for E(Ni-P-B) deposition depends on the variables that affect the plating rate: $[Ni^{+2}]$, $[H_2PO_2]$, $[BH_4]$, [HCOOH], $[H^+]$ and temperature. Because there is no HPO₃⁻² or $B(OH)_4^-$ species before plating and their concentrations are very low during the early stages of deposition, they will not be introduced in the empirical rate equation. The general form of the reaction rate, therefore, will be:

Rate = $dNi^{0}/dt = k[Ni^{+2}]^{a}[H_{2}PO_{2}^{-}]^{b}[BH_{4}^{-}]^{c}[HCOOH]^{d}[H^{+}]^{e} exp[(-Ea)/(RT)]$

(1)

Taking the logarithm:

Log rate (r) = {log k + a log $[Ni^{+2}]$ + b log $[H_2PO_2^{-1}]$ + c log $[BH_4^{-1}]$ + d log [HCOOH] - e pH} (-Ea/2.3RT) where log $[H^+]$ = -pH.

Table 1 Plan of Process Kinetics											
Run No.	Ni ⁺² conc. mol/L	HCOOH conc. mol/L	Na ₂ PO ₂ · H ₂ O conc. mol/L	NaBH ₄ conc. mol/L	рН	Plating temp. °C	Plating parameter	Plating rate mg/cm²/hr	Ni %	P %	B %
1	0.1	0.6	0.2	0.01	5.5	80	Nickel	6.86	74.5	25.1	0.4
2	0.2	0.6	0.2	0.01	5.5	80	sulfate	7.35	84.9	14.8	0.3
3	0.3	0.6	0.2	0.01	5.5	80	$NiSO_4 \cdot 7H_2O$	8.17	86.1	13.6	0.3
4	0.4	0.6	0.2	0.01	5.5	80		8.10	82.4	17	0.6
5	0.5	0.6	0.2	0.01	5.5	80		8.18	82.6	17.1	0.3
6	0.3	0.6	0.00	0.01	5.5	80	Sodium	0.00	_	—	_
7	0.3	0.6	0.05	0.01	5.5	80	hypophosphite	1.14	81.68	7.02	10.4
8	0.3	0.6	0.10	0.01	5.5	80	$NaH_2PO_2 \cdot H_2O$	4.43	83.21	11.19	5.6
9	0.3	0.6	0.15	0.01	5.5	80		5.71	91.6	3.9	4.5
10	0.3	0.6	0.25	0.01	5.5	80		6.88	94.6	4.5	0.85
11	0.3	0.6	0.2	0.00	5.5	80	Sodium	6.20	—	—	—
12	0.3	0.6	0.2	0.005	5.5	80	borohydride	6.26	78.3	21.3	0.4
13	0.3	0.6	0.2	0.015	5.5	80	$NaBH_4$	7.66	92.4	6.1	1.5
14	0.3	0.6	0.2	0.020	5.5	80		8.45	77.8	21.9	0.3
15	0.3	0.6	0.2	0.025	5.5	80	0	—	—	—	
16	0.3	0.2	0.2	0.01	5.5	80	Formic	5.11	78.9	20.7	0.4
17	0.3	0.4	0.2	0.01	5.5	80	acid	6.30	79.9	18.6	1.5
18	0.3	0.8	0.2	0.01	5.5	80	HCOOH	8.39	88.2	10.2	1.6
19	0.3	1.0	0.2	0.01	5.5	80		8.61	92.7	7 0.3	
20	0.3	0.6	0.2	0.01	4.0	80	pH	3.2	86.3	8.4	5
21	0.3	0.6	0.2	0.01	4.5	80		4.82	95.5	4.1	0.4
22	0.3	0.6	0.2	0.01	5.0	80		5.89	83.8	15.9	0.3
23	0.3	0.6	0.2	0.01	6.0	80		8.33	87.4	12.3	0.3
24	0.3	0.6	0.2	0.01	6.5	80		9.3	82.1	17.7	0.2
25	0.3	0.6	0.2	0.01	5.5	60	Plating	2.52	73.7	24.5	1.8
26	0.3	0.6	0.2	0.01	5.5	70	temp	4.60	78.5	21.9	0.6
27	0.3	0.6	0.2	0.01	5.5	85		7.36	85.7	14	0.3
28	0.3	0.6	0.2	0.01	5.5	90		10.25	81.0	18.8	0.2

The reaction orders depend on bulk concentrations of various components of the plating baths. So, as shown in Figs. 1-3, logarithmic deposition rates vs. logarithmic bulk concentrations were plotted and the slopes of the straight lines are the reaction orders, that were determined by linear least-square fit. The effect of each component is discussed separately in the following paragraphs:

Effect of Nickel Ion Concentration It was observed (Fig. 1) that the plating rate is independent of nickel ion concentration, and this agrees with references 8-11, where

 $\log r/\log [Ni^{+2}] = a = slope = zero$

Effect of Sodium Hypophosphite Concentration

Figure 2 illustrates the increase of plating rate with increasing concentration of sodium hypophosphite according to:

