Rapid Spectrometric Determination of Ni(II) In Electroless Nickel Deposition Baths Containing Iron

by R. Liu, C. Gao, S. Hua, Y. Feng, & J. Yang

The influence of complexant, temperature, Fe(III), Fe(II), pH, $NaH_2PO_2 \cdot H_2O$ and KIO_3 on the absorbance of Ni(II) in an electroless nickel (EN) bath was investigated. The results showed that this method was easy-to-operate, and offered quick and accurate determination especially when the EN solution contained iron. The method produced no waste in the analytical process. It can be applied to rapid determination and in-site control of Ni(II) in EN deposition baths when plating on iron.

Because of its properties of compact texture, uniform thickness, high hardness, good wearability and high corrosion resistance, the electroless nickel (EN) process has generated a wide variety of applications in the aerospace, automotive, electronics/computers, machinery, nuclear, oil and gas production and valve industries.[1-3]

With the continuing research into functional materials, more and more EN plating processes are being developed.[3-8] Nickel (II) is continuously consumed in the plating process, so the rapid, accurate determination and adjustment of Ni(II) in the EN solution is therefore critical to the deposition rate, deposit properties, solution stability and successful plating operation.

In our previous work, we showed that iron is dissolved in an acidic EN plating solution during the plating process, when iron sheet is used as a substrate.[5] The reactions are as follows:

$$Fe + 2H^+ \longrightarrow Fe(II) + H_2\uparrow \qquad (1)$$

$$Fe(II) - e \longrightarrow Fe(III) \qquad (2)$$

In another work, we developed a rapid differential spectrophotometric method to determine Ni(II) at the characteristic wavelength of 389.7 nm.[10] There are many methods to determine the concentration of Ni(II) in an EN solution, such as titration, voltammetry[11,12] and spectrometry.[10,13] The accuracy of titration methods can meet the demands of regular production, but it is labor intensive and requires considerable amounts of reagents. The sample taken cannot be reused, which results in more waste. With voltammetry, the scan speed, temperature and condition of the mercury film have a great influence on the peak intensity. Furthermore, the electrode surface must be polished and plated with mercury. So, it is also labor intensive. Even our previous spectrometric method cannot be used to determine Ni(II) when iron-based substrates are used or if Fe(III) or Fe(II) are present in solution. No systematic study on the detection of Ni(II) in the presence of Fe(III) and/or Fe(II) has been reported in the literature. Therefore we undertook to study the influence of complexants, Fe(III), Fe(II), $NaH_2PO_2 \cdot H_2O$, KIO_3, pH and temperature on the spectrophotometric detection of Ni(II). This method can be directly applied to determine the concentration of Ni(II) in the plating process whether there is Fe(III), Fe(II) or neither.

Experimental Procedure

The nominal composition and operating conditions used in the acidic electroless nickel plating solution are given in Table 1. The actual range of variation for the factors studied is given in the section on Results & Discussion later in this article. However, during

Table 1
Main Constituents of the Acidic Nickel Plating Baths Studied

Component	Range	Optimum	Remarks
$NiSO_4 \cdot 6H_2O$	16-35 g/L	27 g/L	Consumed; must be replenished
$NaH_2PO_2 \cdot H_2O$	18-30 g/L	27 g/L	Consumed; must be replenished
$C_4H_6O_4$, Succinic acid	15-28 g/L	20 g/L	Buffer/complexant
$C_4H_6O_5$, DL-malic acid	10-20 g/L	15 g/L	Buffer/complexant
$C_2H_3O_2$, Acetic acid	10-20 g/L	16 g/L	Buffer
Na_2HPO_3	<250 g/L	<100 g/L	Generated in the process; reduces efficiency
KIO_3	14-20 mg/L	16 mg/L	Stabilizer
pH	4.3-5.2	4.8	Adjust with NaOH or H_2SO_4
Temperature	80-93ºC	90ºC	

the plating process, the main constituents were adjusted within the ranges shown.

Reagents Used & General Procedures

With the exception of the DL-malic acid, which was chemical-reagent grade, all chemicals were analytical reagents. All solutions were prepared by first adding suitable amounts of the complexant, sodium hypophosphite, potassium iodide and nickel sulfate and then adjusting to the required pH with either sulfuric acid or sodium hydroxide. Since the concentration of iron in the EN solution varied with time, spectra were referenced versus a cuvette filled with distilled water.

Apparatus

The instrument used for all absorbance spectrophotometry measurements was a dual-wavelength/double-beam recording spectrophotometer. Quartz glass cuvettes having a 1-cm optical path length were employed. The brand width of slit was 2 nm and the scan range was from 360 to 860 nm. The scan speed was 200 nm per minute. Spectra were referenced versus a cuvette filled with distilled water. A pHs-2 typed pH meter was employed.

