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Galvanic corrosion resulting from rupture of a protective metallic coating

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A treatment of corrosion of galvanic couples in which the area of one metal greatly exceeds that of the other has been carried out using mixed potential theory. A ruptured metallic coating on a metal substrate is encompassed by the treatment, as is a metal containing inclusions of a second metal as impurity. Two cases are examined. In the first, exemplified by zinc-plated steel, three reactions are considered: dissolution of the coating and reduction of the oxidizing agent on each metal. In this case, the result of the rupture is often a very marked increase in the corrosion of the coating, leading to an autocatalytic effect. The second case treats an active metal protected by a coating of a more noble metal. The following reactions are considered: both directions of the redox couple generated by the oxidizing agent, and the dissolution of the substrate. It is demonstrated that in the second case the corrosion rate is maximal at vanishingly small porosities. In both cases, variations of the corrosion potential can be used as a measure of porosity.

Introduction

To protect metals or alloys from corrosion by an aqueous environment or the atmosphere, a variety of coatings has been applied, e.g. metallic, inorganic or organic coatings. Metallic coatings are applied by hot dipping, electroplating, spraying, cementation, electroless plating, or gas-phase reactions [1]. These commercially produced metal coatings are all more or less porous and usually become even more porous during shipment and use. In the presence of an electrolyte, which could be a thin film of moisture, galvanic action between coating and substrate will be an important factor determining the protection offered by the coating.

Despite the enormous practical importance of metallic coatings and their porosity, no general attempt has been made to use mixed potential theory [2, 3] to predict the influence of porosity on corrosion rate. A general treatment of galvanic corrosion can be found in Kaesche's book [4]. Stern [5] treated the case of a galvanic couple by assuming that on one metal only oxidation of the metal occurs while on the other metal only reduction of the oxidizing agent occurs. This can be visualized as a very special case of a coated metal. Often, however, the more general case has to be considered where metal oxidation (dissolution) and reduction of the oxidizing agent can occur on both the substrate and the coating. A more general treatment of area relationship in galvanic corrosion has been given by Mansfeld [11].

In this article we are concerned with the corrosion of a bimetallic specimen in which the area of one metal greatly exceeds that of the other. Such a situation will arise if a protective metal coating is ruptured or punctured. Two cases are of practical importance. These are summarized in Table 1. Another situation in which a bimetallic specimen exists with one

Table 1

Case	*Coating* (Me_1)	*Substrate* (Me_2)	*Result of rupture*
I	Active metal, e.g. Zn	Noble metal, e.g. steel	Coating may corrode more rapidly
II	Noble metal e.g. Au	Active metal, e.g. Cu	Substrate corrodes

metal greatly exceeding the other in area arises when an inclusion of impurity occurs at the surface. We shall not specify the oxidizing agent responsible for the corrosion; it could be H_2O, H^+, or O_2.

We denote the coating and substrate metals respectively by Me_1 and Me_2 and the oxidizing agent by Ox. There may be as many as four reactions to consider,

$$Me_1 \rightleftharpoons Me_1^{n_1+} + n_1e^- \quad (1)$$

$$Me_2 \rightleftharpoons Me_2^{n_2+} + n_2e^- \quad (2)$$

$$Ox + n_3e^-(Me_1) \rightleftharpoons Rd \quad (3)$$

$$Ox + n_3e^-(Me_2) \rightleftharpoons Rd, \quad (4)$$

each of which has a cathodic and an anodic component. Reactions (3) and (4) represent the reduction of the oxidizing agent on the coating and substrate metal, respectively.

If the specimen as a whole is electrically insulated, the total current flowing, equal to the algebraic sum of the currents due to reactions (1) through (4), must be zero. Therefore

$$0 = I = \sum_{j=1}^{4} I_j = \sum_{j=1}^{4} I_{ja} - \sum_{j=1}^{4} |I_{jc}|, \quad (5)$$

where I_{ja} and I_{jc} denote the anodic and cathodic partial currents for reaction (j).

We shall concentrate on the condition of very disparate areas

$$A_1 \gg A_2 = A - A_1, \quad (6)$$

where an obvious notation has been used, and seek to determine the way in which the rate of corrosion depends on the exposed area A_2 of the substrate. The ratio A_2/A is often termed the 'porosity' of the coating. Because of inequality (6), $A_2/A \approx A_2/A_1$; either ratio will be called 'porosity' in this paper. Throughout we shall make the assumption that ohmic overpotentials may be neglected. Also, changes of composition and pH of the electrolyte in pores will not be considered. We shall consider the two cases separately, but it is convenient first to define certain quantities which are common to both cases.

