An Analytical Equation to Compute the Composition of Pulse-Plated Binary Alloys

By S. Roy

An analytical equation to predict the composition of binary alloys has been developed. It is applicable to pulse plating of binary alloys when the noble metal ion is deposited under mass-transfer control. It has been shown that the Sand and Cottrell equations can be used to describe the partial current of the more noble species during the pulse *on* time because fluid convection does not affect mass transfer when the *on* time is short. The usefulness of this equation to choose pulse parameters to obtain a specific alloy composition is demonstrated by applying it to copper and nickel codeposition.

Pulse electrodeposition of metallic alloys has been gaining in importance because of the possibility of changing alloy composition and properties by intelligent regulation of pulse parameters. Accordingly, several mathematical models have been proposed to predict the composition of alloys deposited by pulsed currents.¹⁻⁵ The influence of pulse parameters, hydrodynamics, charge transfer reactions, ionic migration, as well as competitive and displacement reactions on the deposit composition and microstructure have been examined in these investigations. Despite the availability of these models, they have not been widely exploited, possibly because they are relatively difficult to implement and use.

To make pulse plating accessible to more users, simpler analytical equations to compute alloy compositions must be developed. In particular, there are no simple design equations for the selection of pulse and engineering parameters for a desired alloy composition. Such equations are difficult to develop for general pulse plating; however, design equations can be derived if certain constraints are imposed on the choice

of pulse parameters, solution composition and hydrodynamics. Indeed, a large number of alloy deposition systems are constrained in terms of electrolyte formulation, electrochemical parameters and fluid dynamics where such equations can prove to be useful. For example, Cu-Zn, Cu-Ni, Cu-Co, Ni-Fe, Ni-Co binary alloys are plated from electrolytes where the more noble (or in the case of anomalous deposition, the less noble) component is mass transport limited, whereas the other component is controlled by reaction kinetics.

In this study, an analytical equation to compute the composition of pulse-plated binary alloys is presented. The equation is derived by analyzing the transient current of the more noble species during the pulse ontime. The current-time response is calculated from a numerical model based on (1) Butler-Volmer charge transfer reactions to describe reaction kinetics, and (2) liquid phase mass transfer through a Nernst diffusion layer to describe ionic transport; the response is compared to the Sand and Cottrell equations. The other constraints used to develop this equation are (1) that the reduction of the noble metal is mass-transfer controlled, (2) that the sum of the partial currents of the reducing metal ions equals the peak current during the *on* time, and (3) that the concentration of the more noble species recovers fully during the *off* time.

The usefulness of this analysis has been demonstrated by simulating galvanostatic Cu-Ni alloy deposition from a 0.0125 M CUSO₄/0.7 M NiSO₄/0.25 M Na₂Cit (sodium citrate) electrolyte using a rotating cylinder. Copper-nickel codeposition was chosen because it is industrially useful.⁶⁻⁸ This system fulfills the criterion that copper, the more noble component, is mass-transfer controlled. The current efficiency during the co-discharge is close to 100 percent,9 which fits the condition that the sum of their partial currents is equal to the peak during the on time. Although recent studies have shown that a displacement reaction occurs during the off time, it has been shown that this reaction is stifled quickly because of formation of a copper-rich layer at the alloy surface.¹⁰ This means that when the *off* time is sufficiently long, the copper and nickel reduction currents are zero and the concentration of cupric species at the electrode surface recovers.

Mathematical Model

A typical square galvanostatic waveform is constructed by passing a high or peak current for a certain time period (*i.e.*, *on* time), followed by a period, the *off* time, when the current is switched off. The *on* time, the peak current, the *off* time and



Fig. 1—Computed values of the partial current for copper and nickel during the on time. Peak current, -0.100 A/cm^2 ; t_{*} , 0.100 sec; cylinder rotation speed, 1000 rpm.