Results & Discussion

Selection of Measurement Wavelength

The constituents of the EN solution are complex. There are three peaks for Ni(II) at 390.0, 655.0 and 715.0 nm,[11,13] which can also be seen in Fig. 1(lines c, d, e). From lines a and b, it can be seen that Fe(III) and Fe(II) have no absorbance between 474 and 860 nm. The absorbance of Fe(III) or Fe(II) is quite significant when the wavelength is lower than 474 nm. Fe(III) or Fe(II) strongly interfered with the absorbance of Ni(II) at 390 nm, while it had no influence on the absorbance of Ni(II) at 655 nm or 715 nm (Fig. 1, lines c, d, e). It is clear that the 390-nm wavelength cannot be used to determine the concentration of Ni(II) when iron sheet is used as the cathode, or when Fe(III) or Fe(II) are present in solution. Thus we selected wavelengths of 655 nm and 715 nm for further research.

Influence of pH on the Absorbance for Ni(II)

The composition of the electroless nickel solution and the concentration of Ni(II) were fixed, while the pH was varied in the range from 1.0 to 5.5. In Fig. 2, we can see that there was a notable change of absorbance at 655 nm and 715 nm with changing pH. As the concentration of hydrogen ions increased, the reaction equilibrium shifted which changed the nature of the bath chemistry.[13] When the pH value was higher than 4.4, the absorbance showed no obvious change.

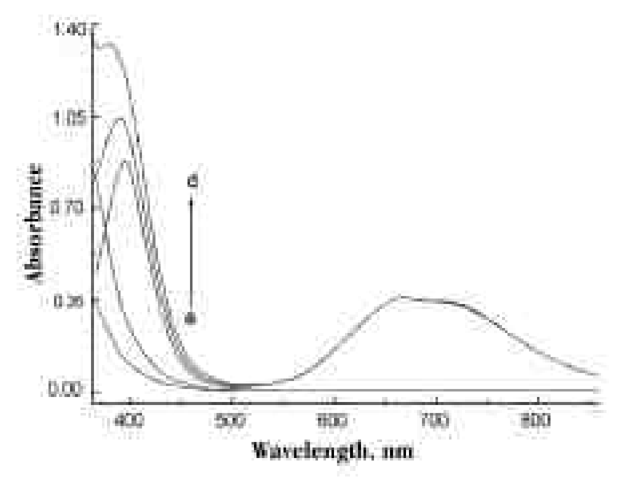

*Fig.1—The absorption of Ni(II) and Fe(III): **(a)** complexant (51g/L) + NaH2PO2·H2O (27g/L) + KIO3 (16g/L) + Fe(III) (20g/L); **(b)** a) + Fe(III) (40g/L) + Fe(II) (40g/L); **(c)** NiSO4·6H2O (27g/L) + complexant (51g/L) + NaH2PO2·H2O (27g/L) + KIO3 (16g/L); **(d)** c)+Fe(III) (20g/L); **(e)** d) + Fe(III) (80g/L).*

This phenomenon can be explained by the fact that the complexant was in an anionic state when the pH was greater than 4.3, and the reaction of Ni(II) with the complexant was balanced.[10,11] If the pH were between 4.3 and 5.5, the measurement would be successful. Too high a pH might cause precipitation of $Ni(OH)_2$. On this basis, we selected a pH value of 4.8 for further research.

Influence of Complexant on the Absorbance for Ni(II)

Again fixing the concentration of the other constituents in the EN solution, the concentration of the complexant was varied between 0.0 and 37.8 g/L. The concentration was increased in steps of 5.4 g/L . The absorbance of Ni(II) is shown in Fig. 3 (the 5.4 g/L increments as lines a thru h), where it can be seen that increasing the concentration of complexant increased the absorbance of Ni(II) at both 655 nm and at 715 nm. With increasing complexant, the complex equilibrium shifted to the side of the complex compound and water was displaced from the $Ni(H_2O)_6(II)$ complex. Therefore, absorbance was increased. From Fig. 3, it can also be seen that the absorbance changed little when the concentration of complexant was in the range of 21.6 to 37.8 g/L. Moreover the quantity of complexant was scarcely consumed and could be adjusted according to the additive process[16]. The complexant concentration could be stabilized in the optimum range. Accordingly the optimum concentration

Table 2
Influence of $NaH_2PO_2 \cdot H_2O$ KIO_3, $NaHPO_3$ & Fe(III) on the Absorbance for Ni(II)

NaH_2PO_2	Concentration, g/L	0.0	4.0	8.0	12.0	16.0	20.0	24.0	27.0	32.0
	Absorbance	0.341	0.342	0.341	0.342	0.341	0.344	0.341	0.342	0.340
KIO_3	Concentration, mg/L	0.0	4.0	8.0	12.0	16.0	20.0	24.0		
	Absorbance	0.342	0.341	0.341	0.343	0.341	0.342	0.341		
NaH_2PO_2	Concentration, g/L	0	50	100	150	200	250			
	Absorbance	0.341	0.342	0.340	0.341	0.342	0.343			
Fe(III)	Concentration, mg/L	0	20	40	60	80	100	120		
Fe(II)	Absorbance	0.342	0.341	0.342	0.342	0.342	0.340	0.341		
	Absorbance	0.342	0.343	0.341	0.342	0.341	0.341	0.340		

Table 3
Inlfuence of Temperature on the Absorbance for Ni(II)

