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May 1980

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PREDICTION OF WORK PIECE GEOMETRY IN
ELECTROCHEMICAL CAVITY SINKING

J. B. Riggs, R. H. Muller and C. W. Tobias

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Berkeley, California 94720

May 1980

ABSTRACT

A computer-implemented model for predicting ECM work piece geometry
has been developed and experimentally verified with a commercial ECM machine
for cavity sinking in copper and 302-stainless steel with 2N KNO₃ electrolyte. Constant tool piece feed rates of 7 - 10 x 10⁻⁴ cm/sec, and applied
voltages of 11 to 25 volts were used. The model predicts the dependence
of work piece geometry on operating conditions and on the electrochemical
and physical properties of the metal-electrolyte pair. Comparison of
eight equilibrium and six unsteady state experimental cavity profiles in
copper showed satisfactory agreement with predictions, as did five equili-
brum profiles for cavity sinking in 302-stainless steel.

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1. **INTRODUCTION**

Electrochemical machining (ECM) involves the shaping of metals by high-rate anodic dissolution. One of the major difficulties associated with the implementation of ECM is the trial-and-error procedure currently used in practice to determine the tool shape and to define process conditions required for a desired cut geometry.

Some of the first modeling efforts\(^{(1,2,3)}\) were concerned with predicting the effect of temperature change and gas evolution on the geometry of the frontal gap. These analyses assumed uniform current efficiency and neglected electrode overpotential effects.

Loutrel and Cook\(^{(4,5)}\) developed a numerical model for the electrochemical machining of a parallel-plate system which appears to consider all the relevant factors affecting the frontal equilibrium ECM gap. Because of the ill-defined inlet and outlet boundary conditions of their system, the experimental results exhibited large deviations from the model predictions in the entrance and exit regions.

A novel mathematical tool piece design procedure which involves a coordinate transformation has been formulated by Nilson and Tsuei\(^{(6)}\). Tsuei, et al.\(^{(7)}\) presented a comparison between model and experiment for the prediction of the combined frontal gap and side gap regions of a cavity profile. They neglected the temperature change of the electrolyte and electrode polarization in their analysis. Although these individual effects are not insignificant, their combined effect on model predictions was small because they appear to have compensated each other. An investigation by Tsuei and Nilson\(^{(8)}\) of the effect of electrolyte conductivity on side gap geometry also assumes constant electrolyte conductivity and neglects electrode polarization.
An approximate analytic analysis of the primary electric field distribution in an electrochemical machining gap has been presented by Rasmussen \(^9\). Ippolito and Fasolio \(^10\) pointed out the importance of cutting rate on side gap taper and suggested in-plant measurement of electrolyte conductivity.

Koenig and Huembs \(^11\) presented a model for calculating the frontal and side gap. Their method was based upon experimental data for current efficiency as a function of current density and electrolyte temperature. Their model showed excellent agreement with experiment although many electrochemical factors such as current-dependent voltage losses at the electrode surfaces, IR drop in surface films, reversible electrode potential, charge transfer overpotential, or the variation in electrolyte conductivity caused by changes in temperature, concentration and gas content were not considered.

This study sought to develop a computer-implemented model for a complete ECM cavity profile and to experimentally verify it by electrochemically sinking cavities with a commercial ECM machine. A cylindrically symmetrical tool piece was chosen because it provided a two-dimensional problem for the model and it could be easily constructed. The model was implemented by a finite difference solution of the Laplace equation for cylindrical coordinates, taking into account temperature effects, electrode polarization, gas evolution and current efficiency. To verify the model, copper and 302-stainless steel were electrochemically machined over a range of operating conditions and with two different tool piece geometries, using a 2N KNO\(_3\) electrolyte.
2. **FUNDAMENTALS**

Under ECM conditions, the solution-side electric field distribution between the electrodes is described by the Laplace equation,

\[ \nabla^2 \phi = 0 \]  

(1)

