Study of System Power Supply Source – the Galvanic Bath with Pulse Plating Deposition of Nickel Coating

Mincho Peev

Abstract: - **This article presents common work of MOSFET key converter from constant voltage into pulse voltage, and galvanic bath for the deposition of metal layers by regime of pulsed electrolysis. Parameters of substitute electric circuit of the galvanic bath are defined with a specific composition of electrolyte and wide range of cathode current density. Experimental simulation studies were performed in the program environment MicroSim DisignLab for polarization of the cathode and anode. For different frequencies is determined impulse and pause durations, for which pulse current of the supply source corresponds to the Faraday current. The experimental studies that are made by real system power supply source - galvanic bath confirmed he results from simulation. The determined parameters of power supply source ensure high efficiency of the process of electroplating. The presented analysis and results can be used in laboratory and industrial conditions to determine the working parameters of the power supply source on the application of pulsed electrolysis.**

Keywords – **Pulse electrodeposition, Pulse plating source**

I. Introduction

The study of pulse electrolysis, as a method for increasing the technological parameters of the coatings obtained in DC electrolysis is presented in some publications from about 20-30 years [1,2]. The development of electronics and improvement of management systems is a prerequisite for development and improvement of supply sources and for new surveys of pulse electroplating technology [3-5]. Galvanic deposition of metal coatings in pulse mode allows improving operational capacities of the coating: better adhesion to the substrate, less internal mechanical tensions, less porosity, higher hardness and straight resistance, better electrical conductivity; and also magnetic properties [4].

In known literature sources, however, is not represented the relationship between process efficiency with change of electrode potential, which change of electrode potential, which substantially affect the electrochemical processes of the cathode.

The purpose of this work is to present researches, allowing optimization of the electrodeposition regime by regulating the pulse current value, frequency and duty cycle of pulses for the most widely used rectangular pulse. Based on theoretical analysis, simulations and experimental studies using of developed specialized programmable source, [5] it is represented the relationship between the cathode potential and current pulse value at different frequencies.

Mincho Peev is with the Technical University of Sofia, Branch Sliven, 59 Burgasko shose Blvd., 8800 Sliven, Bulgaria, E-mail: mfpeev@abv.bg.

II. Basic Characteristics of Pulse Electrolysis

Electrodeposition of metal coatings by the application of rectangular pulses (Fig.1) allows simultaneous the control of three typical parameters of pulse electrolysis: pulse current density (j_p), pulse duration (t_{ON}) and pause duration (t_{OFF}). The application of high pulse current density determines the high cathode polarization [1, 2]. The ultra high cathode potential influences the speed of electrochemical reactions.

The useful range for regulation of parameters (j_p, t_{ON}, t_{OFF}) is determined by the theoretical aspects of pulse electrolysis [1,2]. Great pulse duration (t_{ON}) and pause duration (t_{OFF}) creates conditions similar to DC regime of electrodeposition.

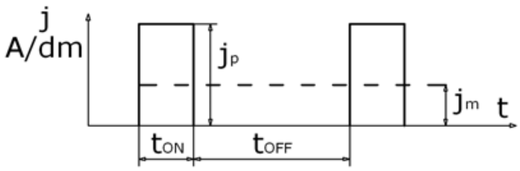

Fig.1. Pulse regime

Very little pause and pulse durations are limited by the capacity of the double electric layer [1]. Double electric layer arises at the border electrode – electrolyte. It has a large capacity and specifies active - capacitive nature of the electrode – electrolyte system (and generally of the galvanic bath). For this reason, in pulse regime, the current in the external electrical chain (i_{REC}) for time of charging double electric layer differs from the current for electrodeposition (i_F- Faraday current). In Fig.2a is presented time-chart at the electrical output of the power source for rectangular pulse. If pulse duration is longer from the time of charging double

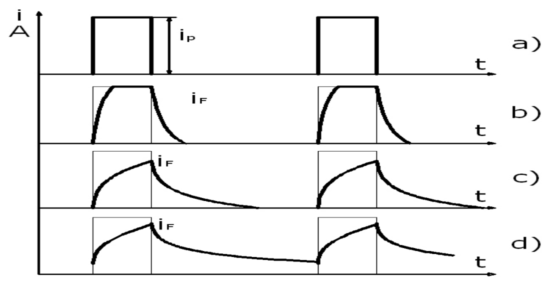

Fig.2 .Damping of Faraday current

electric layer, than Faraday pulse current reaches the source current value (fig.2b). Accordingly, the polarization of the cathode reaches a high value. If pulse duration is shorter towards the charging time of the double layer, than electrodeposition current value (i_F) is below the current value of the power source (fig.2c and fig.2d).

