

### Acknowledgment

Financial support provided by the National Science Foundation under grant No. CBT-8518479 is gratefully appreciated.

Manuscript submitted April 3, 1986; revised manuscript received Dec. 10, 1986.

### REFERENCES

1. A. R. Despic, and K. I. Popov, in "Modern Aspects of Electrochemistry," No. 7, Chap. 4, B. E. Conway and J. O'M Bockris, Editors, Plenum Press, New York (1972).
2. G. Wranglen, *Electrochim. Acta*, **2**, 130 (1960).
3. J. L. Barton, and J. O'M Bockris, *Proc. R. Soc. London, Ser. A*, **268**, 485 (1962).
4. J. W. Diggle, A. R. Despic, and J. O'M Bockris, *This Journal*, **116**, 1503 (1969).
5. A. R. Despic and M. M. Purenovic, *Solid Solution*, **121**, 3, 329 (1974).
6. J. H. Shyu, M. S. Thesis, Case Western Reserve University (1980).
7. J. H. Shyu, Ph.D. Thesis, Case Western Reserve University (1982).
8. U. Landau, and J. H. Shyu, Report EM-2937, Electric Power Research Institute, Palo Alto, CA (1983).
9. R. Aogaki, K. Kitazawa, Y. Kose, and K. Fueki, *Electrochim. Acta*, **25**, 965 (1980).
10. R. Aogaki, and T. Makino, *ibid.*, **26**, 1509 (1981).
11. Y. Oren, and U. Landau, *ibid.*, **27**, 739 (1982).
12. K. E. Yee, and J. Jorne, EDA Monthly Report, Task No. 12240 (1982).
13. S. Tajima and M. Ogata, Comite International de Thermodynamique et de Cinetique Electrochimiques Meeting, Extended Abstracts, p. 170 (1968).
14. S. Tajima, and M. Ogata, *Electrochim. Acta*, **13**, 1845 (1968).
15. Y.-J. Lii and J. Jorne, In preparation (1987).
16. Y.-J. Lii, M. S. Thesis, University of Rochester, (1985).
17. K. E. Yee, Ph.D. Dissertation, Wayne State University, Detroit, MI (1986).
18. J. T. Kim, and J. Jorne, *This Journal*, **127**, 8 (1980).
19. D. Rajhenbah, J. Faltemier, and C. W. Tobias, LBL-15338, Lawrence Berkeley Laboratory, University of California (1983).
20. J. Jorne and E. Roayaie, *This Journal*, **133**, 696 (1986).

## A Mathematical Model for the Electrolytic Codeposition of Particles with a Metallic Matrix

J. P. Celis, J. R. Roos,\* and C. Buelens

Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, de Croylaan 2, 3030 Heverlee, Belgium

### ABSTRACT

Over the last decade the general knowledge of the electrolytic codeposition of inert particles with metals has increased markedly, and a few models have been proposed. In this paper a new model that overcomes several of the shortcomings of the previously proposed models is developed starting from a statistical approach of the incorporation of particles. The validity of the new model is shown for two experimental codeposition systems, namely, Cu-Al<sub>2</sub>O<sub>3</sub> from acidic sulfate baths and Au-Al<sub>2</sub>O<sub>3</sub> from additive-free potassium cyanide baths.

In the early days of composite plating most attention was directed toward practical problems; few efforts were made to elucidate the mechanism of codeposition. Three possible mechanisms were put forward, namely: electrophoresis proposed by Whithers in 1962 (1), mechanical entrapment suggested by Martin in 1964 (2), and adsorption of particles on the cathode mentioned by Brandes (3) in 1967. Various investigators (4, 5) measured the zeta-potential in dilute solutions. Since in electrolytic codeposition solutions of high ionic strength usually are used, extrapolation from dilute solutions gives no reliable evidence of possible electrophoretic effects. Based on a mass transport analysis toward rotating disk electrodes, it was calculated by Van Camp (6) that particles will not reach the surface of a rotating electrode by inertial forces alone as long as

$$0.88\rho_p\omega d^2\nu^{-1} < \frac{3}{4} \quad [1]$$

where  $\rho_p$  = specific weight of particles,  $d$  = diameter of particles,  $\omega$  = rotation speed of the electrode, and  $\nu$  = kinematic viscosity. Concerning a possible adsorption effect of particles onto the cathode by Van der Waals attractive forces, Tomaszewski (7) was the first to point out the effect of monovalent cations on the codeposition process, e.g., thallium ions drastically promote the amount of codeposited particles from copper sulfate plating baths, as was confirmed later by different researchers (8-10). In this respect Foster *et al.* (10) reported a very low degree of adsorption of copper ions on alumina particles, which was supposed to be associated with the rather poor degree of codeposition. However by the addition of tetra ethylene pentamine and especially Tl<sup>+</sup>-ions, ad-

sorption and codeposition behavior improved drastically.

As more and more practical data concerning the effect of electrolysis parameters on the codeposition of inert particles with metals were gathered, a few attempts were made to cast the experimental data into models. Saifullin *et al.* (11) presented a formula to calculate the composition of composite coatings, making abstraction of any mechanism in 1968. Bazzard *et al.* (12) proposed a mathematical expression of the electrolytic codeposition of solid conducting particles with metals. They obtained for the case of the incorporation of one particle during a deposition time,  $t$ , the following equation

$$X_p = \frac{\frac{4}{3} \pi r^3 \rho_p}{\frac{4}{3} \pi r^3 \rho_p + 4 \pi r^2 t e_m} \quad [2]$$

where  $X_p$  = weight percent embedded second phase particles,  $e_m$  = electrochemical equivalent of the metal,  $\rho_m$  = density of the metal,  $\rho_p$  = density of the particle, and  $r$  = radius of the particle. This formula has never been considered as a tool to calculate and predict the composition of the composite coatings since it does not take into account the important effects of pH, temperature, and bath constituents.

An important step forwards was the mathematical model derived by Guglielmi in 1972 (13). Based on a striking similarity of the curves relating the volume percent of codeposited particles (v/o) to the volume percent of particles suspended in the plating bath (C<sub>v</sub>) with the well-known adsorption isotherm (Fig. 1), he postulated a mechanism based on two successive adsorption steps. A

\*Electrochemical Society Active Member.

