

Energetic process modelling of thin-layer electrocrystallization

Abstract. A novel method for improving the energy performance of surface thin layer depositions by pulse currents is presented. We introduce the periodic pulse reverse current supplying an electroplating reactor and then develop a mathematical model of electrocrystallization processes. Next, the energy delivered to the reactor has been determined taking into account particular chemical processes governing the electrocrystallization. The improvement of cycling performance is reached by appropriate matching the period of supplying current to parameters of electroplating reactor.

Streszczenie. W artykule przedstawiona jest nowa metoda ulepszająca sprawność energetyczną nakładania cienkich warstw prądem pulsującym. Elektrolizer zasilany jest prądem pulsującym i opracowany został model matematyczny tego procesu elektrokryształizacji. Następnie wyznaczona została energia pobierana przez elektrolizer z uwzględnieniem szczególnych procesów elektrochemicznych. Poprawę procesu elektrokryształizacji zapewnia dopasowaniu prądu pulsującego do reaktora. (Modelowanie energetycznych procesów w elektrokryształizacji cienkich warstw)

Keywords: electrocrystallization, pulse current, energy performance, mathematical model

Słowa kluczowe: elektrokryształizacja, prąd impulsowy, sprawność energetyczna, model matematyczny.

Introduction

For producing nano- and micro-crystalline materials the electrodeposition appears as versatile technique. Recently, much interest in electrodeposition has evolved due to the low temperatures involved, the ability to coat geometrically complex or non line-of-sight surfaces of porous products, the ability to control the thickness, composition, and microstructure of the deposit, the possible improvement of the substrate/coating bond strength, and the availability and low cost of equipment. Despite the proven cost-effectiveness of these technologies, a significant proportion of potential energy efficiency improvements remain untapped due to numerous understanding barriers.

A novel method for improving the energy performance of surface thin layer depositions by pulse currents is established. Results of computer simulations are presented.

Pulse and Reverse Pulse Producing of Surface Layers

During an electroplating process the deposition of metals and other substances at electrode surfaces occurs. Electrochemical processes use charged electrodes to carry out chemical reactions. A simplified scheme of appliances being widely in using as electrochemical reactors and systems is presented in Fig.1. Various current waveforms supplying the reactors are shown in Fig.2. Metal electrodepositions on high-end thin-layers and on other products in cutting-edge technologies were at the very limit of what DC processes could achieve (Fig.2a).

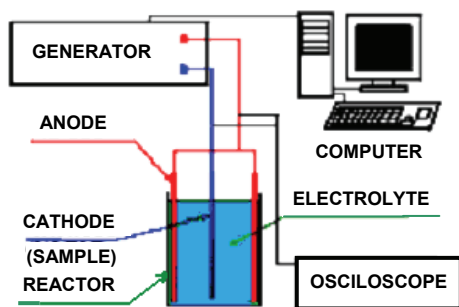


Fig.1. Appliances for electroplating

All major process studies concentrate currently around the PPRC (Fig.2b,c,d,e) electroplating technology and the general metal finishing products. This is common on rough parts or when a bright finish is required (Fig.3). The morphology and composition of electrodeposits vary significantly, and depend on: current density, the nature of the anions or cations in the solution, bath composition and

temperature, solution concentration, power supply current waveform, the presence of impurities, physical and chemical nature of substrate surface. Typically, such reactor elements and characteristics as electrode double layer capacitance, electrode kinetics, diffusion layer, solution resistance contribute to the electroplating effects [1, 2].

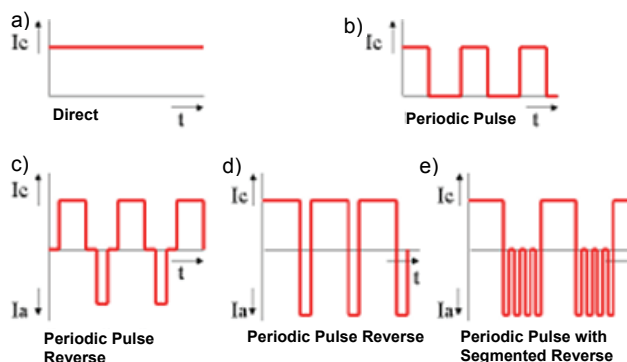


Fig.2. Current waveforms for electroplating

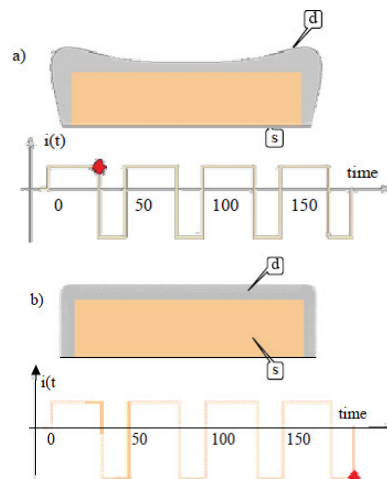


Fig.3. Effects of pulse periodic reverse current plating during: a) direct pulse , b) reverse pulse (s – substrate, d – surface layer)