By i_{oj} where $j = 1, 2, 3$ or 4 we denote the exchange current density of reaction (j). The anodic and cathodic Tafel slopes of reaction (j) are related to the terms a_j and c_j by

$$a_j = 2{\cdot}303\,\beta_{ja} = \frac{\partial\Phi}{\partial \ln(I_{ja})} \quad (7)$$

and

$$c_j = 2{\cdot}303\,\beta_{jc} = \frac{\partial\Phi}{\partial \ln|I_{jc}|}. \quad (8)$$

By Φ_j we mean the reversible potential of reaction (j), i.e. the potential that the specimen would have if reaction (j) was the only one occurring and was at equilibrium. Note that $\Phi_4 = \Phi_3$. By Φ_k we denote the actual potential of the specimen, usually a mixed potential representing some compromise between the competing Φ_j's.

We denote by I_k the corrosion current (of Me_1 in Case I and Me_2 in Case II), while i_k symbolizes the corresponding corrosion current density. It will be convenient to consider also two limiting values of i_k, for which the notations i_{ko} and i_{km} will be used. i_{ko} is the corrosion current density corresponding to $A_2 = 0$, i.e. to an unruptured protective coating. Notice that, even for Case II in which there is no corrosion ($I_k = 0$) in the absence of rupture, the limit

$$\lim_{A_2 \to 0} \left(\frac{I_k}{A_2}\right) = i_{ko} \quad (9)$$

is not always zero. As A_2 increases, I_k also increases in both cases at first, but eventually, when A_2 becomes comparable with A_1, I_k passes through a maximum and then declines. I_{km} is defined as the corrosion current density at the point of maximum I_k, i.e.

$$i_{km} = \frac{I_k}{A_j} \text{ when } \frac{dI_k}{dA_2} \equiv -\frac{dI_k}{dA_1} = 0. \tag{10}$$

Note that i_{km} does not mean the maximum value of the current density, i_k, but corresponds to the maximum value of the current I_k. This maximum corrosion current does not occur until A_2 is large enough to violate inequality (6); nevertheless i_{km} is a useful constant against which to compare corrosion current densities within the range permitted by (6).

Case I

This case, typified by a zinc- or cadmium-plated steel, is one in which rupture of the plating leads to an increase in the corrosion, not of the substrate metal, but of the plate itself. This arises because the exposed metal is noble to the coating and becomes the cathode in the resulting galvanic couple, the coating being the anode. The tendency for the *substrate* metal to corrode is even less than for an unruptured coating, because of cathodic protection.

Whether or not the exposed substrate serves significantly as a cathode depends on the relative magnitudes of the exchange current densities i_{03} and i_{04}. If i_{03} exceeds i_{04} or if the two are of similar magnitude (i.e. if the overvoltage for reduction of Ox is no greater on the coating than on the substrate) then reaction (4) is unimportant and the rate of corrosion of the coating is independent of the porosity. Here we will consider the more interesting (and more common) case in which the overvoltage on the more noble substrate metal is less than that on the coating, so that $i_{04} \gg i_{03}$. In these circumstances the important reactions are

$$\mathrm{Me_1 \rightarrow Me_1^{n_1+} + n_1e^-} \tag{1a}$$

$$\mathrm{Ox + n_3e^-(Me_1) \rightarrow Rd} \tag{3c}$$

and

$$\mathrm{Ox + n_3e^-(Me_2) \rightarrow Rd,} \tag{4c}$$

so that equation (5) becomes

$$0 = I_{1a} - |I_{3c}| - |I_{4c}|. \tag{11}$$

The situation where the reaction proceeds under charge transfer control and that when diffusion of the oxidizer is rate-controlling will be treated separately.

(a) *Charge transfer control*

We resort to standard electrochemical theory which relates the three partial currents to potential by the equations

$$I_{1a} = A_1 i_{01} \exp\left(\frac{\Phi_k - \Phi_1}{a_1}\right) \tag{12}$$

$$|I_{3c}| = A_1 i_{03} \exp\left(\frac{\Phi_3 - \Phi_k}{c_3}\right) \tag{13}$$

and

$$|I_{4c}| = A_2 i_{04} \exp\left(\frac{\Phi_3 - \Phi_k}{c_4}\right) \tag{14}$$

where all terms have been defined previously. Insertion of these equations into (11), together with the definitions of I_k and i_k, gives, on rearrangement

$$i_k = \frac{I_k}{A_1} = \frac{I_{1a}}{A_1} = i_{01} \exp\left(\frac{\Phi_k - \Phi_1}{a_1}\right) = \\ = i_{03} \exp\left(\frac{\Phi_3 - \Phi_k}{c_3}\right) + \frac{A_2 i_{04}}{A_1} \exp\left(\frac{\Phi_3 - \Phi_k}{c_4}\right). \tag{15}$$

