Possible distribution of potential and corrosion current density inside corroding crevices

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A B S T R A C T

The case when the potential distribution inside a corrosion cavity obeys Ohm's law is considered. Mathematically, the potential drop in the crevice is described by a Poisson-type equation with a non-linear source term. A simple method for finding all possible solutions in a one-dimensional approximation and for investigating their stability has been developed. We derive a simple relation for estimating the critical depth of the crevice, L_c (which is defined as the depth at which the active–passive transition just occurs within the crevice) as a function of the width of the crevice, w, electrolyte conductivity, κ, metal potential, E_{met}, and a polarization curve. It is shown that L_c is proportional to $\sqrt{(w\kappa)}$ and is a linear function of E_{met}. Calculation of the corrosion damage (maximum depth of the penetration into the metal, w_{max}) as a function of time and position inside the crevice has been performed. It is shown that during the initial stages of crevice corrosion, when the one-dimensional approximation is valid, w_{max} is determined mainly by the polarization curve for the anodic dissolution of the metal. It is shown that, in the general case, it is impossible to neglect the potential drop in the external environment when quantitatively describing crevice corrosion.

1. Introduction

One of the principal tasks in theoretically describing crevice corrosion is to develop the ability to predict which geometries will be susceptible to this form of attack and to determine the critical crevice geometry that separates the region where crevice corrosion initiates from that where crevice corrosion does not occur [1]. In those cases, when the occurrence of crevice corrosion cannot be avoided, the prediction of the corresponding corrosion damage as a function of time is of great practical importance. In this paper, we estimate quantitatively the value of crevice corrosion damage, which is expressed as the maximum penetration into the crevice wall.

It has been suggested that different mechanisms must be invoked to describe the initiation of crevice corrosion in different systems (geometries). In accordance with the classical point of view, the initiation of crevice corrosion is attributable to the development of a differential aeration cell with the subsequent acidification of the crevice solution and/or migration of aggressive anions (for example, Cl$^-$) into the cavity [1–7], as embodied in the differential aeration hypothesis (DAH). However, as claimed

in Ref. [7] "this classical theory is not able to explain cases of immediate corrosion or cases of crevice corrosion in systems which show no significant acidification or aggressive ion buildup in the crevice solution". In these cases, crevice corrosion can be caused by IR (ohmic) potential drop in the cavity, which places the local metal potential existing in the crevice wall in the active dissolution region of the polarization curve, as developed extensively by Pickering and co-workers [1,7–15]. Generally speaking, in the absence of significant concentration drops in the crevice, the IR drop can be calculated by solving a Poisson-type differential equation relative to the potential in the solution by using a numerical method. In particular, such calculations lead to the definition of the location of the active–passive transition and to the definition of the so-called critical crevice depth. Here, the critical crevice depth, L_c, is defined as the depth, as measured from the crevice mouth, at which the active–passive transition just occurs within the crevice [1,7]. It is assumed that for crevices that are deeper than L_c, the active–passive transition will manifest itself and lead to crevice corrosion. For crevices that are shallower than L_c, the active–passive transition and, accordingly, crevice corrosion will not occur [7]. It has also been stated that computation of the critical crevice depth could be made solely on the basis of the polarization curve and the conductivity of the solution [1].

However, in our opinion, the last conclusion is valid only if the nonlinear, Poisson-type equation has a unique solution for the

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assumed boundary conditions. If the solution is not unique, the location of the active–passive transition (and even the occurrence of this transition) will depend also upon the history of crevice initiation. The fact that the potential and current distributions in a crevice are not unique, especially for the case of metals that show active–passive kinetics, has been mentioned in the literature (see, for example, Refs. [17,18]). In this case, it is also important to investigate if some of the possible solutions that are obtained are unstable and, accordingly cannot be observed [17,18]. Below, it is shown that this situation can occur in practice under certain conditions. We also show that the crevice can remain passive, even when its depth is greater than the critical value, L_c. Generally speaking, the problem of multiplicity and stability of the solutions to the potential distribution are not limited to electrochemical systems that are described by Poisson-type equation. Thus, for example, such problems arise in the case of corrosion of iron rotating disk [19] or differential aeration corrosion under a moisture film [20,21].

