Speciation in Electroless Nickel Solutions

By N. M. Martyak & J.E. McCaskie

The role of complexing agents in electroless nickel solutions is studied using speciation calculations. Electroless nickel solutions, employing lactic or aspartic acids or glycine, decrease the concentration of free nickel. The most predominant nickel species in solution are $Ni(CH_3CH(OH)COO)_3^-$, $Ni(OOCCH_2CH(NH_2)COO)_2^{-2}$ and $Ni(H_2NCH_2COO)_3^-$. All solutions exhibit a fraction of free nickel, which decreased with increasing formation constant of the nickel-ligand species. The plating rate and solution stability are dependent upon the structure of nickel in solution. Higher deposition rates were observed in nickel solutions with fewer chelated sites in the nickel complex.

The chemistry of electroless metal solutions is complex, and the deposition mechanisms are not well understood. The rate of deposition, structure and properties of the coating are dependent upon the chemistry of the solution, concentration of reagents, pH and temperature. Variations in solution components and concentrations may require a concomitant change in the pH and temperature to maintain solution stability or deposit properties. Often, the nature of the chelating agent used in electroless solutions affects not only the plating process and deposit properties but may also influence subsequent waste-avoidance technology of spent solutions.

The complexity of electroless metal deposition is in part a consequence of the structure of the metal in solution. Damjanovic,[1] Conway and Bockris[2] and Mallory and Hajdu[3] showed that the structure of the metal species in solution may affect the kinetics of deposition. It is a necessary condition for the ionic-metal chelate to shed its ligands prior to deposition. As the metal-ligand structure approaches the cathode, part of the solvation or ligand sheath must be bent or removed in a step-wise manner. Conway and Bockris[2] showed that deposition into a vacancy is impossible because the energy required to bend the solvation sheath is too great. The rate of deposition is proportional to the activation energy, E_{act}; therefore, those processes where E_{act} are greater than 200 kJ/mol are considered impossible at speeds measured experimentally during electrodeposition processes. Deposition with the smallest activation energy was shown to occur on a plane where the solvation sheath is bent less, compared to discharge on a kink or edge. Therefore, the number of ligands and the size and shape of the complex metal ion affect the rate of deposition.

The nature and concentration of the chelating agent used to sequester the metal, the pH and the pH-adjusting solution alter the structure of the metal in solution and, consequently, the kinetics (energetics) of deposition. Most electroless nickel and cobalt solutions employ, for example, organic carboxylic acids as the chelating agents. Electroless copper solutions use ethylenediamine derivatives and tartaric acid salts to sequester the cupric ions. The fraction of free acid or free base, protonated and unprotonated species is dependent upon the pH. Metal ions are strong acids and form complexes with bases. Metal complexes may form several species in solution, dependent upon the concentration of the chelating agent and, more importantly, pH. For example, nickel forms six different amine complexes,[4,5] the $Ni(NH_3)_6^{+2}$ species being the predominant species in solution at ammonia concentrations greater than 0.01 molar. Nickel ions, however, exist as the hex-aquo species in ammonia-water solutions with pH less than 8.5, because ammonia is protonated to ammonium ion at a pH < 8.5.

This study was undertaken to examine the effects of various complexing agents on the species of metal in electroless nickel solutions. Speciation calculations are used to determine the fraction of individual species as a function of chelant concentration.

Thermodynamic (Speciation) Calculations

The extent to which organic carboxylic acids exist as free acids or conjugate bases is dependent upon the pH of the solution. The acid-dissociation constant, K_a, is a measure of the ionization equilibrium; the larger the value, the greater the ionization and therefore the lower the pH of the solution. The pK_a is the log of the acid-dissociation constant. Acids commonly used in electroless nickel solutions, such as lactic, glycine and aspartic, exist in equilibrium with their bases and the extent of ionization is shown by the pK_a value of the acid at a given pH. The distribution or fraction of the acid and its base can be calculated from the pK_a of the acid:

$$HA \rightarrow H^+ + A^- \tag{1}$$

$$K_A = \frac{[H^+][A^-]}{[HA]} \tag{2}$$

The fractions of the total concentration [HA] plus $[A^-]$ in the form HA and A^-, $\propto_{HA}$ and $\propto_{A-}$, are expressed as:

