3-D Adaptive Time Domain FEM Analysis of Current Distribution in an Acid-Copper Bath

S. Khorasani[1] and B. Rashidian*

In this paper, three-dimensional Finite Element Method in Time-Domain (FEMTD) has been used to solve the current distribution in an acid-copper bath. The effects of geometric figures on the electrode current distributions and deposited profiles have been studied. A powerful adaptive mesh generator has been carefully designed to meet the requirements on three-dimensional geometries. Almost all practical configurations, even discontinuities and very sharp features, are permitted. A mesh-deformation algorithm is used to follow the change of profiles in the time-domain. For this purpose, instead of becoming involved with complicated mathematical formulations, the morphing techniques of computer graphics have been utilized. The results are rendered to visualize the evolution of profiles, which has considerably simplified the interpretation of the program's output. Several examples have been analyzed numerically.

INTRODUCTION

Rapid growth in the application of electrochemical methods demands accurate analysis of these processes. Low cost and relatively thick metallic deposits could be quickly obtained via electroplating. Electropolishing, which could be considered as a reverse to electroplating, is found to be an invaluable approach to surface finishing.

The above methods can be applied with great success when simple geometries or thin deposits are concerned. For thick films, however, due to non-uniformity in electric current distribution over electrode surfaces, strong non-uniformities in deposits result in as high as a 1:20 difference in thickness [1]. Nevertheless, some small and large scale processes in micromachining and some other areas exist, in which thick treatments (deposition or etching) are involved and electrochemical methods still remain the fundamental solution. Examples of such applications are found in the growth of certain high aspect ratio structures for micro-motors and thick electroforms.

Several analytical and numerical approaches have already been proposed to estimate the current density distribution over the electrodes [2]. Most of these methods are restricted either to one or two dimensions.

Even those few, which have three-dimensional analysis capabilities, are limited to relatively simple geometries, without the ability to predict the time evolution of electrode profiles.

Mainly two competitive methods, the Finite Difference Method (FDM) [3] and Finite Element Method (FEM) [4], have been considered for this case. Both have been used in current distribution problems. The finite difference method is much simpler to implement, but is subjected to convergence problems for complex situations. The finite element method handles complex geometries well, if a powerful mesh generation be available and, as will be discussed later, its convergence is guaranteed in the problems considered here.

The finite element method has previously been applied in two [5] and three [6,7] dimensions but, in both cases, the interpretation of output data has been difficult. Another important concern in the design of a FEM package is the mesh generation method. Best results usually rely on adaptive schemes, which complicate the design of the mesh generator unit. The FEM method is also incompatible with time-domain problems, unless some effective mesh deformation is made available.

In this paper, a time-domain FEM tool has been developed. With the aid of new mesh deformation and automatic adaptive mesh generation modules, it can very efficiently analyze any desired geometrical configuration of electrodes and, also, the evolution of profiles in arbitrary time intervals. This CAD tool is also equipped with computer graphic techniques [8]

1. *Department of Electrical Engineering, Sharif University of Technology, Tehran, I.R. Iran.*

*. *Corresponding Author, Department of Electrical Engineering, Sharif University of Technology, Tehran, I.R. Iran.*

for rendering the results; this interesting approach has simplified the visualization and understanding of the process.

In the following section, the physical system is formulated as a Neumann problem with elliptic Partial Differential Equations (PDEs) and non-linear boundary conditions. Next, the basis and implementation of the numerical method are considered. Then, several examples are presented and, finally, a short conclusion is given.

ANALYTICAL FORMULATION

For an electrolytic system in the liquid steady-state and thermodynamic equilibrium, due to the quasi-neutrality of the electrolyte, the governing equation is the elliptic Laplace equation:

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

where Φ is the electrostatic potential. This equation can be used in the quasi-steady state approximation of the electrolytic cell, in which the boundaries of the system, i.e., electrode profiles, move gradually during electroplating or electropolishing processes. In the absence of transport, due to electrode kinetics or external circuits, this result remains true until the conditions of equilibrium or reversibility are broken. When deviation from reversibility is not so large, i.e., for low current densities, the Laplace equation can still be applied. This is due to the high collisionality in the electrolyte (as a dense, cold liquid plasma,) so that the energy distribution between ion species is nearly uniform and the quasi-neutrality condition is not broken. This is the situation of very low frequency phenomena, so that the displacement current $\partial \mathbf{D}/\partial t$ may be neglected. This situation is discussed in [9] and a general proof for the applicability of the Laplace equation is given in [10].