From a mathematical point of view, in the one dimensional approximation, we have to solve two boundary value problems (boundary conditions are supposed to be satisfied at the mouth and at the bottom of the crevice). In Refs. [1,7,16–18], this problem has been addressed by using the so-called relaxation method, in which a trial solution consisting of values of the dependent variables at each mesh points is developed, with a new trial function being adopted if the previous one did not satisfy the desired finite-difference equations [22]. It is well known that problems with the convergence of the trial solution to the actual solution can arise for the case of non-linear equations [22]. This problem becomes especially important for non-linear equations, which generally have multiple solutions, and it is not evident to which particular solution the numerical iteration will converge. In our opinion, it would much simpler to solve the two boundary value problem by using the so-called shooting method, which reduces the two boundary value problem to an initial value problem. Below, it will be shown how the latter method will allow us to receive all possible solutions, simultaneously, and to investigate their stability. By using the results of the calculations, we suggest a simplified analytical method for estimating the critical depth, L_c, as a function of the width of the crevice, w, electrolyte conductivity, κ, metal potential, E_{met}, and a polarization curve, along with the estimation of corrosion damage during initial stages of crevice corrosion, when the one-dimensional approximation is valid. Special attention will also be paid to the influence of the charge transfer on the external surfaces (outside the crevice) on the process of crevice corrosion. Such a "Coupled Environment Crevice Model (CECM)" follows closely our previous work on developing the Coupled Environment Fracture Model (CEFM) to describe stress corrosion cracking [23,24].

2. Mathematical model

Let us consider the one-sided crevice shown in Fig. 1. It is assumed that the crevice has constant thickness, d (perpendicular
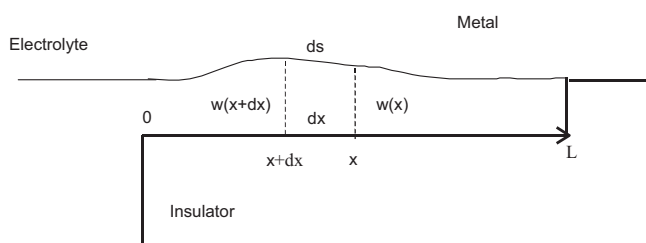

Fig. 1. Schematic of crevice with a gap, $w(x)$, and depth L. It is assumed that the thickness of the crevice (in the direction perpendicular to the plane of the figure) is constant.

to the plane of Fig. 1). Application of the law of charge conservation in Fig. 1 yields:

$$i(x + dx)w(x + dx) - i(x)w(x) = i_s(x)ds(x) \tag{1}$$

where x is the distance from the crevice mouth into the crevice measured along the plane insulated surface, $w(x)$ is the width of the crevice, $i(x)$ is the current density (averaged over the crevice cross-sectional gap), $i_s(x)$ is the charge transfer current density entering the crevice at the metal crevice wall, and $ds = dx\sqrt{1 + (dw/dx)^2}$ is the elementary length of the curve on the metal surface between cross sections x and $x + dx$. Geometrically, $ds = dx/\cos(\beta)$, where β is the angle between the tangent to the metal surface and the x axis and

$$\cos[\beta(x)] = \frac{1}{\sqrt{1 + (dw/dx)^2}} \tag{2}$$

Here, we consider the possibility that, due to the corrosion dissolution, the metal surface may be non-planar.

The differential form of Eq. (1) can be rewritten as

$$\frac{d[iw]}{dx} = i_s \sqrt{1 + \left(\frac{dw}{dx}\right)^2} \tag{3}$$

In the 1-D approximation, the current density, i, can be expressed via Ohm's law (assuming that there are no significant concentration gradients in the crevice) as

$$i = -\kappa \frac{d\varphi}{dx} = \kappa \frac{dE}{dx} \tag{4}$$

Here, κ is the conductivity of the electrolyte, φ is the electrostatic potential in the solution (averaged over crevice cross-section), and E is the potential of the metal measured relative to some reference electrode. If φ is chosen to be 0 at the crevice mouth the relation between φ and E is

$$E = E_0 - \varphi \tag{5}$$

where E_0 is the metal potential at the crevice mouth (at $x = 0$).

Substitution of Ohm's law into the equation of charge conservation yields

$$\frac{d}{dx}\left(w(x)\frac{dE(x)}{dx}\right) = \frac{i_s(E)}{\kappa} \frac{1}{\cos[(\beta(x)]} \tag{6}$$

In this expression, we have taken into account that the charge transfer current density on the metal surface is known as a function of the metal potential, E, rather than as a function of the distance from the crevice mouth. Accordingly, it is more convenient to consider E as an unknown value, rather than the potential drop in the solution, φ.

The boundary conditions for Eq. (6) are follows:

$$E = E_0 \quad \text{at} \quad x = 0 \tag{7}$$

and

$$\frac{dE}{dx} = 0 \quad \text{at} \quad x = L \tag{8}$$

Boundary condition (8) states that the tip of the crevice is an insulator or that, due to the condition $w \ll L$ (the crevice is thin), it is possible to neglect by the current that flows into the crevice through the tip in comparison with the current that flows into the crevice through the side walls. It is important to note that applicability of the 1-D approximation in this case requires, along with the usual condition $w(x) \ll L$, also the fulfilling of the condition $\cos(\beta) \ll 1$. Otherwise, even the term "width of the crevice" looses geometrical sense.