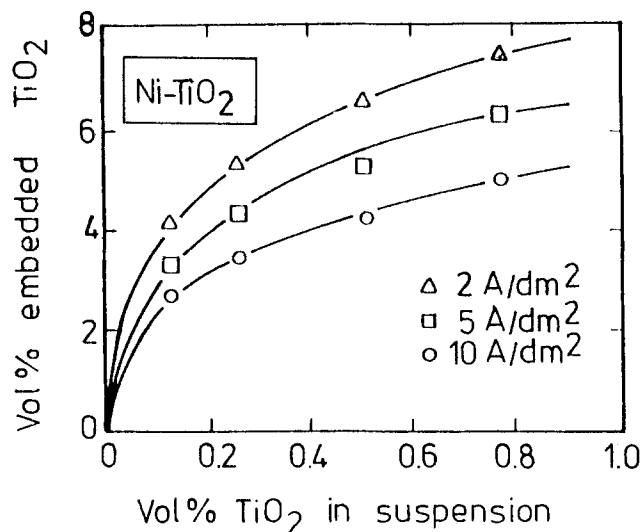


Fig. 1. Volume percent of codeposited particles vs. amount of particles suspended in the plating bath for a Ni-TiO<sub>2</sub> system (13).

loose adsorption ( $\sigma$ ), which has an essentially physical character, results in a rather high degree of coverage of the cathode by particles. A subsequent strong adsorption ( $\theta$ ) which is thought to be field assisted and therefore electrochemical in nature, permits the entrapment of particles in the growing metal layer. The formula so deduced is

$$\frac{C_v}{v/o} = \frac{Mi_o^{B/A}}{nF\rho_m v_o} \cdot i^{(1-B/A)} \cdot \left( \frac{1}{k^*} + C_v \right) \quad [3]$$

where  $F$  = Faraday constant;  $n$  = valence of the electrodeposited metal;  $k^*$  = Langmuir isotherm constant, largely determined by the intensity of interaction between particles and cathode;  $M$  = atomic weight of the electrodeposited metal;  $i_o$  = exchange current density;  $\rho_m$  = density of electrodeposited metal; and  $v_o$ ,  $A$ ,  $B$  = constants. The validity of this model has been verified for different codeposition systems like SiC and TiO<sub>2</sub> with nickel from sulfamate baths (13),  $\alpha$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with copper from acidic copper sulfate baths with and without the addition of thallium ions (14), Al<sub>2</sub>O<sub>3</sub> with nickel from Watts-type electrolyte (15), and TiO<sub>2</sub> with copper from acidic copper sulfate baths (16). This substantiation of Guglielmi's model coming from several investigators proves the soundness and the significance of this mathematical treatment of electrolytic codeposition. However, some objections arrived at by critically examining the derivation and from inexplicable experimental results from literature question the generality of the model. By considering the two parameters  $i$  and  $C$  as solely process controlling, other important process parameters are overlooked as hydrodynamics (17), effect of size type and pretreatment of particles (8, 14), effect of bath constituents (18), and electrolysis conditions as pH (19) and bath temperature. Guglielmi's model does not allow prediction of which way those parameters will affect the electrolytic codeposition.

Foster and Kariapper (20), in 1974, proposed a mathematical expression that could describe the effect of hydrodynamics. They associated the rate of codeposition arbitrarily with the following expression

$$\frac{dV_p}{dt} = \frac{N^*hC_v}{1 + hC_v} \quad [4]$$

where  $N^*$  = number of collisions of particles suitable for codeposition per second and  $V_p$  = volume fraction of particles in the deposit. The parameter  $h$  is further associated with the adsorbed charge density ( $q$ ) on a particle, the potential field at the cathode ( $\Delta E$ ), the rate ( $i$ ) at which the metal is deposited, the bond strength ( $L$ ) of the metal/particle interface per surface area, the shape, size, and density of the particles ( $a$ ), and finally the rate of agitation ( $b$ ), according to Eq. [5], in which  $h^*$  is a constant

$$h = h^*(q\Delta E + Li^2 - ab) \quad [5]$$

Because of the complex interrelationship between some of these factors, only a limited amount of quantitative work was done to prove the validity of expression [4]. Although the calculation or estimation of several parameters incorporated in formulas [3] and [5] is quite impossible, important benefits of Guglielmi's and Foster's models lie in their contribution to a better understanding of the mechanism of codeposition. The mathematical model proposed in this paper (21) contains measurable parameters so that prediction of the amount of codeposited particles for a given system now becomes feasible.

### Description of the Model

The proposed mechanism of electrolytic codeposition of inert particles with metals is based on two fundamental postulates:

1. An adsorbed layer of ionic species is created around the inert particles at the time the particles are added to the plating solution or during the pretreatment of these particles in ionic solutions.
2. The reduction of some of these adsorbed ionic species is required for the incorporation of particles in the metallic matrix.

On its way from the bulk of the solution to the site of incorporation at the active cathode surface the inert particle has to proceed through five stages (see Fig. 2): (i) adsorption of ionic species upon the particle surface; (ii) movement of the particle by forced convection towards the hydrodynamic boundary layer ( $\delta_o$ ) at the cathode; (iii) diffusion of the particle through the diffusion double layer ( $\delta$ ); (iv) adsorption of the particle, still with its adsorbed ionic cloud, at the cathode surface; (v) reduction of some adsorbed ionic species by which the particle becomes irreversibly incorporated in the metal matrix. For the construction of the model it is assumed that steady-state conditions exist, so that neither concentration, pressure, temperature, nor overpotential variations occur during the process, that the cathode surface is uniformly accessible for the plating solution and for the inert particles, and finally that a homogeneous suspension of particles in the plating solution is maintained. We can then focus our attention on what is happening in the diffusion layer.

