Effect of Tool-Electrode Shape on Uniformity of Electrochemical Deposition and Dissolution on Resistive Workpieces

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Abstract

This work is devoted to the theoretical study of the effect of tool-electrode shape and operating conditions on the thickness uniformity of deposited and dissolved metal layer on the resistive workpieces. The Laplace’s equation for the potential in the electrolyte solution, the Poisson’s equation for the potential in the resistive workpiece, and the equation of metal thickness evolution were used as the mathematical model. The numerical solution was performed using the boundary element and finite element methods. The results of computer modeling demonstrate the effect of operating conditions and tool-electrode shape on the uniformity of metal electrochemical deposition and dissolution.

Keywords: Electrochemical deposition and dissolution; Resistive workpiece; Numerical simulation

1. Introduction

Electrochemical deposition and dissolution of metals and alloys on the resistive workpieces are widely used in various industrial processes, for example, for fabricating thin films on printed circuits. A high ohmic resistance leads to the nonuniform deposition or dissolution over the workpiece surface. The problem of the effect of electrode resistance on the distribution of current density and, consequently, the uniformity of metal deposition or dissolution over the electrode surface has long been known [1, 2]. The phenomenon, sometimes referred to as the terminal effect, has been investigated by a number of authors for a variety of applications in several geometries: thin cylindrical wires [3], tubular electrodes [4], and flat plates [5, 6]. In the majority of published works, the distribution of current density during the metal electrodeposition on the substrate with a thin conducting layer was considered. In [7], the case of plane parallel resistive electrodes was studied theoretically in the one-dimensional approximation for various schemes of current leads arrangement, and the nonuniformity of the distribution of current density along the electrode length was estimated. The electrochemical systems with the electrodes of simple shape within one-dimensional approximation were considered in several works [8, 9]. At present, the effect of electrode resistance on the distribution of current density has been well studied for the electrodes of simple shapes (plane long electrodes, rectangular electrodes, cylindrical electrodes, and disk electrodes). Only in a small number of works, the electrodes of more complex shapes or the electrodes of rather simple shape, but with different types of boundary conditions on different surface areas (for example, in the case of partial insulation of electrode surface) were considered [10 - 12]. In contrast to the earlier works devoted to the electrochemical systems with the resistive electrodes, where only the distribution of current density was estimated, in the recent works, the dynamics of the metal deposit growth on the surface of resistive electrode of simple shape has been considered [13 - 15].

The electrode resistance has an effect not only on the metal deposition, but also on the anodic dissolution of long and thin-wall workpieces, for example, turbine and compressor blades, thinning of solar panels, or removal of defect layer of indium-tin oxide [16]. In addition, in the case of high-rate anodic
dissolution, the processes of heat and gas evolution can have an effect on the uniformity of distribution of current density [17].

The uniformity of the distribution of current density and, consequently, the thickness uniformity of deposited or dissolved metal layer over the substrate can be enhanced by using the shaped tool-electrodes. By now, the regularities of the effect of tool-electrode shape on the uniformity of electrochemical deposition and dissolution for the resistive substrates have not been adequately studied.

2. Mathematical model

Fig. 1 presents a scheme of the electrochemical cell with a resistive electrode. A dielectric annulus substrate 1 of inner radius \( r_0 \) and length \( L \) coated with a thin conductive metallic film 2, of thickness \( s_0 \) and conductivity \( x_0 \), acts as the resistive electrode for the cathodic deposition (a, b) or anodic dissolution (c, d). The tool-electrode (TE) 3 is located at a distance \( d \), and the region between the two electrodes, enclosed by concentric insulating walls, is filled with the electrolyte of conductivity \( s_F \). A current collector 4 is attached to the outer edge of the resistive electrode.

Due to the resistance of thin conducting layer, a potential drop develops along the electrode surface, causing the current lines to be more concentrated near the current collector. The resulting variation in the local current density leads to a variation in the thickness of the deposited 5 or dissolved 9 metal layers. To provide more uniform distribution of current density, curved TE 6 and/or insulating shields 8 can be used. In this case, a variation in the thickness of the deposited 7 or dissolved 10 metal layer can be reduced significantly.

The analysis is restricted to deposition or dissolution of a single metal at a current efficiency of 100%:

\[
M \rightarrow M^{\text{n-e}} + ne^-
\]

where \( M \) denotes a metal; \( n \) is the number of electrons, involved in the electrochemical reaction (1); and \( e^- \) denotes an electron.