 $\log r \log [H_2 PO_2^-] = b = slope = 0.4686$

It is proposed that the catalytic oxidation of H₂PO₂ takes place by hydride transfer to the catalytic surface in acidic solutions.12

Effect of Sodium Borohydride Concentration

The reaction order for sodium borohydride can be calculated from the slope of Fig. 3, where

 $\log r \log [BH_{4}] = c = slope = 0.2952$

The borohydride ion is a powerful reducing agent. The mechanisms proposed previously¹²⁻¹⁴ indicated that the molar ratio of reduced nickel to borohydride consumed is 1:1 and this was supported by experimental evidence according to the overall reaction:

 $2Ni_2 + 4H_2O + 2BH_4^- \rightarrow 2Ni^0 + B(OH)_4^- + B + 3H^+ + 9/2 H_2$

Effect of Formic Acid Concentration

The concentration of complexing agent (formic acid) is an important rate-determining factor, as shown in Fig. 4. The rate of deposition increases linearly with increasing formic acid concentration; the reaction order was determined as follows:

 $\log r/\log (HCOOH) = d = slope = 0.3474$

Increasing the rate by use of the concentration of formic acid is attributed to the great ability of formic acid to make nickel

		Specific Rate Constant			
Empiri	Table 2 .cal Parameters	Item [Ni ⁺²] = 1	Rate Constant (k) 78.343	Specific Rate Constant (K') 1421.92	
Item	Reaction Order Value	$[H_{2}PO_{2}] = 1$	13.274	240.92	
[Ni ⁺²]	Zero	$[BH_{4}] = 1$	26.062	473.02	
$[H_2PO_2^{-}]$	0.47 ±0.01	[HCOOH] = 1	8.857	160.76	
$[BH_4]$	0.30 ±0.01	$[H^+] = 1$	1.104	20.04	
[HCOOH]	0.35 ±0.01				
$[H^+]$	0.15 ±0.01	At 80 °C, average value of $K = 463.35$			







Fig. 4—Determination of reaction order for formic acid.

complexes of low kinetic stability ($pK_a = 3.75$). These nickel complexes yield a sufficient quantity of adsorbed nickel ions on the catalytic surface and cause a high deposition rate.

Effect of Hydrogen Ion Concentration

Figure 5 shows that the deposition rate increases slightly with increasing pH, and the order of the reaction with respect to the hydrogen ion concentration $[H^+]$ is very low where

 $\log r/pH = -e = slope = -0.146$

The accumulation of hydrogen ions in the plating bath lowers the pH of the solution and the deposition rate is decreased. It is known that nickel reduction is base catalyzed (*i.e.*, increases with decreasing H^+ concentration). At low pH values, therefore, there is a side reaction that competes with the catalytic deposition of nickel, which agrees with the results of Hung.¹⁵

Activation Energy

The quantity of energy required is one of the most important factors affecting the kinetics and rate deposition reaction. The dependence of reaction rate on temperature is depicted in Fig. 6, where the apparent activation energy can be calculated from the slope of logarithmic rate vs. reciprocal temperature plot (Arrhenius plot) according to the following relation:

 $\log r/(1/T) = -Ea/2.3 R = slope$ E_a = 12.6874 kcal/deg. mol

This value is in agreement with those computed by Feldstein and Amodio¹⁶ for other autocatalytic nickel baths. This low value indicates that the reaction is self-sustaining.

Specific Rate Constant

By using the extrapolation method,¹⁷ the specific rate constant K at 80 °C can be evaluated by extrapolating the lines in Figs. 1-6, where the appropriate concentration is unity and the respective deposition rates are equal to the rate constants (k), where

 $K = k \exp(-Ea/RT)$

 $r [at (Ni^{+2}) = 1] = K [H_2PO_2^{-1}]^{b} [BH_4^{-1}]^{c} [HCOOH]^{d} [H^{+}]^{c}$ $r [at (H_2PO_2^{-1}) = 1] = K [Ni^{+2}]^{a} [BH_4^{-1}]^{c} [HCOOH]^{d} [H^{+}]^{c}$ $r [at (BH_4^{-1}) = 1] = K [Ni^{+2}]^{a} [H_2PO_2^{-1}]^{b} [HCOOH]^{d} [H^{+}]^{c}$ $r [at (HCOOH) = 1] = K [Ni^{+2}]^{a} [H_2PO_2^{-1}]^{b} [BH_4^{-1}]^{c} [H^{+}]^{c}$ $r [at (H^{+}) = 1] = K [Ni^{+2}]^{a} [H_2PO_2^{-1}]^{b} [BH_4^{-1}]^{c} [HCOOH]^{d}$





Fig. 7—Comparison of experimental and computed plating rates.

Empirical Rate Law

For electroless nickel plating using sodium hypophosphite and sodium borohydride as reducing agents, the empirical rate law can be obtained from sufficient data as given in Tables 2 and 3.

