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Current and Potential Distributions in Plating Corrosion Systems*

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ABSTRACT

The numerical determination of current and potential distributions has been performed for plating corrosion systems, where failure to coat a small area leads to corrosion at the pinhole. The distributions depend on characteristic parameters for the disk anode and surrounding plane cathode and reveal that each of the electrodes influences the other due to their proximity. The results were applied to an array of disks, and it was found that the corrosion potential of the system is a linear function of the area ratio of anode to cathode when ohmic effects are important. This may be contrasted to the logarithmic dependence found when ohmic effects are neglected. Other applications are discussed.

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Introduction

The protection of active metals by electroplated noble metals has been an established practice for many years. In the electronics industry, for example, copper is protected by plating gold over the substrate. In order to minimize costs, the thickness of the gold coating is reduced as much as possible, and this introduces pores in the overplate. These pores will permit corrosion of the underlying copper substrate, and if there is a cathodic reaction on the gold, the corrosion of copper will actually be enhanced because of galvanic effects. Therefore, one seeks the minimum thickness of the gold electroplate which will adequately eliminate corrosion.

Several techniques have been introduced to determine the porosity of the electroplate for various plating thicknesses. Chemical etch techniques for the copper-gold system (1,2) decorate the pores and permit them to be counted by microscopic techniques. The measurement of anodic current in a system where the gold is completely inert and only copper is active has been very successful (2,3) in determining the total surface area of copper exposed in pores, but it does not reveal the distribution of pores nor their size on electroplated pieces. A similar technique (4-7) is the determination of resistance when an electroplated specimen is polarized under potentiostatic control. Finally, measurement of the corrosion potential for the galvanic couple, substrate/coat, has been proposed (8-11) as a technique to measure the ratio of areas

of the two metals. We have chosen this final technique for further discussion and study here.

Galvanic corrosion, in this case the corrosion of an active metal in a pore driven by a cathodic reaction on the surrounding noble electrode, is a complex phenomenon which may involve electrode-kinetic effects on both the anode and cathode, mass-transfer effects, and ohmic effects. In addition, the proximity of the two "electrodes" in plating corrosion can lead to interaction effects not normally seen on separated electrodes.

Stern (9) first derived the relationship between the area ratio of a galvanic couple and its corrosion potential. The development was based on the assumptions that the electrochemical reaction kinetics on each electrode were of the Tafel form and that the respective reactions were uniform on the anode and cathode of the couple. This development does not take into account ohmic effects in the solution. The relationship derived is (9)

$$\eta_{\text{CORR}} = - \frac{E_a \beta_c}{\beta_c + \beta_a} - \frac{\beta_c \beta_a}{\beta_c + \beta_a} \ln (A_a i_{a_c}) + \frac{\beta_c \beta_a}{\beta_c + \beta_a} \ln (A_c i_{o_c}) \quad (1)$$

where β = Tafel slope of the respective reaction

i_o = exchange current density of the respective reaction

A_a = area fraction of anode

A_c = area fraction of cathode

η_{CORR} = corrosion potential of the couple relative to the reversible potential of the cathode

E_a = standard reversible potential of the anode with respect to the reversible potential of the cathode

Thus it may be seen that the corrosion potential has a logarithmic dependence on the area ratio $\frac{A_a}{A_c}$, with a slope of $-\frac{\beta_c \beta_a}{\beta_c + \beta_a}$. Stern (9) notes that this equation is not valid in the limit that A_a or A_c approaches 1.

Oldham and Mansfield (11) recently extended this treatment to include both an oxidation reaction and reduction reaction on the cathode of the couple. Their development again does not take ohmic effects into account, but they do treat the case of diffusion control on the cathode.

Mansfield has also treated other special cases (12) including that for diffusion control on both anode and cathode. For this case, the "catchment principle" is derived, i.e., the corrosion potential is found to be linearly related to the area ratio for the galvanic couple.

Levich and Frumkin (13) treated a system of a cathodic disk in a surrounding anodic plane, which is the reverse of the system to be treated here. The current density on the small disk was uniform, and the potential of the surrounding plane was uniform (i.e., completely reversible kinetics on the plane). This treatment specifically includes ohmic effects in solution. More recently, McCafferty (14) has presented an analysis of current and potential distribution for an anodic disk in a surrounding cathodic plane, using an assumed linear form for the electrode kinetics on the disk and plane. This treatment also includes

the effect of ohmic resistance in solution.

The present contribution will describe the general analysis of current and potential distribution for an anodic disk in a cathodic plane. General mathematical expressions for the electrode kinetics will be employed, which reduce to the special treatments listed above as limiting cases. This analysis also provides a systematic treatment of the effect of the proximity of the electrodes on the current and potential distribution of each electrode. The broader understanding of galvanic corrosion in this simple system then allows one to predict the behavior of arrays of disks, and therefore the influence of porosity of the electroplate on the corrosion potential of the couples.

Mathematical Treatment

The system to be studied here is illustrated in figure 1. The anodic disks are distributed randomly on the surface, are coplanar with the surrounding plane, and are all of the same radius, r_d . They are also assumed to be far apart. The effect of recessing the pores will be discussed briefly, but a detailed study will be treated in a later paper.

The current and potential distributions in an electrochemical system may be determined mathematically by solving Laplace's equation

$$\nabla^2 \phi = 0 \quad (2)$$

subject to boundary conditions on the electrodes imposed by the kinetics of the reactions occurring there. Electrodes with highly reversible

FIGURE 1.
CORRODING DISKS IN A CATHODIC SURROUNDING PLANE.

reactions have a constant-potential boundary condition everywhere on the surface since polarization causes an ohmic potential drop in solution without changing the surface potential of the electrode. The current and potential distributions on an electrode with this boundary condition depend on geometric ratios for the system, but do not depend on the absolute size. Boundary conditions suitable for slower reactions cause the current and potential distribution to depend on an absolute length of the electrode, as well as the geometric ratios characteristic of a purely ohmically determined distribution. Also, it will be shown below that the distribution on one electrode depends on the distribution on the counterelectrode as well when the electrodes are near one another.