At the diffusion layer the ions are moving towards the cathode by diffusion and simultaneously take along inert particles onto which a number of ions are adsorbed. Once at the electrode surface, ions are reduced to meet the demands of the reduction process at the applied cathodic overpotential. What is then happening to the

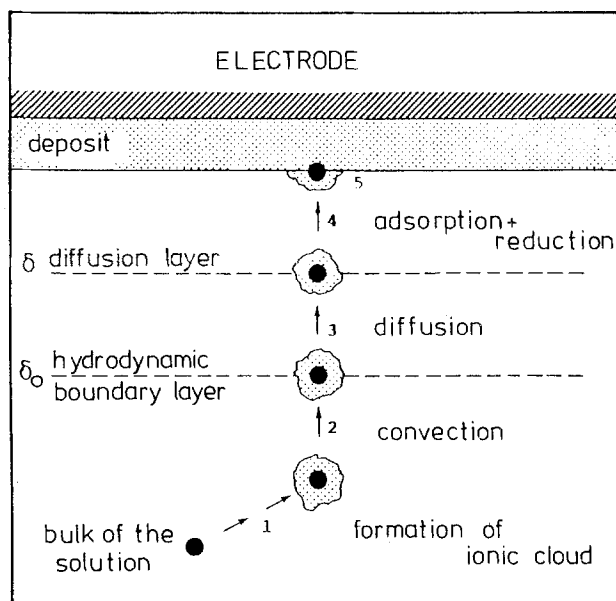


Fig. 2. The five stages in the codeposition of a particle

particles which are populating the cathode surface but are still screened off by their ionic cloud? Here the primary hypothesis of the model is involved: "A particle will only be incorporated when a certain amount  $k$  out of  $K$ -adsorbed ionic species, depending on the combination of plating solution characteristics and particle characteristics, is reduced." As a consequence of this hypothesis still another hypothesis should be added: "No distinction is made between free and adsorbed ionic species and both are considered equal with respect to transport and reduction processes."

The quantitative description of the incorporation of an inert particle into a growing metallic matrix can thus be derived from a statistical approach in which the coefficient  $P$  represents the probability for a particle to become incorporated and  $N_p$  the number of particles crossing the diffusion layer at the working electrode per unit of time and surface area. The primary hypothesis formulated above can now be translated into an expression for  $\Delta W_p$  = weight increase per unit of time and surface area due to particle incorporation

$$\Delta W_p = W_p \cdot N_p \cdot P \quad [6]$$

where  $W_p$  = weight of one particle,  $N_p$  having the dimension of  $m^{-2} \cdot s^{-1}$ . Assuming the particles are all spherical, the weight of one particle is given by

$$W_p = \frac{4\pi r^3}{3} \cdot \rho_p \quad [7]$$

with  $\rho_p$  = density of the particle and  $r$  = radius of the particle. The weight increase per unit of time and surface area due to pure metal deposition ( $\Delta W_m$ ) can be derived from Faraday's law assuming a 100% current efficiency

$$\Delta W_m = \frac{Mi}{nF} \quad [8]$$

with  $M$  = molecular weight of the element deposited,  $n$  = number of electrons participating in the reduction reaction  $M^{n+} + ne^- \rightarrow M$ ,  $F$  = Faraday constant, and  $i$  = current density. The weight percent (w/o) embedded particles in a composite coating can generally be expressed as

$$\begin{aligned} \text{w/o particles embedded} &= \frac{\Delta W_p}{\Delta W_m + \Delta W_p} \cdot 100 \\ &= \frac{W_p \cdot N_p \cdot P}{\frac{Mi}{nF} + W_p \cdot N_p \cdot P} \cdot 100 \quad [9] \end{aligned}$$

**Calculation of the coefficient  $P$ .**—Let us consider the case where a coating is deposited at a current density  $i$ . If one considers that the probability for one ion to be reduced ( $p_i$ ) at current density  $i$  is available, then the probability for the incorporation of one particle based on the reduction of  $k$ -ions out of  $K$ -ions [ $P_{(k/K,i)}$ ] at current density  $i$  can be calculated from a binomial distribution

$$P_{(k/K,i)} = \sum_{z=k}^K C_z^K [1 - p_i]^{K-z} p_i^z \quad [10]$$

The calculation of the probability for one ion to be reduced ( $p_i$ ) is simplified by the consideration that no distinction has to be made between free and adsorbed ions so that both can be treated equal with respect to transport and reduction processes. The number of moles which are reduced per unit of surface area and per unit of time is given by  $i/nF$ . The probability that an ion present in the diffusion layer will be reduced, is the ratio of the previous expression to the number of moles present in the diffusion layer

$$p_i = \frac{\frac{i}{nF}}{\frac{C_{ion} + C_o}{2} \delta + \frac{i}{nF}} \quad [11]$$

with  $C_{ion}$  = bulk concentration of metal ions,  $C_o$  = concentration of metal ions at the working electrode surface, and  $\delta$  = the diffusion layer thickness. The first term of the denominator is an approximation of the mean concentration in the double layer, and the second term represents the moles entering the diffusion layer due to  $i$ . According to the theory of Levich the diffusion layer thickness  $\delta$  is given by

$$\delta = 1.61 D_{ion}^{1/3} \cdot \nu^{1/6} \cdot \omega^{-1/2} \quad [12]$$

with  $D_{ion}$  = diffusion coefficient of the ion,  $\nu$  = the viscosity of the solution, and  $\omega$  = rotation speed of a rotating working electrode. From the equality between diffusion flux and reduction flux, it can be derived that

$$\frac{-D_{ion}(C_{ion} - C_o)}{\delta} = \frac{i}{nF} \quad [13]$$

so that Eq. [11] can be rewritten as

$$p_i = \frac{i}{nFC_{ion} + \frac{i\delta^2}{2D_{ion}} + i} \quad [14]$$

By inserting Eq. [14] in Eq. [10] it is now possible to calculate the probability for the incorporation of one particle  $P_{(k/K,i)}$ , vs. current density, for different values of  $k$  and  $K$  with given values of  $\delta$ ,  $D_{ion}$ , and  $C$ . Figure 3 shows this probability for  $K = 1000$  and Fig. 4 for  $K = 315$ . Some general features of this  $P_{(k/K,i)}$  function are: (i) a higher  $K$  demands a higher current density for an equal probability, (ii) the higher  $K$ , the smaller the probability for the incorporation of one particle at a given current density. In order to take into account hydrodynamic effects, the probability for the incorporation of one particle can hence be written as

$$P = H \cdot P_{(k/K,i)} \quad [15]$$

where  $H = 1$  under laminar flow (where  $\delta$  is defined by Levich's law).  $H = 0$  under high turbulent flow where the particles collide frequently and can hardly enter the very thin diffusion layer. Experimental evidence supporting this hypothesis has already been shown based on rotating disk experiments (22).  $0 < H < 1$  in the transition and early turbulent regimes.