From Eq. (1) and the results of these experiments:

$r = k[Ni^{+2}]^{a}[H_{2}PO_{2}^{-}]^{b}[BH_{4}^{-}]^{c}[HCOOH]^{d}[H^{+}]^{e} exp[(-Ea)/(RT)]$ [new] (1)

Multiplying the right-hand side of Eq. (1) by

 $[\exp(Ea/353R) \exp(-Ea/353R)]$, which equals unity, and because the order of the reaction with respect to nickel ions = 0, then

 $r = k[H_2PO_2^{-1}]^b[BH_4^{-1}]^c[HCOOH]^d[H^+]^e exp[(-Ea)/(RT)] [exp (Ea/353R) exp (-Ea/353R)]$

 $r = [H_{2}PO_{2}]^{b}[BH_{4}]^{c}[HCOOH]^{d}[H^{+}]^{e} exp[(-Ea)/(RT)] Ea/353R) exp(-Ea/353R)$

 $r = [k \exp(-Ea/353R)] [H_2PO_2^{-1}]^{b}[BH_4^{-1}]^{c}[HCOOH]^{d}[H^+]^{e} \exp Ea/R(-1/T + 1/353)$

 $r = K'[H_2PO_2^{-}]^{b}[BH_4^{-}]^{c}[HCOOH]^{d}[H^{+}]^{e} \exp Ea/R [(-353 + T)/353T]$

 $r = K'[H_2PO_2]^b[BH_4]^c[HCOOH]^d[H^+]^e exp Ea/353R [(T-353)/T]$

Because Ea/353R = E = 18.15 °K, the empirical rate equation will be

Rate (r) = $463.33 [H_2PO_2]^{0.47} [BH_4]^{0.30} [HCOOH]^{0.35} [H^+]^{0.15} exp [18.15(T-353)/T]$

Figure 7 shows a comparison between the observed plating rates and those computed using Eq. (2). The agreement is excellent (*i.e.*, the correlation coefficient is 96 percent).

Summary

An empirical rate law equation was developed for an electroless ternary alloy, Ni-P-B, from an acidic bath, deposited on pretreated Al substrate. This equation can be applied only in limited ranges of component bath concentrations at 80 °C. Determination of the reaction order with respect to each of the plating parameters that affect the plating process (NiSO₄, HCOOH, NaBH₄, NaH₂PO₂ and pH) reveals that the sodium hypophosphite concentration is the most significant factor. This indicates that the process is a heterogeneous chemically controlled reaction. The value of the activation energy indicates that the reaction is self-sustaining.

The correlation coefficient between the experimental plating rates and those computed, using the developed empirical rate equation, is 96 percent.

Nomenclature

- Ea the activation energy (kcal/deg. mol)
- R gas constant (1.98 cal/deg. mol)
- K specific rate constant at a particular temperature (80 °C)
- k rate constant in the empirical rate law equation
- T absolute temperature (°K)

Editor's note: Manuscript received, January 1999; revision received, July 1999.

References

- 1. G. Gutzeit, Plating, 46, 1159 (1959).
- M. Pushpavanam & B.A. Shemoi, *Finishing Indust.*, 1(6), 48 (1997).
- 3. L. Aikan, Indust. Fin., 52(12), 229 (1967).
- 4. D.G. McBride, Plating, 59, 858 (Dec. 1972).
- 5. P. Hersch, Trans. Inst. Met. Fin., 33, 417 (1955).
- 6. K.M. Gorbunova, M.V. Ivanov & V.P. Mosiev, J. *Electrochem. Soc.*, **120**(5), 613 (1973).

7. K. Lwamalsu, *Proc. AESF SUR/FIN* 87, Chicago (July 1987).

(2)

- 8. L. Cadrona & P. Gavallotti, Soc. Chim., 53(1), 93 (1960).
- 9. P. Cavallotti & G. Salvago., Electrochim. Metall., 23(3) (1968).
- 10. G. Gutzeit, Plating, 46, 1158, 1275, 1377 (1959).
- 11. D.J. Levy, Proc. Amer. Electroplat. Soc., 50 (1963).
- 12. G. Salvago & P. Cavallotti, Plating, 59, 665 (1972).
- 13. K. Jodaey, G. Woldt & H. Grundel, U.S. patent 3,515,563 (1973).
- 14. M.V. Lvanov & K.M. Gorbunova, *Zaschita Metallov*, No. 2, 477 (1966).
- 15. Aina Hung, Plat. and Surf. Fin., 75, 60 (April 1988).
- 16. N. Feldstein & P.R. Amodio, J. Electrochem. Soc., 117, 1110 (1970).
- 17. F.L. Shippey & F.M. Donahue, *Plating*, **60**, 43 (Jan. 1973).

About the Authors

Dr. S.S. Abd El Rehim* is professor of electrochemistry in the Chemistry Department, Ain Shams University, Cairo, Abbassia, Egypt. He holds a PhD from the Hungarian Academy of Science. Prof. Abd El Rehim is an active member of the Egyptian Corrosion Society. He was awarded the State Prize for Encouragement in Chemistry in 1986 from the Egyptian Academy of Scientific Research and Technology. He has published more than 100 papers in international journals. His research interests are in electroplating of metals and alloys and corrosion of metals in aqueous media.

N.N. El-Ibiari, M. Shaffei and S. Abdel Halem are researchers at the Chemical Eng. and Pilot Plant Dept., National Research Center, Cairo, Egypt.

* To whom correspondence should be addressed.