As electrode boundary condition, the solution-side potential of an electrode is determined by the potential of the metal, \( \phi \), the reversible half-cell potential of the electrode reaction, \( \Delta \phi_{\text{rev}} \), the concentration overpotential, \( \Delta \phi_{\text{conc}} \), the charge transfer overpotential, \( \Delta \phi_{\text{ct}} \), and a possible potential loss in resistive electrode films, \( \Delta \phi_{\text{film}} \). For an anode, the solution-side potential \( \phi_{SS}^a \) is thus given by:

\[ \phi_{SS}^a = \phi^a - \Delta \phi_{\text{rev}}^a - \Delta \phi_{\text{conc}}^a - \Delta \phi_{\text{ct}}^a - \Delta \phi_{\text{film}}^a \]  

(2)

A similar expression can be written for the potential on the solution-side of a cathode. The applied cell voltage, \( \Delta \phi_{\text{appl}} \), is the sum of the ohmic potential drop in the solution, \( \Delta \phi_\Omega \), and the potential drops at both electrodes.

\[ \Delta \phi_{\text{appl}} = \Delta \phi_\Omega + \Delta \phi_{\text{rev}} + \Delta \phi_{\text{conc}} + \Delta \phi_{\text{ct}} + \Delta \phi_{\text{film}} \]  

(3)

Determination of the terms in equation (3) will be discussed in Section 3.

After the potential distribution in the interelectrode space has been determined from Laplace's equation with the proper boundary conditions, the current distribution on the electrodes is calculated from the derivative of the potential \( \phi \) in the direction \( N \) normal to the electrode surface.

\[ i_s = -\kappa \frac{\partial \phi}{\partial N} \]  

(4)

The local current density \( i \) and the Faradic efficiency \( \eta \) of the anode reaction determine the local dissolution rate of the work piece.
during ECM. The rate of recession of the anode surface due to dissolution is

\[
\text{rate of recession} = \frac{1}{nF\rho} \text{ cm/sec.} \quad (5)
\]

The current efficiency, \( \eta \), is the fraction of the total current involved in the dissolution of the metal to form products of valence \( n \). For metals which simultaneously dissolve with multiple valences, an average (effective) valence, that may depend on current density and mass transport conditions, has to be used.

3. THEORETICAL MODEL

3.1 General Approach

A theoretical model was developed to predict the ECM work piece geometry from the operating conditions and the electrochemical characteristics of the system. The operating conditions considered include the tool piece feed rate, applied voltage, electrolyte concentration and inlet temperature. The model takes into account the effect of electrode potentials and overvoltages and variations in electrolyte conductivity caused by cathodic gas evolution and ohmic heating on the shape of the work piece.

Equilibrium ECM geometries were calculated by simulating the cutting process over sufficiently long periods to reach steady-state frontal geometries. Incremental shape changes in the work piece were determined from the current distribution along the work piece and a chosen time step.

3.2 Numerical Solution of the Laplace Equation

For the solution of the Laplace equation in finite difference form, the space between tool and work piece was divided into 10 regions
(blocks), as shown in Figure 1. This approach makes it possible to map regions with sharp local changes in potential (e.g. block 7) with more closely spaced grid points than regions of more gradual change (e.g. block 6). The dotted region along the outside of the tool piece designates an insulating coating of negligible thickness. The outside shape of the tool may also be straight cylindrical, without the lip opposite block 8. The top of blocks 1 and 10, as well as the center line, are treated as insulating boundaries.

The potential distribution in the inter-electrode gap is determined by use of a recursion relation for cylindrical coordinates with an iterative procedure employing an overrelaxation factor of 1.7. Fleck, et al. (12) have presented a comprehensive study of convergence in the numerical solution of the Laplace equation with special emphasis on the optimum overrelaxation factor, which was found to be 1.6 to 1.9. Convergence was assumed when each potential had a relative change between iterations of less than $10^{-6}$. This high degree of accuracy for the potentials was required to insure satisfactory values for the anodic current density which is determined from the numerical derivative of the potential.

The solution of the Laplace equation to obtain the first cut profile required between 300 to 600 iterations. For each subsequent time step, only 100 to 150 iterations were needed, because the potential distribution of the preceding profile was used for the initial estimate, which was closer to the solution than the first guess.

The calculation of an equilibrium ECM profile required approximately 150 time steps which corresponds to about 1000 seconds of computing time on a CDC 7600 computer. The program which implemented the model required storage of about 160,000 bits (Octal). Time steps (3 to 5 seconds) were chosen such that the tool piece was advanced by a
prescribed fraction (5 to 15%) of the frontal gap. Time steps greater than 25 seconds usually resulted in the amplification of errors in the calculation of anode currents in block 6. These currents would oscillate about the equilibrium frontal gap current with increasing amplitude.

