Bi-polar (DC+AC) Pulse-Reverse Technique for the Deposition of Metal Coatings with Improved Properties

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We describe a new pulse-reverse technique, where trains of forward and reverse rectangular pulses are replaced by a single train of bipolar pulses as AC voltage is superimposed over the DC pulses. By applying this technique, five considerable benefits are obtained: (1) the operation is simpler because of a decreased number of variables; (2) the waveform has off-time which allows for diffusive-recovery and desorption; (3) the deposition of nanocrystalline metal coatings becomes possible; (4) there is a decreased risk of anodic passivation; and (5) there is a greater leveling effect resulting in reduction of internal stress and porosity. Theoretical electrochemical considerations and impedance analyses are employed in order to interpret the experimental results for bright copper and nickel coatings deposited by this technique.

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Dr. Mois Aroyo Technical University of Sofia, Sofia 1756, Bulgaria E-mail: <u>mmaroyo@abv.bg</u> Industrial surface finishing of metals employs a diverse range of electrochemical processes. There is a wide variety of anodic and cathodic reactions that play an important role in surface finishing of metals.¹ Because of the dualistic electrochemical nature of the processes of plating and metal finishing based on the simultaneous and competitive reactions of oxidation and reduction, we talk of binary sets of opposite process factors – growth/dissolution, adsorption/adsorption, polarization/depolarization, acidity/alkalinity. In this context, pulse-reverse technologies have the largest potential in controlling not only plating but also other electrochemical metal finishing processes. As we vary the parameters of cathodic and anodic pulses, we can change the relative influence of the above opposite factors and thus define the optimal process conditions.

In our recently published work² we have demonstrated that at definite parameters of pulse periodic reverse (PPR) plating, a large commutative effect of the both trains of forward and reverse pulses can be achieved in terms of the leveling performance and the structural homogeneity of metal deposits. In order to determine the pulse reverse waveform that emerges (Fig.1), we need to know at least nine parameters. From a practical point of view, such a large number of variable parameters presents a considerable obstruction to the application of pulse reverse techniques.



Fig. 1 Pulse periodic reverse waveforme

The main objective of the present work has been to continue to develop these pulse reverse techniques by combining both trains of forward and reverse pulses into a single train of bi-polar (DC+AC) pulses by superimposing AC voltage over the DC pulses (Fig.2).

Electrodeposition of Nanocrystalline Materials

The major advantage of electrodeposition is that a large number of pure metals, alloys, and composites can be electroplated with grain sizes in the nanocrystalline range. One of the key factors in the microstructural evolution of electrodeposits in terms of grain size and shape is inhibition, i.e the reduced surface diffusion of adions by adsorption of foreign species (such as grain refiners) on the growing surface. For example, saccharine, coumarin, thiourea and formic acid have all been successfully applied to achieve grain refinement down to the nanocrystalline range for nickel electrodeposits.³ The scientific literature reports numerous examples identifying electrochemical-processing windows for the producing of nanocrystalline pure metal or alloy deposits. U. Erb and A.M. El-Sherik⁴ have patented an electrodeposition process in which pulsed DC current is applied in order to obtain nanocrystalline nickel coatings with an average grain size of less than 11 nanometers. The cell electrolyte also contains a stress reliever and grain-refining agent such as saccharin in concentrations up to 10 g/l. The optimum value of time on (T_{on}) is 2.5 msec and the peak current density (I_p) may vary between about 1.0 A/cm² and 3.0 A/cm². If the I_p is too high, the deposited material may burn and if it is too low, the grain size will increase.

The new pulse reverse technique that we have developed is based on the application of bi-polar (DC+AC) pulses. It enables us to deposit nanometer-sized crystalline metal coatings because it creates the conditions for the successful application of the above mentioned electrochemical principles, namely:

- The electrocrystalization of metal deposits during the forward pulse polarization should take place under the conditions of highest possible cathodic current density and of reduced surface diffusion rates of adions by the adsorbed brightener species. The higher current density and the lower surface diffusion rates, the finer the grain structure of the coatings.
- The process of metal dissolution of coatings during the reverse anodic polarization should be controlled and effective so that it play the role of an additional non-chemical grain-refining factor as it preferentially dissolves the crystallite's asperities.