By using pulse and reverse pulse plating it is possible to obtain deposits with much more optimized properties than using DC plating. Despite the proven cost-effectiveness of these technologies, great proportions of potential energy efficiency improvements remain untapped due to numerous understanding barriers. For these reasons a fundamental

appreciation of the processes involved in metal surface layer formation is needed to develop a predictive, quantitative model for the effects of deposition variables on resulting film microstructures.

Mathematical Model of Thin-layer Electroplating

To improve the energy performance of metal surface layer depositing by reverse pulse currents consequences of electrode processes exhibiting a number of specific features must be taken into account. During the thin layer metal electrodeposition the complex reaction of charge transfer with intermediate adsorption takes place at least in two elementary steps: reagent adsorption is the first and product desorption is the second. The process can be described by a mathematical model derived from the Maxwell equations and mass balance equations as follows

$$(1) \quad \begin{aligned} \nabla^2 E(M,t) &= -\rho_c(M,t) + \nabla \cdot \vec{P}(M,t), \\ \frac{\partial c_i(M,t)}{\partial t} &= -\nabla \cdot \vec{J}_i(M,t) + \xi_i(M,t) \end{aligned}$$

with $1 \leq i \leq m$, where $E(M,t)$, $\rho_c(M,t)$, $\vec{P}(M,t)$, $c_i(M,t)$, $J_i(M,t)$ and $\xi_i(M,t)$ denote the potential, electric charge density per unit volume, dielectric polarization, concentration, current density and the term representing the sources, respectively, of species i at point M and time t .

It is possible elaborate models which lead to satisfied results when matching them with experimental data. By making a certain number of hypotheses we can generally simplify the governing equations (1) and present them as follows

$$(2) \quad \begin{aligned} C \frac{dV(t)}{dt} + \frac{V(t)}{R_p} + I_F(t) &= I_{prs}(t), \\ L \frac{dI_F(t)}{dt} + R_{ct} I_F(t) - V(t) &= 0, \\ E(t) - R_e I_{prs}(t) - V(t) &= 0 \end{aligned}$$

where $I_{prs}(t)$ denotes the current of the supplying source, and system parameters C , R_p , L , R_{ct} , and R_e are related to the whole surface of the working electrode.

The solution of (2) gives a possibility to explain why the process energy efficiency increases under periodic pulse reverse current conditions, proposing that the lowering of electroplating efficiency was caused by the no matching conditions of the supplied current waveform to the given electroplating reactor. Next, the energy delivered to the reactor can be determined taking into account particular processes governing the electrocrystallization.

The pulse reverse current supplying the reactor (Fig.1) can be represented by

$$(3) \quad I_{prs}(t) = I_{prs}(t+T) = \begin{cases} I_{s,1} & \text{for } 0 \leq t \leq T_1 \\ I_{s,2} & \text{for } T_1 \leq t \leq T_2 \\ I_{s,3} & \text{for } T_2 \leq t \leq T_3 \\ I_{s,4} & \text{for } T_3 \leq t \leq T_4 \end{cases}$$

where T_k , $I_{s,k}$, with $k = 1, 2, 3, 4$, denote the switching moments and magnitudes, respectively, of the pulse reverse current of the supplying source.

Using more convenient formula we can represent the pulse reverse supplying current (3) by

$$(4) \quad I_{prs}(t) = I_{s,1}(t) + \sum_{k=1}^3 H(t, T_k) [I_{s,k+1} - I_{s,k}]$$

where we have introduced the unit Heaviside functions $H_k(t, T_k)$, $k = 1, 2, 3$ which are shifted at the portions T_k of period with respect to the origin point $t = 0$. An illustration plot of a pulse reverse current wave produced by a supplying generator with $I_{s,1} = I_1$, $I_{s,2} = 0$, $I_{s,3} = I_2$ and $I_{s,4} = 0$ with $T = T_4$ is shown in Fig.4a. Surface morphologies of copper films electrodeposited on a technical copper substrate are presented in Fig.4b,c,d, respectively.