$$\propto_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{[H^+]}{[H^+] + K_a} \tag{3}$$

and

$$\propto_A = \frac{K_a}{[H^+] + K_a} \tag{4}$$

Similarly, for dibasic acids and zwitterions, such as glycine, H_2A, the fractions of the various species $\propto_{HA}$, $\propto_{HA-}$ and $\propto_A$– in the forms H_2A, HA^- and A– can be expressed as:

$$C_{H2A} = [H_2A] + K_1[H_2A]/[H^+] + K_1K_2[H_2A]/[H^+]^2 \tag{5}$$

$$\propto_0 = [H_2A]/C_{2H2A} = \frac{[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \tag{6}$$

$$\propto_1 = [\mathrm{HA^-}]/C_{\mathrm{2H2A}} = \frac{K_1[\mathrm{H^+}]}{[\mathrm{H^+}]^2 + K_1[\mathrm{H^+}] + K_1K_2} \tag{7}$$

$$\propto_2 = [\mathrm{A^{-2}}]/C_{\mathrm{2H2A}} = \frac{K_1K_2}{[\mathrm{H^+}]^2 + K_1[\mathrm{H^+}] + K_1K_2} \tag{8}$$

Polyprotic acids (*e.g.*, aspartic acid) can exist as several species, depending on the pH of the solution. Speciation calculations can be performed, using the following general expressions:

$$\propto_0 = \frac{[\mathrm{H^+}]^n}{[\mathrm{H^+}]^n + K_1[\mathrm{H^+}]^{n-1} + K_1K_2[\mathrm{H^+}]^{n-2} + \ldots + K_1K_2 \ldots K_n} \tag{9}$$

$$\propto_1 = \frac{K_1[\mathrm{H^+}]^{n-1}}{[\mathrm{H^+}]^n + K_1[\mathrm{H^+}]^{n-1} + K_1K_2[\mathrm{H^+}]^{n-2} + \ldots + K_1K_2 \ldots K_n} \tag{10}$$

$$\propto_2 = \frac{K_1K_2[\mathrm{H^+}]^{n-2}}{[\mathrm{H^+}]^n + K_1[\mathrm{H^+}]^{n-1} + K_1K_2[\mathrm{H^+}]^{n-2} + \ldots + K_1K_2 \ldots K_n} \tag{11}$$

$$\propto_n = \frac{K_1K_2 \ldots K_n}{[\mathrm{H^+}]^n + K_1[\mathrm{H^+}]^{n-1} + K_1K_2[\mathrm{H^+}]^{n-2} + \ldots + K_1K_2 \ldots K_n} \tag{10}$$

The formation of a complex ion involves the reaction of a metal ion with a ligand. Monodentate ligands include hydroxide, halides, cyanide and ammonia, whereas molecules that can donate two or more electron pairs are called multidentate ligands. Ligands, such as glycine and aspartic acid, are multidentate ligands. Ligands react in a stepwise manner with the metal ion, which may lead to a series of chelated structures. Nickel ions in solutions, for example, react with lactate to form a series of nickel-lactate complexes. The addition of **n** lactate molecules to the nickel ion has an associated equilibrium constant, K_n, where the subscript **n** has an integral value representing the addition of the **n**$^{\mathbf{th}}$ lactate ligand. The stepwise formation for the nickel-lactate species involves three equilibrium expressions, each representing the addition of the next lactate molecule:

$$\mathrm{Ni^{+2} + CH_3CH(OH)COO^- \rightarrow Ni(CH_3CH(OH)COO)^+} \tag{13}$$

$$K_1 = \frac{[\mathrm{Ni(CH_3CH(OH)COO)^+}]}{[\mathrm{Ni^{+2}}][(\mathrm{CH_3CH(OH)COO})^-]} \tag{14}$$

$$\mathrm{Ni(CH_3CH(OH)COO)^+ + CH_3CH(OH)COO^- \rightarrow Ni(CH_3CH(OH)COO)_2} \tag{15}$$