For the analysis which follows, attention is focused on one disk first, and the array of disks will be treated later. The origin of the coordinate system is chosen as the center of the disk. Radial distance, r , is measured from the axis of the disk, parallel to the surface. The distance, z , is measured normal to the surface. We choose the rotational elliptic coordinate system, which has been shown (15,16) to be especially suitable for disk geometries and is related to the coordinates r , z , by

$$z = r_d \eta \xi \quad (3)$$

$$r/r_d = [(1 + \xi^2)(1 - \eta^2)]^{\frac{1}{2}} \quad (4)$$

where r_d is the disk radius. The disk in a surrounding plane is now described geometrically in rotational elliptic coordinates as shown in

figure 2. The disk electrode is at $\xi = 0$, and its axis is $\eta = 1$. The surrounding plane is located at $\eta = 0$. The plane $\xi = \xi_{\max}$ is far from the disk and in cylindrical coordinates is approximately a hemisphere in the solution which intersects the surrounding plane at a radial distance $r_{\max}$.

Laplace's equation in this coordinate system is (16),

$$(1-\eta^2) \frac{\partial^2 \phi}{\partial \eta^2} + (1+\xi^2) \frac{\partial^2 \phi}{\partial \xi^2} + 2\xi \frac{\partial \phi}{\partial \xi} - 2\eta \frac{\partial \phi}{\partial \eta} = 0 \quad (5)$$

and is to be solved subject to the boundary conditions (where κ is the conductivity of the electrolytic solution):

a) on the disk, $\xi = 0$

$$i_d = -\frac{\kappa}{r_d \eta} \left. \frac{\partial \phi}{\partial \xi} \right|_{\xi=0} \quad (6)$$

$$= i_{od} \left[\exp \left\{ \frac{\alpha_{ad} F}{RT} (V_d - \phi_d^\circ - E_d^\circ) \right\} - \exp \left\{ \frac{-\alpha_{cd} F}{RT} (V_d - \phi_d^\circ - E_d^\circ) \right\} \right] \quad (7)$$

b) on the surrounding plane, $\eta = 0$,

$$i_p = -\frac{\kappa}{r_d \xi} \left. \frac{\partial \phi}{\partial \eta} \right|_{\eta=0} \quad (8)$$

$$= i_{op} \left[\exp \left\{ \frac{\alpha_{ap} F}{RT} (V_p - \phi_p^\circ - E_p^\circ) \right\} - \exp \left\{ \frac{-\alpha_{cp} F}{RT} (V_p - \phi_p^\circ - E_p^\circ) \right\} \right] \quad (9)$$

c) ϕ well-behaved at $\eta = 1$

d) at $\xi = \xi_{\max}$ two different boundary conditions were employed, i.e.,

FIGURE 2.
THE DISK-PLANE SYSTEM IN
ROTATIONAL ELLIPTIC COORDINATES.

$$* \frac{\partial \phi}{\partial \xi} = 0 \text{ at } \xi = \xi_{\max} \quad (10)$$

$$* \frac{\partial \phi}{\partial \xi} = - \frac{2\phi}{\xi_{\max}} \left\{ \frac{P_1(\eta) + \frac{3P_2(\eta)}{\xi_{\max} P_2(o) J_p}}{P_1(\eta) + \frac{2P_2(\eta)}{\xi_{\max} P_2(o) J_p}} \right\} \quad (11)$$

Equation (10) would be appropriate for an insulating surface at $\xi_{\max}$, and equation (11) is an approximation to the derivative at $\xi_{\max}$ when the solution actually extends to infinity. In the latter case, the potential ϕ is measured relative to the reversible or open-circuit potential for the surrounding plane. The quantity $(V - \phi^\circ - E^\circ)$ in equations (7) and (9) is the surface overpotential for the respective reaction (16), and ϕ° is the potential in solution at the electrode surface. The derivation of equation (11) is given in Appendix 1.

The Butler-Volmer relationship for kinetics on an electrode is given by Equation (7) or Equation (9). For corrosion systems where simultaneous reactions occur on a homogenous surface, such a relationship would be appropriate for each reaction. Polarization of a reaction far from its reversible potential E° will cause one term of the relationship to dominate, and the polarization is said to be in the Tafel region. For two different reactions occurring simultaneously, one anodic and one cathodic on the same surface, one has for Tafel polarization,

$$i_{\text{anodic}} = i_{\text{oa}} \exp \left[\frac{\alpha_a F}{RT} (V - \phi_a^\circ - E_a^\circ) \right]$$

and

$$i_{\text{cathodic}} = - i_{\text{oc}} \exp \left[\frac{-\alpha_c F}{RT} (V - \phi_c^\circ - E_c^\circ) \right]$$

Following Wagner and Traud (17), the local (net) current density at a point on the surface is the sum of the current density for each reaction, i.e.,

$$i_{\text{net}} = i_{\text{anodic}} + i_{\text{cathodic}} = i_{\text{oa}} \exp \left[\frac{\alpha_a F}{RT} (V - \phi^\circ - E_a^\circ) \right] - i_{\text{oc}} \exp \left[\frac{-\alpha_c F}{RT} (V - \phi^\circ - E_c^\circ) \right]$$

For zero net current

$$i_{\text{anodic}} = - i_{\text{cathodic}}$$

or

$$i_{\text{oa}} \exp \left[\frac{\alpha_a F}{RT} (V - \phi^\circ - E_a^\circ) \right] = i_{\text{oc}} \exp \left[- \frac{\alpha_c F}{RT} (V - \phi^\circ - E_c^\circ) \right] \\ = i_{\text{corr}}$$

where i_{corr} is the corrosion current density at the mixed or corrosion potential. U_{corr} is the corrosion potential identified as

$$U_{\text{corr}} \left[\frac{\alpha_a F}{RT} + \frac{\alpha_c F}{RT} \right] = - \ln \frac{i_{\text{oa}}}{i_{\text{oc}}} - \frac{\alpha_a F}{RT} E_a^\circ - \frac{-\alpha_c F}{RT} E_c^\circ$$

which is identical to equation (1) when E_c° is zero. The expression for the net current may now be written

$$i_{\text{net}} = i_{\text{corr}} \left\{ \exp \left[\frac{\alpha_a F}{RT} (V - \phi^\circ - U_{\text{corr}}) \right] - \exp \left[\frac{-\alpha_c F}{RT} (V - \phi^\circ - U_{\text{corr}}) \right] \right\}$$