This result incorporates a pair of simultaneous equations involving the mixed potential Φ_k. When the latter is eliminated, the equation

$$\left(\frac{i_k}{i_{01}}\right)^{(a_1+c_4)/c_4} - \frac{i_{03}}{i_{01}}\left(\frac{i_k}{i_{01}}\right)^{a_1(c_3-c_4)/c_3c_4} \exp\left(\frac{\Phi_3 - \Phi_1}{c_3}\right) = \frac{A_2 i_{04}}{A_1 i_{01}} \exp\left(\frac{\Phi_3 - \Phi_1}{c_4}\right) \tag{16}$$

results after some algebra.

Before considering the general solution of equation (16) let us first investigate its two limiting cases, so as to derive expressions for i_{ko} and i_{km}. The first limit, it will be recalled, corresponds to the coating being unruptured. Setting A_2 to zero in equation (16) leads straightforwardly to

$$i_{ko} = [(i_{01})^{a_1}(i_{03})^{c_3}]^{1/(a_1+c_3)} \exp\left(\frac{\Phi_3 - \Phi_1}{a_1 + c_3}\right). \tag{17}$$

The second limiting case occurs when A_2 and A_1

are comparable and, in that event, since we are treating the $i_{04} \gg i_{03}$ situation, the second term in equation (16) is negligible. The corrosion current then is

$$I_k = A_1 i_k = [(A_1 i_{01})^{a_1}(A_2 i_{04})^{c_4}]^{1/(a_1+c_4)} \exp\left(\frac{\Phi_3-\Phi_1}{a_1+c_4}\right). \tag{18}$$

The maximum value of I_k can be found by differentiation with respect to A_2, by recalling that A_1 and A_2 sum to a constant A. It is readily shown that this maximum occurs when

$$\frac{A_1}{a_1} = \frac{A_2}{c_4} = \frac{A}{a_1+c_4} \tag{19}$$

and, therefore, following prescription (10)

$$i_{km} = i_{01}\left(\frac{c_4 i_{04}}{a_1 i_{01}}\right)^{c_4/(a_1+c_4)} \exp\left(\frac{\Phi_3-\Phi_1}{a_1+c_4}\right). \tag{20}$$

The relative magnitudes of i_{km} and i_{ko} depend on the Tafel slopes, but to get an idea of the ratio of these two current densities let us consider the typical case when $a_1 = c_3 = c_4$. Then we see from equations (17) and (20) that

$$\frac{i_{km}}{i_{ko}} = \sqrt{\frac{i_{04}}{i_{03}}} \quad \text{for } a_1 = c_3 = c_4. \tag{21}$$

Hence, for this typical case, if the exchange current density for the reduction of Ox on the substrate exceeds that on the coating by a factor of 10^6, the rate of corrosion of Me_1 will be accelerated some thousand-fold for $A_2 = A/2$ compared with $A_2 = 0$.

Turning now to the general case, we find it convenient to replace the constants i_{03} and i_{04} in equation (16) by the constants i_{ko} and i_{km} given in equations (17) and (20). This leads, after further algebra, to

$$\left(\frac{i_k}{i_{ko}}\right)^{(a_1+c_4)/c_4} - \left(\frac{i_k}{i_{ko}}\right)^{a_1(c_3-c_4)/c_3c_4} = \frac{a_1 A_2}{c_4 A_1}\left(\frac{i_{km}}{i_{ko}}\right)^{(a_1+c_4)/c_4}. \tag{22}$$

We would like to invert equation (22) so as to express i_k as an explicit function of the A_2/A_1 ratio. Unfortunately such an inversion is not generally possible in terms of elementary functions. However, as will be demonstrated in an appendix, an approximate solution of equation (22) is

$$\frac{i_k}{i_{ko}} \approx [1+x_I+\gamma_I x_I \ln(1+x_I)]^{c_3/(a_1+c_3)} \tag{23}$$

where

$$x_I = \frac{a_1 A_2}{c_4 A_1}\left(\frac{i_{km}}{i_{ko}}\right)^{(a_1+c_4)/c_4} \tag{24}$$

and

$$\gamma_I = \frac{a_1(c_4-c_3)}{c_4(a_1+c_3)}. \tag{25}$$

Approximation (23) is more precise the smaller is γ_I, becoming exact if $\gamma_I = 0$.