$$K_2 = \frac{[\mathrm{Ni(CH_3CH(OH)COO)_2}]}{[\mathrm{Ni(CH_3CH(OH)COO)^+}][\mathrm{CH_3CH(OH)COO^-}]} \tag{16}$$

$$\mathrm{Ni(CH_3CH(OH)COO)_2 + CH_3CH(OH)COO^- \rightarrow Ni(CH_3CH(OH)COO)_3^-} \tag{17}$$

$$K_3 = \frac{\mathrm{Ni(CH_3CH(OH)COO)_3^-}}{[\mathrm{Ni(CH_3CH(OH)COO)_2}][\mathrm{CH_3CH(OH)COO^-}]} \tag{18}$$

Overall formation constants are related to the stepwise formation constants:

$$K_1 = \beta_1$$
$$K_1K_2 = \beta_2$$
$$K_1K_2 \ldots K_n = \beta_n$$

The corresponding equilibria for the nickel-lactate system, using overall formation constants are:

$$\mathrm{Ni^{+2} + CH_3CH(OH)COO^- \rightarrow Ni(CH_3CH(OH)COO)^+} \tag{19}$$

$$\beta_1 = \frac{[\mathrm{Ni(CH_3CH(OH)COO)^+}]}{[\mathrm{Ni^{+2}}][\mathrm{CH_3CH(OH)COO^-}]} \tag{20}$$

$$\mathrm{Ni^{+2} + 2CH3CH(OH)COO^- \rightarrow Ni(CH_3CH(OH)COO)_2} \tag{21}$$

$$\beta_2 = \frac{[\mathrm{Ni(CH_3CH(OH)COO)_2}]}{[\mathrm{Ni^{+2}}][\mathrm{CH_3CH(OH)COO^-}]_2} \tag{22}$$

$$\mathrm{Ni^{+2} + 3CH_3CH(OH)COO^- \rightarrow Ni(CH_3CH(OH)COO)_3^-} \tag{23}$$

$$\beta_3 = \frac{[\mathrm{Ni(CH_3CH(OH)COO)_3^-}]}{[\mathrm{Ni^{+2}}][\mathrm{CH_3CH(OH)COO^-}]_3} \tag{24}$$

The distribution of several species involving mono- or multidentate ligands uses Eqs. (19)–(24). The concentration of nickel in solutions, for example, includes the free nickel ions as well as the nickel-lactate species:

$$C_{\mathrm{Ni}} = [\mathrm{Ni^{+2}}] + [\mathrm{Ni(CH_3CH(OH)COO)^+}] + [\mathrm{Ni(CH_3CH(OH)COO)_2}] + [\mathrm{Ni(CH3CH(OH)COO)_3^-}] \tag{25}$$

From the equilibrium expressions involving the overall formation constants, Eq. (25) can be rewritten as:

$$C_{\mathrm{Ni}} = [\mathrm{Ni^{+2}}] + \beta_1[\mathrm{Ni^{+2}}][\mathrm{CH_3CH(OH)COO^-}] + \beta_2[\mathrm{Ni+2}][\mathrm{CH_3CH(OH)COO^-}]^2 + \beta_3[\mathrm{Ni^{+2}}][\mathrm{CH_3CH(OH)COO^-}]^3 \tag{26}$$

The concentration of each nickel species in solution is some fraction, ∝, of the total concentration, C_{Ni}:

$$\propto_{\mathrm{Ni^{+2}}} = [\mathrm{Ni^{+2}}]/C_{\mathrm{Ni}} \tag{27}$$

$$\propto_{\mathrm{Ni(CH3CH(OH)COO^-)}} = [\mathrm{Ni(CH_3CH(OH)COO)^+}]/C_{\mathrm{Ni}} = \frac{\beta_1[\mathrm{Ni^{+2}}][\mathrm{CH_3CH(OH)COO^-}]}{C_{\mathrm{Ni}}} \tag{28}$$

$$\propto_{\mathrm{Ni(CH_3CH(OH)COO)_2}} = [\mathrm{Ni(CH_3CH(OH)COO)_2}/C_{\mathrm{Ni}} = \frac{\beta_2[\mathrm{Ni^{+2}}][\mathrm{CH_3CH(OH)COO^-}]^2}{C_{\mathrm{Ni}}} \tag{29}$$

$$\propto_{\mathrm{Ni(CH_3CH(OH)COO)_{3-}}} = [\mathrm{Ni(CH_3CH(OH)COO)_3^-}]/C_{\mathrm{Ni}} = \frac{\beta_3[\mathrm{Ni^{+2}}][\mathrm{CH_3CH(OH)COO^-}]^3}{C_{\mathrm{Ni}}} \tag{30}$$