This expression for the net current is similar to Equation (7) or Equation (9) where i_o is replaced by i_{corr} and E° is replaced by U_{corr} . Therefore, Equation (7) may be written for a corroding disk as

$$i_d = i_{\text{corr},d} \left\{ \exp \left[\frac{\alpha_{\text{ad}} F}{RT} (V_d - \phi_d^\circ - U_{\text{corr},d}) \right] - \exp \left[\frac{-\alpha_{\text{cd}} F}{RT} (V_d - \phi_d^\circ - U_{\text{corr},d}) \right] \right\} . \quad (12)$$

For a corroding plane,

$$i_p = i_{\text{corr},p} \left\{ \exp \left[\frac{\alpha_{\text{ap}} F}{RT} (V_p - \phi_p^\circ - U_{\text{corr},p}) \right] - \exp \left[\frac{-\alpha_{\text{cp}} F}{RT} (V_p - \phi_p^\circ - U_{\text{corr},p}) \right] \right\} . \quad (13)$$

The boundary conditions (12) and (13) along with the expressions for the current in solution at the electrode surfaces yield the characteristic "polarization parameters" for the problem (18). First we have the ratios of the transfer coefficients $\alpha_{\text{ad}}/\alpha_{\text{cd}}$ and $\alpha_{\text{ap}}/\alpha_{\text{cp}}$. For all the calculations reported here, it has been assumed that these ratios are both unity, that is, that the cathodic Tafel slope equals the anodic Tafel slope for either the disk or the plane. Following Newman (18), we identify the additional polarization parameters as

$$J_d = \frac{i_{\text{corr},d} (\alpha_{\text{ad}} + \alpha_{\text{cd}}) F r_d}{\kappa RT}$$

and

$$\delta_d = \frac{|i_{\text{avg},d}| \alpha_{\text{ad}} F r_d}{\kappa RT}$$

for the disk and

$$J_p = \frac{i_{\text{corr},p} (\alpha_{\text{ap}} + \alpha_{\text{cp}}) F r_d}{\kappa R T}$$

for the plane. These three quantities all represent ratios of the ohmic potential drop (of order $i_{\text{avg}} r_d / \kappa$) to the surface overpotential. The quantities J_d and J_p contain i_{corr} and are especially relevant in a potential range where the corresponding equation 12 or 13 can be linearized. The quantity δ_d is especially relevant when the equation 12 can be approximated by a Tafel expression. With retention of the full forms of equations 12 and 13, all these dimensionless parameters can have some influence on the current and potential distributions. The parameter J_p for the plane involves r_d since this is the only characteristic dimension. Since the total current on the anode must be equal in magnitude to the total cathodic current, there is no additional parameter, like δ_d , for the plane. If a net current were being imposed on the disk-plane system by a third electrode, then there would be a total of six parameters for the disk and the plane.

For large values of J_d and δ_d , the current distribution on the disk becomes highly nonuniform and approaches the ohmically determined distribution (uniform potential on the electrode). For small values of these parameters, the current distribution is controlled by the kinetics and becomes uniform.

By the method of separation of variables, one can write the general solution of Equation (5) as

$$\phi = \sum_{n=1}^{\infty} B_n P_n(\eta) M_n(\xi) \quad (17)$$

where P_n is the Legendre Polynomial and M_n is the Legendre Function of imaginary argument (15). The solution for the present problem involves both odd and even orders in both P_n and M_n , and this prevents one from obtaining an orthogonality relationship to calculate the B coefficients in the infinite series. Equation (17) is not very useful for this reason, and it is necessary to seek another means to solve Equation (5) for the present study. It has been found that the numerical solution of Equation (5) by finite difference techniques provides very satisfactory results. The remainder of this paper will be devoted to the discussion of this technique and the results obtained.

As an aside, it is noted that Levich and Frumkin (13) found that only the first term of Equation (17) was needed to solve the problem they treated. From the form of the first few terms in Equation (17), it is expected that the dominant term for large values of ξ (far from the disk) is the first term. This leads one to expect that the present results should show parallel behavior to the results of Levich and Frumkin (13) at large values of ξ . These authors found

$$B_1 = \frac{2 i_d r_d}{\pi K}$$

and thus

$$\phi = \frac{2 i_d r_d}{\pi K} \eta(\xi \cot^{-1} \xi - 1) \quad (18)$$

where i_d is the (uniform) current density on the disk. This result provides a convenient basis for comparison for our results and a means of calculating the contribution of an individual pore to the potential detected by a distant

reference electrode (the measured corrosion potential). See also appendix A which discusses the asymptotic behavior of the potential distribution when electrode-kinetics on the surrounding plane is not ignored.

Numerical Analysis

Following Klingent, Lynn, and Tobias (19) and Fleck (20), we use the five-point, central difference approximation to obtain Laplace's equation in finite difference form,

$$\begin{aligned} \phi_o \left[\frac{2(1-\eta_o^2)}{h_\eta^2} + \frac{2(1+\xi_o^2)}{h_\xi^2} \right] &= \phi_1 \left[\frac{1+\xi_o^2}{h_\xi^2} + \frac{\xi_o}{h_\xi} \right] \\ &+ \phi_2 \left[\frac{1-\eta_o^2}{h_\eta^2} - \frac{\eta_o}{h_\eta} \right] + \phi_3 \left[\frac{1+\xi_o^2}{h_\xi^2} - \frac{\xi_o}{h_\xi} \right] \\ &+ \phi_4 \left[\frac{1-\eta_o^2}{h_\eta^2} + \frac{\eta_o}{h_\eta} \right] \end{aligned} \quad (19)$$

where h_ξ and h_η are mesh spacings as defined in figure 3. This equation is solved for ϕ_o and is identified as $\phi_{o,try}$. A new value of ϕ_o is calculated by

$$\phi_{o,new} = \phi_{o,old} + \Omega (\phi_{o,try} - \phi_{o,old})$$

where Ω is the overrelaxation factor. This value of $\phi_{o,new}$ is used in the calculation of ϕ for adjacent points. All the interior points in the space are treated this way for one iteration, and the iteration procedure is repeated until ϕ converges to within some error limit at each point. The procedure outlined above is the Liebmann (Gauss-Siedel) iteration procedure with successive overrelaxation.