Fig. 2 (*DC*+*AC*) bipolar pulse reverse waveforme

Analysis of AC-circuit, Equivalent to the AC- polarized Plating Cell

In order to explain how the alternating voltage affects the electrode processes, we present a real plating cell as an equivalent circuit of resistors and capacitors^{5,6} as it is shown in Fig. 3. The application of purely sinusoidal voltage $u = U_m \sin \omega t$ on the two-electrode electrochemical system leads to the emergence of the alternating current $i = I_m \sin(\omega t + \varphi)$. Here, ω is an angular frequency, which is 2π times the conventional frequency in hertz, and φ is the phase angle between the sinusoidal voltage and the resulting sinusoidal current, *i*. The later is a sum of both currents:

 i_f - faradaic current of the pure electrochemical electrode reactions i_c - capacitive current of charging and discharging of the double electrical layer on the metal electrode-electrolyte boundary interface

In every AC-polarized electrochemical system the rate of the real electrode process is proportional to the current i_{t} , passing through the combination of an active resistance R_s and a pseudocapacity C_s in series. According to Ohm's this current is in inverse proportion to the faradaic impedance, Z_f :

$$i_{f} = \frac{u}{Z_{f}} = \frac{u}{\sqrt{R_{s}^{2} + X_{s}^{2}}}$$
(1)

Obviously, at a definite value of applied alternating voltage u, the faradaic current i_{e} will depend on the impedance of the electrochemical system. The lower the active resistance $R_{s,r}$, and the reactive resistance $X_s = \frac{1}{\omega C_s}$, the higher i_f . It can be seen that the higher frequency ω results in a lower reactive component of X. An active component of the impedance R is present because the electrical energy supplied by the source is transformed into the energy of the chemical reactions taking place on the electrode surface. It can be proved that the transformed electrical energy will grow in correspondence to the rising values of U_m , I_m and $\cos\varphi$. Thus, at a definite peak of applied alternating voltage u and $\cos\varphi$ the efficiency of the processes on the electrodes will grow while the current I_m increases and while the faradaic impedance, Z_t decreases. Moreover, the application of alternating voltage results in the emergence of a nonfaradaic, capacitive current i_c . This current is in inverse proportion the reactive resistance X_c . thus the following equation is valid:

$$i_c = U\omega C_{dl} \tag{2}$$

Apparently, the values of nonfaradaic, capacitive current i_c are proportional to the double layer capacitance C_{di} . As the capacitance grows, the current of charging and discharging of the double layer increases. Since the double layer capacitance in most plating solutions is close to 50 μ F/

cm², the deposition of metal coatings by application of cathodic AC-polarization is accompanied by the emergence of a small peak of reverse discharging current.



Fig. 3 Equivalent circuit of two-electrode plating system

The Characteristic Features of (DC+AC) Pulse Reverse Plating Technique

In comparison to other pulse reverse plating techniques, the deposition of metal coatings by the application of bi-polar (AC +CD) pulses offers the following benefits:

• *the operation is simpler because of the decreased number of variable parameters*

As one can see from Fig. 2, the superimposing of AC voltage over DC pulses simplifies the resulting waveform of bi-polar (DC+AC) pulses (in comparison to any other pulse-reverse waveform). This allows for the electrodeposition process to be controlled by varying a reduced number of five parameters (Table 1). Given the fact that in all cases of electrodeposition of metal coatings the pulse duration, T_{on} does not change and is usually fixed at small values (optimal 5 *ms*), the number of variable parameters is reduced to four (down from nine parameters of the PPR plating and close to the number of parameters for unipolar pulses).

