Derivation and Rapid Spectrophotometric Determination of Iron In Electroless Nickel Plating Solution

By R. Liu, C. Gao, S. Hua, J. Yang & Y. Lu

Experiment has proved that iron can be dissolved in an acidic electroless nickel (EN) plating solution during the plating process when plating iron sheet. The influence of nickel sulfate, organic acids, sodium hypophosphite, pH and temperature on the absorption of Fe(III) was investigated. A new method, using mono-wavelength, to determine the concentration of Fe(III) was developed. Fe(II) was oxidized to Fe(III) to determine the total iron in the range 0.02 to 19.42 mg/L with recovery of more than 96.6 percent. Results confirmed that this method is easy, uses simple instruments, is quick and offers high accuracy in the process of measurement. This method can be applied to rapid determining whether the substrate is completely covered by Ni-P alloy if iron sheets are used.

Since the accidental discovery in 1944 by Brenner and Riddell, electroless nickel (EN) has grown from a laboratory process to a \$100-million industry.¹ Now, electroless deposition of Ni-P alloys is widely used in diverse fields, such as aerospace, automation, electronics, nuclear, oil and gas production, and valve industries.²

The major reducing agents in an EN bath are sodium hypophosphite, hydrazine and sodium borohydride. In practice, EN deposition baths using sodium hypophosphite as the reducing agent have been preferred. Such baths can be operated under acidic conditions at about 90 °C. Irrespective of the reaction mechanism, the deposit is believed to be initiated by catalytic dehydrogenation of the reducing agent and it is generally accepted that an atomic hydrogen mechanism is involved.³ In this type of EN bath, the overall plating reactions can be approximately described by

$$2H_2PO_2^- + 2H_2O + Ni^{+2} \xrightarrow{\text{catalytic}} Ni + 2H^+ + 2H_2PO_3^- + H_2^{\uparrow}$$
(1)
surface

$$4H_{2}PO_{2} \longrightarrow 2H_{2}PO_{3} + 2P + 2OH + H_{2}\uparrow$$
(2)

These reactions of Ni-P codeposition describe the deposit process most needed for this study. The technology and mechanism or kinetics of EN plating have sparked general interest throughout the industry.⁴⁻⁸ Apart from these reactions, if an iron sheet is dipped into acidic EN plating baths under suitable conditions, Ni-P alloy will be deposited on the substrate. At the same time, iron will dissolve in the solution. The spectrophotometric determination of iron in EN solution has not been reported. Little attention has been focused on this kind of basic reaction, which has not been of significance to researchers, but is as shown in Eqs. (3) and (4).

$$Fe + 2H^{+} \longrightarrow Fe^{+2} + H_{2}^{\uparrow}$$
(3)

If the EN plating solution was thermodynamically unstable, the following reaction could easily occur. (When air was blown into the bath, Fe(II) could be oxidized to Fe(III) by at least 96 percent. If a suitable amount of ammonium persulfate $[(NH_4)_2S_2O_8]$ solution was added, the efficiency of oxygenation could reach 99 percent.)

$$Fe^{+2} - e^{-} \longrightarrow Fe^{+3}$$
 (4)

According to Eq. (4), total iron could be determined by the amount of Fe(III) in the EN solution.

As the plating process continued, with changes of iron sheets, the concentration of Fe ions increased. It is well known that tolerance of foreign ions in EN solutions is limited. Excess of such ions degrades plating and regeneration of the EN solution. Rapid, accurate determination of iron in EN solutions must therefore be important in EN plating



Fig. 1—Absorption spectra of Fe(III) in EN solution.



Fig. 2-Influence of pH on absorbance of Fe(III).

process control, as well as for study of the influence on stability, rate of deposition⁹ and performance of the plated layer.