Four types of boundaries are present in this problem: insulator, centerline, cathode and anode. The anode and cathode boundary conditions are determined from expressions for charge transfer overpotential, as discussed below. There are several ways in which to calculate the potential at the outside corner of the tool piece, the point shared by blocks 6, 7 and 8: as a cathode point, an insulator in the radial direction, or as an insulator in the axial direction. The cavity diameters, as predicted by each of these methods, are different. For the tool pieces used in the experiments, the proper corner potential was found to be the average of treating the point as a cathode point and treating it as an insulator in the radial direction. This procedure was used for all model predictions.

Converged numerical solutions contain a residual error in potential of the order of $h^2$ where $h$ is the grid spacing. The local current density at the electrodes is calculated by a three-point formula for the derivative of the potential normal to the electrode surface.

3.3 Voltage Drop in Electrolyte

The dependence of electrolyte conductivity on temperature and gas void fraction was modeled by equation (6),

$$\kappa = \kappa_{18} \exp \left[ 0.0204 (T - 18) \right] (1 - \varepsilon)^{1.5}. \quad (6)$$

Concentration and temperature dependence had been determined experimentally. Variations in the conductivity have been assumed to occur only in the flow direction, with the effects of gas evolution and temperature change being...
averaged over each cross-section of the electrode gap normal to the flow.

The temperature change of the electrolyte, as it moves from the peak to the side gap (figure 1, blocks 1 to 10), has been apportioned from the experimentally determined inlet and outlet temperatures according to the fraction of the total current that has passed across the electrode gap upstream of the position under consideration.

The gas void fraction has similarly been calculated from the cumulative rate of gas production at the cathode upstream from the cross-section under consideration on the basis of current density distribution and by assuming that the gas behaves as an ideal gas. The effect of local electrolyte pressure on void fraction needs to be taken into account only when the gas volume fraction becomes significant. The cathodic reaction involves both the reduction of the nitrate ion and of water. Although the exact proportion of these competing reactions is not known, it was assumed in this study, that half of the cathodic current is used for hydrogen evolution\(^{(15)}\). The uncertainty in this assumption has only a small effect on the model prediction of the conductivity.

3.4 **Estimation of Other Voltage Drops**

Estimates of the charge transfer overpotential for cathodic and anodic reactions were obtained by use of Tafel equation\(^{(16,17)}\)

\[
\Delta \Phi_{ct} = \beta \ln \left( \frac{i}{i_0} \right), \tag{7}
\]

with parameters given in the literature for similar systems. The Tafel parameters for copper were estimated from previous work\(^{(18)}\) on the high-rate anodic dissolution of copper in acid \(K_2SO_4\), while those for 302-SS were estimated from a study\(^{(19)}\) done on iron dissolution in chloride solution.
Tafel parameters for the principal cathodic reaction, hydrogen evolution, were taken from the literature (16). The cathodic reaction is, however, complicated by the fact that it involves the reduction of the nitrate ion in addition to hydrogen evolution. Parameters used for the computation of charge transfer overpotentials are listed in Table I.

The reversible cell potential $\Delta\phi_{\text{rev}}$ (eq. 3) represents the sum of the half-cell potentials of both electrodes and can be derived from the thermodynamic free energy of the overall cell reaction.

Even with a judicious choice of materials and operating conditions, not all the electrochemical data required by the model are available in the literature. The following procedure has therefore been applied to generate the necessary data: The sum of the reversible cell potential, concentration overpotential and potential drop through electrode films was deduced from equilibrium profiles of calibration experiments (runs 84, 86, 87 and 89 for Cu). As illustrated by Figure 2, the height of the central peak of the cut profile is very sensitive to the applied voltage. Typically, a 0.1V change results in a change in peak height by 1%. Model predictions of work piece geometries were made by use of the Tafel parameters and an additional, current-independent uniform potential drop at the electrodes. The value of this potential drop was varied in the model until the predicted peak heights agreed with the peak heights that were obtained experimentally for the four calibration runs. The additional potential drop thus determined (1.5V for copper under active dissolution and 2.53V for stainless steel) were used in all subsequent computations. In Appendix A it is shown that the above value for copper can be reasonably accounted for by its component parts.
3.5 Simplification of Computations

In order to keep the computational effort within acceptable limits, several simplifications were employed in the implementation of the theoretical model.