To obtain a rough idea of how the corrosion current density depends on the area of the rupture, let us investigate the case where all the Tafel slopes are equal. Then γ_I is zero, approximation (23) becomes exact and simplifies to

$$i_k = \sqrt{i_{ko}^2 + \frac{A_2}{A_1} i_{km}^2} \quad \text{for } a_1 = c_3 = c_4. \tag{26}$$

Moreover, for equal Tafel slopes, equation (21) applies and hence

$$i_k = i_{ko}\sqrt{1+\frac{A_2\, i_{04}}{A_1\, i_{03}}} \quad \text{for } a_1 = c_3 = c_4. \tag{27}$$

This equation indicates that if $i_{04}/i_{03} = 10^6$, the corrosion rate of the coating will be accelerated tenfold even if the porosity is as small as 10^{-4}. This conclusion is for the typical situation $a_1 = c_3 = c_4$, as is Fig. 1 which expresses relationship (27) graphically. This diagram brings out clearly that the strong increase in corrosion rate with porosity at small A_2/A_1 ratios occurs only when the overvoltage for reduction of Ox is much lower on the substrate than on the coating, i.e. when $i_{04} \gg i_{03}$. For such a situation there is a strong 'autocatalytic' effect in that a small rupture will dramatically increase the dissolution rate of the coating, leading to an increase in the area of exposed substrate, which will in turn further increase the rate of corrosion.

The potential Φ_k of the galvanic couple depends on the porosity A_2/A_1 of the coating as given by

$$\Phi_k = \Phi_1 + a_1 \ln \frac{i_{ko}}{i_{01}}\sqrt{1+\frac{A_2\, i_{04}}{A_1\, i_{03}}} \quad \text{for } a_1 = c_3 = c_4 \tag{28}$$

which is evident on combination of equations (15) and (27). Hence the mixed potential change is

$$\Delta\Phi_k = \Phi_k - \Phi_{k_0} = \frac{a_1}{2}\ln\left(1+\frac{A_2\, i_{04}}{A_1\, i_{03}}\right)$$

$$\text{for } a_1 = c_3 = c_4 \qquad (29)$$

compared with the potential Φ_{k_0} of an unruptured specimen ($A_2 = 0$). This equation suggests a method of estimating the porosity of a coated metal. Notice that equation (29) has limiting forms

$$\Delta\Phi_k = \frac{a_1\, i_{04} A_2}{2\, i_{03} A_1} \quad \text{for } a_1 = c_3 = c_4 \qquad (30)$$

or

$$\Delta\Phi_k = \frac{a_1}{2}\ln\left(\frac{i_{04}}{i_{03}}\right) + \frac{a_1}{2}\ln\left(\frac{A_2}{A_1}\right)$$

$$\text{for } a_1 = c_3 = c_4 \qquad (31)$$

according as the porosity A_2/A_1 is much smaller than or much greater than the ratio i_{03}/i_{04}, indicating that the mixed potential varies either linearly or logarithmically with the porosity.

It will be recognized that Case I also corresponds to the condition where an active metal (Me$_1$) contains inclusions of the noble metal (Me$_2$) as an impurity. Zinc with impurities of copper, lead and other metals were the first experimentally investigated examples [8] from which de la Rive [9] and Palmaer [10] developed their local current theory. According to the equation (27) and Fig. 1, where i_{k_0} now is the corrosion rate in the absence of any impurity, the corrosion rate will increase with the amount (area) of the impurity exposed on the surface, impurities with an overvoltage for H^+, H_2O, or O_2 reduction which is low as compared to that of the base metal (high ratio i_{04}/i_{03}) being especially damaging. It has been known in fact for a long time that noble metal impurities (such as Pt in metals like Fe or Zn) increase corrosion rates in acids markedly. These noble metals have a very low hydrogen overvoltage, while the overvoltage for metals such as zinc is relatively high.