Hereafter, it is assumed that stirring of the electrolyte is sufficient to maintain uniform electrolyte temperature and composition in the cell. In addition, the resistive electrode \( s(r,t) \) is considered to be thin as compared to the dimensions of the cell.

The current density \( i \) is determined from the local gradient of electric potential \( \phi \) in the solution by Ohm's law

\[
\mathbf{i} = -\mathbf{x}_{n} \nabla \phi
\]

where \( \mathbf{V} \) is the gradient operator; \( \mathbf{i} \) is the current density in the electrolyte solution; \( \mathbf{x}_{n} \) is the electric conductivity of the electrolyte solution; and \( \phi \) is the potential in the electrolyte solution.

The distribution of potential over the solution is determined from the charge conservation law for electroneutral medium:

\[
\nabla \cdot \mathbf{i} = 0
\]

The distribution of the current inside the resistive electrode is completely governed by ohmic charge transport. Due to the fact that a source term presents the current density of electrochemical reaction, the distribution of the current density over the resistive electrode can be described by the following equations:

\[
\mathbf{i}_n = -\mathbf{x}_{n} \nabla_T \phi_n
\]

\[
\nabla_T \cdot (s \mathbf{i}_n) = -i_s
\]

where \( \nabla_T \) is the tangential gradient operator; \( \mathbf{i}_n \) is the tangential current density along the electrode conductive layer; \( \mathbf{x}_{n} \) is the electric conductivity of the electrode conductive layer; \( \phi_n \) is the potential in the electrode conductive layer; and \( s \) is the thickness of the electrode conductive layer.

The current density \( \mathbf{i}_s \) is related to the current density in the electrolyte solution as follows:

\[
\mathbf{i}_s = -\mathbf{n} \cdot \mathbf{i}
\]

where \( \mathbf{n} \) is the normal vector to the boundary pointing into the electrode.

The rate of local variation of the metal thickness \( s(r,t) \) is simply calculated from Faraday’s law:

\[
\frac{ds}{dt} = \mathbf{i}_s \cdot \mathbf{n} \frac{F}{\rho}
\]
where $F$ is Faraday’s constant and $\rho$ is the molar density of deposited (dissolved) metal.

Along the insulating walls and insulating shield, no current flows in the electrolyte normally to the surface; this results in the following boundary conditions:

$$\nabla \Phi_n \cdot \mathbf{n}|_{\text{wb,sw}} = 0$$  \hspace{1cm} (8)

where IW and IS are subscripts denoting insulating walls and insulating shield, respectively.

Boundary conditions on the TE and resistive electrode are represented by the following equations:

$$\phi|_{\text{TE}} = 0$$  \hspace{1cm} (9)

$$\phi|_{\text{RE}} = \phi_n$$  \hspace{1cm} (10)

where TE and RE are subscripts denoting surfaces of tool-electrode ($z=\zeta_{\text{TE}}(r)$) and resistive electrode ($z=0$), respectively.

The boundary conditions for the resistive electrode are as follows:

$$\frac{\partial \phi_n}{\partial r}|_{r=0} = 0$$  \hspace{1cm} (11)

$$2\pi(r_0 + L)\frac{\partial \phi_n}{\partial r}|_{r=r_0} = \mp \pi \alpha (2r_0 + L) \eta_n$$  \hspace{1cm} (12)

where $\eta_n$ is the average current density over the resistive electrode; sign “−” corresponds to the deposition and “+”, to the dissolution of metal.

Equation (11) gives the condition of zero current passing through the left boundary of the resistive electrode (in the point $r=r_0$), and equation (12) expresses the equality of the currents passing through the right boundary of the resistive electrode and through the electrolyte solution.

The mathematical model involving equations (2) – (12) enables one to calculate the local variation of the thickness of metal layer on the resistive electrode. For convenient solution and analysis of the results, the mathematical model was presented in the dimensionless form. The length of resistive electrode ($L$) was taken as a unit length; the characteristic potential ($\alpha \Phi_n$), as a unit electric potential; the characteristic time ($nf_F^1$), as a unit time; the initial thickness of metal layer on the electrode ($\eta_0$), as a unit resistive electrode thickness; and the characteristic current density ($\eta_n$), as a unit current density:

$$R = \frac{r}{L}, \ Z = \frac{z}{L}, \ S = \frac{s}{s_0}, \ \Phi = \frac{s_0 Z_0}{l_0 L^2} \Phi, \ \eta = \frac{\eta_0}{n F \rho}, \ t = \frac{t}{n F \rho}$$  \hspace{1cm} (13)

Here $R, Z$ are the dimensionless coordinates; $S$ is the dimensionless thickness of metal layer on the resistive electrode; $\Phi$ is the dimensionless potential; $\eta$ is the dimensionless current density; and $t$ is the dimensionless time.