The sum of Eqs. (27)–(30) must equal unity. Substitution of Eq. (26) into Eqs. (27)–(30) yields:

$$\propto_{\mathrm{Ni^{+2}}} = \frac{1}{1 + \beta_1[\mathrm{CH_3CH(OH)COO^-}] + \beta_2[\mathrm{CH_3CH(OH)COO^-}]^2 + \beta_3[\mathrm{CH_3CH(OH)COO^-}]^3} \tag{31}$$

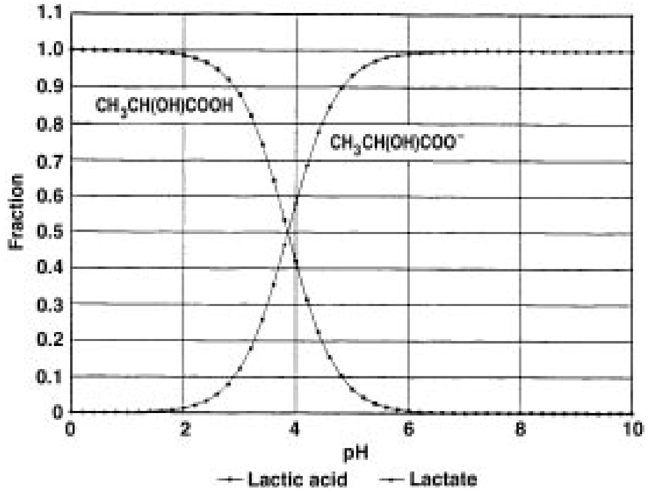

Fig. 1—Speciation plots for the lactic acid-lactate system.

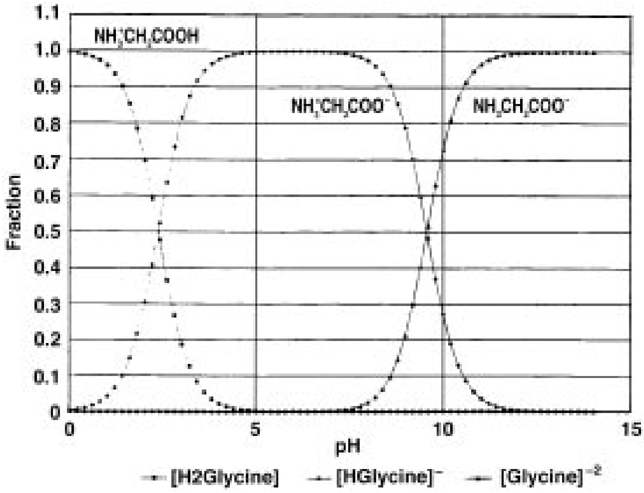

Fig. 2—Speciation plots for the glycine system.

$$\propto_{Ni^{+2}][CH_3CH(OH)COO^-} = \qquad (32)$$

$$\frac{\beta_1[CH_3CH(OH)COO^-]}{1 + \beta_1[CH_3CH(OH)COO^-] + \beta_2[CH_3CH(OH)COO^-]^2 + \beta_3[CH_3CH(OH)COO^-]^3}$$

$$\propto_{Ni^{+2}][CH_3CH(OH)COO^{-2}} = \qquad (33)$$

$$\frac{\beta_2[CH_3CH(OH)COO^-]^2}{1 + \beta_1[CH_3CH(OH)COO^-] + \beta_2[CH_3CH(OH)COO^-]^2 + \beta_3[CH_3CH(OH)COO^-]^3}$$

$$\propto_{Ni(CH_3CH(OH)COO)^3} = \qquad (34)$$

$$\frac{\beta_3[CH_3CH(OH)COO^-]^3}{1 + \beta_1[CH_3CH(OH)COO^-] + \beta_2[CH_3CH(OH)COO^-]^2 + \beta_3[CH_3CH(OH)COO^-]^3}$$