As would be expected, the current density is found to be relatively uniform for the anode surface in blocks 3-6 (Fig. 1). The activation overpotential for copper dissolution was therefore assumed to be a constant, 0.55V (corresponding to an average current density of 25 A/cm²) for this region. For blocks 7-10, where local current density varies greatly, the anodic charge transfer overpotential was determined locally by use of the Tafel equation, as prescribed by the model.

The activation overpotential of the cathode was determined for the whole electrode segment in each block, based on the average current density in that segment and the Tafel parameters for the cathode reaction. The distribution of cathodic activation overpotential and current density thus determined is given in Table II for a typical profile with a large center peak.

The distribution of anode and cathode potentials, resulting from the step-wise representation of charge transfer overpotential for blocks 1 through 6, and Tafel kinetics for blocks 7 through 10, is illustrated in Figures 3 and 4 for small and large center peak. Current density and charge transfer overpotential at the cathode increase with increasing peak height for blocks 1 through 3.

The steplike approximation for taking cathodic charge transfer overpotential into account, rather than applying Tafel kinetics to each electrode surface element (grid point on the electrode) to represent a continuous function, has been found to reduce the number of iterations for a converged solution by about a factor of four. The predicted work piece
geometry obtained by this approximate method for run 84 (Fig. 3) has shown no noticeable difference from that obtained by use of the Tafel expression for each surface element.

4. EXPERIMENTAL

4.1 Selection of Work Piece Material and Operating Conditions

For the comparison of computed work piece profiles with experimental profiles, metal-electrolyte combinations were employed for which at least some of the input parameters for the computations had been determined previously.

The copper-KNO$_3$ system was chosen because of earlier work conducted in this laboratory$^{(18,20,21)}$ with this metal-electrolyte pair. Because of a lack of quantitative data on the properties of anodic films formed during transpassive dissolution, the operating conditions for the electrochemical machining of copper were adjusted to avoid any part of the anode being in the transpassive region. For this purpose, the electrolytic flow was maintained as high as possible (300-400 cc/sec) and the tool piece feed rate was not allowed to exceed $1.3 \times 10^{-3}$ cm/sec. Even with these restrictions, the theoretical frontal gap could be varied from 0.05 to 0.13 cm, resulting in a rather wide range of ECM cut profiles. The apparent valence of the dissolution process in the active regime, $n = 2$, has been shown before to be independent of current density$^{(20)}$. The use of high volumetric flow rates and relatively low current densities (20 to 35 A/cm$^2$ for copper) also circumvented the problem of modeling electrolyte conductivity at large gas void fractions.

The electrolyte concentration was held at about 2N KNO$_3$ ($\rho \approx 1.12$ g/cm$^3$) for all runs to avoid any effects that significant variations in electrolyte concentration might have on the course of electrode reactions. The applied voltage was varied from 11 to 25 volts.
Modeling of the machining of SS 302 was successful because this material demonstrated a reasonably constant current efficiency over the range of current densities considered. The apparent valence of dissolution (+3.8) was determined from cavity sinking experiments. This value indicates the occurrence of anodic side reactions, e.g., oxygen evolution.

Physical properties of the two anode materials used in the model are listed in Table III. Attempts at modeling a mild steel-nitrate system, in which current efficiency depends sharply on current density\(^{(22)}\), were unsuccessful because a quantitative description of the current efficiency as a function of current density, and its dependence on hydrodynamic conditions, were not available.

4.2 Equipment and Procedures

An 8-inch ECM Job Shop Gun Drill (Hanson-VanWinkle-Munning) was used to obtain the experimental cuts. The power system provided up to 25 volts and 500 amperes D.C.

The tool pieces were constructed from a 10 cm long section of brass rod usually 1.9 cm in diameter, and a 1 cm slice of a 5 cm diameter rod. The outside of the tools was coated with a 25 to 40 micron thick layer of Kynar\(^{\text{R}}\) vinylidene fluoride resin. Before each run, the inside part and the front end of the tool piece were polished on a lathe using 000 emery paper. Before each set of runs, the electrolyte system was cleaned and a fresh batch of electrolyte prepared.

