Effects of Heavy Metal Ions on the Rate of Electroless Nickel Plating*

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The effects of heavy metal ions (Zn²⁺, Cd²⁺, Tl⁺, Pb²⁺) on the rate of electroless nickel plating were studied by the potential sweep method and also by a radiotracer technique using ²⁰⁴Tl⁺. With the exception of ZnCl₂, an addition of heavy metal salts studied resulted in the cessation of electroless nickel deposition at the concentration of about 2.0 mM. The effects of the heavy metal ions on the electroless nickel plating were elucidated through the analysis of the partial anodic and cathodic reactions in the electroless nickel plating bath. The inhibiting action of ZnCl₂ for the oxidation of sodium borohydride at the nickel electrode is not so strong as that of the other metal salts studied because Zn was not incorporated into nickel. A definite correlation was found between the deposition rate of nickel and the mixed potential in the electroless nickel plating bath. Radiochemical study of the deposition of Tl indicated that the incorporation of thallium into the nickel deposit is controlled by the diffusion of thallous ions. The incorporation of thallium decreased the catalytic activity of the nickel surface for the anodic oxidation of sodium borohydride.

1 Introduction

Electroless nickel plating bath essentially consists of a reducing agent and nickel ion, then such a system is thermodynamically unstable, however, kinetically stable under optimum conditions for the deposition of nickel. The electroless deposition of nickel occurs selectively only at a catalytic surface by the controlled chemical reduction of nickel ion. A reducing agent such as sodium borohydride supplies electrons for converting nickel ion to nickel. If electroless nickel bath is operated at a high temperature or with a high borohydride concentration, powder deposits are formed spontaneously in the bulk of the solution, and the rapid decomposition of the bath may occur. It is well known that trace amounts of various stabilizers are used effectively to prevent undesirable bath decomposition. In the previous paper¹, the effect of thiourea on the deposition rate of nickel has been discussed in relation to the stability of the electroless nickel plating bath. The primary purpose of this study is to make clear the change in the deposition rate of nickel with an addition of heavy metal salts on the basis of the mixed potential theory.

From the practical point of view, it is interesting to know the behavior of these metal ions in the electroless nickel plating bath³.

2 Experimental

2.1 Reagents

Special grade chemicals were used without further purification in preparing the electroless nickel bath except for nickel chloride which was purified by the same method as described in the previous paper¹. The radioactive thallous nitrate was obtained from New England Nuclear Corp. (U.S.A.) and was reduced to thallous nitrate by metallic thallium⁴. The completion of the reduction of thallous to thallium ions was confirmed by the polarographic method. Radioactive ¹⁴⁴Tl⁺ was diluted with inactive thallous nitrate to give the specific activity of 0.213 mCi/mM. In each experiment, an appropriate amount of radioactive ¹⁴⁴Tl⁺ was added to the electroless nickel plating bath. The amount of thallium incorporated in the nickel deposit was determined by the same techniques as described in the previous paper¹.

2.2 Deposition rate

Bath A shown in Table 1 was used for evaluating the effect of various metal ions on the deposition rate of nickel. A copper sheet (50cm²) was used as a substrate, which was sensitized by the same method as described previously³, and electroless nickel plating was carried out at

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* Studies on the Electroless Nickel Plating with NaBH₄ as a Reducing Agent (Part 9)
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Table 1 Bath composition

<table>
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<tr>
<th>Type</th>
<th>NiCl₂</th>
<th>Na₃T</th>
<th>Gly</th>
<th>NaOH</th>
<th>NaBH₄</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.04 M</td>
<td>0.16 M</td>
<td>0.1 M</td>
<td>0.3 M</td>
<td>variable</td>
<td>variable</td>
</tr>
<tr>
<td>B</td>
<td>0.04 M</td>
<td>0.16 M</td>
<td>0.1 M</td>
<td>0.3 M</td>
<td>-------</td>
<td>variable</td>
</tr>
<tr>
<td>C</td>
<td>0.16 M</td>
<td>0.1 M</td>
<td>0.3 M</td>
<td>variable</td>
<td>variable</td>
<td>variable</td>
</tr>
</tbody>
</table>

Additives: ZnCl₂, CdCl₂, TlCl, PbCl₂, Na₃T; Sodium Tartrate, Gly; Glycine

60°C for 30 min. The deposition rate of nickel was determined from the weight gain during the electroless plating and the amount of hydrogen gas evolved was measured with a gas buret.

2.3 Electrochemical measurement

The steady-state mixed potential of the test electrode in the electroless nickel plating baths was measured with a recording potentiometer against an Hg/HgO electrode at 60°C. In each experiment the test electrode was freshly prepared by the electrodeposition of nickel on platinum wire (0.5 mm, 0.64 mm) sealed in a glass tube. Baths B and C, given in Table 1, were used for the measurement of cathodic and anodic polarization curves. The measurement was carried out by the potential sweep method using the same instrument and cell assembly as described in the previous paper. After removal of oxygen from the test solution by bubbling purified nitrogen, potential scan was performed at 500 mV/min.