At boundary points on the electrodes, use of the five-point central difference technique produces "image" points outside the physical space. These image points are eliminated by using the boundary conditions (6) and (8) along with (12) and (13) (or (7) and (9)), expressed in finite difference form. This yields on the plane electrode,

FIGURE 3.

RELATIONSHIP OF THE MESH POINTS AND MESH DISTANCES h_ξ AND h_η .

$$\begin{aligned}
 \phi_o \left[\frac{2 (1-\eta_o^2)}{h_\eta^2} + \frac{2 (1+\xi_o^2)}{h_\xi^2} \right] &= 2 \phi_2 \left(\frac{1-\eta_o^2}{h_\eta^2} \right) \\
 &+ \phi_1 \left[\frac{1+\xi_o^2}{h_\xi^2} + \frac{\xi_o}{h_\xi} \right] + \phi_3 \left[\frac{1+\xi_o^2}{h_\xi^2} - \frac{\xi_o}{h_\xi} \right] \\
 &+ 2 \xi_o h_\eta F_p \left[\frac{1-\eta_o^2}{h_\eta^2} + \frac{\eta_o}{h_\eta} \right] \quad (20)
 \end{aligned}$$

where

$$\begin{aligned}
 F_p &= \frac{r_d}{\kappa} i_{\text{corr},p} \left\{ \exp \left[\frac{\alpha_{ap} F}{RT} (V_p - \phi_p^\circ - U_{\text{corr},p}) \right] \right. \\
 &\quad \left. - \exp \left[\frac{-\alpha_{cp} F}{RT} (V_p - \phi_p^\circ - U_{\text{corr},p}) \right] \right\}
 \end{aligned}$$

A similar relationship is obtained for boundary points on the disk.

Equation (20) is a nonlinear equation in ϕ_p° . The treatment of these nonlinear boundary conditions is discussed in more detail in Appendix 2.

For convenience, $U_{\text{corr},p}$ was taken to be zero for the calculations.

The boundary at $\eta = 1$ was treated by dropping the term

$$(1-\eta^2) \frac{\partial^2 \phi}{\partial \eta^2}$$

from Equation (5) and using backward difference relations in η , central differences in ξ , to obtain

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$$\begin{aligned}
\phi_0 \left[\frac{2(1+\xi_0^2)}{h_\xi^2} + \frac{3}{h_\eta} \right] &= \phi_1 \left[\frac{1+\xi_0^2}{h_\xi^2} + \frac{\xi_0}{h_\eta} \right] \\
&+ \phi_3 \left[\frac{1+\xi_0^2}{h_\xi^2} - \frac{\xi_0}{h_\eta} \right] + \phi_4 \left[\frac{4}{h_\eta} \right] \\
&- \phi_8 \left[\frac{1}{h_\eta} \right]
\end{aligned} \tag{21}$$

where the points are identified on Figure 3. The iteration procedure and successive overrelaxation used for these boundary points were similar to that employed for the interior points.

The boundary at $\xi = \xi_{\max}$ was treated with two different boundary conditions. The boundary condition expressed by Equation (10) was used to simulate the situation which would be encountered for a single disk in a plane with an insulating surface at $\xi_{\max}$. The boundary points were treated in the same way as interior points, and the image points were eliminated by using equation (10) in finite difference form. The iteration procedure and successive overrelaxation for these points were the same as for interior points. The boundary condition expressed by Equation (11) was used to obtain results which could be used with multiple disks in the plane. The relationship (11) was expressed in finite-difference form to eliminate image points, and the iteration procedure and successive overrelaxation were used as before. For large values of $\xi_{\max}$, both boundary conditions give essentially identical results for the potential and current distribution on and near the disk. The results differ in the region near $\xi_{\max}$ where boundary

condition (10) causes the current density on the plane to be higher near $\xi_{\max}$ than does (11), for the same total current to the disk. This will be discussed in more detail below.

Results and Discussion

The results which have been obtained are rather complex. In order to discuss them clearly and concisely, the presentation of the results will be divided into four parts. In the first part, the general behavior will be discussed with particular emphasis on accuracy and the influence of boundary conditions. Following this will be the description of the calculated current and potential distributions as influenced by system parameters. The third part will discuss the implications of these results for disk arrays, and the final part will present other applications.

A. General

The finite difference technique used here was found to be efficient, fast, and accurate for determining the current and potential distribution on the disk and plane. The use of overrelaxation and successive iteration procedures discussed earlier reduces the computational time required for convergence as compared to other iteration procedures without overrelaxation (see Fleck (20)). Iteration was concluded when all points in the domain changed less than a given error limit for two successive iterations. Accuracy was assumed adequate when (1) reducing the error limit caused a change of less than 0.1%, and (2) doubling the number of

mesh points in each direction caused a change of less than 0.1%. Finally, calculations were made for the disk-insulating plane system discussed by Newman (15), and the uniform disk-reversible plane system discussed by Levich and Frumkin (13). It was possible to achieve agreement with both cases to within 0.1%. Therefore, it is believed that the results presented here are accurate to 0.1%, unless otherwise noted.

In general, the current density on the disk and plane is larger in absolute magnitude near the edge of the disk than elsewhere. The effect of slow kinetics, small size, and high conductivity is to reduce this non-uniformity. In the limit of uniform current density on both the disk and surrounding plane, the system behavior should approach that described by Stern (9) and Oldham and Mansfeld (11).

The use of the insulator boundary condition, equation (10), forces the total current on the plane to be equal in magnitude to the total current on the disk. These results would be useful for studies of galvanic corrosion of a single disk in a surrounding plane, with an insulator surface at $\xi_{\max}$. Since the primary interest here is for disk arrays, and the insulator boundary condition results are not relevant to arrays, they will not be discussed further. It is sufficient to state that the current distribution on the disk is unaffected by the boundary condition at $\xi_{\max}$ for the range of parameters discussed below. The current distribution on the plane is affected only near $\xi_{\max}$, where current is forced to go due to the insulator boundary condition. Therefore, the general behavior of the system is identical for either boundary condition, except as noted, and the behavior will be described only for equation (11).