To complete the definition of the problem, a boundary condition in the form of known potential values or its normal derivative is required. When electrode kinetics are present in the electrolyte system, it may be shown, using theoretical studies [11,12], that the so-called Butler-Volmer equation describes the local current density over the electrode-electrolyte interface:

$$J = I_0 \Big\{ \exp[-\alpha_a z \mathrm{F}\eta/\mathrm{RT}] - \exp[(1-\alpha_a)z\mathrm{F}\eta/\mathrm{RT}] \Big\}, \tag{2}$$

where J is the current density, I_0 is the exchange current density, α_a is the anodic transfer ratio, R is the universal gas constant, T is the absolute temperature, F is the Faraday constant and η is the electrochemical overpotential. The direction of the current density vector, $\mathbf{J}$, is normal to the electrode-electrolyte interface

and is related to the electric potential Φ, according to:

$$\mathbf{J} = -\kappa \nabla \Phi, \tag{3}$$

where κ is the conductivity of the electrolyte.

Here, it is pointed out that the Butler-Volmer equation for electrode kinetics could not be applied to closed regions, simply because two electrodes with different potentials should not touch each other. However, an elliptic problem, such as the Laplace equation considered here, usually models an interior problem [13], i.e., problems with closed solution regions. In order to satisfy this criterion, the homogeneous boundary condition is applied over non-electrode boundaries, that is:

$$\nabla \Phi . \mathbf{n} = 0. \tag{4}$$

This condition guarantees that all of the anodic electric current reaches the cathode and, therefore, no leakage of electric current density lines exists, i.e., the conservation of mass and electric current is satisfied. In the numerical implementation, a current conservation of better than 2% is observed.

It is easily seen that the total mathematical formulation consists of a non-linear boundary condition of Neumann's type on electrodes (Equation 2), i.e., on the normal derivative of the unknown electric potential function and an elliptic PDE (Equation 1) with the homogenous boundary condition (Equation 4) on the rest of the solution region periphery.

A thorough practical study [14] of the electrode kinetics, with the aid of statistical models, shows that for the acid-copper bath, the following similar expression can be used instead of Equation 2, with the standard deviation of about 11% for current densities in the range of 1-400 A/mm^2:

$$\mathbf{J} = I_0 \Big\{ \exp[-\alpha_a z \mathrm{F}\eta/\mathrm{RT}] - \exp[\alpha_c z \mathrm{F}\eta/\mathrm{RT}] \Big\}. \tag{5}$$

Here, α_c is the cathodic transfer ratio and I_0 is the exchange current density. The same study gives approximate expressions to the conductivity, κ, and the exchange current density, I_0, of the solution:

$$\kappa = 0.011163 + 0.030798[\mathrm{CuSO_4}]$$
$$+ 0.423553[\mathrm{H_2SO_4}] - 0.045224[\mathrm{H_2SO_4}]^2$$
$$- 0.135359[\mathrm{H_2SO_4}][\mathrm{CuSO_4}]_{\mathrm{mho/cm}}$$

$$I_0 = i_0[\mathrm{Cu}]^\gamma \exp\Big\{ -\mu[\mathrm{H_2SO_4}] \Big\}, \tag{6}$$

in which the brackets stand for the molar concentration. The values for the parameters in Equations 5 and 6 are shown in Table 1 [14].

The mathematical formulation of an acid-copper electroplating bath is, thus, established in this way. In the next section the numerical solution of the problem is presented.

Table 1. Values of the parameters in Equations 5 and 6.

Parameter	Value
α_a	1.08
α_c	0.39
γ	0.67
μ	0.37
i_0	15.8 mA/cm^2

NUMERICAL METHOD

The family of finite element methods falls into two main categories: The variational or Rayleigh-Ritz method, which is used in this work, and the Weighted-Residual or Galerkin method. Here, the variational approach is considered due to its simpler implementation. Further discussion on this subject can be found in [4,13].