III. Replacement Scheme of the Galvanic Bath. Determination of Parameters.

The replacement scheme of the galvanic bath is made in order to study its joint work with power supply source of pulses during nickel electro deposition developed in [5].

A. Mathematical Model

During the electrodeposition of metals most limiting stage is the discharge of metal ions on the surface of the cathode The creation of a mathematical model of the galvanic bath for electrochemical processes with delayed stage of ion's discharge is possible by the following assumptions [2]: It is assumed that the cathode process involves two parallel electrochemical reactions with the following substances - metal that deposits on the cathode and hydrogen. Dependencies between the partial current density and electrode overvoltage is expressed by the emergence of electrode polarization, the separation of oxygen to the anode is ignored; the electrolyte is homogeneous; the surface of the electrodes is plane; the migratory movement of ions at cathode electrolyte layer is ignored.

Under these conditions, the dynamic processes in galvanic bath are described by the following nonlinear differential equations system [2]:

$$j_k(t) = \frac{i}{S_k} = j_{мк}(t) + j_H(t) + j_{ck}(t) \qquad (1)$$

$$j_a(t) = \frac{i}{S_a} = j_{ма}(t) + j_{ca}(t) \qquad (2)$$

$$j_{мк}(t) = j^0_{мк}\left\{\exp\left[-\alpha_м \frac{z \cdot F}{R \cdot T}\left(E_k - E_{рм}\right)\right] - \exp\left[(1-\alpha_м)\frac{z \cdot F}{R \cdot T}\left(E_k - E_{рм}\right)\right]\right\} \qquad (3)$$

$$j_{ма}(t) = j^0_{ма}\left\{\exp\left[\beta \frac{z \cdot F}{R \cdot T}\left(E_a - E_{рм}\right)\right] - \exp\left[-(1-\beta)\frac{z \cdot F}{R \cdot T}\left(E_a - E_{рм}\right)\right]\right\} \qquad (4)$$

$$E_k - E_{pH} = \begin{cases} R_n \cdot j_H(t) \to npu\left|E_k - E_{pH}\right| \le \dfrac{RT}{F} \\ a + b \cdot \lg j_H(t) \to npu\left|E_k - E_{pH}\right| > \dfrac{RT}{F} \end{cases} \qquad (5)$$

$$u(t) = E_a(t) - E_k(t) + \frac{d}{\gamma \cdot \sqrt{S_k \cdot S_a}}\, i(t) \qquad (6)$$

Where: E_k is the cathode electrode potential, V; - E_a - electrode potential of the anode, V; - $E_{рм}$ - equilibrium potential of reaction of the discharge and ionization of the metal ions, V; - E_{pH} - equilibrium potential of the reaction of discharge of hydrogen ions, V; - J_k - the current value of cathode current density, $A.dm^{-2}$; - J_a - current value of anode current density, $A.dm^{-2}$; - $J_{мk}$ - partial current density of discharge of metal ions on the cathode, $A.dm^{-2}$; - J_H - partial current density of discharge of hydrogen ions on the cathode, $A.dm^{-2}$; - $J_{ма}$ - partial current density of ionization of metal ions on the anode $A.dm^{-2}$; - $j_{мк}{}^0$ - density of the current exchange of the cathode, $A.dm^{-2}$; -$j_{ма}{}^0$- density of the current exchange of the anode $A.dm^{-2}$; - J_{ck} - capacitive current density of cathode $A.dm^{-2}$; - J_{ca} - density capacitive current rating, $A.dm^{-2}$; - a, b - constants determined experimentally; - $\alpha_м$ - activity of metal ions on the cathode; - β - activity of metal ions on the anode; - F - Faraday number, F = 96486,7 $C.mol^{-1}$;- R - gas constant, R = 8,31434 $J.K^{-1}.mol^{-1}$; - T - absolute temperature, K; - z - valence (charge of ions); - γ - specific conductivity of the electrolyte, $\Omega^{-1}.m^{-1}$; - d - distance between electrodes, m; - $S_к$, S_a – surface of cathode and anode.

Under System of equations corresponds to electrical replacing scheme of the galvanic bath shown in Figure 3.