Condition (11) relates the potential ϕ and the gradient $\partial\phi/\partial\xi$ at $\xi_{\max}$, and current may pass through this surface. The amount of current that "leaks" through this surface at $\xi_{\max}$ will depend on the location of $\xi_{\max}$ as well as the non-uniformity of current density on the plane. For a given value of J_p for the plane, the fraction of current that leaks past $\xi_{\max}$ decreases as $\xi_{\max}$ increases.

The current distribution on the disk is determined by the parameter J_d for $i \ll i_{\text{corr}}$, and is independent of the current level and therefore the potential difference between the disk and plane. For currents much larger than i_{corr} , the current distribution is determined by the current level as measured by δ_d . For intermediate currents, values of $\alpha_{\text{ad}}/\alpha_{\text{cd}}$ and δ_d characterize the current distribution. In addition, the polarization characteristics of the plane influence the current distribution on the disk as will be shown.

B. Current and Potential Distribution on the Disk and Plane

The potential distribution in the solution on the disk and plane for an insulating plane is shown in figure 4. The potential at the surface is highest near the center of the disk and decreases to zero far from the disk. This is compared to the potential distribution calculated for a conducting plane with reversible kinetics ($J_p \rightarrow \infty$) shown in the lowest curve on this figure. The influence of the conducting plane is to lower the potential near the center of the disk, and the potential becomes zero at the edge where the two electrodes join. The gradient of the potential is larger near the edge of the disk for a conducting plane.

To make the influence of the plane polarization more quantitative, the potential difference across the disk is shown in figure 5 as a function of J_p for different values of δ_d . $\Delta\phi$ is made dimensionless by multiplying

FIGURE 4.
POTENTIAL DISTRIBUTION AT THE SURFACE
OF THE DISK AND SURROUNDING PLANE.

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FIGURE 5.
POTENTIAL DIFFERENCE BETWEEN THE CENTER AND EDGE OF THE
DISK AS A FUNCTION OF PLANE POLARIZATION PARAMETER J_p .

XBL 765-1790

by $4r_d k/I$ where I is the total (disk) current. The influence of increasing δ_d is to decrease the importance of electrode kinetics relative to the ohmic potential drop, and thus to decrease the potential difference between the center and edge of the disk. The intercept as $J_p \rightarrow 0$ for each curve was calculated for an insulating plane, and the general curve is shown in figure 6, where the intercept is from Newman (15). In the other extreme, as $J_p \rightarrow \infty$, the potential difference across the disk is shown in figure 7 as a function of δ_d . The intercept for $\delta_d \rightarrow 0$, $J_p \rightarrow \infty$, is that for the Levich-Frumkin calculation, i.e., $8/\pi^2$. The results shown on figure 7 are less accurate than other results reported herein because of the large gradients in the corner where the disk and plane join. Problems with accuracy were also encountered for the calculations of figure 5 for values of J_p greater than 20. The results for large values of J_p and δ_d will be reported at a later date.

The current distribution on the disk is shown in figure 8 where the curve for $J_p = 0$ is for an insulating plane and agrees with the results of Newman (15). The other curves were calculated for a conducting plane with different values of the plane polarization parameter. As noted already, increasing J_p distorts the current distribution on the disk, causing a larger current density at the edge of the disk. This results from decreasing the influence of electrode kinetics on the plane as compared to the ohmic influence. All curves were calculated for Tafel polarization on the disk, with identical values of δ_d . The influence of a conducting plane on a disk with linear kinetics is qualitatively the same.

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FIGURE 8.

CURRENT DISTRIBUTION ON A DISK IN A CONDUCTING PLANE
FOR DIFFERENT VALUES OF THE PLANE POLARIZATION PARAMETER, J_p .

The current density on the cathodic plane is shown in figure 9 as a function of distance from the disk. The polarization behavior of the disk influences the current distribution on the plane only very near the disk for large values of J_p . The potential and current distribution far from the disk are then rather insensitive to the disk polarization parameters. Also shown in this figure is the calculation for a uniform current disk and reversible plane, labeled "Levich." The parallel behavior of the two curves indicates that for large values of ξ , the current and potential distribution for both cases have the same dependence on ξ . Thus one expects that only the first term of the expansion for the potential, equation (17), is important for the present case for J_p greater than about 1. The two curves were calculated for identical values of the total disk current.

These observations lead us to propose that the value of B_1 for equation (17) may be calculated by comparison with the Levich-Frumkin result, even though it may not be calculated directly as discussed earlier. The ratio B_1/B_{1L} (B_{1L} is the value obtained by Levich and Frumkin, see Equation (18)) is equivalent to the ratio of the current density from figure 9 to the Levich-Frumkin current density at a particular value of ξ . Knowledge of the value of B_{1L} for the uniform current disk, reversible plane permits calculation of B_1 . The ratio B_1/B_{1L} is influenced by the value of J_p as shown in figure 10, but nearly independent of the disk behavior as shown in figure 11. It should be mentioned that the parallel behavior of the two curves in figure 9 for large values of ξ is also observed for the boundary condition (8) except near $\xi_{\max}$.

FIGURE 9.

THE CATHODIC CURRENT DENSITY TO THE SURROUNDING PLANE AS A FUNCTION OF THE DISTANCE ξ FROM THE EDGE OF THE DISK, COMPARED TO THE LEVICH-FRUMKIN BEHAVIOR FOR A REVERSIBLE PLANE.

FIGURE 10.

THE DEPARTURE OF THE BEHAVIOR OF THE CATHODIC PLANE FROM LEVICH-FRUMKIN BEHAVIOR, MEASURED BY THE RATIO B_1/B_{1L} , AS A FUNCTION OF THE RECIPROCAL OF THE PLANE POLARIZATION PARAMETER, $1/J_p$.

FIGURE 11.

THE DEPARTURE OF THE BEHAVIOR OF THE CATHODIC PLANE FROM LEVICH-FRUMKIN BEHAVIOR, MEASURED BY THE RATIO B_1/B_{1L} , AS A FUNCTION OF THE DISK POLARIZATION PARAMETER, δ_d , AT THREE VALUES OF J_p .