In the variational method, the main goal is to minimize a functional, usually as an integral, in terms of the coefficients (node values) of interpolating functions. The coefficients and interpolating functions will approximate the value of the unknown function at the nodes and entire solution domain, respectively (the piece-wise linear functions are the simplest case). When the solution region is in one or two dimensions, each of the continuous linear pieces, namely finite element, is in the form of lines or triangles, respectively. In three dimensions, the problem becomes more difficult, as the elements get the form of tetrahedrons. The solution region should, therefore, be properly subdivided into a complete set of constituting elements. This is the function of a mesh generation module, which has been specially designed for this work.

It could easily be shown that the minimization of the following functional is equivalent to the solution of the current distribution problem [9]:

$$I(\Phi) = \frac{1}{2}\iiint_\Omega |\nabla\Phi|^2 d\Omega$$

$$- \frac{I_0 \mathrm{RT}}{\kappa \mathrm{F}}\oint\oint_\Gamma \frac{-1}{\alpha_a}\exp\left[-\frac{\alpha_a \mathrm{F}(\Phi_M - \Phi)}{\mathrm{RT}}\right]$$

$$+ \frac{1}{\alpha_c}\exp\left[\frac{\alpha_c \mathrm{F}(\Phi_M - \Phi)}{\mathrm{RT}}\right]d\Gamma. \qquad (7)$$

Here, Φ and Φ_M are electrolyte and metal phase potentials, respectively. It is seen that the surface integral term represents the non-linear boundary condition, while the volume integral term represents the elliptic Laplace equation.

The unknown function is, then, approximated by piece-wise linear functions in each element and by applying the continuity condition at the vertices of the neighboring elements, or the so-called nodes. The non-linearity of the integrand in the surface integral makes the application of the numerical scheme very difficult, especially when three dimensions are involved

and a great deal of computation is necessary (iterative schemes are applied in these kinds of problem). A reasonable solution to this problem is to linearize the non-linear term by means of Taylor expansion, after which the functional in Equation 7 becomes:

$$I(\Phi) = \frac{1}{2}\iiint_\Omega |\nabla\Phi|^2 d\Omega$$

$$- \frac{I_0}{\kappa}(\alpha_a + \alpha_c)\oint\oint_\Gamma (\Phi_M - \Phi)d\Gamma. \qquad (8)$$

The above linearization is valid, as long as the current density is far from the limiting current density, which is typically of the order of 100 mA/mm^2 for most of the practical baths. Since an exponential term is to be approximated by this method, the accuracy may be easily estimated to be better than 4% for electrode overpotential of about 7 mV, which is equivalent to about 50 mA/cm^2. For samples having an area of several cm^2, therefore, the total bath current should not exceed a few 100 mA. More discussion on the validity of this approximation is presented in the next section.

The above minimization process using linear interpolations, leads to an algebraic, simultaneous, linear system of equations, which can be solved by several existing methods:

$$[K_{ij}][\Phi_j] = [f_i], \qquad (9)$$

where $[\Phi_j]$ is a vector of unknown potentials $\{\Phi_j, j = 1, 2, ..., n\}$ at the n nodes and $[K_{ij}]$ and $[f_i]$ are also the stiffness matrix and force column vector [4], respectively. The stiffness matrix is always sparse and symmetrical for variational methods. This feature has been considered in the development of the code, so that both the storage capacity and efficiency are improved significantly. For the present problem, with thousands of unknowns, this is an important advantage.

The conjugate-gradient algorithm [15] has been chosen to solve the system of equations. The convergence of this algorithm is guaranteed and is able to find the exact solution (limited to round-off errors) in, at most, n iterations for elliptic problems [16], where n is the number of unknowns. In practice, convergence to three decimal figures has been achieved within $n/100$ iterations.

The stiffness matrix and force vector are obtained from the superimposing of elementary parts $[K^e]$ and $[f^e]$ belonging to each element, with the e superscript standing for the index of element:

$$[K^e] = \frac{I_0(\alpha_a + \alpha_c)\mathrm{F}}{6\kappa \mathrm{RT}}\begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 2 \end{bmatrix}V^e, \qquad (10)$$

$$[f^e] = \frac{I_0(\alpha_a + \alpha_c)f\Phi_M}{3\kappa \mathrm{RT}}\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}A^e,$$

where V^e is the volume of the "e" hedronal element and A^e is the area of the "e" triangular boundary element on electrodes. The corresponding value for non-electrode boundary elements would be identically zero.