3 Results and Discussion

3.1 Deposition rate of nickel and hydrogen evolution

Electroless nickel plating is very sensitive to impurities in the bath. It is very interesting, therefore, to find out the effect of trace amounts of heavy metal ions on the deposition rate of nickel and also on hydrogen evolution. The deposition rate of nickel, shown in Fig. 1, was affected by the type of additive used and its concentration. The deposition rate of nickel substantially increased with an addition of CdCl₂ or TlCl up to about 0.4 mM, however, a further increase in the concentration of the additives caused the rate of deposition to fall off steadily and to become nil at about 2.0 mM since the heavy metal ions act as a catalytic poison. An addition of PbCl₂ up to 1.0 mM gave rise to a steady decrease in the deposition rate of nickel and a further increase in the concentration of PbCl₂ resulted in the complete cessation of the nickel deposition. However, such inhibitions for the nickel deposition could not be detected even in the presence of 2.0 mM ZnCl₂.

The electroless deposition of nickel is always accompanied by hydrogen evolution, and hence the dependence of the molar ratio of hydrogen to nickel (H₂/Ni) on the concentration of heavy metal salts was examined in the course of electroless nickel deposition. The value of H₂/Ni, given in Fig. 2, decreased with the addition of a small amount of TlCl or PbCl₂, and led to the limiting value (1.0). In the case CdCl₂, the H₂/Ni ratio had a maximum at about 0.2 mM and then decreased gradually with increasing concentration of CdCl₂. An addition of ZnCl₂, however, caused the H₂/Ni ratio to increase appreciably with the concentration, which can be explained in terms of hydrogen overvoltage of the electrode. With the exception of Zn, the
heavy metals which have the higher hydrogen overvoltage than that of nickel were codeposited on the electrode in the course of electroless plating of nickel, whereas the reduction of zinc ion scarcely occurred in the potential region investigated as will be shown in the following section. Incorporation of Cd, Tl or Pb into nickel reduced the value of H$_2$/Ni to about 1.0 and gave lustrous nickel deposits. However, the electroless plating bath containing TlCl greater than 1.0 mM gave rise to many cracks in the nickel deposit. The high value of H$_2$/Ni in the case of cadmium might be due to the less noble deposition potential of Cd compared with Tl or Pb. From the practical point of view, TlCl and PbCl$_2$ seemed to be effective as a stabilizer in the electroless nickel plating bath.

3.2 Electrochemical analysis of the electroless nickel plating on the basis of the mixed potential theory

The electroless nickel plating process is essentially comprised of the partial anodic and cathodic reactions. Electrons consumed in the reduction of nickel and hydrogen ions are fed by the catalytic oxidation of sodium borohydride. Effects of the foreign metal ions on the rate of nickel deposition and hydrogen evolution would be elucidated by the systematic analysis of the partial reactions. The cathodic polarization curves for the nickel electrode in bath B containing various heavy metal salts are shown in Fig. 3. In the absence of heavy metal salts, two reduction peaks corresponding to the nickel deposition were observed at about −0.3 V and −1.0 V (vs. Hg/HgO), respectively. With an addition of 1.0 mM ZnCl$_2$ to the bath, the first peak was shifted to the less noble potentials and the second peak became obscure owing to hydrogen evolution. No deposition of zinc was observed at the potentials more noble than about −1.3 V because bizincate or zinicate anions were predominant in the bath B. Consequently, changes in cathodic polarization curves with an addition of ZnCl$_2$ may be ascribed to the adsorption of these anions. An addition of CdCl$_2$, TlCl, or PbCl$_2$ diminished the first peak in the cathodic polarization curve owing to the deposition of the corresponding metals.

The anodic polarization curves shown in Fig. 4 were measured by the potential sweep method, in which the potential of nickel electrode was held at −1.13 V (vs. Hg/HgO) for 1 min prior to anodic sweep. In the absence of heavy metal salts, the oxidation of sodium borohydride took place at the potentials more noble than −1.3 V. A limiting current, which was observed in the potential range from −0.9 V to −0.7 V, was found to be controlled by the diffusion of borohydride ions. Hydrogen evolution in the potential
region tested resulted in fluctuation of the limiting current, which indicated that the borohydride ion could hardly be oxidized via an electrochemical reaction involving eight electrons as pointed out by many authors\(^7\)\(^1\)\(^\text{12}\). An addition of 1.0 mM ZnCl\(_2\) to the bath slightly inhibited the oxidation of sodium borohydride as shown in Fig. 4. This type of inhibition might be due to the adsorption of the bizincate or zincate ions on the active sites of the nickel electrode. The oxidation of borohydride ions was completely inhibited by the addition of TICl or PbCl\(_2\) at potentials less noble than \(-0.75\) V, however, borohydride began to oxidize at the potentials more noble than \(-0.6\) V, because of the appearance of an active nickel surface by the dissolution of Tl or Pb. In the presence of 1.0 mM of CdCl\(_2\), the borohydride was no longer oxidized since the active nickel surface taking part in the catalytic reaction was diminished by the formation of a cadmium oxide film at about \(-0.85\) V\(^{11}\).