Experimental Procedure

Nickel solutions were composed of reagent-grade nickel sulfate hexahydrate, the nickel concentration being 4 g/L. Various chelating agents, lactic acid, glycine and aspartic acid were added, so that the final concentration of the chelant was 0.4 M. The pH was adjusted to 7.0, using ammonium hydroxide. Thiourea was added as a stabilizer at 1.5 mg/L. The temperature was maintained at 90 °C. Weight gain measurements were made by plating electroless nickel on low-carbon steel substrates.

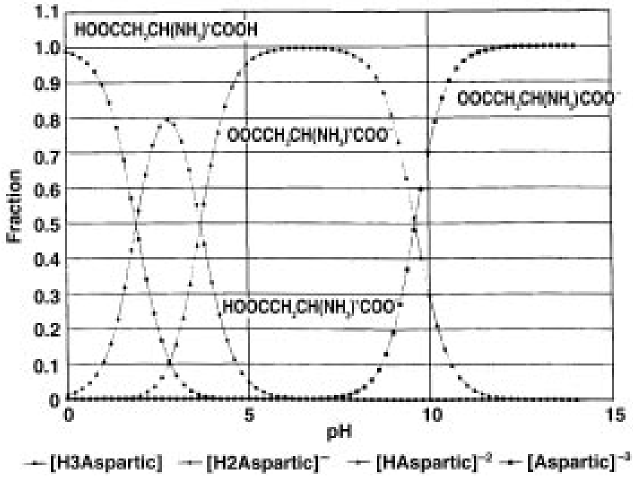

Fig. 3—Speciation plots for the aspartic acid-aspartate system.

Results and Discussion

The results of the speciation calculations show that at pH 7.0, greater than 99 percent of lactic acid exists as the unprotonated species (Fig. 1). In a low-pH solution, the amino group of the glycine molecule is protonated: $NH_3^+CH_2COOH$. At a pH of approximately 5, the carboxylate group deprotonates, yet the amino group remains protonated, forming a zwitterion. Figure 2 shows that at very high pH, the amino group deprotonates, forming a monoanion, $NH_2CH_2COO^-$. Aspartic acid behaves in a manner similar to glycine (Fig. 3). At a low pH, the amino group is protonated as are the carboxylate groups. At a pH of approximately 3, one of the carboxylate groups loses a proton. Between pH 5 to 8, a second proton is lost from the remaining carboxylate group and at pH greater than 9, the amino group loses the last proton. Addition of lactic acid to a nickel solution at pH 7.0 decreases the free nickel concentration from 100 percent to approximately 30 percent at 0.4 M lactic acid concentration (Fig. 4). Three nickel-lactate species form as a result of the addition of lactic acid, the $Ni(CH_3CH(OH)COO)_3^-$ species being predominant at about 30 percent. About 20 percent each of the $Ni(CH_3CH(OH)COO)^+$ and the $Ni(CH_3CH(OH)COO)_2$ species are also present in solution. There is a considerable amount of free nickel in solution at 0.4 M lactate.

In the nickel-glycine solution, Fig. 5, the free nickel decreases to about two percent, the $Ni(H_2NCH_2COO)^+$

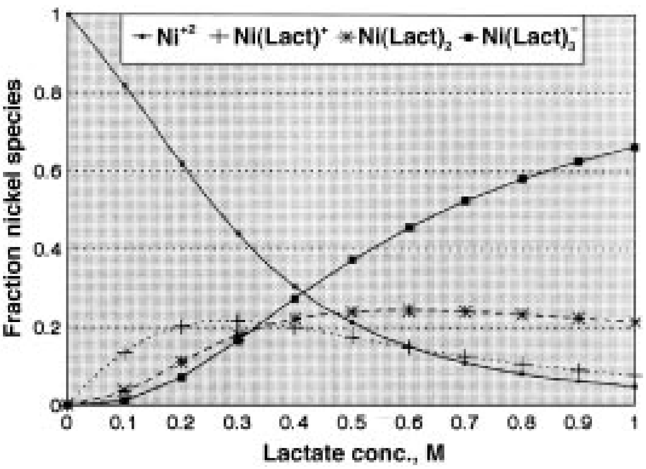

Fig. 4—Speciation plots for the nickel-lactate system.

