Boundary element model of electrochemical dissolution with geometric non-linearities
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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.

1 Introduction

Large scale changes in geometry due to corrosion of polycrystalline pure copper is modeled using the BEM. To characterize the behavior, large plate axisymmetric samples are tested, where measurements of geometrical changes vs. time are correlated to measured current density
Boundary Elements

vs. time. A 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.

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]. A Newton-Raphson iterative procedure is used to solve for equilibrium at each solution step. 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 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, 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 cubic spline fit was found to be sufficiently smooth for the parametric representation of data points.

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 NH₄OH solution.

2 BOUNDARY ELEMENT MODEL

The behavior of an electrochemical system under charge transfer control can be modeled using the Laplace equation, which neglects mass-transport considerations. The rational behind neglecting these equations, 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).
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). Polarization curves are determined from experiments which relate the potential to current density. These were used as the nonlinear boundary conditions. Initially, a potential distribution is assumed on $\Gamma$, then a solution obtained and the resulting fluxes calculated. These fluxes, after being multiplied by the electrolyte conductivity to yield current densities, were compared to the current densities calculated from the polarization data. A Newton-Raphson iterative procedure was used to solve this nonlinear boundary condition problem.

### 3 Moving Boundaries

The moving boundary problem has been approached in this research as quasi-static, thus reducing to Laplace's equation [5,6]. A discrete time marching algorithm and predictor-corrector iterative scheme is used to track the moving front. At each time step, the boundary moves in a direction normal to itself, as defined in a point wise sense. The magnitude of the movement (at low current densities) is based on the current density which is linearly proportional to the flux and to properties inherent to the metal itself. At the end of each time step, the resulting flux distribution is known. Since $\partial \phi / \partial n = k \bar{J}$, where $k$ is the conductivity of the electrolyte, and $\bar{J}$ is the current density, the resultant current density along each element is determined. At each node the integral of current density from the adjacent elements is calculated, to give the mean current density in the neighborhood of the node. Faraday's Law is then used to determine the dissolution resulting from the mean current density and the quantity of time represented by the time step as [1]

$$m = \frac{I t a}{nF}$$

(1)

where $m$ is the mass reacted per unit area, $I$ is the current density, $t$ is the duration of the time step in seconds, $a$ is the atomic weight of the metal (63.55 for Copper), $n$ is the number of electrons released by an atom released from the lattice (2 for Copper), and $F$ is the Faraday constant 96,500 Coulombs/$n$. The direction of node movement is in the normalized
direction of the vector sum of the fluxes. Movement in both directions is possible, simulating dissolution and plating.

Because small errors in the direction of the normal to the boundary can result in significant errors in subsequent iterations, a curvilinear representation of the boundary was used. Since any one element may be subject to complex changes in geometry, it was necessary to describe all elements in a parametric sense. A cubic spline fit was used to generate a smooth curve through the data points. For even very complex boundaries, the algorithm which generates the locations of the data points provides a sufficiently dense mesh of nodes to allow cubic splines to adequately describe the surfaces. This representation of the boundary allows accurate generation of the normals at every node in the element. After each node in an element is moved proportional to its flux, a new spline fit is performed.

Modeling of corners is accomplished by using the following equations to generate the change in position of the node common to both elements:

$$\Delta r = \frac{k_2n_{z,2}q_{downstream} - k_1n_{z,1}q_{upstream}}{k_1k_2n_{r,1}n_{z,2} - k_1k_2n_{r,2}n_{z,1}} \quad (2)$$

$$\Delta z = \frac{k_2n_{r,2}q_{downstream} - k_1n_{r,1}q_{upstream}}{k_1k_2n_{r,2}n_{z,1} - k_1k_2n_{r,1}n_{z,2}} \quad (3)$$

where $n_{r,1}$, $n_{z,1}$, $n_{r,2}$, and $n_{z,2}$ are the $r$ and $z$ component of the outward drawn normal to the upstream and downstream sections of the corner, $q_{downstream}$ is the downstream flux, and $q_{upstream}$ is the upstream flux, see Figure 1. The constants $k_1$ and $k_2$ are determined for the upstream and downstream locations using Faraday's law as $nF/\tau a$.

Figure 1. A corner node.
If the elements are collinear, the common node is moved by an amount halfway between that of each element, when considered independently

\[ \Delta r = r_{r,1}(q_{\text{downstream}}/k_1 + q_{\text{upstream}}/k_2)/2 \]  
(4)

\[ \Delta z = z_{z,1}(q_{\text{downstream}}/k_1 + q_{\text{upstream}}/k_2)/2 \]  
(5)

If the elements are orthogonal, the common node is moved by the amount of each element, when considered independently

\[ \Delta r = r_{r,1}q_{\text{downstream}}/k_1 + r_{r,2}q_{\text{upstream}}/k_2 \]  
(6)

\[ \Delta z = z_{z,1}q_{\text{downstream}}/k_1 + z_{z,2}q_{\text{upstream}}/k_2 \]  
(7)

Figure 2. Axisymmetric section dissolving in an electrolytic bath.