After each run, the tool piece was inspected for insulation failure or formation of cathodic films. The work piece was milled to expose the cross-section of the cavity that had been electrochemically machined (Fig. 5). The cross-section was deburred using a small diameter circular file and then photographed (Polaroid Projection film type 46-L). The diameter of the cavity and the height of the peak that forms in the bottom
of the cavity were measured on the specimen using a Vernier caliper. The experimental ECM profile was traced on an enlarged projection of the photograph, using the independently measured cavity diameter for scale.

Experimental conditions and results obtained in steady-state cavity sinking and in cavity starting are listed for representative groups of runs in Tables IV and V, respectively.

5. RESULTS

5.1 Active Dissolution of Copper

Experimental ECM cavity profiles and those predicted by the model were compared for the steady-state and nonsteady-state electrochemical machining of copper. Equilibrium geometries were obtained for a 1.9 cm and a 1.27 cm diameter tool piece. All tool pieces used had a 0.63 cm internal diameter.

Representative comparisons between model and experiment are shown in Figure 6 for a 1.9 cm diameter tool piece with a 0.32 cm radius of curvature on the inside lip and in Figure 7 for a 1.27 cm diameter tool piece with a 0.16 cm radius inside lip.

5.2 Transient Cavity Profiles

In order to investigate transient ECM processes, two sets of cavity starting experiments were conducted by stopping the ECM process at different stages of cavity formation. In Figure 8, the experimental ECM profile from an early stage of cavity formation is compared with a model prediction. It demonstrates the initiation of the center peak, the establishment of a frontal gap and the rounding of the outside corner at the original work piece surface.

The transient development of cut profiles in cavity sinking, starting from a flat surface, and the unsteady state response of cavity
profiles to changes in applied voltage, tool advancement rate and electrolyte conductivity have been graphically demonstrated in a computer-generated motion picture\textsuperscript{(23)}.

5.3 Transpassive Dissolution of Copper

After the transient and steady-state modeling of the electrochemical machining of copper had been accomplished for conditions of active dissolution, the modeling of a cavity in which part of the metal is dissolving in the transpassive regime was attempted. For ECM cavity sinking in copper, the onset of transpassive dissolution is marked by the formation of a bright ring at the base of the peak (Fig. 9). The comparison between model and experiment for this cavity (Fig. 10) shows a good prediction by the model. The bright ring does not show as an anomaly on the profiles because with the high flow rate employed, the dissolution occurs just barely in the transpassive regime and the effect of the resistive transpassive film, which forms on the bright area, was apparently offset by the reduction in valence of dissolution\textsuperscript{(20)}.

Figure 11 shows an experimental profile for which the transition from transpassive to active dissolution is more obvious. Here, an extremely low electrolyte flow rate caused dissolution in the frontal gap to proceed deeply in the transpassive regime (probably due to lack of removal of reaction products from the anode surface). The frontal gap is much smaller than would be expected for active dissolution with the same applied voltage (extrapolation of the cut profile from the active region of the side gap). The smaller frontal gap results from the voltage losses in the anodic resistive film formed during transpassive dissolution\textsuperscript{(20,24,25)}. The right edge of region TT denotes the location where transpassive dissolution ends and high rate active dissolution begins. The region TT connects the cavity profile for active dissolution (A) with that for transpassive dissolution (T).
It would be extremely difficult to model this complex profile without precise information on the transpassive dissolution behavior of the metals, particularly the effects of hydrodynamics and current density on the onset of transpassive dissolution, and the resistance of the passive film.

5.4 Dissolution of 302-Stainless Steel

Equilibrium cavity profiles in 302 SS have been investigated with a 1.9 cm diameter tool piece. The applied voltage was varied from 20 to 26 volts, while the tool piece feed rate ranged from $7 \times 10^{-4}$ to $1 \times 10^{-3}$ cm/sec (runs 125 through 129). Figure 12 shows the comparison of an experimental profile with the theoretical prediction. The relatively high additional voltage drop of 2.53V, that had to be assumed for this prediction in order to obtain the proper height for the center peak, coupled with the observation of a bright surface on the peaks and the frontal gaps of cavities in 302 SS, indicates dissolution in the transpassive regime.