**Calculation of coefficient  $N_p$ .**—The next parameter in formula [7] to be determined is  $N_p$ , the number of particles crossing the diffusion layer at the working electrode per unit of time and surface area. In analogy with the calculation where the probability to incorporate one particle ( $P$ ) was related to the probability to reduce one ion ( $p_i$ ) (cf. formula [10]),  $N_p$  is here associated with the number of ions being reduced ( $N_{ion}$ )

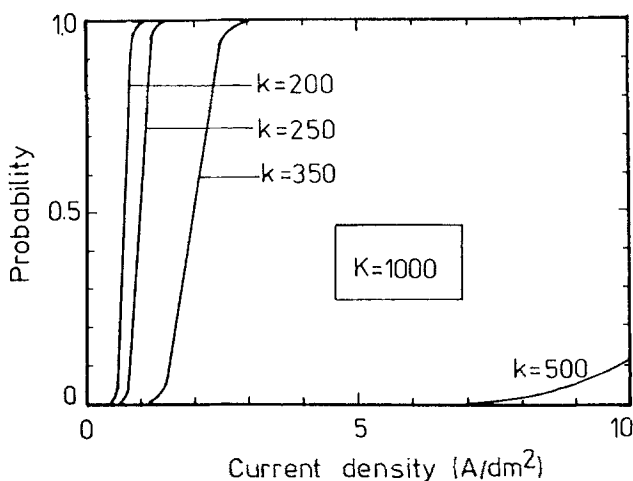


Fig. 3. Probability for the incorporation of one particle vs. current density for  $K = 1000$ .

$$N_p = N_{ion} \cdot \frac{C_p^*}{C_{ion}^*} \quad [16]$$

with  $N_p$  = number of particles crossing the diffusion layer per second and per unit of surface area,  $N_{ion}$  = number of ions crossing the diffusion layer per second and per unit of surface area,  $C_p^*$  = number of particles in the bulk of the solution,  $C_{ion}^*$  = number of ions in the bulk of the solution. Calculation of  $C_p^*$  and  $C_{ion}^*$  can be done by converting, respectively, mass concentrations of particles and ions into number of particles and ions according to the following equations

$$C_p^* = \frac{C_p}{W_p}$$

$$C_{ion}^* = \frac{C_{ion} N_A}{M}$$

$$N_{ion} = \frac{i \cdot N_A}{nF}$$

with  $C_p$  = concentration of particles in plating bath and  $N_A$  = Avogadro's number.

Equation [16] is valid as long as particles and ions move at the same rate. This is only the case when the reaction is under charge-transfer overvoltage control, i.e., when the reduction of ions, either free or adsorbed, is the rate controlling step while diffusion is fast enough to provide the ions for reduction. In the concentration overvoltage region the transport step, which takes place by diffusion in the diffusion layer, dominates the reaction rate. Since the particles with their ionic cloud diffuse much slower than the free ions, and since this effect is more pronounced at higher current densities, the relative diffusion of the particles can be written as

$$N_p = N_{ion} \cdot \frac{C_p^*}{C_{ion}^*} \cdot \left( \frac{i_{tr}}{i} \right)^\alpha \quad [17]$$

where  $i_{tr}$  = transition current density from charge transfer to concentration overvoltage control and  $\alpha$  = measure of interaction between free and adsorbed ions due to current density effects.  $\alpha$  is equal to zero for a reduction process under charge transfer overvoltage control. For a reduction process which is under mass transfer control  $\alpha$  is not equal to zero.

By combination of formula [9], with [7], [15], and [17] one can now derive the final expression for the weight percent embedded spherical particles as a function of current density

w/o emb. spherical part. =

$$\frac{4\pi r^3 \rho_p \cdot N_{ion} \cdot \frac{C_p^*}{C_{ion}^*} \cdot \left( \frac{i_{tr}}{i} \right)^\alpha \cdot H \cdot P_{(k/K, i)}}{\frac{3Mi}{nF} + 4\pi r^3 \rho_p N_{ion} \cdot \frac{C_p^*}{C_{ion}^*} \cdot \left( \frac{i_{tr}}{i} \right)^\alpha \cdot H \cdot P_{(k/K, i)}} \cdot 100 \quad [18]$$

One of the main parameters of the model is  $i_{tr}$ , i.e., the current density at which the reduction reaction changes from charge-transfer to mass transport control. It determines the position of the maximum in the curve of  $N_p$  vs.  $i$  and indirectly the value of the maximum codeposition level. Hence an extremely accurate measurement or calculation of the value of  $i_{tr}$  is necessary for the prediction of any codeposition curve. Any shift of the polarization curve due to the addition of particles in the solution must thus be determined since it will influence  $i_{tr}$ . With increasing bath load of particles,  $i_{tr}$  will change and consequently the location of the maximum of the curve  $N_p$  vs.  $i$  will change.

The formulation of the present model shows that the process depends on many variables of which the most important are: (i) the current density or overpotential which influences all the terms in formula [18] except those related to the particle: (ii) the adsorbed layer on

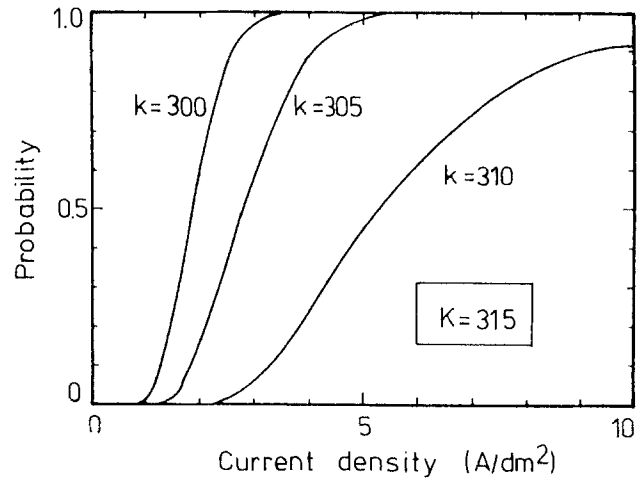


Fig. 4. Probability for the incorporation of one particle vs. current density for  $K = 315$ .

the particle which determines the probability for codeposition through the ratio  $k/K$ , the position of the maximum on the current-axis, and the factor  $N_p$  in the concentration overvoltage zone; (iii) the particle itself with its proper weight and its amount in suspension; (iv) the metal ions to be reduced which determine where the codeposition goes through a maximum and the factor  $N_p$ ; (v) hydrodynamic conditions which influence to a great extent  $N_p$  and the probability for codeposition.

