Estimation of electroless metal deposition rate from measured bath potential

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SUMMARY — Studies have indicated that the potential changes in an electroless metal plating system is affected by chemical constituents of the baths. A hypothesis is tested to estimate metal deposition rates from the potential changes. A comparison has been made between the theoretical and experimental estimates.

INTRODUCTION
Electroless deposition of a metal consists of two electrochemical reactions; the reduction of metal ions and the oxidation of a reducing agent. Simultaneously, the potential of metal plating bath changes. The extent of potential change depends on the change in the chemical composition of the bath. The purpose of this paper is to compare the experimentally determined metal deposition rates with the theoretical rates estimated from a hypothesis based on mixed potential theory and the potential/current curves of the electrochemical reactions.

Various electroless nickel and cobalt bath formulations with hypophosphite or hydrazine as the reducing agent have been described in the literature, but hypophosphite has found much more extensive technical application probably due to its high reducing power. However, a high hypophosphite concentration is not desirable because it results in bulk reduction of metal ions as opposed to selective catalytic deposition on the metal surface to be coated. In other words, bath stability decrease is a direct function of hypophosphite concentration. In this work, sodium hypophosphite was used as the reducing agent for nickel and cobalt ions in electroless systems and the influence of increasing metal ion concentration was studied.

EXPERIMENTAL PROCEDURES
Mild steel specimens were pretreated by being dipped in 30% HCl for 60 seconds, rinsed in deionized water, dried, weighed and stored in a desiccator. All chemicals used in preparing plating solutions were of analytical grade. The water used was deionized. Bath pH was adjusted with concentrated ammonia solution or concentrated H2SO4. The following electroless plating formulations were used:

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Concn.</th>
<th>Temp.</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO4</td>
<td>Variable*</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Sodium hypophosphite</td>
<td>10g/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycine</td>
<td>40g/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>10g/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>90°C</td>
<td></td>
</tr>
</tbody>
</table>

*50, 100 and 150g/l Ni ion

Cobalt Chloride Variable†
Sodium hypophosphite 20g/l
NH4Cl 50g/l
Thiourea 17g/l
pH 9.5
Temp. 85°C

†25, 50 and 75g/l Co ion

Potentials were measured using freshly deposited nickel or cobalt using the equipment shown in Fig 1. The auxiliary electrode (1cm² platinum sheet), the working electrode and the reference electrode already immersed in the plating solution were connected to the appropriate terminals of the potentiostat. The reference electrode (SCE) was used in combination with a Luggin capillary whose tip was placed 0.5mm from the 1cm² working electrode. Plating kinetics were obtained from the cathodic polarization data with the sweep-generating unit set at 50mVmin⁻¹ for a sweep time of 30 minutes. The current was monitored on the chart recorder.

RESULTS AND DISCUSSION
The Wagner and Traud theory of mixed potential postulates that the rate of a Faradaic process is independent of other Faradaic processes occurring simultaneously at the electrode and thus depends only on the electrode potential. Plating of metals involves a reaction proceeding at a rate controlled by activation and diffusion. In the case of Ni and Co plating, the polarization curves (Figs 2 and 3) show that diffusion is insignificant. The cathodic reactions are predominantly activation controlled.

Theoretical plating rate estimation
It is assumed that electroless plating electrochemical reactions is composed of the following reactions:

\[ \text{R} = \text{R}^* + \text{xe}^- \quad \text{(H}_2\text{PO}_2)^- \text{oxidation} \]
\[ \text{M}^* + \text{xe}^- = \text{M} \quad \text{Metal deposition} \]

When these two reactions are at steady state, the plating rate, \( i_p \), is given by:

\[ i_p = i_m = i_n \]

where \( i_m \) and \( i_n \) are respectively the cathodic and anodic reaction rates.
Table 1. Comparison of theoretical and experimental metal deposited in 30 minutes

<table>
<thead>
<tr>
<th>Ni ion concentration (g/l)</th>
<th>Bath steady potential (mV SCE)</th>
<th>wt deposited (mg)</th>
<th>theoretical</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>-633</td>
<td>3.03</td>
<td>7.60</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-613</td>
<td>4.22</td>
<td>7.90</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>-610</td>
<td>4.46</td>
<td>10.40</td>
<td></td>
</tr>
</tbody>
</table>

**Co ion concentration (g/l)**

<table>
<thead>
<tr>
<th></th>
<th>Bath steady potential (mV SCE)</th>
<th>wt deposited (mg)</th>
<th>theoretical</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-610</td>
<td>5.41</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-583</td>
<td>8.65</td>
<td>7.40</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>-552</td>
<td>14.6</td>
<td>10.30</td>
<td></td>
</tr>
</tbody>
</table>


Fig 2. Nickel ion reduction kinetics measured in plating solution containing (a) 25 g/l NiSO₄, (b) 10 g/l sodium hypophosphite, (c) 40 g/l glycine, (d) 10 g/l acetic acid maintained at 90°C and pH5.