The influence of the disk on the behavior of the plane is concentrated to a region near $\xi = 0$. This influence is depicted on figure 12 where the value of $|i_p|/i_{\text{corr},p}$ at $\xi = 0$ is given as a function δ_d for different values of J_p . This reveals that $|i_p|/i_{\text{corr},p}$ at $\xi = 0$ is large, even for small values of J_p . For all values of J_p shown here, the value of $|i_p|/i_{\text{corr},p}$ is smaller by at least five orders of magnitude at $\xi = 200$. The decrease is sharper for larger values of J_p .

The wide range of current density on the plane in figure 9 indicates how essential it is that the general expression for the kinetics, equation (13), be used. For large values of J_p , the ratio $|i_p|/i_{\text{corr},p}$ approaches a large value at $\xi = 0$. For small J_p , the value of $|i_p|/i_{\text{corr},p}$ at $\xi = 0$ is still large, and in either case $|i_p|/i_{\text{corr},p} \rightarrow 0$ as $\xi_{\text{max}} \rightarrow \infty$. Both the large value of $|i_p|/i_{\text{corr},p}$ and its large variation from $\xi = 0$ to $\xi \rightarrow \infty$, preclude the use of linear kinetics on the plane, except for extremely large values of J_p and small values of δ_d . The Tafel approximation for plane kinetics would not be appropriate either because of the value of $|i_p|/i_{\text{corr},p}$ at $\xi \rightarrow \infty$. Therefore, the present technique provides results which could probably never be obtained theoretically, because boundary condition (13) or (7) describes the kinetic behavior everywhere on the plane, including the extremes at small and large ξ .

C. Array of Disks

The results discussed in the previous section provide a background for the analysis of the behavior of an array of disks. The random array of disks which are all of the same radius and are far apart will be treated here. Following Levich (13b), the average potential in solution at some large distance from the surface is

FIGURE 12.

THE CURRENT DENSITY TO THE PLANE AT $\xi = 0$,
AS COMPARED TO THE CORROSION CURRENT DENSITY FOR THE
PLANE, AS A FUNCTION OF δ_d AND FOR THREE VALUES OF J_p .

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$$\bar{\phi}_{(\text{large } z)} = \bar{n} \int_0^{\infty} \phi(r) 2\pi r dr \quad (22)$$

where $\bar{n}$ is the number of disks per square centimeter of surface. In the previous section it was found that the potential far from the surface can be approximated by the first term of equation (17), i.e.,

$$\begin{aligned} \phi &= B_1 P_1(\eta) M_1(\xi) \text{ at large } \xi \\ &= \left(\frac{B_1}{B_{1L}} \right) B_{1L} \eta [\xi \cot^{-1} \xi - 1] \end{aligned} \quad (23)$$

For large z , ξ is also large and

$$\phi = - \frac{B_1}{B_{1L}} (B_{1L}) \eta \left[\frac{1}{3\xi^2} \right] \text{ as } \xi \rightarrow \text{large} \quad (24)$$

where $B_{1L} = \frac{-2 I_d}{\pi^2 r_d^2 \kappa}$. The equation for $\bar{\phi}_z$ now becomes

$$\bar{\phi}_z = - \frac{2\pi B_1 \bar{n}}{3B_{1L}} (B_{1L}) \int_0^{\infty} \frac{\eta}{\xi^2} r dr \quad (25)$$

Using the relationships in equations (3) and (4), for large ξ , it may be shown that

$$\bar{\phi}_z = - 2\pi \left(\frac{B_1}{B_{1L}} \right) B_{1L} \bar{n} (r_d^2) \quad (26)$$

The ratio of anode area to cathode area, A_a/A_c , is

$$A_a/A_c = \bar{n} \pi r_d^2$$

and

$$\bar{\phi}_z = \frac{4 I_d}{3\pi^2 r_d \kappa} \left(\frac{B_1}{B_{1L}} \right) \left(A_a/A_c \right) \quad (27)$$

Thus, the corrosion potential of an array of disks will be proportional to the area ratio when ohmic effects are important. This is contrasted to the behavior expected when only kinetic effects are important, e.g., equation (1). It should be noted that the corrosion potential, $\bar{\phi}$, is independent of the value of z , and may be measured with an appropriate reference electrode in any arbitrary location far from the disk-plane surface.

Equation (27) was derived with the assumption that the pores are far enough apart that they interact to a negligible extent through the small ohmic drop far from a disk. This should be a good approximation when the distance separating the disks is large enough that only a small current density flows to the midpoint of the separation distance. This suggests that the minimum distance of separation for negligible interaction is dependent on the magnitude of J_p . The larger the value of J_p , the smaller may be the separation distance for the disks for independent behavior. The polarization parameters on the disk have a small influence on the plane behavior, as noted previously, so the most important parameter influencing interaction will be J_p . Preliminary calculations indicate that 99% of the plane current would go to a distance less than ξ_{max} when the product

$$J_p \xi_{max} \cong 195. \quad (28)$$

For large values of ξ_{max} ,

$$\begin{aligned} \xi_{\max}^2 &\approx \frac{\text{area of cathode (plane)}}{\text{area of anode (disk)}} \\ &= \frac{r_{\max}^2 - r_d^2}{r_d^2} \end{aligned}$$

and from equation (28) one may obtain a value of the minimum separation distance or area ratio for this level of interaction for given J_p (and r_d).

For example, if

$$J_p = 0.7$$

the area ratio of cathode to anode is 10^6 . This would then be the minimum area ratio for which the corrosion potential would be expected to obey equation (27). More detailed results will be reported at a later date.

D. Applications

The importance of ohmic effects in galvanic corrosion in plating systems may be estimated by calculation of the polarization parameters of the disk and plane. These calculations require the values of the corrosion current density for both surfaces, the value of a characteristic dimension for the disk, r_d , the average current density on the disk, and the conductivity of the electrolyte. Small values of the polarization parameters for the disk and plane would indicate that the kinetic effects are more important than ohmic considerations, and that the current distribution on each will tend to be uniform. As the polarization parameters approach zero, the behavior of a disk array will tend toward that predicted by Stern (9) and Oldham and Mansfeld (11). These

polarization parameters are very important and very useful diagnostic criteria.

The exposed substrate disk in a plating system would be expected to be small, and this small characteristic dimension would be expected to force both J_d and δ_d to be small. Therefore, the current distribution on such a disk would be rather uniform.

