BE study of SVE measurement of localized corrosion rate

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Abstract

In order to analyze the electric field disturbance due to the sensor probe, a new effective BEM is developed. In this method, the analysis is divided into three stages and the size of matrix to be solved is reduced. A new line-shaped element is developed and the boundary integrals for far area are also approximated. Two example problems are solved. It is found that the result obtained by this method agrees well with the conventional method and the computation time was reduced 1/15. It is also found that the SVET overestimates the electric field due to the sensor probe.

1 Introduction

Localized corrosion such as intergranular or pitting corrosion causes serious damage to various machines and structures. For the estimation of these localized corrosion, Scanning Vibrating Electrode Technique (SVET),\(^1,2\) which measures the electric potential difference near the sample surface submerged in the electrolyte as shown in figure 1, has been recently used. It is impossible to measure the current density distribution from the surface directly. In this technique, the current density distribution is estimated from electropotential gradient at the points just above the sample surface. We can get only vague information when the measuring points are far away from the surface.\(^3\) However, when the measuring points approach the sample surface, accurate determination of the correct electropotential field becomes difficult due to the electric field disturbance by the sensor probe itself. As shown in figure 2, equipotential lines, which are expected to be parallel, are distorted.
2 Governing equation

In this paper, we estimate the errors caused by disturbance due to sensor probe itself. The size ratio of sample region to instrument vessel is over $10^4$ and a huge number of elements is needed. It seems impossible to analyze the electric field by conventional BEM when we consider the sensor probe scanning. We propose a new effective BEM for this problem and show the effectiveness with some results.

Let us assume that the surface of the electrolyte domain $\Omega$ is surrounded by $\Gamma(=\Gamma_d + \Gamma_n + \Gamma_m)$ where the potential values and current densities are prescribed on $\Gamma_d$ and $\Gamma_n$, respectively while $\Gamma_m$ is the sample metal surface. If we ignore the ion distribution in the electrolyte, the electropotential within the electrolyte, $\phi$, obeys the Laplace's equation:

$$\kappa \nabla^2 \phi = 0 \quad \text{in} \Omega$$  \hspace{1cm} (1)

where $\kappa$ denotes the conductivity of the electrolyte. The density of current across the boundary, $q$, is related to the potential as

$$q = \kappa \frac{\partial \phi}{\partial n}$$  \hspace{1cm} (2)

where $\partial/\partial n$ is the outward normal derivative.

The boundary conditions are given by

$$\phi = \phi_0 \quad \text{on} \quad \Gamma_d$$  \hspace{1cm} (3)

$$q = q_0 \quad \text{on} \quad \Gamma_n$$  \hspace{1cm} (4)

$$\phi = f(q) \quad \text{on} \quad \Gamma_m$$  \hspace{1cm} (5)

where $\phi_0$ and $q_0$ are the prescribed values of potential and current density, respectively. The nonlinear function $\phi = f(q)$ represents polarization curve.
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Electrolyte surface

Cathode (Line element) Anode (Line element) Vessel wall

Figure 3: Boundary elements for the 1st stage analysis.

Figure 4: Boundary elements for the 2nd stage analysis.

3 Analysis method

Following the ordinary boundary element formulation, we derive the boundary integral equation from equation (1):

\[ \kappa \phi = \int_\Gamma \phi^* q d\Gamma - \int_\Gamma q^* \phi d\Gamma \]  

(6)

where \( \phi^* \) is a fundamental solution. Then, the boundary \( \Gamma \) is discretized to the boundary elements and we can get the following simultaneous equations:

\[ \frac{1}{\kappa} Gq - H\phi = 0 \]  

(7)

where \( \phi \) and \( q \) are vectors that are composed by nodal values of \( \phi \) and \( q \), respectively. \( G \) and \( H \) are the known matrices determined by the boundary shape and size. As described above, it takes a huge amount of calculation to analyze electric field of SVET. We propose a method that divides the analysis into three stages to perform the calculation effectively.