Fig 3. Co²⁺ reduction kinetics measured in plating solution containing (a) 25 g/l cobalt chloride, (b) 20 g/l sodium hypophosphite, (c) 50 g/l NH₄Cl, (d) 17 g/l thiourea, (e) Trisodium Citrate 100 g/l maintained at 85°C, pH8.

Fig 4. Effect of Ni ion concentration on Ni plating.

Fig 5. Effect of Ni ion concentration on electroless Ni solution potential.

Fig 6. Effect of Co ion concentration on Co plating.

Fig 7. Effect of Co ion concentration on electroless cobalt plating solution potential.
The potential associated with this equilibrium condition is the mixed potential and the equation for the plating rate as a function of potential is given by:

\[ i_p = i_n = nF \exp(1-\beta) F/V \]

where \( K \) = reaction rate constant
\( V \) = electrode potential
\( \beta \) = symmetry factor (\( \approx 0.5 \))
\( n \) = number of electrons involved in the reaction.

Using the data for nickel deposition from Fig 2, at \(-620mV\) SCE, the deposition rate expressed as current density is about 7mA/cm\(^2\), i.e.

\[ i_{-0.620} = nF \exp ((1-\beta)F \times 0.620/RT) \]
\[ = 0.0076 Acm^{-2} \]

This expression can be used to calculate the theoretical nickel deposition rates at different potentials and then compared with those obtained experimentally at the same steady potentials obtained at different metal ion concentrations.

For example:
(i) When the above potential is decreased by 0.13V, the theoretical deposition rate (i.e. at \(-0.633V\)) is

\[ i_{-0.620} = nF \exp ((1-\beta)F \times 0.620/0.13/RT) \]
\[ = 0.0056 Acm^{-2} \]

(ii) when the plating potential is increased by 0.007V, the theoretical deposition rate is

\[ io_{0.613} = i_{-0.620} \exp ((1-\beta)F \times 0.007/RT) \]
\[ = 0.0078 Acm^{-2} \]

(iii) At the plating potential of \(-0.610mV\) SCE, the theoretical deposition rate becomes

\[ i_{-0.610} = i_{-0.620} \exp ((48250) \times 0.10/RT) \]
\[ = 0.0082 Acm^{-2} \]

Similarly for cobalt deposition, at 820mV SCE, the deposition rate is about 0.00035A/cm\(^2\) as indicated in Fig 3, i.e.

\[ i_{-0.820} = nF \exp ((1-\beta)F \times 0.820/RT) \]
\[ = 0.00035Acm^{-2} \]

Using this to calculate the theoretical rates at the different potentials:

1. When the plating potential is raised (by 0.21V) to \(-610mV\) SCE, the theoretical deposition rate becomes:

\[ i_{-0.610} = i_{-0.620} \exp (0.5 \times 96500 \times 0.210/RT) \]
\[ = 0.010 Acm^{-2} \]

2. Similarly, at the potentials of \(-0.583\) and \(-0.552mV\) SCE, the respective theoretical plating rates are 0.016 and 0.027 Acm\(^{-2}\).

The theoretical and experimental metal deposition rates at these potentials are compared in Table 1. The theoretical deposition currents are converted to "weight deposited in 30 minutes", the period for which the experimental weight gain was obtained. The weight gain at various bath potentials were extracted from the results in Figs 4, 5, 6 and 7.

The discrepancies between the theoretical and experimental deposition rates are due to the difficulties encountered in obtaining very accurate measurements under the operating conditions of the baths. Parts of the substrates may be lost due to solution attack at high temperatures, and deposited metal may be lost into solution. Nevertheless, the theoretical and experimental estimates for cobalt are close, and for both nickel and cobalt also agree in another respect – the deposition rates increase as the potentials become noble (less negative).

CONCLUSION

The metal plating rate \( i_p \) may be predicted from the measured bath potential \( V \) in an electroless metal plating system using the expression

\[ i_p = nF \exp ((1-\beta)F V/RT) \]

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REFERENCES