Boundary Element Model for Stress Field - Electrochemical Dissolution Interactions

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Introduction

This paper aims to model the effects of low levels of stress (in the elastic range) on the dissolution rate of metals by means of experiments and to incorporate these into a boundary element code in order to predict dissolution rates of corroding structures. Corrosion, ignoring the effects of stress, is thoroughly documented, and the effects of micromechanical damage caused by strains in the plastic region are well recognized. However, very little is known regarding the effects of low levels of stress on the behavior of metals in general. To quantify this effect, a system consisting of stainless steel in seawater was investigated. The two primary aspects of this research are the experimental determination of the effects of low level stresses on the corrosion behavior of samples and the incorporation of these effects in a boundary element method-based code which was written to predict long-term changes in geometry due to the stress modified dissolution. The initial experimental system used is high purity copper with aerated NH_4OH as the electrolyte. This system is used to verify the functionality of the numerical code in predicting large changes in geometry due to long-duration dissolution. Analysis of time-dependent measurements of the specimens yields the geometry changes in the corrosion region as a function of time. The second electrochemical system used is type 304 stainless steel in a saline electrolyte which simulates seawater composition.

A Boundary Element Method (BEM) code is written to predict the electrochemical dissolution activity in 2D and axisymmetric geometries of partially corroding systems. The nonlinearities in this problem are due to boundary conditions of the third kind in which the ratio of the potential to the current density at the corroding surface is provided as highly non-linear polarization curve measured by experiment.

This curve is particular to each specimen, electrolytic environment, stress, time, and potential other factors, such as temperature. A Newton-Raphson iterative procedure to is used to solve for equilibrium at each solution step. A nodal optimization routine dynamically modifies the number of nodes and their location on the boundary. This is necessary due to the large changes in geometry experienced during long duration dissolution. The term "super-element" is used to denote one section of the boundary where nodes are dynamically located along the boundary and which is defined by a curvilinear fit

through the previous nodal locations. Corners, edges, and other geometrically important features as well as changes in material properties occur only at the juncture of super-elements. Since any super-element may be subject to complex changes in geometry, it was necessary to describe all elements in a parametric sense. A fit consisting of orthogonal Chebyshev polynomials was found to be sufficiently smooth for the parametric representation of the data points.

Comparison between numerical predictions using polarization curves determined by experiment for the Copper/ammonium system reveals that the BEM code developed to model recession of corroding surfaces faithfully reproduces recession fronts measured in the experiments.

Background

BEM is adopted because the knowledge of physical quantities (potential and current density) on the surface of corroding materials is of prime importance in corrosion problems. The BEM does not require discretization of the domain with internal elements in comparison to other conventional analysis techniques, e.g. finite-difference-method (FDM) and finite-element-method (FEM). Fu and Chow [1] introduced the use of a boundary integral formulation of the Laplace equation to solving corrosion problems. An axisymmetric problem was modeled and compared to experimental results of potential and current distributions. In their model, the behavior of the electrode double layer, where the electoneutrality law is not valid, is expressed as an experimentally determined polarization curve, and the Laplace equation is applied only to the bulk electrolyte. This is the most common approach taken by researchers in modeling corrosion, and this framework has been adopted in this dissertation.

Other research using BEM in the modeling of potential and current density distribution in cathodic protection systems was undertaken by Santiago, *et al*. [2]. The method was expanded to cover galvanic couples by analyzing distributions of current density and potential on a carbon steel stainless steel in NaCl electrolyte by Varela, Kurata, and Sanada [3]. Santiago and Telles [4] used BEM to predict the evolution of current density and potential distributions with respect to time that appear when cathodic protection systems are employed to prevent corrosion of metallic structures in contact with an electrolyte.

An example of the application of the BEM to model corrosion and cathodic protection for large geometries are presented by Degiorgi *et al*. [5], where studies of the corrosion prevention capability of shipboard impressed current cathodic protection (ICCP) systems are undertaken. Butler *et al*. [6] have used BEM to generate time-to-failure estimates for roofing fastener/structure systems subject to corrosion resulting from galvanic couples, and subsequently this work was extended to model pit growth using new curvilinear super-elements by Butler *et al*. [7]. A detailed review of literature associated with the application of BEM to corrosion problems is provided in Butler [8].

Governing Equations

The governing equation for corrosion can be reduced down to the Laplace equation for the potential Φ,

$$\nabla^2 \Phi = 0 \tag{1}$$

The above equation and the assumptions on which it is predicated hold true in the bulk region of the electrolyte, while they fail in the double layer region close to the corroding surface(s). This is described in standard references, Brebbia, Telles, and Wrobel [9]. In this region, reminiscent of the boundary layer in fluid mechanics, a nonlinear relationship exists between the current density and the potential. This is reflected in the boundary conditions imposed at the surfaces of the system. *Robin* boundary conditions are needed to specify the empirically measured relationships between potential and current, which are typically nonlinear. These boundary conditions can only be specified from experiment, in the form of typical polarization curves for the specimen.