Fig. 2—(a) Effect of peak current on transition time for t_p 0.100 sec. Values calculated numerically for cylinder rotation speed, 1000 rpm & 3000 rpm; values computed from the Sand equation; (b) values of i_{cu} for $i_p = -0.100 \text{ A/cm}^2$ and 0.100 sec. Symbols show numerical values for cylinder rotation speeds of 1000 and 3000 rpm; i_{cu} from the Cottrell equation.

the *off* current are denoted by t_p , i_p , t_p , and i_p , respectively. The codeposition of copper and nickel during the *on*-time is described by the following charge transfer equations,

$$i_{k} = i_{0,b,k} \left\{ -\frac{C_{k}(0,t)}{C_{b,k}} \exp[-\beta_{c,k}\eta_{k}(t)] \right\}$$
(1)

where i_k is the partial current, i_0 is the exchange current density, - is the overpotential, C is concentration, and β is the Tafel constant. Subscripts k refer to Cu or Ni, and 0 and b refer to surface and bulk, respectively. During *off* time, the values of i_k for both copper and nickel are set to zero. The mass transfer to the cathode surface is described by diffusion through a Nernst diffusion layer

$$\frac{\partial C_k}{\partial t} = D_k \frac{\partial^2 C_k}{\partial x^2} \tag{2}$$

subject to the boundary conditions

$$C_k(\delta_k, t) = C_{b,k}, \qquad (3)$$

$$\frac{\partial C_k(0,t)}{\partial x} = -\frac{i_k}{z_k F D_k} \qquad (4)$$

and the initial condition

$$C_k(x,0) = C_{b,k} \tag{5}$$

where $_k$ is the thickness of the Nernst diffusion layer of each species,¹¹ z is the number of electrons exchanged in the charge transfer reaction, F is Faraday's constant and D is the diffusion coefficient. The final condition is that the total applied current has to equal the sum of the partial currents for copper and nickel,

$$i_p = \sum_k i_k$$
 (6)

The amount of metal deposited is computed from the total reduced charge, Q_{t} , corresponding to each metal:

$$Q_k = \int_{0}^{t_p} i_k \tag{7}$$

Equations (1) to (7) are solved using the kinetic, physical and transport parameters shown in the table. The solution procedure of this model has been presented previously in detail⁵ and, therefore, is not elaborated here.

To cover a representative range of

practical pulse plating conditions, i_{Cu} and i_{Ni} were calculated for i_p values ranging from -0.050 A/cm² to -0.400 A/cm² and the t_p values between 0.050 and 0.300 sec. The effect of hydrodynamics on the partial currents was examined by setting the cylinder rotation speed at either 1000 or 3000 rpm.

Figure 1 shows the typical response of the partial currents for copper and nickel for different values of t_p . As shown in the figure, for a certain period of time, t_1 , the entire current is consumed by the copper discharge reaction. This is because copper is more noble and there is sufficient quantity of cupric ions near the cathode. The copper current begins to decrease after t_1 because the consumption of Cu^{+2} resulting from the surface reaction cannot be replenished by ionic transport. The nickel reduction current, on the other hand, is zero during the transition time, and increases only when the partial current of copper relaxes. Interestingly, the transition time was found to depend only on i_p ; when the value of t_p was changed from 0.050 to 0.300 sec and the rotation speed was varied from 1000 rpm to 3000 rpm, no variation in t_1 occurred. These results indicate that fluid convection does not affect the



Fig. 3—Atomic percentage of copper in the deposit. Numerical calculation: -0.100 A/cm² and -0.200 A/cm². Alloy composition from Eq. (18).

concentration changes near the cathode during the pulse *on* time.