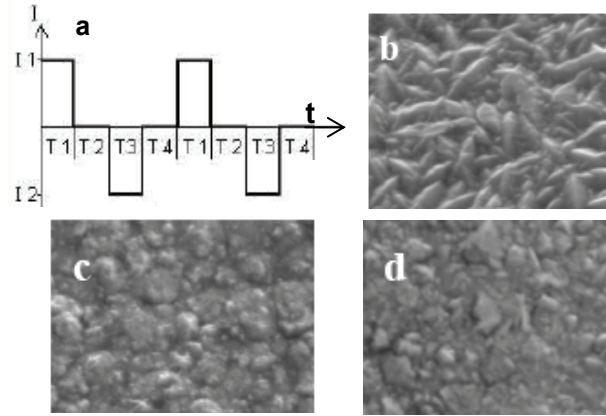


Fig.4. Copper surface electrodeposits; a) PPRC waveform, b) DC surface morphology, c) PPRC surface morphology at $f = 0.5$ kHz, d) PPRC surface morphology at $f = 10$ kHz, (c), (d) with $T_2 - T_1 = T_4 - T_3 = 0$ and $I_1 = 2A$, $I_2 = -1A$

Solutions

Possible improvements of cycling performance can be determined by the following analysis.

A steady-state periodic solution of equations (2) depends on system eigenfrequencies

$$(5) \quad \begin{aligned} s_1 &= -\alpha + j\omega \quad \text{and} \quad s_2 = -\alpha - j\omega, \quad j = \sqrt{-1}, \\ \alpha &= \frac{1}{2} \left(\frac{R_{ct}}{L} + \frac{1}{CR_p} \right), \quad \omega = \sqrt{\omega_0^2 - \alpha^2}, \quad \omega_0 = \sqrt{\frac{R_{ct} + R_p}{CLR_p}} \end{aligned}$$

It is easily seen from (2) and (3) that the resulting steady state voltage $E(t)$ can be expressed as follows

$$(6) \quad E(t) = E(t+T) = E_1(t) + \sum_{k=1}^3 H(t, T_k) [E_{k+1}(t) - E_k(t)]$$

where $E_k(t)$, $k=1,2,3,4$ denote the voltage components in the successive parts, respectively, of the supplying current period. When $t \in (T_k, T_{k+1})$ and the supplying current is equal to $I_{s,k}$ with $k = 1, 2, 3, 4$ we obtain

$$(7) \quad E_k(t) = A_k(t) e^{s_1 t} + B_k e^{s_2 t} + E_{f,k}$$

where $E_{f,k}$ denotes the steady state term forced by $I_{s,k}$, and A_k and B_k are constants to be determined from continuity and periodicity conditions fulfilled by respective components of the whole system response [3].

The steady state forced term $E_{f,k}$ follows from equations (2) when successively substituting $I_{s,k}$, respectively. In results we get

$$(8) \quad E_{f,k} = (R_e + R) I_{s,k}$$

where $k = 1, 2, 3, 4$ and $R = R_p R_{ct} / (R_p + R_{ct})$ denotes the equivalent resistance of parallel connection of resistances R_p and R_{ct} . To determine integration constants A_k and B_k we take into account the continuity and periodicity conditions which are fulfilled by the voltage $V(t)$ and current $I_F(t)$ [3, 4].

Results of Computations

Results of computer simulations performed for an electrodeposition process characterized by the following system parameters: $R_e=12.78\Omega$, $C=0.3075\mu\text{F}$, $R_p=2690\Omega$, $R_{ct}=0.47472\Omega$ and symmetric supplying current source with $I_{s,1}=7\text{A}$, $I_{s,2}=-7\text{A}$ and $2T_1 \approx T_0=0.1859\text{s}$ and $2T_2=4T_1$ are presented in Fig.5, respectively. Comparing the responses exhibited by the electrolyzer for different periods of the supplying pulse reverse currents but with the same magnitudes it is easily seen that the electrode voltage is strongly sensitive on the rate of supplying current period T with respect to natural period T_0 of the electrolyzer.