The singular boundary integral equations

$$c(\xi)\phi(\xi) + \int_{\Gamma} \Phi^*(\xi,x)\frac{\partial\phi(x)}{\partial n}\,d\Gamma(x) - \int_{\Gamma} \frac{\partial\Phi^*(\xi,x)}{\partial n}\phi(x)d\Gamma(x) = 0 \qquad (2)$$

where $c(\xi,x)$ is the free term which depends on the local boundary geometry, x and ξ are the locations of the field and source point respectively and Φ^* is the free-space fundamental solution. For axi-symmetric problems, assuming that all boundary conditions also have no dependence on the polar angle, the dependent variables are reduced to $R - Z$ by integrating the 3-D boundary integral equation in the polar direction and where upon using the axisymmetric fundamental solution:

$$\overline{\Phi}^*(\xi,x) = \frac{4K(m)}{\sqrt{a+b}} \qquad (3)$$

the governing boundary integral equation is written as:

$$c(\xi)\overline{\phi}(\xi) + \int_{\overline{\Gamma}}\overline{\phi}(x)\frac{\partial\overline{\Phi}^*}{\partial n}(\xi,x)\,R(x)\,d\overline{\Gamma}(x) = \int_{\overline{\Gamma}}\frac{\partial\overline{\Phi}^*}{\partial n}(x)\overline{\phi}(\xi,x)R(x)\,d\overline{\Gamma}(x) \qquad (4)$$

while $K(m)$ is the elliptic function of the second kind.

Numerical Implementation

Using conventional BEM practice, by introducing the discretizations of the boundary, the potential, and its normal derivative into the boundary integral equations, the boundary element equations are derived in the following standard form:

$$[H]\{\phi\} = [G]\{q\} \qquad (5)$$

where $\{\phi\}$ is the vector of nodal values of the potential, $\{q\}$ is the set of nodal values of the normal derivative of the potential, while the influence matrices $[H]$ and $[G]$ are computed numerically using Gauss-type quadratures. Upon specification of the boundary conditions, the above are solved for the unknowns to finally determine both the potential and its normal derivative everywhere at the boundary.

In the BEM code, a nodal optimization routine dynamically modifies the number of nodes and their location on the boundary. This is necessary due to the large changes in geometry

experienced during long-duration dissolution. The term "super-element" (Butler [8]) is used to denote one section of the boundary where nodes are dynamically located along the boundary, which is defined by a curvilinear fit through the previous nodal locations. Corners, edges, and other geometrically important features as well as changes in material properties occur only at the juncture of super-elements. The node spacing routine optimally places nodes along the current surface, whereas changes in the surface are also carried out using a remeshing scheme. This adaptive strategy modifies the number and location of the nodes and is based on several criteria, including the normalized magnitude of the field variable (the potential), normalized magnitude of the flux (current density), the normalized magnitude of the normal stress, and the rate at which these parameters are changing (Butler [8]).

Examples

Comparison of BEM Analysis with Experimental Results on Thick Cylinder
For this example, a 8.89 cm diameter x 2.54 cm thick cylindrical section was prepared. The specimen was composed of C12000 Copper (99.9% Cu). The specimen was sealed with a dielectric material only on the back, with the sides and front exposed to the electrolyte. The electrolyte was NaOH which was held at 20^0 C and aerated using bubbled air. Samples of the copper were tested to determine its polarization response (see Figure 1). All polarization samples were previously scanned several times to achieve a surface profile typical of the full size specimens. The results were used as the polarization response boundary condition for the numerical model.

The laboratory specimen displays an unusual flatness in the region $0 \leq r \leq 1.14$ cm which is a result of formation of a copper precipitate film in this region directly under the cathode. This film prevented further dissolution of material in this area which resulted in the accelerated loss of material in the remaining exposed surfaces, particularly note the corner region. Attention is now shifted to the effect of stress on the polarization curve characteristics of stainless steel under stress.
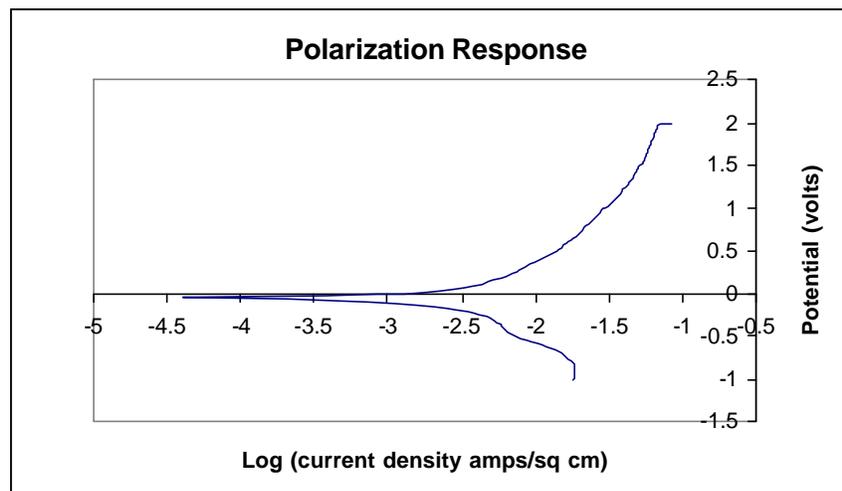