At this stage of the discussion, one has to give some attention to the applicability of the present model. Considering the electrolytic codeposition of particles, one has to differentiate between the codeposition of electrical nonconducting particles and conducting particles. Conducting particles are generally codeposited to a much larger weight percent than nonconducting particles, and they also tend to cause dendritic outgrowth of the metallic matrix. Looking back to the present model, one could object that the specific electrical conductivity of the particles is not included as a parameter. Nevertheless the effect of this electrical conductivity is indirectly reflected by the  $k$  value selected for the calculation of the coefficient  $P_{(k/K, i)}$ . Indeed, in the case of conducting particles, the number of adsorbed ions to be reduced out of  $K$  adsorbed ions necessary to obtain a codeposition, will be smaller than in the case of nonconducting particles because of the polarization of conducting particles. This means that for all other parameters being constant, a higher probability of codeposition is expected for conducting particles. The outgrowth of the metallic matrix is strictly related to the polarization of these conducting particles which allows the formation of metallic nuclei over the outward surface of the particles once these are in direct contact with the cathode.

Finally, one can wonder why a critical waiting time of particles at the cathode is not considered explicitly in the present model. Indeed some researchers (10) have tried, but without success, to include a critical time in their model. In the present model a possible critical time is incorporated in the calculation of the probability coefficient  $P_{(k/K, i)}$ . Considering the collision of incoming particles with partly embedded particles, one can say that in the case of nonconducting particles a codeposition at the top of a partly embedded particle will not occur since the reduction of  $k$  adsorbed ions cannot occur. In the case of conducting particles the polarization of the particles can indeed allow the codeposition of an incoming particle at the top of a partly embedded particle. In analogy with the preceding discussion this will further increase the probability of codeposition through the lowering of the value  $k$  in  $P_{(k/K, i)}$ .

#### Application of the Present Model to Real Codeposition Data

The codeposition of  $Al_2O_3$ -particles with copper from acidic sulfate plating baths has been extensively re-

Table I. Experimental conditions and relevant data for Cu-Al<sub>2</sub>O<sub>3</sub> codeposition using rotating disk electrodes

Solution	CuSO <sub>4</sub> · 5H <sub>2</sub> O pH 0.3	C <sub>Cu<sup>2+</sup></sub> = 30 g/liter M <sub>Cu</sub> = 63.5 g/mol d <sub>Cu<sup>2+</sup></sub> = 2.2 Å n = 2 ν = 2 cSt D = 0.147 × 10 <sup>-3</sup> cm <sup>2</sup> /s T = 20°C
Particles	γ-Al <sub>2</sub> O <sub>3</sub>	ρ <sub>p</sub> = 3.7 g/cm <sup>3</sup> d <sub>p</sub> = 0.05 μm C <sub>Al<sub>2</sub>O<sub>3</sub></sub> = 20 g/liter Specific surface area 80 m <sup>2</sup> /g
Adsorbed ions on particles	Cu <sup>2+</sup> , H <sup>+</sup>	0.2 mg Cu <sup>2+</sup> on 1g Al <sub>2</sub> O <sub>3</sub>
Reduction reaction	Cu <sup>2+</sup> → Cu	i <sub>tr</sub> = 2 A/dm <sup>2</sup> i <sub>lim</sub> = 10 A/dm <sup>2</sup>
Flow regime	Laminar	Rotation speed: 400 rpm δ = 50 μm

ported in literature (7, 8, 14, 23, 24). Experimental conditions used in the present study and data necessary for the calculation are summarized in Table I. Based on these data the different parameters of the model can be calculated separately

$$W_p = \frac{4\pi r^3}{3} \rho_p = 2.4 \times 10^{-19} \text{ kg} \quad [19]$$

$$\Delta W_m = \frac{Mi}{nF} = 0.33 \times 10^{-6} \times i \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \quad [20]$$

$$N_p = N_{\text{ion}} \cdot \frac{C_p^*}{C_{\text{ion}}^*} \cdot \left(\frac{i_{\text{tr}}}{i}\right)^\alpha$$

$$= 9.187 \times i \times \left(\frac{2}{i}\right)^\alpha \times 10^{11} \text{ m}^{-2} \cdot \text{s}^{-1} \quad [21]$$

$$p_i = \frac{i}{C_{\text{ion}} \delta n F + \frac{i \delta^2}{2D_{\text{ion}}} + i} = \frac{i}{45.3 + 6.4 i} \quad [22]$$

$$K = 740 \text{ ions/particle}, \quad H = 1$$

$P = H \cdot P_{(k/K, i)} = 1 \cdot P_{(k/K, i)}$  plotted in Fig. 5, for different ratios of  $k/K$ . For the application of the model two parameters have still to be determined, namely  $k$  and  $\alpha$ . According to the model it is assumed that in the charge-transfer control region  $\alpha = 0$ . From the comparison between experimental and theoretical results  $k$  may be evaluated. The final formulation of the model in the charge-transfer overvoltage region is then

$$\text{w/o embedded Al}_2\text{O}_3 = 66.8 \times P_{(5\%, i)} \quad [23]$$

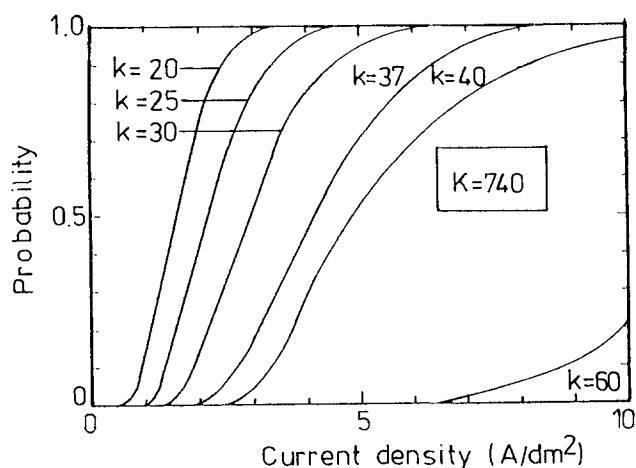


Fig. 5. Probability for the incorporation of one particle vs. current density for  $K = 740$ .

