Engineering Analysis with Boundary Elements 34 (2010) 714–720

Contents lists available at ScienceDirect

Engineering Analysis with Boundary Elements

journal homepage: www.elsevier.com/locate/enganabound

Boundary element model of electrochemical dissolution with geometric non-linearities

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ARTICLE INFO

Article history:
Received 6 October 2009
Accepted 21 March 2010

Keywords:
Boundary elements
Corrosion
Non-linear polarization
Electrochemical dissolution

ABSTRACT

Large scale changes in geometry due to corrosion of polycrystalline pure copper are modeled using the Boundary Element Method. Axisymmetric geometries are considered. A quasi-static analysis is performed and a nonlinear polarization curve is determined from experiments to impose third kind boundary conditions. Super-elements, based on a cubic spline fit interpolation, are introduced to model the motion of the boundaries. Faraday's law is used to relate boundary motion to the surface flux. An set of controlled experiments using nearly pure (99.99% and 99.9%) copper with aerated NH_4OH electrolyte was used to test the experimental methods developed for this study and to verify the functionality of the numerical code in predicting large changes in geometry due to long duration dissolution. Polarization curves were measured and input into the BEM code and recession profiles were predicted. Comparison between experiment and predictions reveal that, given the polarization curves measured in the lab, the BEM code predicts accurate recession profiles.

1. Introduction

This paper reports on a methodology based on the Boundary Element Method (BEM) with the ultimate aim 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, has been 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, an experimental program was undertaken to study a system consisting of stainless steel in seawater. Results of this study will be reported in a follow-up publication focusing on experimental determination of the effects of low level stresses on the corrosion behavior of samples and the ultimate incorporation of these effects in the boundary element method-based code which was written to predict long-term changes in geometry due to the stress modified dissolution.

This paper develops a BEM strategy to model large changes in geometry due to long-duration dissolution. Moreover, integration with experimental input and verification of the predictions from the code are undertaken using two experiments. An initial experimental system using high purity copper with aerated NH_4OH as the electrolyte was used to determine polarization curves and to verify the functionality of the numerical code in predicting corrosion-induced large geometric changes. Analysis of time-dependent measurements of the specimens yields the geometry changes in the corrosion region as a function of time.

BEM is utilized to predict the electrochemical dissolution activity in two dimensional 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 a highly non-linear polarization curve measured by experiment. This curve is specific to each specimen, electrolytic environment, stress, time, and other potential factors, such as temperature. A Newton–Raphson iterative procedure 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

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doi:10.1016/j.enganabound.2010.03.007

only at the junction 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.

Nonlinearities in this problem are large scale changes in geometry and boundary conditions given by the highly non-linear polarization response of the specimen, which is a function of both time and potential [1–4]. Copper was selected due to its relatively low cost, because it is thermodynamically reactive, undergoes dissolution at room temperature, and it has been the subject of numerous studies. It can easily be obtained in single crystal, foil, thin plate, and poly-crystalline form in purities of up to 99.999%. The electrolyte used is an aerated NH_4OH solution.

Comparisons 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. Here, axisymmetric samples are tested, where measurements of geometrical changes with time are correlated to measured current density versus time, and the BEM model is used to predict electrochemical dissolution activity in these axisymmetric samples. Analysis of time-dependent measurements of the specimens yields geometry changes in the corrosion region as a function of time. Combining geometrical changes and total current yields average current density on the surface as a function of time.

2. 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 [4] 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 electroneutrality 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 the present study.

Other research using BEM in the modeling of potential and current density distribution in cathodic protection systems was undertaken by Santiago et al. [5]. 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 et al. [6]. Santiago and Telles [7] 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. [8], where studies of the corrosion prevention capability of shipboard impressed current cathodic protection (ICCP) systems are undertaken. Butler et al. [9] 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. [10]. A detailed review of literature associated with the application of BEM to corrosion problems is provided in Butler [11].

3. Governing equations

The behavior of an electrochemical system under charge transfer control is modeled using the Laplace equation for the electric field potential ϕ, which neglects mass transport considerations using the following equation:

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

The rationale behind neglecting mass transport, is the fact that in typical corrosion systems where neither the electrolyte nor the electrodes are thin films, the behavior tends to bulk electrolyte behavior when the electrolyte is thicker than 0.1–0.3 cm. The conductivity of the metal is assumed infinite, thus only one region (the electrolyte) is modeled. This assumption is reasonable, unless the metal is very thin (as in printed circuit boards) or highly resistive (composite electrodes composed of metal plus other materials). Further, as the electromagnetic field changes gradually over time, a quasi-static model provided by Eq. (1) is adequate. For example, the experiments carried out in this study involved periods of the order of several weeks. The above equation is solved using the boundary element method for axisymmetric systems. In particular, for purely axisymmetric problems, the governing boundary integral equation can be expressed as [7,8]:

$$c(\xi)\Phi(\xi) + \int_{\overline{\Gamma}} \Phi(x)\overline{q}^*(\xi,x)\,d\overline{\Gamma}(x) = \int_{\overline{\Gamma}} \overline{\Phi}^*(x)q(\xi,x)\,d\overline{\Gamma}(x) \tag{2}$$

where $c(\xi)$ is equal to one when ξ lies within the domain and 1/2 is ξ is on a smooth boundary. The generating curve for the axisymmetric body is denoted by $\overline{\Gamma}$. Here, the axisymmetric kernels are defined as

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

$$\overline{q}^*(\xi,x) = \frac{4}{\sqrt{a+b}}\left\{\frac{1}{2r(x)}\left[\frac{r^2(\xi)-r^2(x)+[z(\xi)-z(x)]^2}{a-b}E(m)-K(m)\right]\eta_r(x) + \frac{z(\xi)-z(x)}{a-b}E(m)\eta_z(x)\right\} \tag{4}$$

Here, $K(m)$ is the complete elliptic integral of the first kind, $E(m)$ is the complete elliptic integral of the second kind, $\eta_r(x)$ and $\eta_z(x)$ are the direction cosines of the outward drawn normal to the generating curve, $a = r^2(\xi)+r^2(x)+[z(\xi)-z(x)]^2$, $b = 2r(\xi)r(x)$, $m = 2b/(a+b)$, and $r(x)$ and $z(x)$ are the polar coordinates [12]. Using a standard boundary element method, the above equation can be discretized and solved for the given boundary conditions. In our code, a library of elements is available ranging from constant to fourth order isoparametric boundary elements. Quadratic elements are usually used in all numerical analyses.

For electrochemical models, the field variable is the electrochemical potential in the system and its derivative is proportional to the current density (the proportionality constant being the conductivity of the electrolyte), i.e. at the anodic or cathodic surface the relation

$$k\frac{\partial\phi}{\partial n} = h(\phi)\phi \tag{5}$$

is used to model the boundary condition. Polarization curves, plots of $\partial\phi/\partial n$ vs. ϕ, which provide the function $h(\phi)$, are determined from experiments. This Robin boundary condition is nonlinear, and resolution of the potential field thus requires