Passing to the dimensionless variables, the following system of equations is obtained:

$$\nabla \cdot (\nabla \Phi_n) = 0$$  \hspace{1cm} (14)

$$\nabla \cdot (\nabla \phi_n) = -I$$  \hspace{1cm} (15)

$$\frac{d \eta_n}{d t} = I$$  \hspace{1cm} (16)

where $I = -K_0 \frac{\partial \phi_n}{\partial Z}|_{r=0}$ is the dimensionless current density in electrolyte solution on the resistive electrode and $K_0 = \pi L \alpha L (\eta_0, \eta_n)$ is the dimensionless initial resistance of the resistive electrode.

Dimensionless boundary conditions for equations (14) and (15) are as follows:

$$\nabla \Phi_n \cdot \mathbf{n}|_{\text{wb,sw}} = 0$$  \hspace{1cm} (17)

$$\Phi|_{\text{TE}} = 0$$  \hspace{1cm} (18)

$$\Phi|_{\text{RE}} = \Phi_n$$  \hspace{1cm} (19)

$$\frac{\partial \phi_n}{\partial R}|_{r=0} = 0$$  \hspace{1cm} (20)

$$S \frac{\partial \phi_n}{\partial R}|_{r=r_0} = \mp 0.5 + \frac{R_n}{r + R_n}$$  \hspace{1cm} (21)

The initial condition for equation (16) is as follows:

$$S(R, \eta)|_{t=0} = 1$$  \hspace{1cm} (22)

For a straight TE and in the absence of insulating shield, the solution of system of equations (14) – (16) depends on three dimensionless parameters: the dimensionless initial resistance of resistive electrode ($K_0$); the dimensionless interelectrode distance ($D = d/L$); the dimensionless inner radius of resistive electrode ($R_n$) and the type of electrode process (metal deposition or dissolution), which determines the sign of the right-hand side of equation (21).

To provide the comparability of the results for the straight and curved TE, assume that an average interelectrode distance is equal to that of the straight electrode.

Assume that the surface of TE is prescribed by the following equation:

$$Z_m(R) = a R^2 + b R + c$$  \hspace{1cm} (23)

Parameters of equation (23) can be determined by the values of TE shift in the extreme points ($\Delta D_0 = \Delta d / L$; $\Delta D_1 = \Delta d / L$) and from the condition that an average gap is equal to the given value $D$:

$$Z_m(R_0) = D + \Delta D_0$$  \hspace{1cm} (24)

$$Z_m(R_0 + 1) = D + \Delta D_1$$

$$2 \pi \int_{R_0}^{R_0 + 1} Z_m(R) dR = \pi (R_0 + 1)^2 - R_0^2 \frac{D}{\Delta D_1}$$  \hspace{1cm} (24)

The solution of system of equations (24) is as follows:
Thus, in the case of curved TE, the solution of system of equations (14) – (16) additionally depends on two more dimensionless parameters \((\Delta D_1, \Delta D_2)\) that characterize the shape of tool-electrode.

In the presence of insulating shield \(L_{in} = h/L\) in length and \(H_{in} = h/L\) thick, which is located at a distance \(Z_{in} = z_{in}/L\) from the resistive electrode, there are three more dimensionless parameters \((L_{in}, H_{in}, Z_{in})\).

Thus, in the general case, there are 8 dimensionless parameters as compared with 3 dimensionless parameters for the straight TE.

3. Results and discussion

The numerical solution of Laplace’s equation for the potential in the electrolyte solution (14) and Poisson’s equation for the potential in the resistive electrode (15) was performed by the boundary element and finite element methods. The number of boundary and finite elements and the time step were determined from the condition that these parameters have no effect on the numerical solution. The numerical method was described in detail in the earlier works [17, 18].

At the first stage, the initial distributions of potential and current density over the electrochemical cell with a straight TE at various values of parameters \(K_e, D, R_e\) are calculated (Figs. 2 and 3). The range of values of parameter \(K_e\) was chosen from the condition that a typical value of metal conductivity is by approximately \(10^6\) times higher than the conductivity of electrolyte solution, the initial thickness of conducting layer is of the order of tenths of a micrometer, and the length of resistive electrode is from tens to hundreds millimeters.