4 Element Order and Node Location

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" 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 transition between super-elements which have significant differences in dissolution behaviors, whether due to material characteristics or differences in boundary conditions, can lead to numeric difficulties unless treated carefully. Careful examination of experimental specimens indicates that a sigmoidal shape most closely models the actual transition zone. This is modeled in the BEM code using a very narrow (0.01 times the length of the adjacent super-elements) special "transition zone" element (tz-element) between each super-element. The displacement and normal at either end of the tz-element is set equal to that of the adjacent super-element. A cubic polynomial is then fit to this data, with n equally spaced nodes where n is a function of the order of the 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 cubic spline fit generated this parametric smooth curve through the data points. The node spacing adaptive strategy is based on several criteria, including the normalized magnitude of the field variable (the potential) and of the normalized magnitude of the flux (current density), as shown below:

\[
\begin{align*}
\text{\text{u}}_{\text{max}} & = \text{maximum absolute value of the potential in one super-element} \\
\text{q}_{\text{max}} & = \text{maximum absolute value of the flux in one super-element} \\
L & = \text{length of the super-element} \\
S_0 & = \text{coordinate of one end of the super-element} \\
S_i & = \text{coordinate of node-}i
\end{align*}
\]

then

\[
s_i = L \frac{0.05}{0.1 + |u_i| + |q_i|} + s_{i-1} \tag{8}
\]

This approach allows a very fast modification of the number of nodes and their locations. Because the number and location of nodes within a super-element are dynamically adjusted, the order of the elements within a super-element is easily changed. The BEM code at present can automatically vary the order of the elements from linear through 4th order as required. Every super-element may use a different order, the only restriction at present is that all of the elements within a super-element are the same order. This gives the code tremendous flexibility as the number of nodes,
location of nodes, and order of the elements can vary with location on the boundary and with time.

5 Experimental Work

For the axisymmetric problem, a 20 cm x 0.6 cm square thick 99.99% pure copper plate was prepared. The specimen was sealed with a dielectric material on the back, sides, and front except for a 15.875 diameter circular area. The ammonium hydroxide electrolyte was held at 20°C and aerated using bubbled air. The specimens were prepared by polishing with 600 grit silicon carbide and then thoroughly cleaned and dried using clean compressed air. To allow the surface of the specimen to achieve equilibrium with the solution, a delay of 48 hours was used between placing the specimen in the solution and the application of a potential. This resulted in some dissolution of material with a corresponding roughening of the surface. A 0.635 cm diameter x 0.635 cm long graphite cathode was used, with the end of the cathode placed 0.635 cm from the surface of the plate in its initial configuration. The cathode was held at a constant potential of 0.70 volts above the equilibrium half-cell electrode potential.

An analog/digital control board operating from a 486 PC provided the constant potential to the graphite cathode centered on the unprotected circular region of the copper plate. The A/D board recorded the total potential and potential drop across a fixed resistance, which allowed calculation of the potential drop across the electrolyte and the two interfaces (graphite/ammonium hydroxide and copper/ammonium hydroxide). Samples of the solution were taken to determine the conductivity as a function of time. The conductivity is necessary to relate the flux to the current density in the BEM formulation, and to determine the potential drop across just the two interfaces.

Knowing the total potential and the potential drop across the fixed resistance allows calculation of the total resistance of the circuit, thus the current as a function of time is known. This is then compared with the integral of the current density over the specimen surface as calculate by the BEM model. To measure the changes in geometry as a function of time, molds of the specimen surface were prepared at intervals. Elastomeric vinyl polysiloxane impression material was used to capture the fine details of the surface without contaminating the copper surface. A high resolution high strength molding compound was then poured into the molds allowing
recreation of the specimen geometry as a function of time. These molds could then be sectioned and measured.

Samples of the copper were tested to determine its polarization response. All polarization samples were previously scanned several times to achieve a surface profile typical of the full size specimens. A potentiostat conforming to ASTM F5-69 was used with a scan rate of 2 millivolts/second. The scanning was performed in both a forward and backward direction to verify minimal hysteresis in the material behavior. The results were used as the polarization response boundary condition for the numerical model which are displayed below in Figure 3.

![Polarization Response](image1)

![Electrolyte Conductance](image2)

Figure 3. Experimental data: plot the polarization and conductivity
The surface recession of the laboratory Cu sample was modeled using the above as input and the quasi-static BEM model described above. It is noted that there is a reasonable correlation between the BEM predicted behavior and the experimental results. This validates that our approach is successful in predicting long term large scale changes in geometry due to corrosion induced dissolution. Possible sources of deviation between experiment and model variation include the fact that the experimental surface profiles are an average of the radial profiles, noise in the measurements of conductivity, slight variations in the electrolyte properties due to fluid flow, and small random changes in the polarization curves over time.

![Comparison between Experimental Results and BEM Model](image)

Figure 4. Plot of surface dissolution as a function of time.

### 6 Conclusions

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 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. Experiments were carried out to determine the conductivity and polarization curves for a test sample of Cu in an ammonium hydroxide electrolyte. Using these data as input, the BEM model successfully predicts dissolution rates.
7 References