Justification for the sufficient accuracy of the linear formalism can be observed through several arguments: First of all, the application range of the Butler-Volmer kinetics is limited to the regions where the overpotential, η, could be approximated by the electrochemical overpotential, η_e, which occurs at low current densities [11]. For large current densities, the system actually enters the diffusion or transport limited regime, for which the results of the Butler-Volmer kinetics are far from those in practice. Secondly, only slowly developing processes, with low deposition rates, in which transport effects are negligible, have been of interest. Thirdly, analysis of highly non-linear regimes (with high current densities,) requires a further division of the solution region into electrolyte and two electrode double-layers (because the effect of this phenomenon would not be negligible here), which makes the problem extremely complex. In such situations, the numerical method usually becomes ineffective, in addition to developing severe convergence problems. Finally, the linearization of boundary conditions has been performed previously [6,7] and the overall magnitude of errors has been reported to be no more than 10%.

The deformation of all meshes is the next essential problem in the time stepping process. A very difficult and time-consuming approach is to rework the mesh generation. However, an efficient method has been designed for this case. An optimized 3-D Lagrange interpolation was developed over the velocity vectors. This interesting scheme enabled the monitoring of the deposition (or etching) rate and profile changes during a complete typical electroplating or electropolishing process. Some results of the program are demonstrated in the next section.

Using an Object-Oriented approach in the C^{++} language, the numerical method was successfully applied with reasonable computation time on a Pentium workstation. An optimized memory organization system managed 32 Megabytes of memory for more than 300,000 nodes in a single precision storage.

PROGRAM RESULTS

Typical installation of an electroplating bath is shown in Figure 1. The anode and cathode electrodes are above and below, respectively and the space between them is filled with a conducting liquid electrolyte. Cell voltage is applied to the electrodes with a positive polarity to the anode.
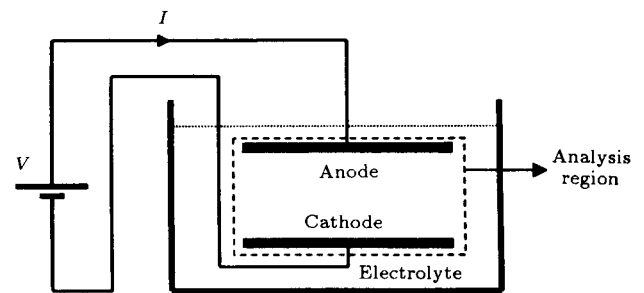
For an example of the adaptive mesh generation,

Figure 1. Typical electrolytic bath installation.

refer to Figure 2, where it can be seen that the meshing grids are finer near the regions with more concave or convex features (electroplating of the same object is represented in Figure 7).

To demonstrate the capabilities of the program, three basic defect structures, in the forms of concave edge, cylindrical and pin holes, have been simulated with flat anodic profiles (Figure 3). The dimensions for all figures are chosen as 10×10 cm^2 and the distance between anode and cathode is, also, 10 cm. The cell voltage is 10 Volts and the time step for this figure, as well as for the others, is 10 minutes. The anodic profile is removed in the rendering procedure, because it is of no special interest.

It can be seen that the bottom of the holes are exposed to much lower current densities and, therefore, to a much lower growth speed. In the case of a pin hole,
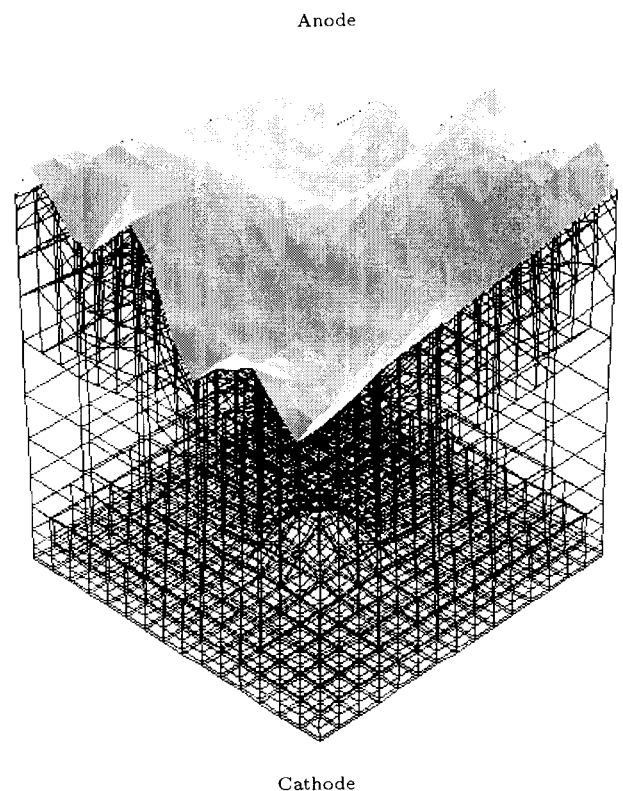