3.1 Three-stage analysis

In order to analyze the area of interest, the total current from sample surface must be known. If the domain is assumed to be infinite, we cannot take account of the shape of the vessel and cannot get accurate total current.

In the first stage, taking the vessel shape into account, we analyze the electric field roughly using the mesh as shown in figure 3, which contains line-shaped elements. A description of the line-shaped element is given in section 3.2. There are no mesh wall regions in figure 4, because we make use of mirror image.

In the second stage, the line-shaped elements which are located near the sensor probe are replaced by ordinary face elements, as shown in figure 4. Equation (6) can now be written as follows,

\[ \kappa c_i \phi_i - \int_{\Gamma_{st.2}} \phi^* q d\Gamma + \int_{\Gamma_{st.2}} q^* \phi d\Gamma = \int_{\Gamma_{st.1-st.2}} \phi^* q d\Gamma - \int_{\Gamma_{st.1-st.2}} q^* \phi d\Gamma \]  

(8)
where \( \Gamma_{st.1} \) and \( \Gamma_{st.2} \) are each domain of the first and second stages as shown in figures 3 and 4. The right-hand side of the above equation is already known. Hence the equation can be solved and \( \phi \) and \( q \) of the face elements are obtained.

In the third stage, the effect of sensor probe is considered. The area just below the sensor probe is discretized with fine face elements as shown in figure 5. Similarly to the equation (8), the values obtained in the first and second stages are put into the right-hand side of the following equation as known terms,

\[
\kappa c_i \phi_i - \int_{\Gamma_{st.3}} \phi^* q \, d\Gamma + \int_{\Gamma_{st.3}} q^* \phi \, d\Gamma = \int_{\Gamma_{st.1-st.2}} \phi^* q \, d\Gamma - \int_{\Gamma_{st.1-st.2}} q^* \phi \, d\Gamma + \int_{\Gamma_{st.2-st.3}} \phi^* q \, d\Gamma - \int_{\Gamma_{st.2-st.3}} q^* \phi \, d\Gamma
\]

where \( \Gamma_{st.3} \) is the domain of the third stage.

Using this method, a huge number of elements can be reduced. Besides, it needs iteration only in the third stage to consider the scanning probe.
Then it become possible to reduce much amount of calculation time. As shown in figure 6, in the conventional BEM the large matrix is solved at one time, while in this method, the large matrix is divided into three small parts.

3.2 Approximate analysis of slender current source

We approximated slender structures as line-shaped current source which has circle-shaped cross section of radius \( r \) as shown in figure 7. Each matrix components \( h_{ij} \) and \( g_{ij} \) of equation (7) can be written as follows by this approximation.

\[
\begin{align*}
c_i &= 1 \\
h_{ij} &= 0 \\
g_{ij} &= \frac{2\pi a}{4\pi r} dl \\
g_{ii} &= \frac{1}{4\pi r} d\Gamma
\end{align*}
\]  

where \( l \) is the length of the line element and \( \Gamma \) is the surface of the element.

In this study, slender rectangle-shaped current sources are treated, and the current changes remarkably along the width-direction as shown in figure 8, so that the above approximation become inaccurate. In order to improve the accuracy, we develop a new line-shaped element. Let us consider a rectangular plate with width \( 2c \) (x-direction) and length \( 2b \) (y-direction). Since we make use of mirror image as described above, we assume that current flows from both sides of the plate.

When the poralization can be neglected, current distribution is give by following equation,

\[
q(x, \bar{q}) = \frac{2c\bar{q}}{\pi \sqrt{c^2 - x^2}}
\]
where \( \bar{q} \) is the average of the current density. Then each matrix components of the line-shaped element with length \( 2b \) are given as follows.

\[
\begin{align*}
\mathbf{c}_i &= 1 \\
\mathbf{h}_{ij} &= 0 \\
\mathbf{g}_{ij} &= \int_{l_j} \frac{2c \times 2}{4\pi r} \, dl \\
\mathbf{g}_{ii} &= \frac{2c \times 2}{\pi^2} \int_0^c \int_0^b \frac{1}{\sqrt{x^2 + y^2}} \frac{1}{\sqrt{c^2 - x^2}} \, dy \, dx 
\end{align*}
\]