The cathodic plane would tend to have a nonuniform distribution of current because of its size unless both the corrosion current density is low and the conductivity is high. For values of the parameters of

$$\kappa = 0.001 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$F = 96,500 \text{ C equiv}^{-1}$$

$$T = 298.15^\circ\text{K}$$

$$R = 8.315 \text{ joules } (^\circ\text{K})^{-1} \text{ mole}^{-1}$$

$$r_d = 10^{-3} \text{ cm}$$

$$i_{\text{corr,p}} = 10^{-2} \text{ A cm}^{-2}$$

$$(\alpha_{\text{ap}} + \alpha_{\text{cp}}) = 1$$

then

$$J_p = 0.3893$$

For a value of $\delta_d = 10^{-3}$ (virtually uniform disk current), and the above value of J_p , the current density to the plane is found to be nonuniform. The plane current density at a distance of three disk radii is decreased by an order of magnitude from the value at $\xi = 0$. It is reduced by five orders of magnitude at about 98 disk radii. This nonuniform current distribution on the plane would cause the corrosion potential to follow equation (27).

More specifically, the transition in behavior from that described in Equation (27) to that given by Equation (1) occurs at a specific area ratio for a given system. The quantity

$$J_p \xi_{\max} \cong 195$$

may be used to estimate the area ratio at which this transition occurs. For

$$J_p = 10$$

the value of $\xi_{\max}$ is 19.5 and this corresponds to a ratio of anode area to cathode area of

$$\frac{A_a}{A_c} \cong 2.6 \times 10^{-3}$$

For smaller area ratios the system would follow Equation (27). For larger area ratios the system would behave as described in Equation (1). The transition between the two regions would be smooth, and the behavior would not follow either relationship exactly. The size of the transition region has not been determined here, but is the subject of a continuing study.

For a single pore in a finite plane, the behavior will be similar to that described above in general. That is, at area ratios $\left(\frac{A_a}{A_c}\right)$ smaller than that given by

$$J_p \xi_{\max} \cong 195$$

the ohmic effects will be important. At larger area ratios the transition to the behavior given by Equation (1) will occur. The exact description of the behavior of this finite system with ohmic effects is being determined and will be reported later, along with the behavior of interacting arrays of pores which is another finite system of considerable importance.

For systems where δ_d is unknown because $i_{avg,d}$ is unknown, one may estimate δ_d from figure 13. Here, the value of U , the corrosion potential difference of the separated metals, J_p , and J_d can be used to predict δ_d . For small values of $\left[\frac{\alpha_a FU}{RT} + \ln J_d\right]$, the polarization parameter of the plane does not influence δ_d because kinetic effects predominate. For larger values of $\left[\frac{\alpha_a FU}{RT} + \ln J_d\right]$, figure 13 may be used and the value of J_p is important for predicting δ_d . The total spread of values between $J_p = 0$ and $J_p = \infty$ is not large until $\left[\frac{\alpha_a FU}{RT} + \ln J_d\right]$ becomes greater than 10, a value seldom encountered in practice. Knowledge of δ_d with the other parameters can then be used to predict current distribution on the disk and plane from figures 8 and 9. The potential distribution across the disk can be estimated from figure 5. For an insulating plane, the value of $\ln \delta_d$ becomes proportional to, $\left[\frac{\alpha_a FU}{RT} + \ln J_d\right]$ at small values of δ_d . At large δ_d , a linear relationship between δ_d and $\left[\frac{\alpha_a FU}{RT} + \ln J_d\right]$ is observed with a slope of $4/\pi$. A disk with a reversible plane has the same behavior at small δ_d , as shown. For large δ_d , a linear relationship between δ_d and $\left[\frac{\alpha_a FU}{RT} + \ln J_d\right]$ is again observed, but with a slope of $16/\pi$. These results will be discussed in a forthcoming publication (21). It should be noted that these curves have been determined for a surrounding plane of infinite extent.

Knowledge of these parameters allows one to estimate B_1/B_{LL} from figures 10 and 11. This can be used to predict the slope of the corrosion potential - area ratio curve for a collection of pores in a plating system, and this can be verified by experiment.

These results would also be applicable to the situation of a cathodic inclusion on an anodic plane. The physical consequences predicted by this

treatment are nonuniform anodic dissolution on the plane, with the largest dissolution near the inclusion. This could lead to undermining the inclusion with eventual pit formation if the inclusion is dislodged.

Summary

Numerical analysis of a conducting disk in a conducting plane has been performed by finite difference techniques. The current and potential distribution on both the disk and the plane have been determined for a wide range of parameters. The distributions have been shown to depend not only on the individual parameters of the disk and plane, but the disk and plane influence each other as well because of their proximity. The results have been used to determine the behavior of an array of disks, and the application and use of the results for other situations have been discussed.

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Appendix 1

Boundary Condition Far from the Disk

The surface $\xi = \xi_{\max}$ defines a hemisphere in r, z coordinates. If the hemisphere is an insulator, no current may pass through it, and one uses the boundary condition specified in Equation (8). We have also used a second boundary condition in which current is allowed to pass through this hemispherical boundary, and we approximate the potential gradient in solution nearby by a relationship which is similar to the Levich-Frumkin distribution. We have found that both boundary conditions give the same results for current and potential distribution everywhere except near the boundary $\xi = \xi_{\max}$. The insulator boundary condition forces more current to flow to the plane in the corner near $\xi = \xi_{\max}$.

Levich and Frumkin found, for a reversible plane and uniform current on the disk, that the potential far from the disk is

$$\phi = \frac{2i_d r_d}{\pi K} \eta [\xi \cot^{-1} \xi - 1] \quad (18)$$

where i_d is the (uniform) current density on the disk.