Once  $k$  is known, the value of  $\alpha$  in the concentration overvoltage region can be deduced from the experimental codeposition results. The model in the region of concentration overvoltage then becomes

$$\text{w/o embedded Al}_2\text{O}_3 = 66.8 \times (2/i)^\alpha \times P_{(5\%, i)} \quad [24]$$

Theoretical and experimental results are plotted in Fig. 6 and are found to fit well. Based on these values of  $\alpha$  and  $k$  obtained on a rotating disk electrode under controlled mass transport conditions, data published earlier for the codeposition of alumina with copper on a vertical cathode with vibrating perforated bottom plate providing the necessary agitation (14) can be checked. Since an identical codeposition system is considered, where only the agitation rate varies, the model parameters do not need to be modified, except  $H$  that will differ from unity while  $i_{\text{tr}}$  derived from a polarization measurement is taken equal to 1.65 A/dm<sup>2</sup>. With  $H = 0.25$  the model is then expressed by

$$\text{w/o embedded Al}_2\text{O}_3 = 0.167 \left(\frac{1.65}{i}\right)^\alpha \times P_{(5\%, i)} \quad [25]$$

with  $\alpha = 0$  for  $i < 1.65$  A/dm<sup>2</sup> and  $\alpha = 6$  for  $i > 1.65$  A/dm<sup>2</sup>.

The comparison between experimental and theoretical data is shown in Fig. 7. The deviation between theory and experiment is probably due to the experimental setup, in which no constant double layer thickness is obtained, and the flux of ions and particles is not uniform over the electrode surface. Notice the lower predicted and experimentally verified codeposition when one goes from a rotating electrode setup to a nonrotating vertical electrode setup.

A second codeposition system which was studied using rotating electrode is the codeposition of alumina with gold from a potassium gold cyanide solution. Experimental conditions and data necessary for calculation are summarized in Table II. Two different  $i_{\text{tr}}$  values have to be used since two transitions from charge transfer overvoltage control to concentration overvoltage control appear from potentiokinetic polarization measurements (25). Derived data are

$$W_p = 2.4 \times 10^{-19} \text{ kg} \quad [26]$$

$$\Delta W_m = 2.04 \times 10^{-6} \times i \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \quad [27]$$

$$H = 1 \quad [28]$$

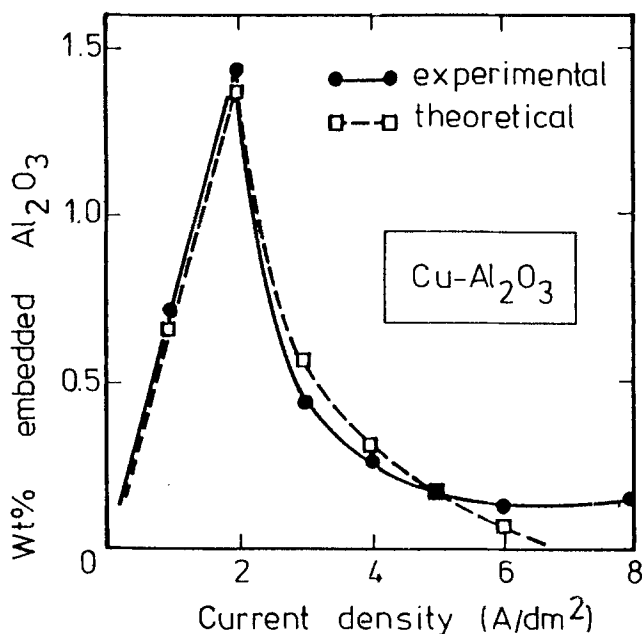


Fig. 6. Experimental and predicted results for Cu-Al<sub>2</sub>O<sub>3</sub> codeposition on a rotating disk electrode.

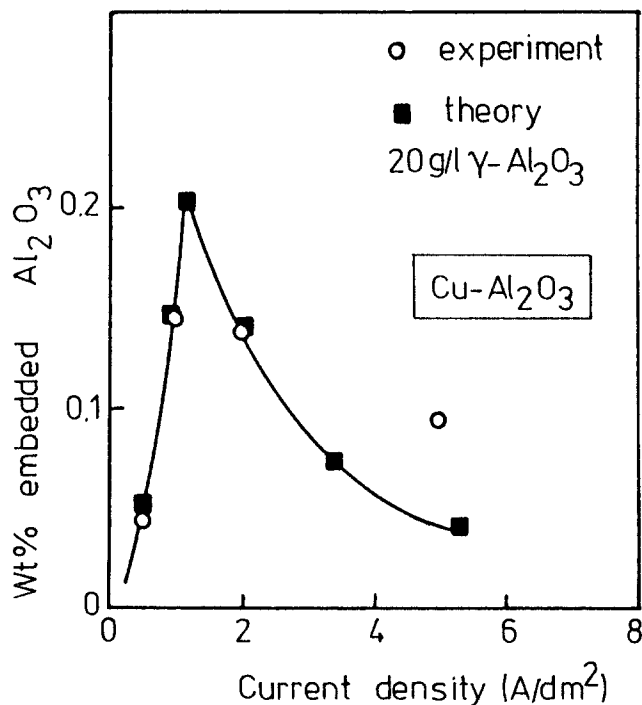


Fig. 7. Experimental and predicted results for Cu-Al<sub>2</sub>O<sub>3</sub> codeposition on a vertical cathode.

$$N_p = 1.65 \times 10^{13} \times i \times \left( \frac{i_{tr}}{i} \right)^\alpha \quad \text{m}^{-2} \cdot \text{s}^{-1} \quad [29]$$

In the absence of data, the amount of components involved in the reaction is assumed to be proportional to the concentration of gold in solution

$$P_i = \frac{i}{1.88i + 2.12} \quad [30]$$

$P = P_{(k/K, i)}$  plotted in Fig. 3 for  $K = 1000$  and different values of  $k/K$ .

For the parameters of the model, three parameters still have to be determined for the reduction of the two species, namely,  $k$ ,  $K$ , and  $\alpha$ , with  $\alpha = 0$  in charge-transfer overvoltage region. The best fit of the experimental results is found by inserting the following values for the first species:  $k/K = 0.15$  and  $K = 200$ . For the second species, the best fit is obtained with  $k/K = 0.15$  and  $K = 500$ . The model is expressed as:

For the reduction of the first species

$$\text{w/o embedded Al}_2\text{O}_3 = 1.55 \times P_{(15\%, i)} \times \left( \frac{0.35}{i} \right)^\alpha \quad [31]$$

with  $\alpha = 0$  for  $i < 0.35$  A/dm<sup>2</sup> and  $\alpha = 0.6$  for  $i > 0.35$  A/dm<sup>2</sup>.