3.3 The mixed potential

The mixed potential in the electroless nickel plating bath is determined by the partial anodic and cathodic reactions, which are influenced by the presence of foreign metal ions as described in the preceding section. It is, therefore, interesting to know the mixed potential established in the course of the electroless nickel deposition. The mixed potential of the test electrode, shown in Fig. 5, gradually became noble with increasing concentration of the CdCl\(_2\), TICl or PbCl\(_2\) up to the critical amount, above which the mixed potential was shifted drastically in the noble direction (about \(-0.6\) V \(\text{vs. Hg/HgO}\)). This potential shift corresponded to the cessation of the electroless nickel deposition. (cf. Fig. 1)

On the other hand, such a positive shift in the mixed potential was not observed with an addition of ZnCl\(_2\). The behavior of zinc chloride in the electroless nickel plating bath can be explained on the basis of the deposition potential of Zn which was less noble than that of the other metals studied.

3.4 Radiotracer technique

The incorporation of thallium into the nickel deposit was pointed out by the electrochemical analysis of the partial cathodic reaction in the electroless nickel plating bath as described above. Chemical analysis is available for the determination of the additives in the nickel deposit. However, the methods are somewhat troublesome to use and sometimes they are not sensitive enough to detect the impurities in trace amounts, whereas a radiotracer technique is very convenient for this purpose. The amount of incorporated thallium was determined by using radioactive thallous nitrate (\(^{203}\)Tl\(^{+}\)). The amount of thallium in the nickel deposit increased with plating time as shown in Fig. 6. This finding indicated that the incorporation rate of thallium depends upon the concentration of thallous ion and is constant during the electroless nickel plating. The Tl content in the nickel deposit shown in Fig. 7 increased with an increase in the concentration of TINO\(_3\) up to 1.5 mM, but a further increase in the thallous ions resulted in a decrease of Tl content. As the deposition rate nickel decreased drastically above the concentration of 1.5 mM TINO\(_3\), the atomic ratio of thallium to nickel in the deposit

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**Fig. 6** Effect of plating time on the amount of Tl incorporated into nickel deposit

**Fig. 5** Effect of the concentration of additives on the mixed potential
Effect of TlNO₃ concentration of the amount of Tl incorporated into nickel deposit

Potential (V vs. Hg/HgO)

Greatly increased, which indicated that all active sites on the nickel surface are covered with thallium.

The diffusion of the thallous ion has an important role in determining the incorporation rate of thallium in the electroless nickel plating. Effect of agitation of the bath on the deposition rate of thallium is shown in Fig. 8. Thallium was electrodeposited on a copper substrate at a constant potential for 1 min and then the electrode was washed with acetone instead of water to prevent its dissolution in water and then dried quickly. The deposition rate of Tl was substantially increased by stirring the bath in the less noble potentials where the electroless nickel deposition was actually taking place. These results imply that the incorporation rate of Tl into the nickel deposit is controlled by the diffusion of thallous ions from the bulk of the solution to the electrode surface.

4 Conclusions

The effect of the heavy metal ions on the rate of nickel deposition and hydrogen evolution was investigated by means of the potential sweep method and radiotracer technique. The codeposition of Cd, Tl or Pb with nickel was pointed out by the electrochemical analysis of the partial cathodic reaction in the electroless nickel plating bath. The incorporation of Tl into the nickel deposit was detected by the radiotracer technique by using thallous nitrate (²²⁸Tl). The complete cessation of the nickel deposition was observed in the presence of about 2.0 mM of CdCl₂, TlCl or PbCl₂ owing to the adsorption or deposition of the corresponding metals. The behavior of the ZnCl₂ in the electroless nickel plating bath was explained from the fact that zinc has the less noble deposition potential compared with the other metals studied. Inhibiting action of the foreign metals in the electroless nickel bath was elucidated by the assumption that the active sites eligible for the oxidation of sodium borohydride is completely covered with the foreign metals which have a high hydrogen overvoltage. Higher efficiency of borohydride utilization is achieved by an addition of TICl or PbCl₂ in the electroless nickel plating bath with a high rate of nickel deposition.

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