The determination of Fe(II) and Fe(III) has been widely reported. A.E. Harvey et al.¹⁰ solved the interference of Fe(II) and Fe(III) with each other, using dualwavelength measurement by subtraction and rectification, but the operation was labor intensive. Wang Dimin used the theory of dual-wavelength and equal absorption to eliminate the interference.11 He rapidly determined Fe(II) and Fe(III) in groundwater by triwavelength spectrophotometry. Sun Dengming determined trace iron in water by extraction catalytic kinetic spectrophotom-

					Tabl	le1						
		Mai	n Consti	ltuents	ofAcio	dicNic	kel Pla	atingB	aths			
	Component	Ran g/I	ge Optin g/]		imum ;/L	Re	Remarks					
	$NiSO_4 \cdot 6H_2O$	16-3	35	2	27	cor	sumed	, must l	oe reple	enished	1	
	$NaH_2PO_2 \cdot H_2O$	18-3	30	27		consumed, must be replenished						
l	$C_4H_6O_4$	15-2	28	2		buffer/complex compound						
l	$C_4H_6O_5$	10-2	20	15		buffer/complex compound						
	Na ₂ HPO ₃	<25) <100		100	harmful when formed						
	pН	4.00-5	5.20	4	.80	dec	reases,	must b	e buffe	ered an	d adjus	sted
l	Temp, °C	85-9	95	ç	92	pro	vides r	eaction	energy	, must	be sta	bilized
l	Ferrous substrate	Perrous substrate with radius of 1.60 cm,			em,	substrate and catalyst						
		thick	ness of	about 5	10 µm	c		.1 1	, .			
	Fe(III)					for	med in	the pla	ting pro	ocess		
						•						
	Tnfluence	e of Co	molev (Tabl J Nicl	.e∠ ∞⊃l ⊆ul	fate	Sodium		hognh	nito	
1			& Tempe	erature	on Abs	orband	ce of Fe	e(III)	unypor	piloppi	iiice	
	Parameter											
l	Complex compound	l (g/L)	0.00	0.70	1.40	2.10	2.80	3.50	4.20	4.90		
	Absorbance		0.256	0.270	0.289	0.303	0.318	0.311	0.322	0.326		
	Nickel sulfate (g/L)		0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.0		
l	Absorbance		0.321	0.322	0.321	0.322	0.319	0.318	0.319	0.320		
,	X 1 1 1 1 1	A 1	0.0	o -	1.0		•		•			
	Na hypophosphite (g	g/L)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.0		
	Ausorbalice		0.525	0.521	0.528	0.525	0.515	0.522	0.518	0.525		
L	Temperature (°C)		25	30	35	40	45	50	55	60	65	70
l	absorbance		0.321	0.321	0.320	0.319	0.318	0.317	0.318	0.315	0.314	0.317

etry.¹² Lu Guoliang determined iron in sillimanite with oxytetracyline using spectrophotometry.¹³ All these methods could not be applied to determine the concentration of iron in EN solution, however. The focus of this paper is to investigate the factors that may influence the absorption of Fe(III) systematically, and to develop the optical analytical method of iron in EN solution, which is produced in the plating process.

Without use of an extra color reagent, we oxygenated Fe(II) to Fe(III), dispelling the interference at 312.0 nm for the measurement. We could then determine total iron in EN solution by monowavelength spectrophotometry rapidly and accurately.

Experimental Procedure

Reagents	

Chemicals used were: $NiSO_4 \cdot 6H_2O$, $NaH_2PO_2 \cdot H_2O$, NaOH, H_2SO_4 , $(NH_4)_2S_2O_8$, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, *dl*-malic acid and succinic acid. All except *dl*-malic acid were analytical reagents. All experiments were prepared by adding suitable amounts of the organic acids (referred to as the complex compound), sodium hypophosphite and nickel sulfate together, then using H_2SO_4 or NaOH to adjust the pH.

During the plating process, the concentration of Ni⁺² was determined by spectrophotometry.¹⁴ When the concentration of Fe(III) was very high, the probable concentration was estimated, then diluted to a suitable concentration for the determination. At different stages, the diluted times were

different and the influence of bland reagents and diluting water was very small. Spectra were referenced vs. a cuvette filled with distilled water.

Apparatus

Absorbance spectrophotometry

The instrument used for all absorbance measurements was a dualwavelength/double-beam recording spectrophotometer. The cuvettes were quartz glass of one cm optical path length. The bandwidth of the slit was 2 nm, the scan range was from 250 to 420 nm. The scan speed was 200 nm/min.