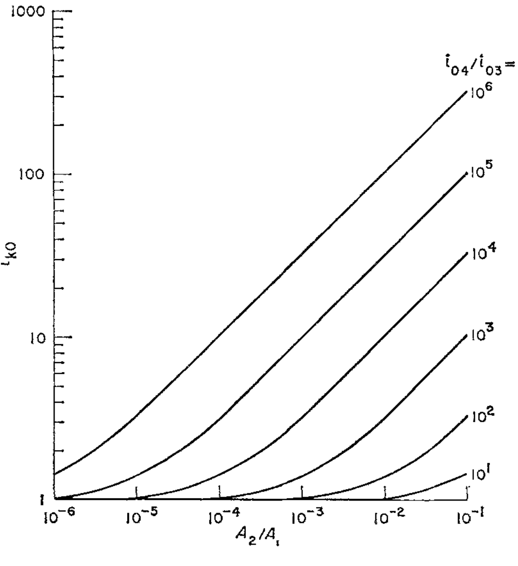

Fig. 1. Logarithmic graphs of the function $(i_k/i_{k_0}) = \sqrt{1+(A_2 i_{04}/A_1 i_{03})}$ versus A_2/A_1 for values of the parameter i_{04}/i_{03}. These plots relate to Case I and demonstrate the marked increase in corrosion rate which attends increasing porosity, provided that reduction of Ox is sufficiently favored on metal Me$_2$ compared with Me$_1$.

(b) *Diffusion control*

Here the rate of corrosion is determined by the rate at which the oxidizer diffuses to the surface of the metal. An example is corrosion of metals in aerated neutral media.

As in equation (11) we can write $I_{1a} = |I_{3c}| + |I_{4c}|$, but now:

$$I_{3c} = I^L_{0_2} = i^L_{0_2} A_1 \qquad (32)$$

$$I_{4c} = I^L_{0_2} = i^L_{0_2} A_2 \qquad (33)$$

assuming that the diffusion current density $i^L_{0_2}$ is the same on the coating as on the substrate.

It follows that:

$$I_{1a} = i^L_{0_2}(A_1 + A_2) = i_{1a} A_1. \qquad (34)$$

For the dissolution current density of the coating, we obtain:

$$i_k = i_{1a} = i^L_{0_2}\left(1+\frac{A_2}{A_1}\right). \qquad (35)$$

Since the ratio A_2/A_1 will always be small in Case I, it follows that

$$i_{1a} = i^L_{0_2} = \text{const.} \qquad (36)$$

which means that the dissolution rate of the coating is independent of porosity when the corrosion process is diffusion controlled.

Case II

When an active metal is imperfectly coated with a noble metal such as gold, the system will acquire a mixed potential Φ_k lying between the reversible potentials Φ_2 and Φ_3 of reactions (2) and (3) but, on account of inequality (6), Φ_k will lie closer to Φ_3 than to Φ_2. Under these conditions the substrate metal corrodes and the noble coating serves as a redox electrode. The important reactions are therefore

$$\mathrm{Me_2 \rightarrow Me_2^{n_2+} + n_2e^-} \tag{2a}$$

$$\mathrm{Ox + n_3e^-(Me_1) \rightarrow Rd} \tag{3c}$$

and

$$\mathrm{Ox + n_3e^-(Me_1) \leftarrow Rd.} \tag{3a}$$

Under these conditions dissolution under diffusion control does not have to be considered as long as porosity of the coating is low. We assume that the overpotential for the reduction of Ox on substrate metal Me_2 is not significantly less than that on coating metal Me_1, so that reaction (4) plays a negligible role.

In this case, equation (5) reduces to

$$0 = I_{2a} + I_{3a} - |I_{3c}| \tag{37}$$

which becomes

$$I_k = I_{2a} = A_2 i_{02} \exp\left(\frac{\Phi_k - \Phi_2}{a_2}\right) = \\ = A_1 i_{03} \exp\left(\frac{\Phi_3 - \Phi_k}{c_3}\right) - A_1 i_{03} \exp\left(\frac{\Phi_k - \Phi_3}{a_3}\right) \tag{38}$$

on substitution of the usual electrochemical relationships. When Φ_k is replaced as the dependent variable in this equation by i_k, the corrosion current density I_k/A_2, we obtain, after rearrangements

$$\left(\frac{i_k}{i_{02}}\right)^{(a_2-a_3)/a_3} - \left(\frac{i_k}{i_{02}}\right)^{-(a_2+c_3)/c_3} \exp\left(\frac{(a_3+c_3)(\Phi_3-\Phi_2)}{a_3 c_3}\right) = \\ = -\frac{A_2 i_{02}}{A_1 i_{03}} \exp\left(\frac{\Phi_3 - \Phi_2}{a_3}\right). \tag{39}$$

As with Case I, we tackle limiting forms of equation (39) before solving it generally. Applying definition (9), we find

$$i_{ko} = i_{02} \exp\left(\frac{\Phi_3 - \Phi_2}{a_2}\right) \tag{40}$$

for the limit of zero porosity. For large A_2/A_1 ratio, the oxidation of Rd is inappreciable and the first term in equation (39) may be ignored. Thence it follows that

$$I_k = A_2 i_k = [(A_1 i_{03})^{c_3} (A_2 i_{02})^{a_2}]^{1/(a_2+c_3)} \\ \exp\left(\frac{\Phi_3 - \Phi_2}{a_2 + c_3}\right). \tag{41}$$