Table II. Experimental conditions and derived data for Au-Al<sub>2</sub>O<sub>3</sub> codeposition using rotating disk electrodes

Solution	KAu(CN) <sub>2</sub> pH 4	$C_{\text{Au}^+} = 10.3$ g/liter $M_{\text{Au}} = 197$ g/mol $n = 1$ $d_{\text{Au}^+} = 2.5\text{\AA}$ $\nu = 0.867$ cSt $D = 0.98 \times 10^{-5}$ cm <sup>2</sup> /s $T = 40^\circ\text{C}$
Particles	$\gamma\text{-Al}_2\text{O}_3$	$\rho_p = 3.7$ g/cm <sup>3</sup> $d_p = 0.05$ $\mu\text{m}$ $C_{\text{Al}_2\text{O}_3} = 20$ g/liter
Adsorbed ions on particles	Au complexes, H <sup>+</sup>	Au(CN) <sub>2</sub> <sup>-</sup> , Au(CN)
Reduction reaction	First species Second species	$i_{tr} = 0.35$ A/dm <sup>2</sup> $i_{tr} = 4.25$ A/dm <sup>2</sup>
Flow regime	Laminar	Rotation speed: 600 rpm $\delta = 43$ $\mu\text{m}$

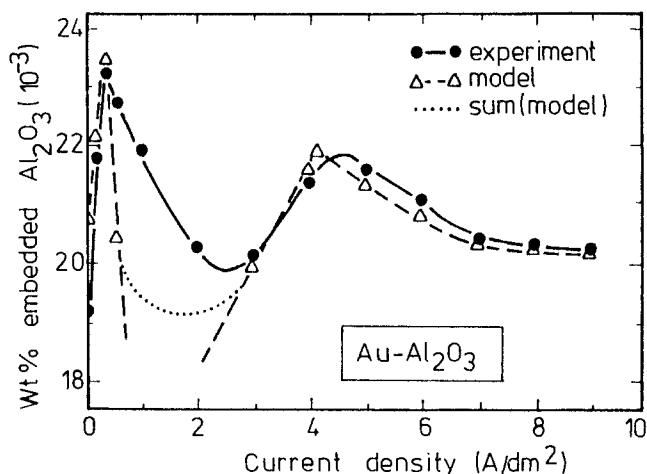


Fig. 8. Experimental and theoretical codeposition curve for the Au-Al<sub>2</sub>O<sub>3</sub> codeposition system.

For the reduction of the second species

$$\text{w/o embedded Al}_2\text{O}_3 = 1.94 \times P_{(15\%, i)} \times \left( \frac{4.25}{i} \right)^\alpha \quad [32]$$

with  $\alpha = 0$  for  $i < 4.25$  A/dm<sup>2</sup> and  $\alpha = 0.5$  for  $i > 4.25$  A/dm<sup>2</sup>.

Experimental and theoretical codeposition curves for the Au-Al<sub>2</sub>O<sub>3</sub> on RDE are compared in Fig. 8.

### Conclusions

A new model (21), based on a statistical approach, has been developed for the electrolytic codeposition of inert particles with metals. The basic hypothesis for the development of the model is expressed as follows: a particle will only be incorporated when a certain amount of adsorbed ions, depending on the codeposition system itself, is reduced. This is translated into the expression

$$\text{w/o particles embedded} = \frac{W_p \cdot N_p \cdot P}{\Delta W_m + W_p \cdot N_p \cdot P} \cdot 100$$

where  $W_p$  = weight of one particle (kg),  $N_p$  = amount of particles crossing the diffusion layer at the working electrode per unit of time and surface area at current density  $i$  (s<sup>-1</sup> m<sup>-2</sup>),  $P$  = probability for the incorporation of one particle at a current density  $i$ ,  $\Delta W_m$  = mass of metal matrix deposited per unit of time and surface area at current density  $i$  (kg m<sup>-2</sup> s<sup>-1</sup>).

The model was found to be valid for the electrolytic codeposition of Cu-Al<sub>2</sub>O<sub>3</sub> from acidic sulfate baths and Au-Al<sub>2</sub>O<sub>3</sub> from cyanide baths and therefore we expect it to be valid for all other composite plating systems. If the necessary data for the calculation of the probability coefficient  $P$  are not available, the model parameters can be determined by comparing theory and experiment. We believe this model will contribute to a deeper and more complete insight into the mechanism of the electrolytic codeposition processes.

Manuscript submitted June 27, 1986; revised manuscript received Dec. 17, 1986.

### LIST OF SYMBOLS

$C_{i, \text{ion}}$	bulk concentration of metal ions (mol m <sup>-3</sup> )
$C_o$	concentration of metal ions at the working electrode surface (mol m <sup>-3</sup> )
$C_p$	concentration of particles in plating bath (kg m <sup>-3</sup> )
$C_p^*$	number of particles in the bulk of the solution (m <sup>-3</sup> )
$C_{i, \text{ion}}^*$	number of ions in the bulk of the solution (m <sup>-3</sup> )
$C_v$	volume percent of particles in the plating bath (%)
$d$	diameter of particles (m)
$D_{i, \text{ion}}$	diffusion coefficient of the ion (m <sup>2</sup> · s <sup>-1</sup> )
$e_m$	metal equivalent (kg A <sup>-1</sup> s <sup>-1</sup> )
$E$	potential gradient (V)
$F$	Faraday constant (96,500 A, s mol <sup>-1</sup> )
$H$	coefficient of hydrodynamic effects (-)
$i$	current density (A · m <sup>-2</sup> )