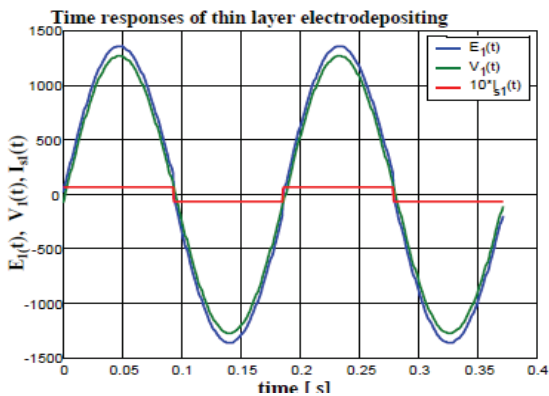


Fig.5. Time responses for $2T_1 \approx T_0$

The relative decrease of the amplitude because of damping phenomena during one half of the natural period ($t=T_0/2$) equals $\exp(-\alpha T_0/2)$. So the down and upper extreme separations from $E_{1,0}$ for the left half-loop are related to one another through this exponential factor giving the damping decay for a half-cycle: $(E_{1m} + E_{1,0}) \exp(-\alpha T_0/2) = E_{1m} - E_{1,0}$. For the case in which $\alpha \ll \omega_0$, that is, $\alpha T_0 \ll 1$ (electrolyzer with relatively weak damping), we can assume $\exp(-\alpha T_0/2) \approx 1 - \alpha T_0/2$. Using this approximation in the above relation and solving for E_{1m} , we obtain the following estimate

$$(9) \quad E_{1m} \approx E_{1,0} \frac{2}{\alpha T_0 / 2} = \frac{4}{\pi} Q E_{1,0}$$

where the product of the damping constant α and the self oscillation period T_0 is expressed here in terms of the quality factor $Q = \omega_0/2\alpha$.

Equation (9) shows that for the voltage excited by the external symmetric pulse reverse current ($T = T_0$) the amplitude of steady-state oscillation is approximately Q times greater than the magnitude $E_{1,0}$ induced by stationary direct current. When the driving period is an even-numbered multiple of T_0 , the maximal voltage of the supplying current source in steady-state cannot exceed $2E_{1,0}$. This is easily seen from the shape of the corresponding voltage $E_i(t)$ presented in Fig.5. For high frequencies of the external current, when the square-wave period T is very short compared to the natural period T_0 of the reactor, in steady-state oscillation the voltage executes only small oscillations about the mid-point $E_{1,0} = 0$.

Energy Consumption by Electroplating Reactor

The rate of an electroplating process can best be described as the electric energy consumption; i.e., a measure of the quantity of electric charges moving in a certain volume of space during a specified unit of time.

The steady state energy $W(\Delta t)$ delivered by the source $I_s(t)$ to the electroplating reactor during the time interval $\Delta t = nT$, (T is the period, $n \gg 0$ is an integer) is expressed by

$$(10) \quad W(\Delta t) = n \cdot W_T$$

where W_T denotes the one-period energy delivered by the source. This means that in the periodic state (Fig.4) it is sufficient to evaluate W_T and by multiplying it by n we obtain the energy absorbed by an electroplating element during the given time interval Δt .

The derivation of the corresponding expression for W_T leads to

$$(11) \quad W_T = T \int_0^T v(t) I_s(t) dt = \int_{q(0)}^{q(T)} v(t) dq(t) \\ = \int_{\psi(0)}^{\psi(T)} I_s(t) d\psi(t), \quad q(t) = \int I_s(t) dt, \quad \psi(t) = \int v(t) dt$$

where $q(t)$ and $\psi(t)$ denote the electric charge and magnetic flux delivered by the source $I_s(t)$, respectively.

Several experiments performed on real testing specimens verified the efficiency of the method in electrochemical process analysis of many practical systems. Illustrations are shown in Fig.6. The PPRC supplying current leads to the one-period energy loops having the form of a rectangle on the $(\psi(t), i(t))$ plane

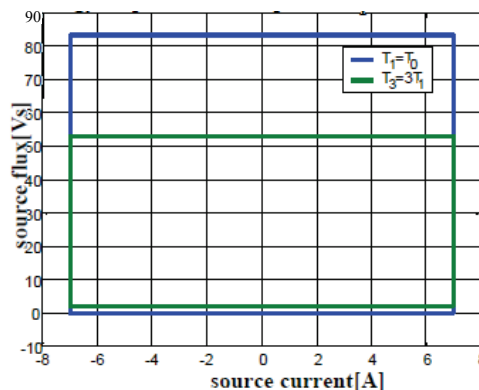


Fig.6 One-period energies in reversal pulse plating

Conclusions

In this work an attempt is put on description of a new method for electrocrystallization process realizations which takes into account the activation energy and mass transfer effects. With use of quantitative methods, many salient features of electrolyzer operations can be modeled in concise forms. The use of the typical mathematical tools, such as the Fourier series and Fourier transforms is avoided. Results of appropriate computations are given.

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