Ignoring the resistance of resistive electrode, the initial distribution of current density over the electrode is uniform and the dimensionless current density is equal to unity. From the above results (Figs. 2 and 3), it is clearly seen that the presence of resistive electrode has a pronounced effect on the distribution of current density. An increase in the relative resistance of the electrode (parameter \(K_e\)) and inner radius of the electrode \(R_e\) leads to an increase in the nonuniformity of distribution of current density, and an increase in the relative interelectrode distance \(d/e\) enables one to decrease the nonuniformity of current density distribution. These results agree well with the literature data [10]. The initial distribution of current density enables one to estimate possible nonuniformity of current density during the electrodeposition.

To enhance the uniformity of deposited metal layer thickness, the versions of electrochemical cells with curved electrodes were considered. The following equation was used as the target function:

\[
Q = \min_{\omega_n} \left\{ \int_{\omega_n} |S(t) - \omega_n| \, dt \right\}
\]

Equation (26) characterizes a root-mean-square deviation of the deposited layer thickness \(S\) from the rated value \(S_0 = 1 + r'\cdot t\).

The optimal shape of TE was determined by the gradient descent method. Fig. 4 gives the schemes of the cell at \(K_e = 1\), \(D = 1\), \(R_e = 0\) with a straight TE (Fig. 4a) and curved TE (Figs. 4b – 4d), corresponding to different values of the step in the direction of antigradient of function (26).

At \(r' = 10\) corresponding to a tenfold increase in the average thickness of conducting layer, the most uniform distribution of the deposited layer thickness is reached at \(\Delta D_1 = 0.2\) and \(\Delta D_2 = 0.6\) (Fig. 4c). Fig. 5 gives the dependences of the local nonuniformity of the deposit thickness along the resistive electrode length. By varying the shape of TE, it is possible to raise the metal deposition rate on the areas of the resistive electrode far from the current lead. However, near the current lead, the effect of TE shape is rather weak. Therefore, to decrease the metal deposition rate in the zone adjacent to the current lead, it is advantageous to use the insulating shield (Figs. 6 and 7).

The insulating shield leads to the nonmonotonic variation of current density and, consequently, nonmonotonic thickness of deposited metal layer near the current lead (Fig. 7). The case that the absolute values of the local minimum and local
maximum of nonuniformity of the deposited layer thickness are approximately equal is most favorable (Fig. 7, curves 3 and 5). A combination of the straight TE and insulating shield levels off the distribution of deposit thickness only near the current lead. The best results are obtained by combining the curved TE and the insulating shield. Due to the mutual effect of TE shape and insulating shield, the optimal shapes of TE with and without the insulating shield are different. In the latter case, more uniform thickness of deposited layer is achieved. This makes possible to decrease the value of target function (26) by more than 20 times.

At other values of parameters, the character of the effect of TE shape and the insulating shield is similar. At a higher resistance of the resistive electrode and a smaller interelectrode distance, a relatively lower nonuniformity of deposited metal layer thickness can be achieved.

The electrode resistance decreases during the electrodeposition; therefore, the terminal effect decreases with the time. In the case of electrochemical dissolution, an opposite situation is observed: the electrode resistance increases with the time leading to an increase in the nonuniformity of current density distribution and the thickness of removed metal layer. In the case of straight TE, the highest metal removal rate is reached near the current lead. Therefore, at a certain instant of time, the electric contact between the current lead and the resistive electrode can be broken. The electrochemical dissolution of the resistive electrode was simulated similarly to the electrodeposition. The only distinction was the opposite sign at the right-hand side of equation (21).

Figs. 8 – 10 give the time dependences of the distribution of metal layer thickness along the resistive electrode length for the electrochemical cells at $K_0 = 0.5$, $D = 0.25$, $R_0 = 10$ with straight TE (Fig. 8) and curved tool-electrodes of optimal shape and dimensions without the insulating shield (Fig. 9) and with the insulating shield (Fig. 10). The inserts show the scheme of electrochemical cell and the initial potential distribution.

In the case of straight TE (Fig. 8) the anodic dissolution is highly nonuniform and, at $t = 0.25$, the electric contact between the resistive electrode and the current lead is broken. The application of the curved TE enables one to enhance the uniformity of the dissolved layer thickness (Fig. 9) to a certain extent. However, the best results are achieved by combining the curved TE and the insulating shield (Fig. 10).
The results give the upper estimate of nonuniformity of the resistive electrode thickness: with regard for the polarization, the nonuniformity will be lower. Further development of the proposed method can be associated with more complicated approximation of TE surface.

Acknowledgements

The reported study was funded by RFBR and Tula region according to the research project № 15-48-03250p_a and by the Ministry of Education and Science of the Russian Federation, Project no. 1096 of the Basic Part of the State Program.

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