$i_0$	exchange current density ( $A \cdot m^{-2}$ )
$i_{tr}$	transition current density from charge-transfer to concentration overvoltage control ( $A \cdot m^{-2}$ )
$k^*$	Langmuir constant (-)
$K$	amount of ions adsorbed on a particle (-)
$M$	atomic or molar mass ( $kg \cdot mol^{-1}$ )
$n$	valence of electrodeposited metal (-)
$N_{ion}$	number of ions crossing the diffusion layer per unit of time and surface area ( $s^{-1} \cdot m^{-2}$ )
$N_p$	number of particles crossing the diffusion layer at the working electrode per unit of time and surface area ( $s^{-1} \cdot m^{-2}$ )
$N^*$	number of collisions of particles suitable for co-deposition per unit of time and surface area ( $s^{-1} \cdot m^{-2}$ )
$N_A$	Avogadro's number ( $6.022 \cdot 10^{26} \cdot kg^{-1}$ )
$p_i$	probability for the ion to be reduced (-)
$P$	probability for a particle to become incorporated (-)
$r$	radius of a particle (m)
$X_p$	weight percent of embedded particles (%)
$W_p$	weight of one particle (kg)
$W_m$	weight increase of deposited metal per unit of time and surface area
$\alpha$	measure of interaction between free and adsorbed ions due to current density effects (-)
$\delta$	diffusion layer thickness (m)
$\delta_0$	hydrodynamic boundary layer thickness (m)
$\theta$	strong adsorption coverage (-)
$\nu$	kinematic viscosity ( $kg \cdot m^{-1} \cdot s^{-1}$ )
$\rho_m$	density of electrodeposited metal ( $kg \cdot m^{-3}$ )
$\rho_p$	density of particles ( $kg \cdot m^{-3}$ )
$\sigma$	loose adsorption coverage (-)
$\omega$	rotation speed of the electrode ( $s^{-1}$ )

## REFERENCES

- J. C. Whithers, *Prod. Fin.*, **8** (1962).
- P. W. Martin and R. V. Williams, Proc. Interfinish '64, pp. 182-188, British Iron and Steel Research Ass., London (1964).
- E. A. Brandes and D. Golthorpe, *Metallurgica*, 195 (1967).
- J. E. Hoffman and C. L. Mantell, *Trans. Met. Soc. AIME*, **236**, 1015 (1966).
- D. W. Snaith and P. D. Groves, *Trans. Inst. Met. Finish.*, **51**, 27 (1973).
- M. Van Camp, Engineering Thesis, KU. Leuven (1979).
- T. W. Tomaszewski, L. L. Tomaszewski, and H. Brown, *Plating*, **56**, 1234 (1969).
- E. S. Chen, G. R. Lakshminarayanan, and F. K. Sautter, *Met. Trans.*, **2**, (4), 937 (1971).
- J. R. Roos, J. P. Celis, and J. A. Helsen, *Trans. Inst. Met. Finish.*, **55**, 113 (1977).
- J. Foster and A. M. J. Kariapper, *ibid.*, **50**, 207 (1972).
- R. S. Saifullin and R. G. Khalilova, *J. Appl. Chem. USSR*, **43** (1970).
- R. Bazzard and P. J. Boden, *Trans. Inst. Met. Finish.*, **50**, 63 (1972).
- N. Guglielmi, *This Journal*, **119**, 1009 (1972).
- J. P. Celis and J. R. Roos, *ibid.*, **124**, 1508 (1977).
- N. Masuko and K. Mushiake, *J. Met. Finish. Soc. Japan*, **28**, 534 (1977).
- M. K. Totlani and S. N. Athavale, *J. Electrochem. Soc. India*, **31**, 119 (1982).
- J. Zahavi and J. Hazan, *Plating Surf. Finish.*, **70**, 57 (1983).
- T. Hayashi, in Proc. Interfinish '76, Amsterdam (1976).
- F. K. Sautter, *This Journal*, **110**, 557 (1963).
- A. M. J. Kariapper and J. Foster, *Trans. Inst. Met. Finish.*, **52**, 87 (1974).
- C. Buelens, Ph.D. Thesis, KU. Leuven (1984).
- J. P. Celis, J. R. Roos, W. Van Vooren, and J. Vanhumbecq, Paper K, pp. 1-10, Proc. 3rd AESF Pulse Plating Symposium, Washington, DC (1986).
- C. White and J. Foster, in Proc. Annual Technical Conference IMF, Torquay (1978).
- J. E. Hoffmann and R. C. Ernst, INCRA-Project No. 31 (1964).
- C. Buelens, J. P. Celis, and J. R. Roos, *J. Appl. Electrochem.*, **13**, 541 (1983).

## The Composition of Electrodeposited Zinc-Nickel Alloy Coatings

Mark F. Mathias\*\* and Thomas W. Chapman\*

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

## ABSTRACT

The composition of zinc-nickel alloy films deposited on a rotating disk electrode is analyzed in terms of a one-dimensional transport-reaction model. The mass-transfer model includes the effects of migration and complexation of zinc by chloride. It is found that migration in this system can enhance the interfacial concentration of nickel deposition to levels exceeding that in the bulk solution. A simple electrode kinetics model is postulated to describe the partial current density of each metal-reduction reaction in terms of electrode potential, interfacial concentrations, and temperature. Kinetics parameters appearing in the model are estimated from experimental deposit composition data. The resulting model can predict alloy composition over a range of plating conditions, but electrode polarization is not predicted accurately. A more complete kinetics model, describing zinc-nickel interactions, is needed.

Alloy coatings on base metal substrates can provide desirable surface properties with respect to corrosion protection, wear resistance, and electromagnetic phenomena. For example, zinc-nickel coatings on steel give better corrosion protection than do pure zinc films (1). In many cases, including zinc-nickel, the alloy coating can be formed by electrodeposition (2). This paper considers the question of how bath composition and operating conditions determine electrodeposited alloy composition. In particular, a mass transfer model is developed for zinc-nickel chloride baths that permits correlation of the composition of the deposit on a rotating disk electrode (RDE) with plating conditions in terms of electrode kinetics parameters. Such a correlation, based on interfacial conditions, should apply to other electrode configurations.

The premise of this work is that alloy composition is determined by the relative rates, or partial current densi-

ties, of the individual metal reduction reactions and that the kinetics of these reactions are determined by the local interfacial conditions of solute concentrations, potential, temperature, and surface properties. While the electrode kinetics may be expressed in terms of these interfacial conditions, the latter must be related to bulk solution conditions by means of a mass transfer model.

Large-scale alloy electrodeposition is usually done at high current densities from baths in which the reacting species are also major constituents of the solution. For example, a zinc-nickel alloy can be electrodeposited successfully at 400 mA/cm<sup>2</sup> from a bath containing mainly nickel and zinc salts (3). Under these conditions ionic migration is clearly an important mechanism of mass transport that must be included in a complete analysis of the deposition process. Because migration effects depend strongly on the concentrations and charges of the species in the solution, the speciation of the solute metal ions must also be considered. This paper considers zinc-nickel alloy deposition on an RDE and relates average al-

\* Electrochemical Society Active Member.

\*\* Electrochemical Society Student Member.