This equation is similar to (18) and by the procedure used in connection with that equation we establish

$$i_{km} = i_{02} \left(\frac{c_3 i_{03}}{a_2 i_{02}}\right)^{c_3/(a_2+c_3)} \exp\left(\frac{\Phi_3 - \Phi_2}{a_2 + c_3}\right) \tag{42}$$

as the second limiting corrosion current density.

Combining equations (40) and (42) we arrive at the simple relationship

$$i_{km} = i_{ko} \left(\frac{c_3 i_{03}}{a_2 i_{ko}}\right)^{c_3/(a_2+c_3)} \tag{43}$$

between the two limiting corrosion current densities. For the typical $a_2 = c_3$ situation, the interrelation becomes

$$i_{km} = \sqrt{i_{03} i_{ko}} \quad \text{for } a_2 = c_3 \tag{44}$$

indicating that the corrosion current density corresponding to maximum corrosion current is the geometric mean of the corrosion current density in the small-puncture limit and the exchange density for oxidant reduction on the coating metal.

We now return to the general equation (39) and replace the constants i_{02} and i_{03} in that equation by substitution from equations (40) and (42). After some algebra, this leads us to

$$\left(\frac{i_k}{i_{ko}}\right)^{(a_2-a_3)/a_3} - \left(\frac{i_k}{i_{ko}}\right)^{-(a_2+c_3)/c_3} = \\ = -\frac{c_3 A_2}{a_2 A_1} \left(\frac{i_{ko}}{i_{km}}\right)^{(a_2+c_3)/c_3}. \tag{45}$$

As with Case I, there is no general solution to this equation; that is, there is no exact explicit expression possible for i_k. By the method explained in the appendix, however, an approximate solution, namely

$$\frac{i_k}{i_{ko}} \approx \left[\frac{1-x_{II}-(\gamma_{II}-1)x_{II}\ln(1-x_{II})}{(1-x_{II})^2}\right]^{c_3\gamma_{II}/(a_2+c_3)} \tag{46}$$

may be derived, where x_{II} is the negative expression

$$x_{II} = -\frac{c_3 A_2}{a_2 A_1}\left(\frac{i_{ko}}{i_{km}}\right)^{(a_2+c_3)/c_3}. \tag{47}$$

This approximation is better the closer is the term

$$\gamma_{II} = \frac{a_3(a_2+c_3)}{a_2(a_3+c_3)} \tag{48}$$

to unity; that is, the more nearly equal are a_2 and a_3.

To appreciate the implication of equation (46), it is useful to consider the simplification engendered when all Tafel slopes are equal. Approximation (46), then exact, becomes

$$i_k = \frac{i_{ko}}{\sqrt{1+\dfrac{A_2 i_{ko}^2}{A_1 i_{km}^2}}} \quad \text{for } a_2 = a_3 = c_3. \tag{49}$$

Moreover, for equal Tafel slopes interrelation (44) applies, permitting the alternative formulation

$$i_k = \frac{i_{ko}}{\sqrt{1+\dfrac{A_2 i_{ko}}{A_1 i_{03}}}} \quad \text{for } a_2 = a_3 = c_3. \tag{50}$$

Equation (50) indicates that the rate of corrosion, initially large and equal to i_{ko}, will fall as A_2 increases, becoming one-tenth of its initial value when the ratio A_2/A_1 exceeds i_{03}/i_{ko} one-hundredfold. At first encounter this result may appear paradoxical: the corrosion, zero when the coating is unruptured, occurs at a maximal rate when the porosity is minute. The paradox is resolved, however, when the corrosion current (rather than the current density) is considered in the $A_2 \to 0$ limit.

It must be emphasized that the reduction from the general expression (46) to the simple equation (50) requires the assumption of the typical equalities $a_2 = a_3 = c_3$. The same assumption was made in constructing Fig. 2, which shows how the dissolution current density (corrosion rate) depends on porosity for Case II. However, the same qualitative description holds even if the Tafel slopes are unequal.