When the penalization cannot be neglected, equations (15), (16) and (17) are available, but there are no analytic solution like equation (14). We have to know current density distribution along x-direction. Functions \( \phi(x, \bar{q}) \) and \( q(x, \bar{q}) \) are obtained by 2-dimensional analysis in a infinite domain. These functions are nonlinear with respect to \( \bar{q} \) and it is impossible to have expressions like equation (18). So that we rewrite equation (6) as follows.

\[
\kappa \phi_i(0, \bar{q}_i) - \int \int_{\Gamma_i} \phi^* q_i(x_i, \bar{q}_i) \, dx \, dy = \int_{\Gamma_i} \phi^* q \, d\Gamma - \int_{\Gamma_i} q^* \phi \, d\Gamma
\]

The left-hand side of this integral equation is regarded as a function of \( \bar{q} \) and plays a role of \( \mathbf{g}_{ii} \cdot \bar{q} \). Then the nonlinear simultaneous equations are solved by Newton-Raphson method, and the average current densities of each line-shaped elements can be obtained.

### 3.3 Approximation of boundary integral \( \int_\Gamma q^* \phi \, d\Gamma \)

The fundamental solution \( \phi^* \) and its derivative \( q^* \) in equation (6) is described as follows.

\[
\begin{align*}
\phi^* &= \frac{1}{4\pi r} = O(r^{-1}) \\
q^* &= \kappa \frac{\partial \phi^*}{\partial n} = O(r^{-2})
\end{align*}
\]

The second term of the right-hand side of equation (6) are not sensitive to the position of observation points when the observation points are away from the source point. After the second stage, the boundary integral, \( \int_\Gamma q^* \phi \, d\Gamma \), in the first stage area which is away from the area of interest can be approximated as follows. Instead of each source points of elements, the center of the area of interest (this position is written by \( y_{center} \)) can be used as each source points. In short, it is expressed as follows.

\[
\begin{align*}
\mathbf{h}_{ij} &= h_{centerj} \\
h_{centerj} &= \int_{\Gamma_j} q^*(x, y_{center}) \, d\Gamma(x)
\end{align*}
\]

Then the boundary integrals which need much calculation time are reduced.
Figure 9: Polarization curve of the sample.

Figure 10: Calculated potential difference without polarization.

Figure 11: Calculated potential difference with polarization.

4 Results

Let us consider a measurement, where the current flows out from the sample to the cathodic counter electrode. The sample has a metal foil of $10\mu m$ thickness between insulators.

Two cases are considered. One is the case where the sample has no polarization, i.e. the potential of the surface is constant. Another is the case where the polarization characteristics of the sample is shown in figure 9. As shown in figures 3-5, the mesh has 247, 30 and 289 elements in the first, the second and the third stages respectively. In order to ascertain the validity of this method, the conventional BEM is also performed. In this case, the mesh has 715 elements.

The sensor probe vibrates between $10\mu m$ and $30\mu m$ above the sample surface. The results which corresponds to the measurement data are shown as symbols ($\circ, \Box$) in figures 10 and 11 for both cases. The broken lines in both figures represent the result without the sensor probe disturbance. Figures 12 and 13 show the current distribution on the sample with and
without a sensor probe respectively. It is found that the measurement overestimates the electric field by the disturbance. It is also found that good agreements are achieved between the conventional method and the present method. Computation time was reduced to 1/15 by proposed method.

5 Concluding remarks

In order to analyze the electric field disturbance due to the sensor probe, a new effective BEM is developed. This method agrees well with the conventional method and the computation time was reduced 1/15. It is found that the SVET overestimates the electric field due to the sensor probe.

Although the disturbance due to a sensor probe is considered in this study, the composition of the electrolyte near the sample surface deviates from the bulk's and that also disturbs the electric field. Further study would be necessary to estimate the effect of this phenomenon.

Reference