6. CONCLUSIONS

A numerical modeling procedure which involves the repetitive evaluation of the contour of moving boundaries has been shown to allow the prediction of entire work piece geometries over a range of operating conditions for cavity sinking in copper and 302-stainless steel. The computer implemented model was able to predict not only the shape of the front and side gap, but also the shape of the center peak for both equilibrium and unsteady-state cavity sinking operations. The precise modeling requires input data on the thermodynamic and kinetic behavior of metal-electrolyte pairs of greater accuracy and over wider ranges of conditions than are
presently available in the literature. There is a particularly serious lack of information on kinetic behavior at high current densities, on current efficiency, and on all dissolution parameters pertaining to the transpassive regime.

In the absence of adequate electrochemical data, relevant input parameters can be determined by computation from a series of calibration experiments. Although this procedure does not provide details on the reactions, it can furnish the valence of dissolution and the current-independent part of electrode potentials.

For the simple tool geometries considered here, it has been found possible to introduce approximations in the numerical analysis which greatly reduce the computational effort. The complete evaluation of more complex three-dimensional geometries of industrial interest would probably involve unreasonably high costs; only very large computers would have adequate speed and sufficiently large memory capacity for such an approach.
This work was supported by the Division of Materials Sciences, Office of Basic Energy Science, U. S. Department of Energy under contract No. W-7405-ENG-48.
REFERENCES


Table I. Parameters of the Tafel equation (Eq. 7) used for the estimation of activation overpotential, $\Delta \phi_{ct}$

<table>
<thead>
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<th>$\beta$ (V)</th>
<th>$i_o$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper anode</td>
<td>0.052</td>
<td>0.000063</td>
</tr>
<tr>
<td>SS 302 anode</td>
<td>0.066</td>
<td>0.001</td>
</tr>
<tr>
<td>Brass cathode</td>
<td>0.052</td>
<td>0.0000001</td>
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Table II. Activation overpotential and current density along the cathode surface

<table>
<thead>
<tr>
<th>Block Number</th>
<th>$\Delta \phi_{ct}$ (volts)</th>
<th>$i_{ave}$ (A/cm$^2$)</th>
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<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>0.85</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>0.95</td>
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</tr>
<tr>
<td>4</td>
<td>0.98</td>
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<td>5</td>
<td>1.0</td>
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</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>22.5</td>
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Table III. Properties of anode materials

<table>
<thead>
<tr>
<th></th>
<th>Copper</th>
<th>SS 302</th>
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<tbody>
<tr>
<td>Formula Weight, M</td>
<td>63.5</td>
<td>56.4</td>
</tr>
<tr>
<td>Density, $\rho$</td>
<td>9.4</td>
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<tr>
<td>Apparent Valence of Dissolution, $n$</td>
<td>+2</td>
<td>+3.8</td>
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### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>F</td>
<td>Faraday's constant (96500 coul/equivalent)</td>
</tr>
<tr>
<td>$F_r$</td>
<td>tool piece feed rate (cm/sec)</td>
</tr>
<tr>
<td>h</td>
<td>grid dimension (cm)</td>
</tr>
<tr>
<td>i</td>
<td>current density ($A/cm^2$)</td>
</tr>
<tr>
<td>$i_s$</td>
<td>current density at the surface ($A/cm^2$)</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight of anode metal (grams/mole)</td>
</tr>
<tr>
<td>n</td>
<td>valence of dissolution of anode metal</td>
</tr>
<tr>
<td>N</td>
<td>unit vector normal to electrode surface</td>
</tr>
<tr>
<td>T</td>
<td>electrolyte temperature ($°C$)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Tafel parameter (volt)</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>gas void fraction</td>
</tr>
<tr>
<td>$\eta$</td>
<td>current efficiency of anodic reaction</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>electrolyte conductivity ($\Omega^{-1}cm^{-1}$)</td>
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<td>$\kappa_{18}$</td>
<td>electrolyte conductivity at $18°C$ ($\Omega^{-1}cm^{-1}$)</td>
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<td>$\rho$</td>
<td>density ($g/cm^3$)</td>
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<tr>
<td>$\phi$</td>
<td>electric field potential (volt)</td>
</tr>
<tr>
<td>$\phi^a$</td>
<td>potential in anode metal</td>
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<tr>
<td>$\phi^a_{rev}$</td>
<td>reversible half-cell potential of anode reaction (volt)</td>
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<td>$\Delta\phi_{appl}$</td>
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<tr>
<td>$\Delta\phi_{ct}$</td>
<td>charge transfer activation overpotential (volt)</td>
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<tr>
<td>$\Delta\phi_{conc}$</td>
<td>concentration overpotential (volt)</td>
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<td>$\Delta\phi_{film}$</td>
<td>potential drop through electrode films (volt)</td>
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<tr>
<td>$\Delta\phi_{\Omega}$</td>
<td>ohmic potential drop in the electrolyte (volt)</td>
</tr>
<tr>
<td>$\Delta\phi$</td>
<td>reversible cell potential (volt)</td>
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FIGURE CAPTIONS