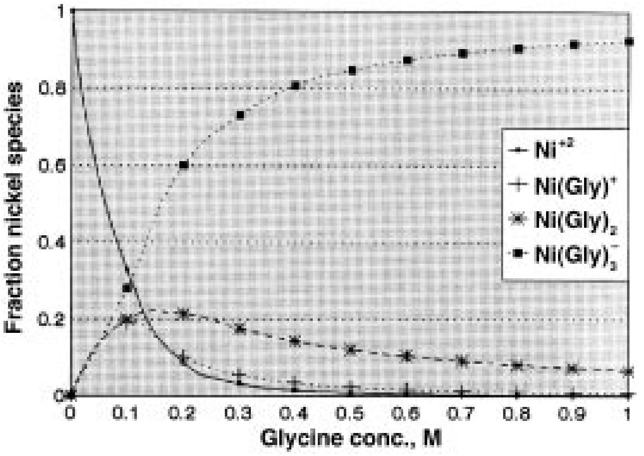

Fig. 5—Speciation plots for the nickel-glycine system.

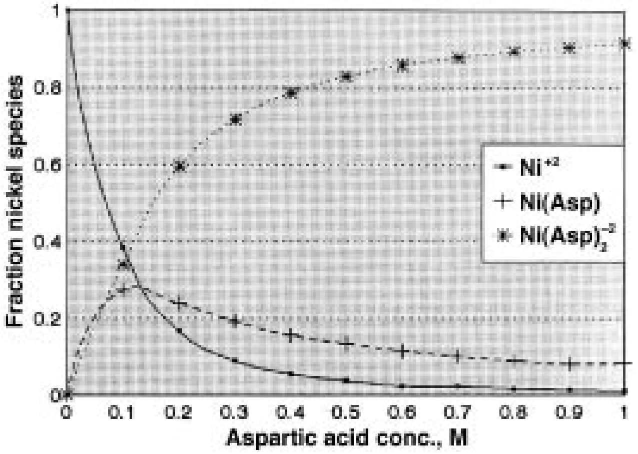

Fig. 6—Speciation plots for the nickel-aspartate system.

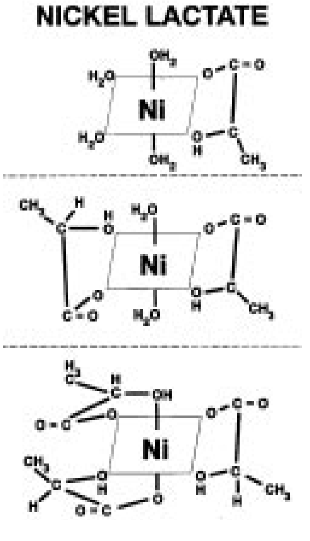

Fig. 7—Structure of nickel-lactate molecules.

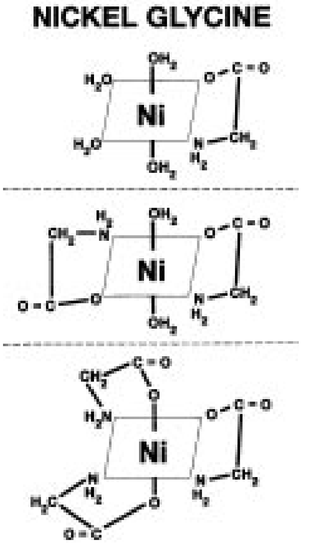

Fig. 8—Structure of nickel-glycine molecules.