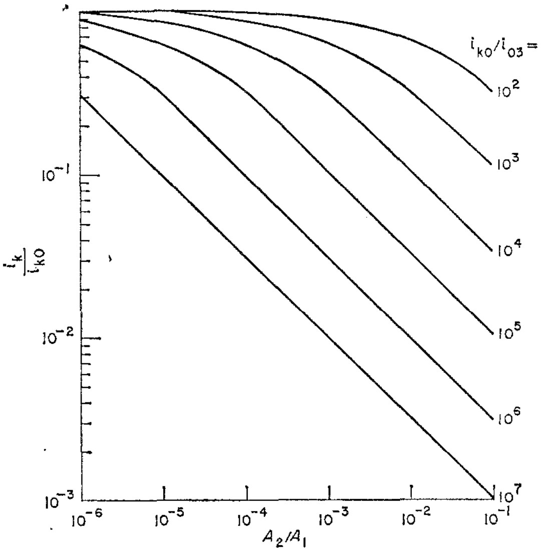

Fig. 2. Logarithmic graphs of the function $(i_k/i_{ko}) = [1+(A_2 i_{ko}/A_1 i_{03})]^{-\frac{1}{2}}$ versus A_2/A_1 for the indicated values of the parameter i_{ko}/i_{03}. These plots relate to Case II and demonstrate that increasing porosity leads to a decrease in corrosion rate (though the total corrosion, $I_k = A_2 i_k$, does increase with porosity).

Even though it refers to an unruptured surface, equation (40) shows that the value i_{ko} is a function of the parameters of the substrate (i_{02}, Φ_2, a_2) and the oxidizer (Φ_3). but not of the coating. Taking some approximate values for iron in aqueous solution at pH = 4 [$i_{02} = 10^{-6}$ A/cm^2, Φ_2 (for a ferrous ion activity of 10^{-6} mole/l) = −0·6 V, Φ_3 = −0·24 V, a_2 = 0·04 V], one obtains about 6×10^{-3} A/cm^2 for i_{ko}. Since for iron at pH 4 the exchange current density for hydrogen evolution is about 10^{-7} A/cm^2 [3], the i_{ko}/i_{03} ratio is about 10^5. Reference to Fig. 2 shows that, as the porosity of a coated iron specimen increases in a medium at pH 4, the rate of corrosion of the substrate is only modestly decreased until a porosity of about 10^{-4} is reached. Thereafter the corrosion rate decreases about threefold for each tenfold increase in exposed area.

Analogously to equation (29), the change in mixed potential is expressible as

$$\Delta\Phi_k = \frac{a_2}{2}\ln\left(1+\frac{A_2 i_{ko}}{A_1 i_{03}}\right) \quad \text{for } a_2 = a_3 = c_3. \tag{51}$$

This equation predicts a negative drift in mixed potential as porosity increases (Fig. 3). This phenomenon was employed by Morrissey [6]

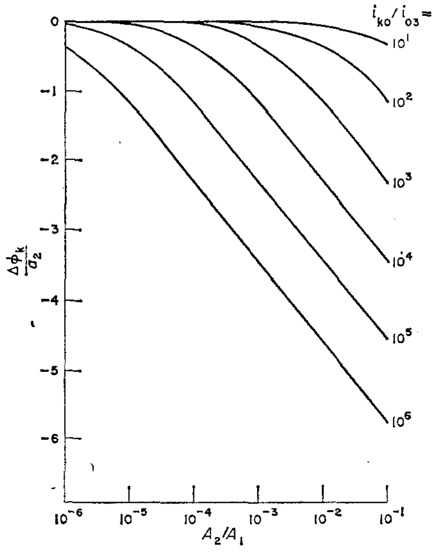

Fig. 3. Semilogarithmic graphs of $(\Delta\Phi_k/a_2) = -1{\cdot}15 \log[1+(A_2 i_{ko}/A_1 i_{o3})]$ versus A_2/A_1 for values of the parameter i_{ko}/i_{o3}. These plots relate to Case II and demonstrate how the mixed potential becomes more negative as corrosion proceeds and porosity thereby increases.

to estimate the porosity of gold-plated copper specimens.

The relationship between Φ_k and porosity as derived by Stern [5] was in the form

$$\Phi_k = \frac{\Phi_3+\Phi_2}{2} - \frac{a_2}{2}\ln\left(\frac{A_2\, i_{o2}}{A_1\, i_{o3}}\right) \quad \text{for } a_2 = c_3. \quad (52)$$

In Stern's treatment it was assumed that the only reaction on the substrate is metal oxidation and the only reaction on the noble coating is reduction of the oxidizer, i.e. reactions (2a) and (3c) in our notation. In the present treatment, however, the possibility of an additional reaction (oxidation of H_2 or OH^-) on the coating is admitted. The deviation from a logarithmic relationship between $\Delta\Phi_k$ and porosity at small values of A_2/A_1 which was observed by Morrissey [6] for the Cu–Au couple in 0·1 M KCl is predicted by Equation (51) and Fig. 3, although Morrissey attributes it to experimental difficulties.