Figure 1 - Tool and work piece geometry. Identification of blocks in the inter-electrode gap used for the numerical solution of the Laplace Equation.

Figure 2 - Experimentally determined effect of applied voltage on equilibrium cavity profiles. Run 84, 21.2 volts; Run 86, 10.9 volts. (For other experimental data see Table IV.)

Figure 3 - Distribution of cathode and anode solution-side potentials (in volts) for run 84. Block numbers shown in italics. \( \Delta V_{\text{appl}} = 21.2 \text{ volts}, F_r = 8.05 \times 10^{-4} \text{ cm/s}. \) Tafel kinetics were used to determine anode solution-side potentials for blocks 7 through 10: \( \Delta \Phi_{\text{ct}} = 0.052 \ln (i/0.00063). \)

Figure 4 - Distribution of cathode and anode solution-side potentials (in volts) for run 15. Block numbers in italics. \( \Delta V_{\text{appl}} = 19.9 \text{ volts}, F_r = 12.28 \times 10^{-4} \text{ cm/s}. \) Tafel kinetics were used to determine anode solution-side potentials for blocks 7 through 10; \( \Delta \Phi_{\text{ct}} = 0.052 \ln (i/0.00063). \)

Figure 5 - Work piece after milling to expose cross-section of ECM cuts with different center peaks.

Figure 6 - Comparison between model and experiment. Equilibrium cavity profile using 1.90 cm diameter tool piece, copper, Run 86. (Table IV.)

Figure 7 - Comparison between model and experiment. Equilibrium cavity profile using 1.27 cm diameter tool piece, copper, Run 22. (Table IV.)

Figure 8 - Comparison between model and experiment for unsteady state cavity profile, tool piece diameter 1.85 cm, copper, Run 21. (Table V.)

Figure 9 - Cut-away view of cavity obtained in Run 15, (Table V). Arrow indicates bright ring formed by transpassive dissolution.
Figure 10 - Comparison between model and experiment for the onset of transpassive dissolution. Equilibrium cavity profile, 1.85 cm diameter tool piece, copper, Run 15. (Table IV.)

Figure 11 - Experimental equilibrium cavity profile resulting from localized active and transpassive dissolution. A - region of active dissolution, TT - region of transition between active and transpassive dissolution regions, T - region of transpassive dissolution; tool diameter - 1.73 cm, copper, Run 39. (Table IV.)

Figure 12 - Comparison between model and experiment for the dissolution of 302-stainless steel. Equilibrium cavity profile, 1.85 cm diameter tool piece, Run 125. (Table IV.)
Figure 1
Figure 3
Figure 4

MODEL

18.25

Cu

18.27
18.25
18.25
18.34
18.54
18.80

0.75
0.91
0.95
0.99
1.0
1.0
1.0

15

1
2
3
4

XBL 771-7217
Figure 6
Figure 8
APPENDIX A

Components of the Current Independent-Potential Drop

The additional voltage drop derived from the computed work piece contours by comparison with experimental calibration contours in section 3.5 represents the sum of reversible cell potential, concentration overpotential, possible potential drop through electrode films and any error in charge transfer overpotential resulting from the use of approximate Tafel parameters.