To assess the relative importance of diffusive and convective transport during the *on* time, i_{Cu} values from numerical computations were compared to those obtained from diffusion-controlled mass transfer. These comparisons are illustrated in Figs. 2a and 2b. Numerically calculated values of t_1 are represented by the open circles and squares in Fig. 2a. The dotted line in the same figure is obtained from the Sand equation:

$$t_1 = \frac{\pi D_{Cu} z^2 F^2 C_{b,Cu}^2}{4 i_p^2}$$
(8)

Because the Sand equation is based on pure diffusion, the filled circles and the solid line show the comparison between transition times in the presence and absence of fluid convection. The excellent agreement between the transition times calculated from the model and those predicted by the Sand equation shows that the transport of cupric species to the surface during t_1 is controlled solely by diffusion. The importance of diffusion on the mass transport of Cu^{+2} during the remaining period of *on* time (*i.e.*, t_1 to t_p , is shown in Fig. 2b. Numerically calculated values of i_{Cu} are not only independent of cylinder rotation speed, but agree well with those computed from the Cottrell equation:

$$i = zFC_{b,Cu} \sqrt{\frac{D_{Cu}}{\pi t}}$$
(9)

The excellent agreement between the copper reduction current in the presence and absence of convection substantiates that diffusion is the dominant mechanism for Cu⁺² species transport.

Analytical Equation

The preceding results show that the partial current for copper is exactly described by the Sand and Cottrell equations for time periods from 0 to t_1 and between t_1 and t_p , respectively. The amount of copper discharged during the *on* time, therefore, can be computed by integrating these two analytical expressions. The quantity of copper plated during time t_1 is

$$Q_1 = i_p t_1 \tag{10}$$

When the Sand equation is used to replace the transition time by solution properties and the peak current, Eq. (10) reduces to:

$$Q_1 = \frac{\pi z^2 F^2 C_{b,Cu}^2 D_{Cu}}{4i_p}$$
(11)

.

or

After the transition time, the amount of copper plated, Q_2 , is calculated from Eq. (9)

$$i_{k} = i_{0,b,k} \left\{ -\frac{C_{k}(0,t)}{C_{b,k}} \exp[-\beta_{c,k} \eta_{k}(t)] \right\}$$
(12)

(13)

$$Q_2 = 2zFC_{b,Cu} \sqrt{\frac{D_{Cu}}{\pi}} t_1^{1/2} (R^{1/2} - 1)$$
 where $R = \frac{t_p}{t_1}$

The copper plated during the on-time is given by the summation of Q_1 and Q_2 , which is

$$Q_1 + Q_2 = z^2 F^2 C_{b,Cu}^2 D_{Cu} \left\{ \frac{\pi}{4i_p} + \frac{\left(R^{1/2} - 1\right)}{i_p} \right\} \quad (14)$$

The atomic percentage of copper in the deposit is easily calculated by dividing the charge of copper reduced by the total amount of metal deposited

$$\chi_{Cu} = \frac{Q_1 + Q_2}{i_p t_p}$$
(15)

Electrolyte* Properties⁵

Kinetic and Transport Parameters	Copper	Nickel
V _{rev} (V)	-0.2	-1.0
i _{0,b} (A/cm ²)	5 x 10 ⁻⁵	1 x 10 ⁻⁴
$\beta_{c}(V)$	19.5	17.5
D (cm ² /sec)	1.8 x 10 ⁻⁶	5.5 x 10 ⁻⁶

* 0.0125 M $\rm CuSO_4/0.7$ M $\rm NiSO_4/0.25$ M $\rm Na_3Cit$

The overpotential $-_{k}$ is calculated by setting $- = E - V_{rev,k}$, where E is the cathode potential.

The denominator in Eq. (15) can be rewritten as

$$i_p : t_1 : \frac{t_p}{t_1}$$
,

which is equal to

$$\frac{z^2 F^2 C_b^2 \pi D}{4i_p} R$$

It can now be shown that the atomic percentage of copper in the deposit is

$$\chi_{Cu} = \frac{1}{R} \left[1 - \frac{4}{\pi} \right] + \frac{4}{\pi R^{1/2}}$$
(16)

or

$$\chi_{Cw} = \frac{-0.273}{R} + \frac{1.2732}{R^{1/2}}$$
(17)