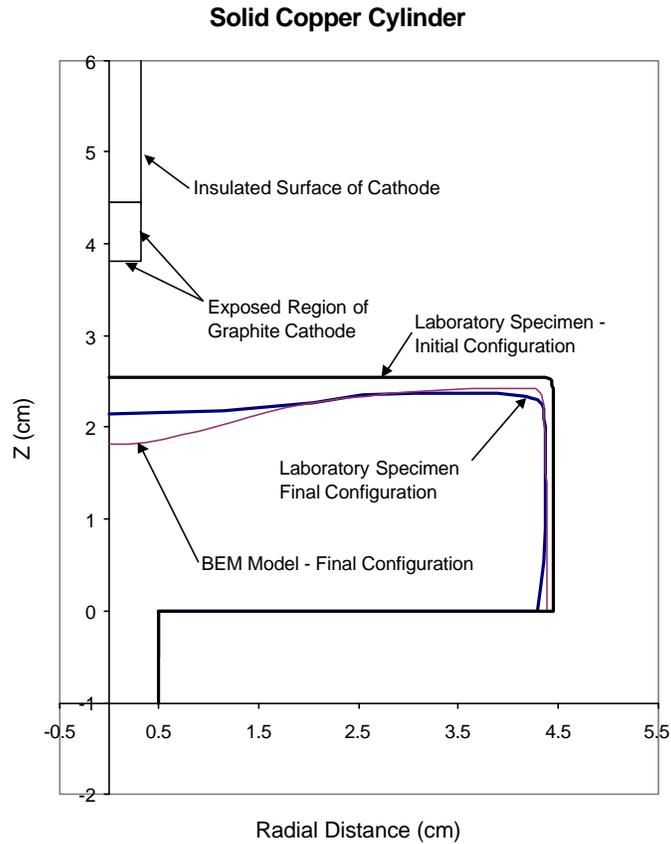Figure 1.   Copper cylinder - polarization response.

Solid Copper Cylinder

Figure 2.   Copper cylinder surface profile - BEM vs. experimental.

Experiments on Dissolution Behavior of Steel with Stress
A series of low stress (0 - 40 MPa) tests were conducted under compressive stresses to measure the change in polarization response to stress. As an initial step, three polarization curves were generated for a specimen at different stress levels is shown in Figure 3. To clearly measure the effect of the stress field and the rate of change of stress on the current/potential relationship (the polarization function) a constant stress field in the area being measured is desirable. To achieve this a four-point bend test was constructed. It can be seen that the shape of the curves are not appreciably changed, especially in the region around the equilibrium potential, E_{corr}. There is an apparent trend in the magnitude of the exchange current density, but as this has very little effect on the corrosion rate at any meaningful deviation from E_{corr} and may be due to subtle changes in the surface profile from preceding scans, it is not considered significant.

All of the data clearly showed a linear relationship between stress and shifts in E_{corr}. Furthermore, more data presented in Butler [0] clearly indicates that there is a correlation between $\frac{\partial E_{corr}}{\partial \sigma}$ and the stress rate $\frac{\partial \sigma}{\partial t}$. In this test, the effects of an applied stress field on the long term dissolution behavior of type 304 stainless steel were quantified and incorporated into a boundary integral numerical scheme.
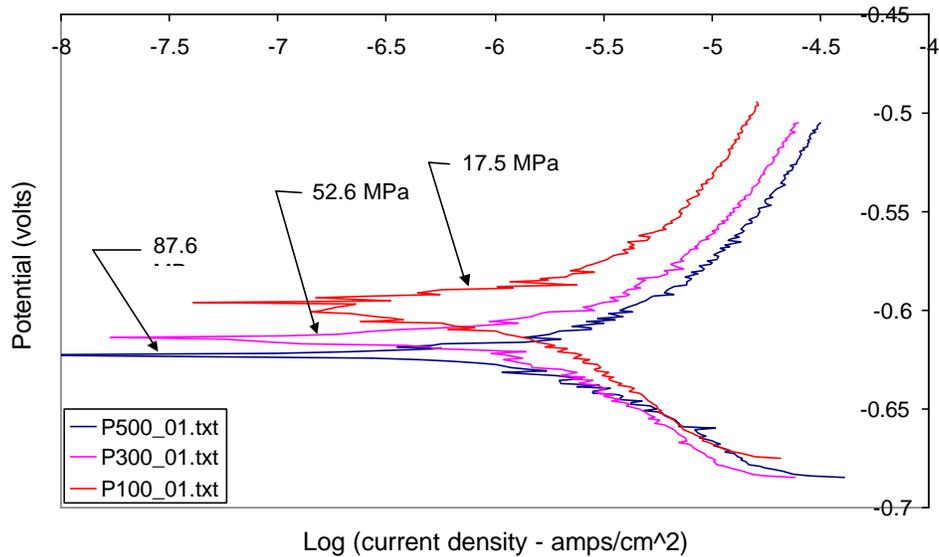
Change in Polarization Scans with Stress

Figure 3. Typical Change in Polarization Scans with Stress

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