For copper dissolution in the active regime, only the first two contributing potentials are deemed important. For a possible overall reaction according to

\[ \text{Cu} + 2\text{H}_2\text{O} = \text{Cu(OH)}_2 + \text{H}_2, \]

the standard potential at 25°C is

\[ E^0 = 0.6V. \]

The pH of the electrolyte after discharge is normally between 10 and 11. It can therefore be assumed that the pH at the cathode would be greater than 11 and thus result in a concentration overpotential of at least 0.5V. The concentration overpotential at the anode may account for another 0.4V. The additional potential drop of 1.5V determined by computation from the calibration profiles is therefore reasonable.
## Summary of Experimental Data

**TABLE IV. Experimental data for equilibrium ECM profiles**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Work Piece Metal</th>
<th>Cavity Diam. (cm)</th>
<th>Peak Height (cm)</th>
<th>Tool Diam. (cm)</th>
<th>Soln. Density and Temperature (OC)</th>
<th>Tool Piece Feed Rate (cm/sec. x 10^4)</th>
<th>Inlet Temperature (OC)</th>
<th>Temperature Change (OC)</th>
<th>Total Current (A)</th>
<th>Applied Voltage (V)</th>
<th>Inlet Pressure (BARS)</th>
<th>Flow (cc/sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>Cu</td>
<td>2.14</td>
<td>0.264</td>
<td>1.90</td>
<td>1.1204/19.5</td>
<td>8.04</td>
<td>24.5</td>
<td>0.5</td>
<td>82</td>
<td>21.2</td>
<td>2.3</td>
<td>400</td>
</tr>
<tr>
<td>86</td>
<td>Cu</td>
<td>2.03</td>
<td>0.538</td>
<td>1.90</td>
<td>1.1195/22.0</td>
<td>7.54</td>
<td>26.2</td>
<td>0.8</td>
<td>69</td>
<td>10.8</td>
<td>3.9</td>
<td>330</td>
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<tr>
<td>87</td>
<td>Cu</td>
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<td>0.594</td>
<td>1.90</td>
<td>1.1195/22.0</td>
<td>10.24</td>
<td>25.9</td>
<td>0.6</td>
<td>89</td>
<td>12.4</td>
<td>3.9</td>
<td>340</td>
</tr>
<tr>
<td>89</td>
<td>Cu</td>
<td>2.05</td>
<td>0.444</td>
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<td>1.1201/20.0</td>
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<tr>
<td>39</td>
<td>Cu</td>
<td>2.60</td>
<td>---</td>
<td>1.73</td>
<td>1.12925/21.5</td>
<td>5.84</td>
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<td>1.1204/20.0</td>
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<td>118</td>
<td>20.5</td>
<td>3.7</td>
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<td>1.1204/20.0</td>
<td>7.62</td>
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<td>3.0</td>
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<td>1.1205/20.5</td>
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<td>155</td>
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<td>3.6</td>
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APPENDIX B (cont'd)

TABLE V. Experimental data for transient ECM profiles (cavity starting)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Work Piece</th>
<th>Start Point (cm above surface)</th>
<th>Stop Point (cm above surface)</th>
<th>Solution Density and Temp. (°C)</th>
<th>Tool Piece Feed Rate cm/sec. x 10^4</th>
<th>Inlet Temp. (°C)</th>
<th>Temp. Change (°C)</th>
<th>Applied Voltage</th>
<th>Inlet Pressure (BARS)</th>
<th>Flow cc/sec.</th>
<th>Tool Diameter (cm)</th>
</tr>
</thead>
<tbody>
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<td>Cu</td>
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<td>0.0635</td>
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<td>7.83</td>
<td>24.5</td>
<td>0.5</td>
<td>21.4</td>
<td>2.2</td>
<td>400</td>
<td>1.85</td>
</tr>
<tr>
<td>17</td>
<td>Cu</td>
<td>0.127</td>
<td>0.000</td>
<td>1.1200/20.0</td>
<td>7.83</td>
<td>24.5</td>
<td>0.5</td>
<td>21.4</td>
<td>2.2</td>
<td>400</td>
<td>1.85</td>
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<td>7.83</td>
<td>24.5</td>
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<td>1.1200/20.0</td>
<td>10.16</td>
<td>26.0</td>
<td>1.0</td>
<td>13.4</td>
<td>3.9</td>
<td>340</td>
<td>1.85</td>
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