Appendix

If y is a function of two parameters, γ and x, such that

$$y^{1-\gamma} - y^{-\gamma} = x, \qquad \text{(A1)}$$

then only for certain special values of γ may y be written as an explicit function of x. Included in these special solutions are

$$y = \tfrac{1}{2} \pm \sqrt{x+\tfrac{1}{4}};\ \ \gamma = -1 \qquad \text{(A2)}$$

$$y = 1+x;\ \ \gamma = 0 \qquad \text{(A3)}$$

and

$$y = \frac{1}{1-x};\ \ \gamma = 1 \qquad \text{(A4)}$$

as well as other algebraic expressions when $\gamma = -2, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{3}{2}, 2$ or 3.

When γ has a value other than one of these special values, the only possible explicit expression for $y(\gamma,x)$ are approximations or infinite series. Consider one of these latter, the Taylorian expansion

$$y(\gamma,x) = y(\gamma_s,x) + [\gamma-\gamma_s]\frac{\partial y}{\partial \gamma}(\gamma_s,x) + \frac{[\gamma-\gamma_s]^2}{2!}\frac{\partial^2 y}{\partial \gamma^2}(\gamma_s,x) + \ldots \qquad \text{(A5)}$$

where γ_s is one of the special γ values. Now if γ is close to γ_s the coefficient $[\gamma-\gamma_s]^2/2!$ of the third right-hand term in (A5) will be small and later terms will be even smaller. Hence the approximation

$$y(\gamma,x) \approx y(\gamma_s,x) + \frac{[\gamma-\gamma_s]y(\gamma_s,x)[y(\gamma_s,x)-1]\ln y(\gamma_s,x)}{\gamma_s+[1-\gamma_s]y(\gamma_s,x)} \qquad \text{(A6)}$$

is valid, wherein we have inserted the expression derived from (A1) for $\partial y(\gamma_s,x)/\partial\gamma$.

Now consider equation (22) of Case I and let

$$\left(\frac{i_k}{i_{ko}}\right)^{(a_1+c_3)/c_3} = y_I. \qquad \text{(A7)}$$

Then, with definitions (24) and (25), equation (22) may be recast as

$$y_I^{\,1-\gamma_I} - y_I^{\,-\gamma_I} = x_I \qquad \text{(A8)}$$

appearing as an example of equation (A1). Moreover, definition (25) ensures that γ_I will not be very different from the special γ value, zero. Insertion of $\gamma_s = 0$ and $y_I(\gamma_s,x_I) = 1+x_I$ into equation (A6) yields

$$y_{\mathrm{I}} \approx 1+x_{\mathrm{I}}+\gamma_{\mathrm{I}}x_{\mathrm{I}}\ln(1+x_{\mathrm{I}}) \qquad \text{(A9)}$$

from which equation (23) follows immediately.

In similar fashion the definition

$$y_{\mathrm{II}} = \left(\frac{i_{\mathrm{k}}}{i_{\mathrm{ko}}}\right)^{a_2(a_3+c_3)/a_3c_3} \qquad \text{(A10)}$$

converts equation (45) into another example of (A1) wherein $x = x_{\mathrm{II}}$ and $\gamma = \gamma_{\mathrm{II}}$, a quantity close in magnitude to the special value $\gamma = 1$. Insertion of $\gamma_s = 1$ and $y(\gamma_s, x) = 1/(1-x)$ into (A6) now give a result to which equation (46) is equivalent.

List of symbols

Me_1	Coating
Me_2	Substrate
Ox	Oxidizing agent (H^+, H_2O or O_2)
Rd	Reduced form of Ox (H_2 or OH^-)
I	Current
i	Current density (c.d.)
A_1	Area of coating
A_2	Area of substrate
$A = A_1+A_2$	Total area
A_2/A_1	Porosity
β	Tafel slope
a	Anodic Tafel constant related to β
c	Cathodic Tafel constant related to β
Φ_{k}	Corrosion potential
I_{k}	Corrosion current
i_{oj}	Exchange c.d. of reaction (j)
Φ_j	Reversible potential of reaction (j)
i_{ko}	Corrosion c.d. corresponding to unruptured coating
i_{km}	Corrosion c.d. at maximum i_{k}
i_{02}^{L}	Limiting oxygen diffusion c.d.

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