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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.

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

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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

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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 χ_m, 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 χ_s. A current collector 4 is attached to the outer edge of the resistive electrode.

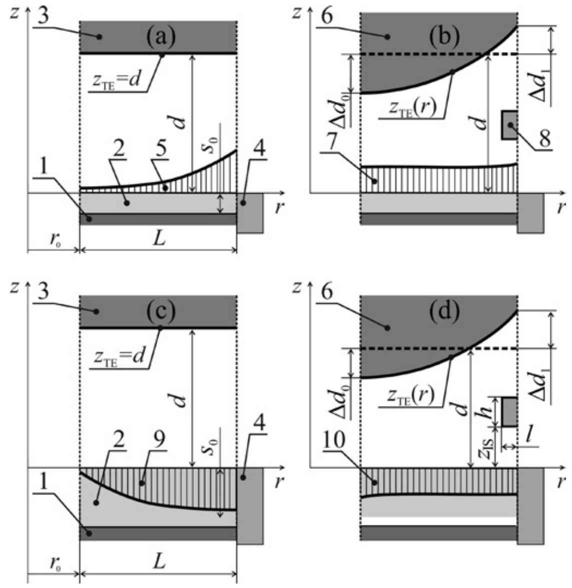

Fig. 1. Schemes (not drawn to scale) of electrochemical deposition (a, b) and electrochemical dissolution (c, d) for the resistive electrodes: 1 – dielectric substrate, 2 – initial metal layer on the electrode of thickness s_0, 3 – counter electrode with straight surface, 4 – current collector, 5 – layer of deposited metal with non-uniform thickness, 6 – counter electrode with curved surface, 7 - layer of deposited metal with uniform thickness, 8 – insulating shield; 9 - layer of dissolved metal with non-uniform thickness, 10 - layer of dissolved metal with uniform thickness.

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 %:

$$\mathrm{M} \Leftrightarrow \mathrm{M}^{+n} + ne^{-} \qquad (1)$$

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 $\mathbf{i}_\mathrm{s}$ is determined from the local gradient of electric potential φ_s in the solution by Ohm's law

$$\mathbf{i}_\mathrm{s} = -\chi_\mathrm{s} \nabla \varphi_\mathrm{s} \qquad (2)$$

where ∇ is the gradient operator; $\mathbf{i}_\mathrm{s}$ is the current density in the electrolyte solution; χ_s is the electric conductivity of the electrolyte solution; and φ_s is the potential in the electrolyte solution.

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

$$\nabla \cdot (\mathbf{i}_\mathrm{s}) = 0 \qquad (3)$$

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:

$$\mathbf{i}_\mathrm{m} = -\chi_\mathrm{m} \nabla_\mathrm{T} \varphi_\mathrm{m} \qquad (4)$$

$$\nabla_\mathrm{T} \cdot (s\mathbf{i}_\mathrm{m}) = -i_n \qquad (5)$$

where ∇_T is the tangential gradient operator; $\mathbf{i}_\mathrm{m}$ is the tangential current density along the electrode conductive layer; χ_m is the electric conductivity of the electrode conductive layer; φ_m is the potential in the electrode conductive layer; and s is the thickness of the electrode conductive layer.

The current density i_n is related to the current density in the electrolyte solution as follows:

$$i_n = -\mathbf{i}_\mathrm{s} \cdot \mathbf{n} \qquad (6)$$

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:

$$\frac{ds}{dt} = \frac{i_n}{nF\rho} \qquad (7)$$