Temperature, ˚C	20	25	30	35	40	45	50	55	60	65	70	75
Absorbance	0.342	0.342	0.342	0.342	0.342	0.342	0.342	0.342	0.342	0.342	0.342	0.342

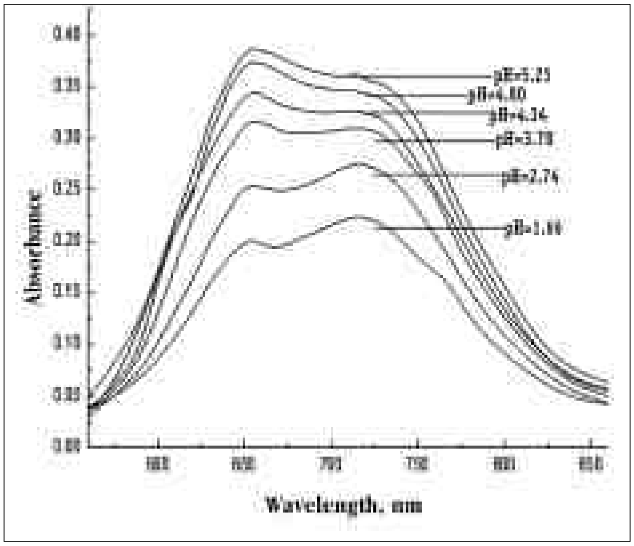

Fig.2—The influence of pH on the absorbance of Ni(II).

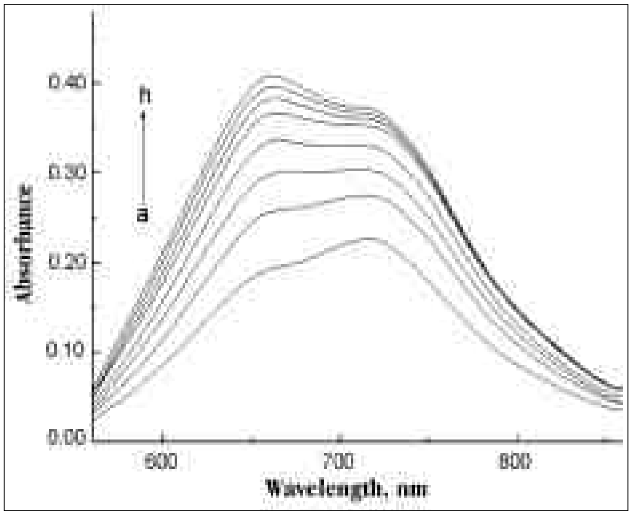

Fig.3—The influence of complexant on the absorbance of Ni(II).

of the mixed complexant (51.0 g/L) was selected for measurement. From Figs. 2 and 3, it can be seen that the pH and concentration of complexant have a larger influence on the absorbance of Ni(II) at 655 nm than that at 715 nm for the same composition change. Therefore, a wavelength of 715.0 nm was selected for further research.

Influence of NaH$_2$PO$_2$·H$_2$O, KIO$_3$, NaHPO$_3$, Fe(II) & Fe(II) on the Absorbance for Ni(II)

While the other constituents in the EN solution were fixed, the concentrations of sodium hypophosphite, KIO$_3$, NaHPO$_3$ (Fe(II) and Fe(III) changed according to the values shown in Table 2. The results show that the concentration of NaH$_2$PO$_2$, KIO$_3$, NaH$_2$PO$_3$ and Fe(III) and Fe(II) had virtually no influence on the absorbance of Ni(II). So the change on the concentration of NaH$_2$PO$_3$ in EN solution during the plating process is negligible and the optical concentration of NaH$_2$PO$_2$·H$_2$O, KIO$_3$, NaHPO$_3$ and Fe(III) was selected at the suitable concentration for measurement.

Influence of Temperature on Absorbance for Ni(II)

While the constituents in the EN solution were fixed at the optimum concentrations, the temperature was varied from 20º C to 75 ºC. As shown in Table 3, the change of temperature had no influence on the absorbance for Ni(II). Therefore, the EN solution can be directly used in the cuvette for *in situ* determination during the plating process without having to correct for change in temperature.

Working Curve

The pH and the concentration of the other components were adjusted to the optimum conditions from this study. The absorbance was measured at 715 nm. The relationship between Ni(II) concentration and absorbance followed Beer's law when the concentration of nickel sulfate was varied from 0 to 30 g/L. The working curve could be described by the relationship:

$$A = 0.01263C_{Ni} + 0.00434 \qquad (3)$$

with a correlation coefficient of 0.9996.

Summary

The factors that may influence the absorbance of Ni(II) in electroless nickel solutions were investigated. A rapid and convenient method was developed for determining the concentration of Ni(II) when iron-based cathodes are used or if Fe(III) and or Fe (II) are present in solution. This method has a good linear correlation coefficient and can be applied to *in situ* control of Ni(II) in electroless nickel plating processes for iron-based substrates.

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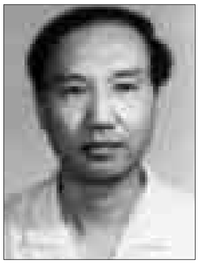

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