Equation 17 has only one variable parameter, R, or t_p/t_1 . In the equation there are two terms, of opposing signs, containing R. The negative term will always be smaller than the positive term, because the former is dependent on R⁻¹ and the latter on R^{-1/2}, and t_1 is much smaller than t_p . For the case of sufficiently small values of t_1 ($t_1 \approx 0.1 t_p$), the negative term can be neglected. Because this is true for applied currents greater than -0.050 A/cm², the copper content in the deposit is

$$\chi_{Cu} = \frac{1.2732}{R^{1/2}}$$
(18)

The applicability of Eq. (18) for computing the alloy composition is illustrated in Fig. 3. The symbols represent the values obtained from numerical calculations and the lines represent Eq. (18). The two values are in good agreement for the entire range of pulse parameters examined.

Discussion

Equation (18) can be viewed as a design equation for determining the peak current during pulse deposition of alloys. Although Eq. (18) is applicable only for the case when the *off* time is sufficiently long, previous studies have shown that pulse *off* times on the order 0.5 to 1 sec are usually adequate to satisfy this criterion. In this case, *R* can be computed from Eq. (18) when the desired alloy composition is known. Inasmuch as *R* is dependent only on t_p and t_1 , and t_1 is completely described by the physical properties of the electrolyte and i_p , the value of i_p can be computed from *R*.

These results have certain implications for pulse-plated alloys. One is that a layer of pure copper will always precede the deposition of nickel. The thickness of this layer, for a peak current of -0.050 A/cm², is calculated to be 1.2 Å, which is half a monolayer. In practice, thicker layers are usually plated during a single pulse; therefore, this may not pose any limitation during pulse plating of a nickel-rich alloy. It is nevertheless important to note that the partial current for both metals varies for the first 40 msec and, therefore, only graduated alloys are plated during this period. The thickness of the alloy plated during this time is 7.9 Å, about 3 atomic layers. In effect, therefore, thicker deposits must be plated when nickel-rich alloys of a relatively constant alloy composition are desired.

A second implication lies in the choice of engineering and pulse parameters used in practice. During deposition of nanostructured metallic Cu-Ni multilayers, for example, to lower the copper content in the nickel layer, a low concentration of cupricions in the solution and low flow velocities have been used.^{7,8} Current results indicate that this is not the defining parameter for alloy composition, however, because the pulse time is too short for flow velocities to affect mass transport. Indeed, deposits with copper content below five percent can be deposited from a solution containing higher concentrations of Cu⁺² (see Fig. 3) and high flow velocities, as long as the peak current is high.

It must be mentioned that Eq. (18) can be used to calculate the alloy composition only when mass transfer of Cu+2 ions to the cathode is controlled by diffusion, and the effect of fluid convection is negligible. An estimate of the time when diffusion governs the transient surface concentration after a step change in current has been estimated in previous heat and mass transfer studies.¹²⁻¹⁴ These investigations have revealed that a dimensionless time τ , given by Dt/ δ^2 , can be used to estimate the time when convection effects are not felt at the electrode surface. It has been shown that surface concentration changes are governed solely by diffusion for $\tau < 0.05$, because the flow velocity close to the electrode surface is small and a certain time is necessary before the effects of bulk stirring are felt at the electrode surface. The dimensionless time for the electrochemical parameters used in this study is approximately 0.03, which is in accordance with the findings of previous mass transfer work.

Conclusions

An analytical equation has been developed to predict the composition of binary alloys when the more noble species is plated under mass transfer control. Simulation of codeposition of copper and nickel, with a rotating cylinder from a 0.0125 M CuSO₄/0.7 M NiSO₄/0.25 M Na₃Cit electrolyte, showed that the discharge rate for copper is controlled solely by diffusion for an *on* time of less than 0.300 sec. Fluid convection does not play any role in the transport of the cupric species to the cathode surface during this period. The partial current for mass transfer controlled species, therefore, can be described by the Sand and Cottrell equations. It was shown that this equation can be employed to compute the peak current necessary to obtain a particular alloy composition.

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Continued on page 84.