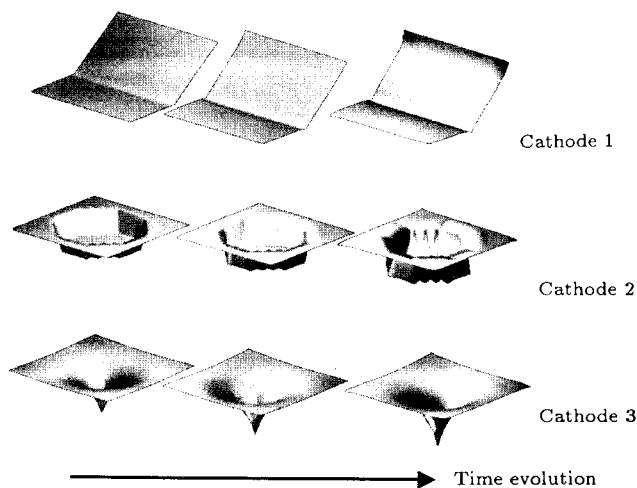**Figure 2.** Adaptive mesh generation.

Figure 3. Electroplating of concave features with dimensions $10 \times 10 \times 10$ cm^3 and time step 10 minutes.

in fact, the current density becomes zero. This clearly explains why such microscopic defects can cause large scale problems in thick deposits.

The same configurations for peaking defects, i.e., convex edge, cylindrical peak, etc. are demonstrated in Figure 4. In this case, it is expected that defects of the convex type will result in thick standing columns. The results could be compared with the prediction above. These types of defect grow rapidly in electroplating processes, leading to major problems.

To overcome these difficulties, the electropolishing process may be proposed. Notice that this process is not a thermodynamic reverse to electroplating, because electroplating is an irreversible process in non-equilibrium, thermodynamic conditions. Therefore, reversing cell polarity does not return us to the starting profiles. This situation is illustrated in Figures 5 and 6. Now, the situation is such that the cathode profile
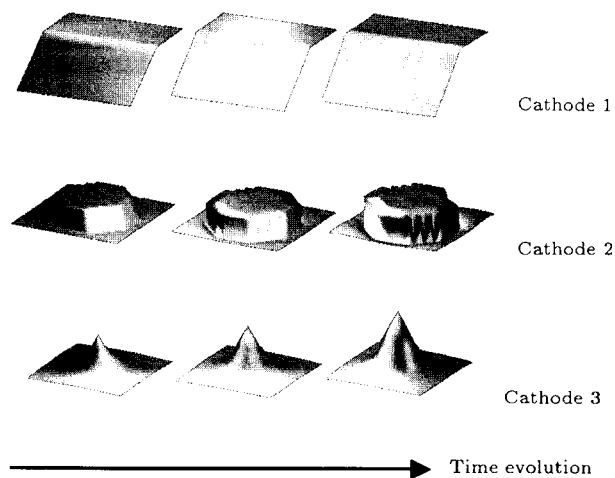