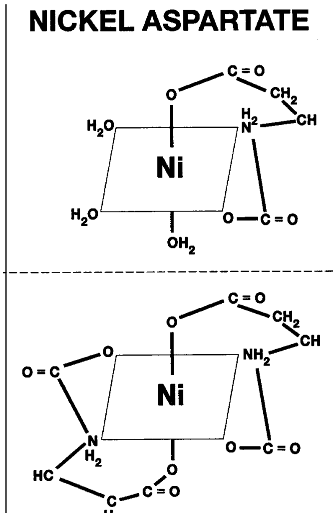

Fig. 9—Structure of nickel-aspartate molecules.

contributing about five percent to the total nickel concentration. The $Ni(H_2NCH_2COO)_2$ species is 13 percent of the total nickel concentration. The most predominant species at 0.4 M glycine is the $Ni(H_2NCH_2COO)_3^-$ complex, contributing about 80 percent to the total nickel concentration.

In the nickel-aspartate system (Fig. 6), the divalent $Ni(OOCCH_2CH(NH_2)COO)_2^{-2}$ species contributes about 78 percent to the total nickel concentration, whereas approximately five percent of the nickel is free. The $Ni(OOCCH_2CH(NH_2)COO)$ complex contributes 17 percent to the nickel concentration.

The plating rate is affected by the chelant. The greatest deposition rate is from the lactate solution, 30.5 μm/hr. The deposition rates from the glycine solution and the aspartate solution are 12.2 μm and 4.3 μm/hr, respectively. The number of bound water molecules in the nickel chelate structure is believed to influence the plating rate and solution stability. In the nickel solution without chelating agent, the deposition rate is 35 μm/hr and exhibits instability, depositing nickel over the sides of the plating vessel. The deposit is unacceptable from a commercial standpoint.

There are six water molecules in the coordination structure. In the nickel lactate system, there are several nickel species with varying numbers of water molecules bound to the nickel (Fig. 7). In the nickel glycine system, most of the nickel is completely complexed, but there is a fraction of nickel species with water bound to the central nickel atom (Fig. 8). Similarly, in the nickel aspartate solution, a small fraction of nickel exists with water bound either in the axial or equatorial positions, as seen in Fig. 9. This is in accord with the finding of Rorabacher *et al.*,[6] who showed alcoholic oxygen atoms are also available for bonding to nickel. Coordination of nickel to alcoholic oxygen in branched polyamino-alcohols facilitated nickel chelation to the nitrogen atoms. The plating rate and solution stability are, accordingly, affected by the number of open sites (bound water molecules) in the nickel structure. During deposition, nickel must shed its coordination sheath.[1,2] The high lability and rapid exchange between alcoholic oxygen atoms with water molecules facilitates nickel deposition in the lactate solutions. For nickel glycine and nickel aspartate, substitution by water molecules into the inner coordination sphere is difficult, as reflected by the large formation constants for these species. The enhanced plating rate of nickel glycine compared to nickel aspartate results from the second carboxylate group on the aspartate molecule coordinating a third site in the octahedral structure of nickel, whereas glycine coordinates only two sites per molecule.

Potential-pH studies[7] show that the nature of the chelating agent used in electroless nickel solutions does not affect the thermodynamics of electroless nickel deposition. It was postulated that the chelating agents therefore affect the kinetics of nickel deposition. This study shows that the plating rates were inversely related to the strength of the nickel-ligand complex. Electrochemical studies also show that the reduction reaction mechanism for electroless nickel deposition is independent of the chelating agent.[8] Cathodic Tafel slopes are similar for nickel deposition from the lactate, glycine and aspartate solutions and are similar to those from a Watts nickel solution. Consequently, the rate of electroless nickel deposition appears to be dependent upon the rate at which the nickel-ligand structure dissociates.

Findings

Speciation calculations were used to determine the fraction of nickel species in three electroless nickel solutions. The deposition rate and solution instability may be functions of the fraction of free nickel and the number of bound water molecules in the octahedral nickel structure. Nickel lactate solutions typically have the highest plating rate. Nickel-glycine and nickel-aspartate solutions are very stable, but the deposition rate is lower than from the lactate solutions.

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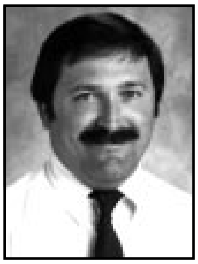

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