In the replacing scheme $R_{electrolyt}$ is the resistance of the electrolyte in the space between anode and cathode. R_a is the resistance of the anode surface during the transmission of electrical charges between the anode and electrolyte. R_{cathod} is the resistance on the cathode surface during transmission of electrical charges (electrons) from the cathode to the metal ions of the electrolyte. C_a and C_{cathod} are the capacities of electric double layer on the anode and cathode surfaces. The elements of the replacement scheme have nonlinear character as their values depend greatly on current density.

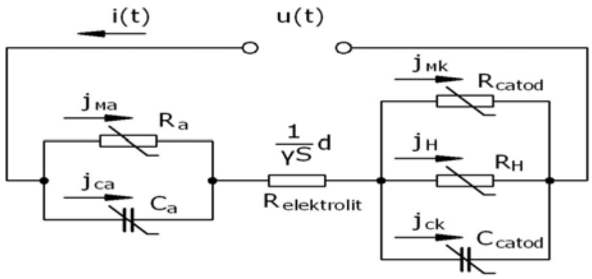

Fig.3 Electrical replacing scheme of the galvanic bath

B. Determination of Parameters

The parameter's determination of the replacing scheme was made for galvanic deposition of nickel coating trough following electrolyte deposition: $NiSO_4.7H_2O$ – 145 g/l; $Na_2SO_4.10H_2O$ – 45 g/l; H_3BO_3 – 25 g/l; NaCl – 7 g/l. During the process the maintaining temperature of electrolyte is T=25 ^oC (298 K); pH = 5,5. Recommended current density in a constant current mode j_{DC} = (0,8 to 2,0) $A.dm^{-2}$ [2]. In a pulse mode the average current density j_m (Figure 1) must correspond to the current density in a constant current mode. The average current density is determined by the expression:

$$j_m = j_p \frac{t_{ON}}{t_{ON} + t_{OFF}} \qquad (7)$$

The constants in the equations for the used electrolyte composition have the following values [1]: $j^0_{мк} = 3{,}1.10^{-5}, A.dm^{-2}$; $j^0_{ма} = 7{,}94.10^{-6}, A.dm^{-2}$; $\alpha_м$=0,3; β=0,4; $E_{рм}$=-0,25,V; $E_{рН}$=-0,226,V; $C^*_{Ni} = 80.10^6, F.dm^{-2}$; $\gamma_{ел} = 12.7, \Omega^{-1}.m^{-1}$; S_a=2S_k.

Determination of the values of the elements of the replacing scheme was made by the following sequence:

- Elaboration of polarization curves $E_k = f(j_{мк})$ $E_a = f(j_{ма})$ (Fig.4 and Fig.5).

The elaboration is done with calculations by equations (3) and (4).

- Determination of the cathode's area value for the performed experiment;
- Determination the duty cycle of pulses value

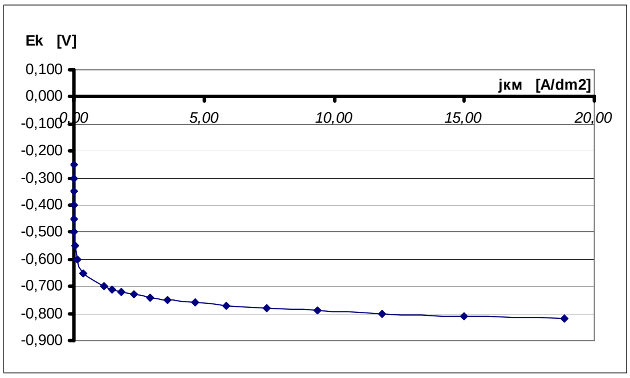

Fig.4 Polarization curve of nickel cathode

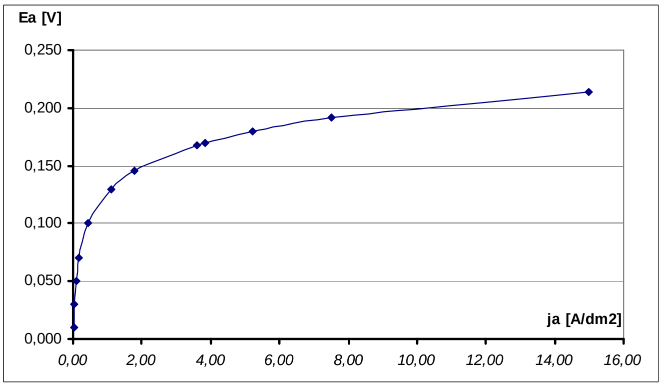

Fig.5 Polarization curve of nickel anode

$$k_з = \frac{t_{ON}}{t_{ON} + t_{OFF}}$$

and calculation of the pulse current density value $j_p = \frac{j_m}{k_з}$

- Determination the value of pulse current of the external circuit (the current of power source)