Figure 4. Electroplating of convex features with dimensions $10 \times 10 \times 10$ cm^3 and time step 10 minutes.
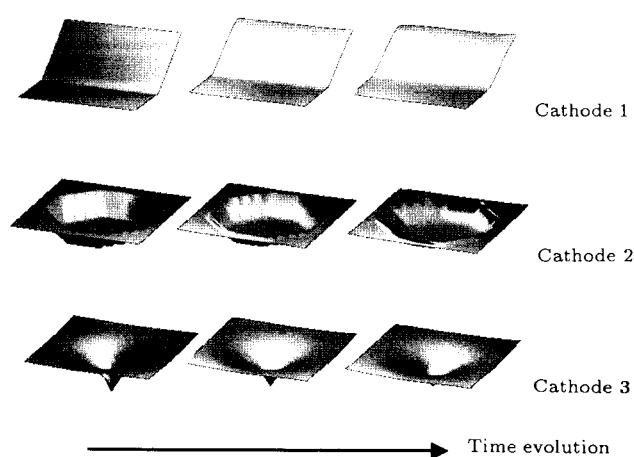

Figure 5. Electropolishing of concave features with dimensions $10 \times 10 \times 10$ cm^3 and time step 10 minutes.
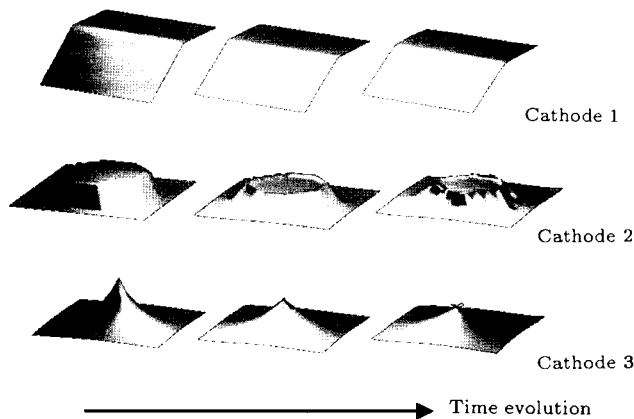

Figure 6. Electropolishing of convex features with dimensions $10 \times 10 \times 10$ cm^3 and time step 10 minutes.

tends to become flatter and the initial configuration can never be restored. This interesting concept forms the basis for the so-called periodic-reversed electroplating [17], which provides a much better uniformity in the deposit thickness compared to conventional methods. An optimization of this method as an instability production scheme demonstrates the possibility of obtaining relatively defectless deposits, with more than 1200 mm of thickness, including improved uniformity, adhesion, residual stress and brightness [18].

The results of electroplating two complicated geometries are presented in Figure 7 to illustrate the capabilities of this package (the dimensions and cell voltage are as before).

As a final remark, the total current and current density, respectively, vary proportionally and inversely proportionally to the cell dimensions, with the voltage staying the same. However, if the voltage is changed proportional to the cell dimensions, the current density will remain the same, while the square root of the total current would change proportionally.
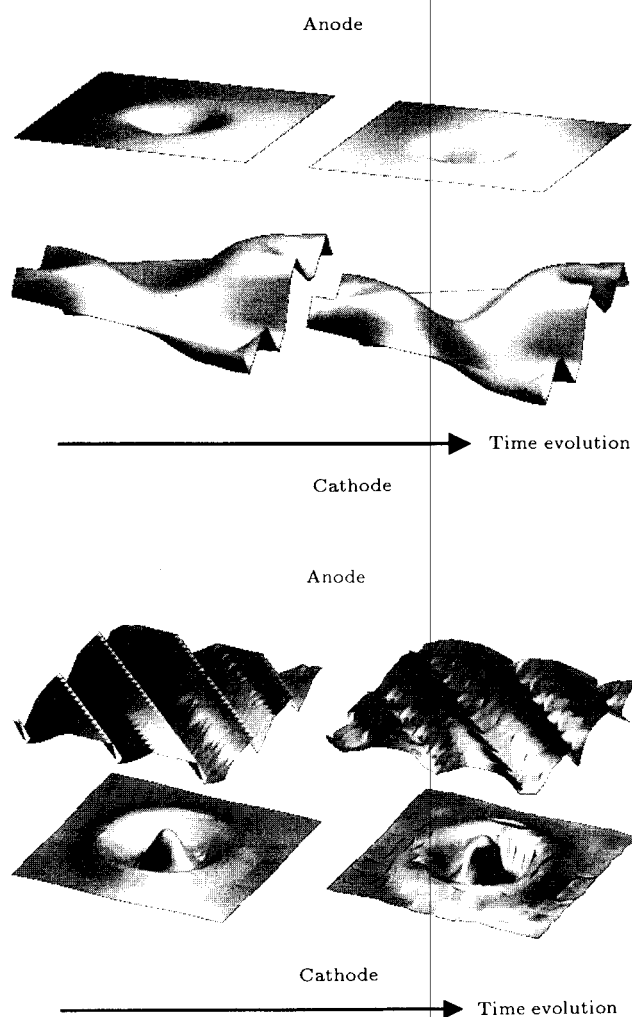
Figure 7. Electroplating of two complicated profiles with an anode electrode on top of each profile and with dimensions $10 \times 10 \times 10$ cm^3 and time step 10 minutes.