The plating experiments were conducted at 90 ± 2 °C. The concentration of nickel sulfate was determined every 20 min.¹⁴ After determination of Ni⁺², other constituents in the EN plating baths were added according to the usual procedures of EN plating.¹⁵

Results & Discussion

Selection of Wavelength for Measurement

The constituents of EN solutions are complex. There are many peaks of absorbance in the range 800-200 nm. Fe(III) had absorption at a wavelength lower than 450 nm. The absorbance peak at 390 nm represents absorption of Ni⁺²,¹⁶ shown in Fig. 1. From curve a, it can be seen that there was almost no absorption between 340 and 310 nm, especially between 312.0 and 326 nm. The absorbance almost reached zero when there was no iron. From curves b and c, it is clear that



Fig. 3-Relationship of oxidation efficiency vs. air-blast time.



Fig. 4—Concentration increase of iron during plating.

with increasing Fe(III), absorption in this range increased correspondingly. To eliminate the interference of the other components and to increase the sensitivity of measurement, the maximum absorption peak cannot be selected. The least interference and largest absorption selected was at 312.0 nm.

Influence of pH on Absorbance of Fe(III)

In Fig. 2, the constituents of the EN solution and the concentration of Fe(III) were fixed-only their pH varied in the range 1.00 to 7.00. From Fig. 2 it can be seen that there was a sudden change of absorbance, which increased correspondingly. It could be explained that as the concentration of H+ increased, the balance of the complex reaction moved, which led to change in the structure of the complex compound.¹⁴ When the pH was greater than 4.40, the absorbance showed almost no change. This phenomenon could be explained as the complex compound being in the anionic state. When the pH was greater than 4.40, the reaction of Fe(III) with the complex compound was balanced. So if the pH was only between 4.40 and 6.00, the measurement would be successful [too high a pH might cause precipitation of Ni(OH), and $Fe(OH)_2$].

Influence of Complex Compound On Absorbance of Fe(III)

The other constituents (Table 1) in the EN solution were fixed, with the concentration of Fe(III) at 6.07 mg/L. The concentration of the complex compound was varied between 0.0 and 5.0 g/L. The absorbance of Fe(III) is shown in Table 2, where it can be seen that with increasing concentration of the complex compound, the absorbance of Fe(III) at 312.0 nm showed a tendency to increase. With the concentration of

complex compound increased, the complex balance moved to the side of the complex compound and water was displaced from the complex $Fe(H_2O)_6^{+3}$ so that absorbance was increased.¹⁴ From Table 2, it can also be seen that the absorbance changed little when the concentration of complex compound was in the range 2.8 to 4.9 g/L. Moreover, the quantity of complex compound was scarcely consumed and could be adjusted according to the additive process,¹⁵ so their concentration could be stabilized in the optimum range (see Table 1). Accordingly, the optimum concentration of the complex compound (3.5 g/L) was selected for measurement.

Influence of Nickel Sulfate

& Sodium Hypophosphite on Absorbance of Fe(III) The other concentrations in the EN solution were fixed and the concentration of Fe(III) was 6.07 mg/L. The concentrations of nickel sulfate and sodium hypophosphite were varied over the range of 0.0 to 5.0 g/L, respectively. Their absorbance is shown in Table 2. From the results, it can be seen that when their concentration was changed in this range, there was almost no influence on the absorbance of Fe(III). So 2.7 g/L was selected for both nickel sulfate and sodium hypophosphite as the suitable concentration for measurement.

Influence of Temperature on Absorbance of Fe(III)

Everything in the EN solution, including Fe(III) was fixed and the temperature was varied from 25 to 70 °C. The absorbance is shown in Table 2, where it can be seen that temperature had little effect on the absorbance of Fe(III). We selected 25 °C, therefore, which was the normal temperature for our experiments.