$i_{REC} = j_p \cdot S_к$

- Determination of the pulse current density of cathode $j_{мк} = \frac{i_{REC}}{S_k}$ and of anode $j_{ма} = \frac{i_{REC}}{S_a}$

- Determination of polarization of the cathode E_k and anode E_a from polarization curve by received values of $j_{мк}$ and $j_{ма}$;

- Calculation of the replacing scheme elements by dependencies:

$$R_{catod} = \frac{E_k - E_{рм}}{j_k.S_k}, \Omega \qquad (8)$$

$$R_a = \frac{E_a - E_{рм}}{j_a.S_a}, \Omega \qquad (9)$$

$$C_{catod} = S_k \cdot C_{Ni}, \mu F \qquad (10)$$

$$C_a = S_a \cdot C_{Ni}, \mu F \qquad (11)$$

$$R_{electrolit} = \frac{d}{\gamma_{ел} \cdot \sqrt{S_k \cdot S_a}}, \Omega \qquad (12)$$

In order to carry out the simulation study during producing nickel coating with cathode surface S_k = 0,1 dm^2, duty cycle pulse k_z = 0,1 and average current density j_m = 1 $A.dm^{-2}$ are obtained the following values for the elements of the replacing scheme: R_{cathod} = 0.543 Ω, C_{cathod} = 800 µF, R_a = 0.428 Ω, C_a = 1600 µF, $R_{electrolyt}$ = 5,57 Ω.

IV. Simulation Studies

Current state of the theory of galvanic deposition of metals by pulsed currents is not yet possible to give a definite answer to the question of rational choice of form and parameters of the polarizing pulses [2]. Therefore, for each metal deposition processes in the laboratory have tried many variations of the current forms and regimes of work. Mathematical modeling has significant opportunities and advantages over laboratory tests.

In the programming environment PSpice is created a simulation model of the system MOSFET key converter pulses - galvanic bath (Fig. 6).

The galvanic bath's replacement scheme is represented with ignoring of hydrogen separation at the cathode (cathode current utilization in nickel electrodeposition is about 97%). The equilibrium potential of the electrodes (anode and cathode) is represented by constant voltage souses E_{pNi_a} and E_{pNi_c}. R_{cathod} is the resistance on the cathode surface during transmission of electrical charges from the cathode to the metal ions of the electrolyte. R_a is the resistance of the anode surface during the transmission of electrical charges between the anode and electrolyte. $R_{electrolyt}$ is the resistance of the electrolyte in the space between anode and cathode. C_a and C_{cathod} are the capacities of electric double layer on the anode and cathode surfaces.

The key converter is able to set the pulse and pulse reverse mode of galvanizing. Through transistors M5 and M7 it is possible to set a positive impulse. By M8 and M6 it is possible to set the reversible impulse. A study of cathode electric regimes (E_k, i_F,, i_{ck}) for frequencies from 10 Hz to 10000 Hz at average current density j_m = 1 $A.dm^{-2}$ and $k_з$ = 0,1 is done using this model. Measurement of Faraday current (i_F) is not possible in real conditions but it determines the character of the processes flowing on the cathode.

Fig.7 and fig.8 of presents the results of simulation for cathode: current of the power source; the potential of the cathode; Faraday current; current of the electric double layer. These results are received at the duty cycle $к_3$=0,1 and frequencies 10 Hz and 10000 Hz.

The received results from the simulation studies for cathode potential values and current pulse value at low frequencies correspond to these, received in real conditions. For frequency