CONCLUSIONS

A powerful software package for current distribution problems in three dimensions has been developed, using the variational finite element method in time domain, for the study of growing defects. Two fully automatic mesh generators in adaptive and non-adaptive versions, have been designed and applied. The mesh generators produce finer grids near the electrodes, over which larger variations of electrostatic potential is expected. An efficient mesh deformation was designed to permit tracking changes in electrode profiles over the time domain, without needing to regenerate the meshes in the total solution domain at each time step. The output of the program is rendered by computer graphic techniques which simplifies visualization and interpretation of the results. Several examples of the program capabilities for various forms of defect have been demonstrated. It is possible to extend this work to other plating baths with minor modifications.

REFERENCES

1. Durney, L.J., Ed., *Electroplating Engineering Handbook*, 4th Ed., Van Nostrad, New York, p 52 (1984).

2. Prentice, G.A. and Tobias, C.W. "A survey of numerical methods and solutions for current distribution problems", *J. Electrochem Soc.*, **129**(1), pp 72-78 (1982).

3. Klingent, J.A., Lynn, S. and Tobias, C.W., *Electrochim. Acta*, **9**, p 297 (1964).

4. Zeinkiewics, O.C. and Taylor, R.L., *The Finite Element Method*, 4th Ed., McGraw-Hill, London, **1**, chap 9 (1989).

5. Morris, R. and Smyrl, W., *AIChE J.*, **34**, p 5 (1988).

6. White, R.E., Jagush, F. and Burney, H.S. "Three-dimensional current distributions in a bipolar chlor-alkali membrane cell", *J. Electrochem. Soc.*, **137**(6), pp 1846-1848 (1990).

7. Jagush, F., White, R.E. and Ryan, W.E. "Predicted secondary current distributions for linear kinetics in a modified three-dimensional Hull cell", *J. Electrochem. Soc.*, **137**(6), pp 1848-1851 (1990).

8. Rogers, D.F. and Adams, J.A., *Mathematical Elements for Computer Graphics*, McGraw-Hill, New York (1976).

9. Khorasani, S., *Field Analysis in Electrolytic Media*, M. Sc. Dissertation, Department of Electrical Engineering, Sharif University of Technology, Tehran, chap 4 (1997).

10. Darcy, E. and White, R., *J. Electrochem. Soc.*, **135**(1), p 3 (1988).

11. Antropov, L.I., *Theoretical Electrochemistry*, Mir Publishers, Moscow (1977).

12. Newman, J.S., *Electrochemical Systems*, Prentice-Hall, Inc., New York (1977).

13. Sadiku, M.N.O., *Numerical Techniques in Electromagnetics*, CRC Press, New York, chap 1 (1992).

14. Caban, R. and Chapman, T.W. "Statistical analysis of electrode kinetics measurements-copper deposition from $CuSO_4$-H_2SO_4 solutions", *J. Electrochem. Soc.*, **124**(9), p 1371 (1977).

15. Hamming, R.W., *Numerical Methods for Scientists and Engineers*, McGraw-Hill, New York (1962).

16. Hestenes, M.R. and Stiefel, E., *J. Res. Nat. Bur. Stand.*, **49**, p 409 (1982).

17. Durney, L.J., Ed., *Electroplating Engineering Handbook*, 4th Ed., Van Nostrad, New York, chap 24 (1984).

18. Khorasani, S. and Rashidian, B. "Optimization of electroplating via modern methods", *1st Iranian Nat. Conf. Non-fer. Metal.*, Sarcheshmeh, Iran, **2**, pp 593-602 (1996).