Working Curve

The pH and concentration of all components was adjusted to the selected conditions. Their absorbance was measured at 312.0 nm; it followed Beer's law when the concentration of Fe(III) was changed in the range 0.02 to 19.42 mg/L (in steps of 1.21 mg/L). The working curve could be described by: A = $0.05041 C_{E_2} + 0.00905$, with a correlation coefficient of 0.99971. Its molar absorptivity coefficient was 2.94 x 103 mol⁻¹ cm⁻¹.

Oxidation of Fe(II) to Fe(III)

The concentration of iron in the EN process was different at different metal turnovers (MTO). A certain amount of iron was in the Fe(II) oxidation state. Moreover, its molar extinction coefficient at 312.0 nm was different. To determine the concentration of iron in an EN solution with high accuracy, the Fe(II) must be oxidized to Fe(III). There were many methods that could accomplish the oxidation, but an experimental method was tried. We alkalized a certain amount of EN solution with Fe(III), plus an oxygen-enriched air blast for many minutes, then diluted it and measured. The relationship of blasting time with efficiency of oxygenation is shown in Fig. 3, which indicates that the efficiency of oxygenation could be as great as 96 percent. In this study, we also used $(NH_4)_2S_2O_8$ solution as the oxidant to oxidize Fe(II) to Fe(III), shown in the following recovery test.

Iron Produced & Accumulated in EN Solution By Spectrophotometry

The EN solution listed in Table 1 was used. When the iron sheet was immersed, the absorbance at 312.0 nm increased greatly in the initial stage. With increasing time, the deposited Ni-P alloy covered the substrate completely, halting

RecoveryTest							
Added iron (m	ıg/L)	Recovery by Alkalization & Air Blast %	Recovery by Oxidation with $(NH_4)_{,S_2}_{,s_2}$ %				
Fe(II)	Fe(III)		4220				
2.9613	3.64146	96.13	97.46				
5.9226	3.6678	97.33	99.00				
3.5719	7.2829	99.83	99.46				
8.8839	0.0000	94.22	96.64				

further dissolution and therefore the increase in absorbance at 312.0 nm. A new iron sheet produced the same result, as shown in Fig. 4. This proved that the reactions of Eqs. (3) and (4) had occurred, confirming our expectations.

Recovery Test

According to Table 1, after oxidation of Fe(II) to Fe(III), it was diluted 10 times, using the same method as in the working curve, with results as shown in Table 3. From Fig. 3 and Table 3, it was clear that the method of blowing air was labor intensive and that if $(NH_4)_2S_2O_8$ solution was the oxidizer, the efficiency was very good, so $(NH_4)_2S_2O_8$ was the oxidizer of choice.

Determination of Total Iron in EN Solution

The iron sheet was changed every 80 min. During the plating process, samples were taken from the EN solution, a certain amount of $(NH_4)_2S_2O_8$ solution was added, and the samples diluted, then measured at 312.0 nm. Then the concentration of iron in EN solution could be obtained using the equation of the working curve. The concentration of iron in the EN solution at different times is shown in Fig.4, where it can be seen that the concentration of iron increased rapidly at the beginning of immersing the sheet. Moreover, from Fig. 4 it was apparent that the dissolution of iron was different with different substrate sheets. The reason was that as plating progressed, by-products accumulated, the deposit rate became slower and complete coverage of the substrate required more time. At different stages of the plating process, we assessed the probable concentration of iron in the EN solution, diluted it, then determined. From Fig. 4, we could also see that after the substrate was covered by Ni-P alloy, phosphate was generated continuously, but the absorbance of Fe(III) was stabilized. Our conclusion was that phosphate has almost no effect on the absorbance of Fe(III).

Summary

It was proved that there is a reaction involving partially dissolved iron sheets during EN plating by use of spectrophotometry, setting up a new method to determine the concentration of iron in EN solution using mono-wavelength at 312.0 nm. To determine the concentration of iron in EN solution at this wavelength, the linear range was wide, with other constituents of the EN solution having almost no influence on the absorbance of iron.

From these facts, it may be concluded that if the concentration of iron in EN baths did not increase during the plating process, the iron sheet must be covered completely by Ni-P alloy. It was of great importance to investigate every reaction during EN plating, to study the mechanism of EN plating and to improve the stability and the properties of the Ni-P alloy.

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