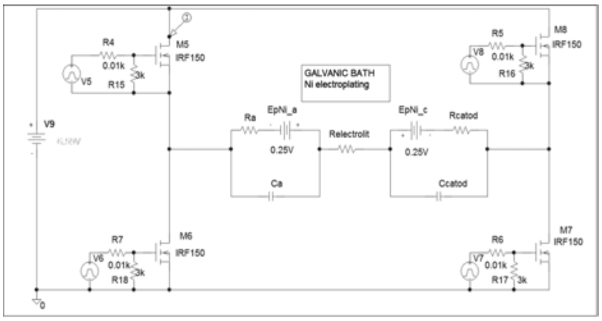

Fig.6 Replacing scheme MOSFET transistor switch - galvanic bath

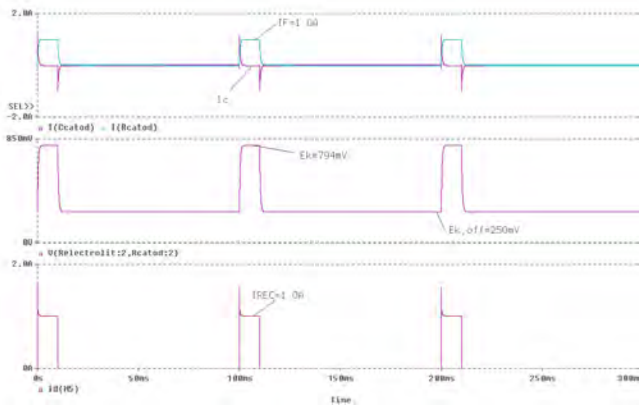

Fig.7 Pulse mode k_3 = 0,1; f=10 Hz

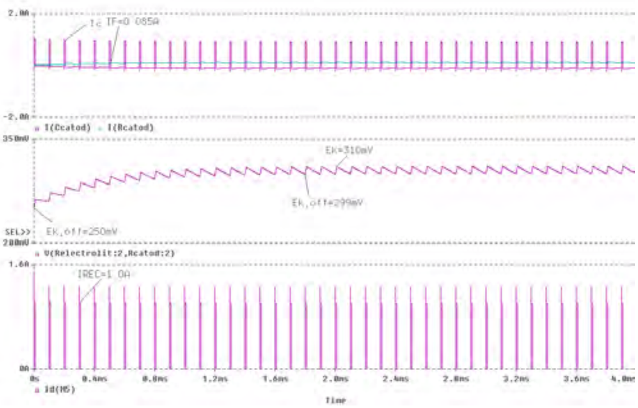

Fig.8 Pulse mode k_3 = 0,1; f=10000 Hz

10 Hz (fig.7) the value obtained for E_k is 0.79V (at calculated 0,79V), Faraday current also corresponds to the calculated - 1A. For frequency 100Hz cathode potential does not reach the estimated value (E_k = 0,75 V - 95% of the set one), Faraday current reached 93% (i_F = 0,93). With increasing frequency Faraday current decreases because during the pulse electric double layer was unable to be charged up to the established value and thus current from the power source is distributed between the capacitive current of the electric double layer (i_c) and Faraday current (i_F).

At frequencies above 2000 Hz Faraday current strongly decreases and the cathode potential reduces too. The resulting effect is rectification of Faraday current. This effect is greatly expressed at a frequency of 10000 Hz (fig8): current from the power source is a pulse, but Faraday current fluctuates around an average of 0.09 A. Cathode potential fluctuates around an average of 0,3 V. The regime is similar to DC electrodeposition.

V. Conclusion

A simulation model of the system MOSFET key converter from dc to pulse voltage - galvanic bath is developed in the programming environment PSpice; thus the electrical replacing scheme of the galvanic bath is reported.

The systematization of sequence for calculations to determine the electrical parameters of the galvanic bath was made. For specific parameters of galvanic coating deposition in pulse mode are defined the parameters of electrical circuit replacing scheme of the galvanic bath.

Simulation researches in PSpice for the polarization of cathode, current of the electrodeposition and current of the electric double layer on the cathode for a nickel coating under pulse mode and under range of frequency variation from 10 Hz to 10000 Hz were carried out.

The proposed survey approach can be used in laboratory and industrial conditions to determine the operating parameters of the power source for pulse electrolysis (current density, duty cycle pulse, frequency of pulses).

References

[1] J. Cl. Puippe, N. Ibl, Influence of charge and discharge of electric double layer in pulse plating, J. of Applied Electrochem. 10 (1980) 775-784

[2] Костин Н.А., В.С. Кублановский, В.А. Заблудовский, Импульсной электролиз, Киев, Науковая думка, 1989.

[3] M.S.Chandrasenar, Malathy Pushpavan, Pulse and pulse reverse plating – Conceptual, advantages and applications, Electrochemica Actaq 53 (2008), pp 3313-3322.

[4] M. Lindblom, H.M. Hertz, A. Holmberg, Pulse reverse plating for uniform nickel height in zone plates, Vac. Sci. Technology, Vol. 24, Nr.6, Nov/Dec 2006, pp 2848-2851.

[5] Анастасия Кръстева, Минчо Пеев, Йовчо Стоянов, Георги Кънов, Реверсивен програмируем източник на импулси за нанасяне на галванични покрития, Електротехника и Електроника, 2005, бр 5-6 стр. 10-16.