For the present problem we use the expansion

$$\phi = \sum_{n=1}^{\infty} B_n P_n(\eta) M_n(\xi) \quad (17)$$

and retain only the first two terms of the expansion in anticipation that higher terms are negligible for large values of ξ . The first term is identical to the Levich-Frumkin result except for the value of B_n , i.e.,

$$P_1(\eta) = \eta \quad (A1-1)$$

$$M_1(\xi) = - [\xi \cot^{-1} \xi - 1] \quad (A1-2)$$

and the second term is

$$P_2(\eta) = \frac{1}{2} (3\eta^2 - 1)$$

$$M_2(\xi) = -\frac{2}{\pi} [(3\xi^2 + 1) \cot^{-1} \xi - 3\xi].$$

For large values of ξ (see (22)),

$$\left. \begin{aligned} M_1(\xi) &\rightarrow \frac{1}{2\xi^2} \\ M_2(\xi) &\rightarrow -\frac{8}{15\pi\xi^3} \end{aligned} \right\} \text{ as } \xi \rightarrow \infty$$

and

Near the plane, the potential must also satisfy the boundary condition for passage of current to the plane, and this provides a relationship between B_1 and B_2 . On the plane, it is assumed that we are far enough from the disk that the kinetics may be approximated by the linear relationship i.e.,

$$-\frac{\kappa}{r_d \xi} \left. \frac{\partial \phi}{\partial \eta} \right|_{\eta=0} = i_p = \frac{(\alpha_{ap} + \alpha_{cp})F}{RT} (U_{\text{corr},p} - \phi_{op}) i_{\text{corr},p} \quad (\text{A1-7})$$

We arbitrarily set $U_{\text{corr},p} = 0$, and find

$$-\frac{1}{\xi} \left[\frac{B_1}{2\xi^2} \right] = J_p \left[\frac{8}{15\pi\xi^3} B_2 P_2(0) \right] \quad (\text{A1-8})$$

where terms of order $(1/\xi^4)$ have been neglected, and

$$J_p = \frac{(\alpha_{ap} + \alpha_{cp}) r_d F}{\kappa RT} i_{\text{corr},p} \quad (\text{A1-9})$$

This leads to

$$B_1 = -\frac{16}{15\pi} J_p P_2(0) B_2 \quad (\text{A1-10})$$

and with this relationship we may now derive an expression for the potential gradient near ξ_{max} valid for large values of ξ_{max} .

Now,

$$\begin{aligned}\phi &= \frac{B_1}{2\xi^2} P_1(\eta) - \frac{16 B_2}{15\pi \xi^3} P_2(\eta) \\ &= \frac{8B_2}{15\pi} \left\{ \frac{P_2(0) P_1(\eta) J_p}{\xi^2} + \frac{2P_2(\eta)}{\xi^3} \right\} \quad (A1-11)\end{aligned}$$

and

$$\begin{aligned}\frac{\partial \phi}{\partial \xi} \Big|_{\xi=\max} &= \frac{8 B_2}{15\pi} \left\{ \frac{2P_2(0) P_1(\eta) J_p}{\xi^3} + \frac{6 P_2(\eta)}{\xi^4} \right\} \\ &= - \frac{2\phi}{\xi_{\max}} \left\{ \frac{P_1(\eta) + \frac{3P_2(\eta)}{\xi_{\max} P_2(0) J_p}}{P_1(\eta) + \frac{2P_2(\eta)}{\xi_{\max} P_2(0) J_p}} \right\} \quad (A1-12)\end{aligned}$$

and this reduces to the Levich-Frumkin functional relationship as

$$\xi_{\max} \rightarrow \infty.$$

Appendix 2

Finite Difference Approximations for Nonlinear Boundary Conditions

Equation (20) is a finite difference relationship for the surrounding plane involving a function F_p which is exponential in ϕ_p° . This nonlinear relationship for ϕ_p° is rather unstable, and diverges rapidly unless the initial potential approximation is near the final, converged value. We have adopted the following treatment which eliminates these divergence problems.

We approximate the value of F_p by

$$F_p = F_p (V_p - \phi_p^\circ - U_{\text{corr},p}) + (\phi_p^\circ(r) - \phi_{p,\text{old}}^\circ) F_p' \quad (\text{A2-1})$$

where

$\phi_{o,\text{old}}$ is the previous value of ϕ_p° at the central point

$\phi_o(r)$ is the value of ϕ_p° at the central point to be calculated

F_p' is the derivative of F_p with respect to the overpotential $(V_p - \phi_p^\circ - U_{\text{corr},p})$.

Equation (19) becomes now,

$$\begin{aligned} \phi_o \left[\frac{2(1-\eta_o^2)}{h_\eta^2} + \frac{2(1+\xi_o^2)}{h_\xi^2} + 2F_p' \xi_o h_\eta \left(\frac{1-\eta_o^2}{h_\eta^2} + \frac{\eta_o}{h_\eta} \right) \right] \\ = 2\phi_2 \left(\frac{1-\eta_o^2}{h_\eta^2} \right) + \phi_1 \left[\frac{1+\xi_o^2}{h_\xi^2} + \frac{\xi_o}{h_\xi} \right] \\ + \phi_3 \left[\frac{1+\xi_o^2}{h_\xi^2} - \frac{\xi_o}{h_\xi} \right] + 2\xi_o h_\eta (F_p + \phi_{o,\text{old}} F_p') X \\ \left[\frac{1-\eta_o^2}{h_\eta^2} + \frac{\eta_o}{h_\eta} \right] \end{aligned} \quad (\text{A2-2})$$

or

$$\begin{aligned}
& \phi_o \left[\frac{2}{h_\eta^2} + \frac{2(1+\xi_o^2)}{h_\xi^2} + 2 F_p' \xi_o \left(\frac{1}{h_\eta} \right) \right] \\
&= \frac{2\phi_2}{h_\eta^2} + \phi_1 \left[\frac{1+\xi_o^2}{h_\xi^2} + \frac{\xi_o}{h_\xi} \right] \\
&+ \phi_3 \left[\frac{1+\xi_o^2}{h_\xi^2} - \frac{\xi_o}{h_\xi} \right] + \frac{2\xi_o}{h_\eta} (F_p + \phi_{o,old} F_p') \quad (A2-3)
\end{aligned}$$

where we have introduced $\eta_o = 0$ on the plane.

This equation is solved for ϕ_o , called $\phi_{o,try}$, and a new value of ϕ_o is calculated by

$$\phi_{o,new} = \phi_{o,old} + \Omega (\phi_{o,try} - \phi_{o,old}).$$

The same value of the overrelaxation parameter is used for the boundary as for interior points.

An analogous treatment of the generally nonlinear boundary condition on the disk was adopted.

Successive iterations with this approximation technique leads to convergence and a rigorous result, since the second term of (A2-1) approaches zero as the potential approaches the converged value.

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