Table 1 Pulse Plating Parameters				
UNIPOLAR PULSE PLATING	BI-POLAR (DC+AC) PULSE REVERSE PLATING			
Pulse Duration, <i>T_{on} ms</i>	Pulse Duration, T_{on}			
Pulse Frequency, $f_p Hz$	Pulse Frequency, $f_p Hz$			
Pulse Current Density, $i_p A/cm^2$	Cathodic Pulse Current Density, $i_{p,c} A/cm^2$			
-	Anodic Pulse Current Density, $i_{p,a} A/cm^2$			
-	Frequency of Alternating Voltage, $f_{a-v}kHz$			

• *there is an off-time between two (DC+AC) pulses*

The *off-time* influences directly the structure of the deposits and their properties as it provides a relaxation time for 1) the recovery of metal ions in the depleted diffusion layer and 2) the adsorption and diffusion of adatoms as well as brightener species on the electrode surface.

One of the stages of the electrocrystallization of the metal coatings is taken up by the time consuming process of surface diffusion and incorporation of the adatoms in the crystal lattice. If all other plating conditions are equal, low surface diffusion rates and high population of adatoms enhance the creation of new nuclei and favor the grain refinement. Elsewhere⁷ we have already described the leveling mechanism and focused on the relationship between the rates of adsorption and diffusion of adatoms and brightener species on the one hand, and the pulse frequency on the other. It was established that the fine-grained metal coatings deposited at pulse frequency that guarantees maximum leveling should demonstrate superb qualities because of the high degree of structural homogeneity. By varying the pulse frequency, at definite pulse duration T_{on} , we can find the exact off-time that enables a maximum value of leveling power and thus creates the plating conditions for electrodeposition of metal coatings with improved properties.

• It is a possible to apply very high pulse current densities, which promotes the deposition of nanocrystalline metal coatings

Since the average current density i_m , is the product of duty cycle, $t_d = \frac{T_a}{T_a + T_{off}}$ and the pulse current density i_p , we can write:

$$i_m = i_p \cdot T_{on} f_p \tag{3}$$

When the average current densities for both types of pulse plating (unipolar & bi-polar DC+AC) are the same, the following equation is valid:



$$i_{p}^{'}.T_{on}^{'}f_{p}^{'} = i_{p}^{''}.T_{on}^{''}f_{p}^{''}$$
 (4)

Fig. 4 Comparison between pulse current peaks of the unipolar and bi-polar (DC+AC) pulses

Comparing the both waveforms in their geometric appearance (shown in Fig.4), we can conclude that for the pulse duration of unipolar pulse plating (UPP):

$$T_{on}' = 2T_{on}''$$
 (5)

Substituting the expression (5) in equation (4) we obtain that the peak of pulse current i_p of the (DC+AC) plating has to be two times greater than the pulse

current i_p of the UPP plating. Moreover, according to the expression (1), the high frequency of the superimposed AC-voltage (up to 5 *kHz*) causes the reduction of faradaic impedance, which results in an additional increase of the pulse current peak. Thus, we can achieve a rise of the cathodic current peaks of the bi-polar (DC+AC) pulses that is nearly of three times greater than that of the unipolar pulse plating (UPP). This high pulse current, in combination with brighteners and other organic additives in plating electrolyte, will promote a deposition of nanocrystaline metal coatings.



Fig. 5 Graphical presentation of depolarization effect of applied alternating voltage on the anodic reaction of active metal dissolution

• *AC-polarization leads to the more effective anodic dissolution of the metal and decreases the risk of passivation*

Tafel's slope
$$g \beta = \frac{\eta_a, Volt}{I, Amp}$$
, has a dimension of an electrical resistance (in *ohms*). This

means that the steeper the slope, the greater resistance of the anodic process stages – destruction of the crystal lattice, ionisation, or transportation, e.g. the greater anodic polarization. For example, a slow diffusion of positively charged metal ions Me^{n+} , from the electrode surface to the bulk solution will result in accumulation of these ions near the metal-electrolyte interface and, hence, in increased anodic polarization. Similarly, retardation in the other stages of the process gives rise to the electrode potential in a positive direction and the potential of passivation

 E_{MxOy} can be reached even at fairly low values of anodic current density (Fig. 5). Conversely, when the anodic polarization is reduced, the Tafel's slope becomes flatter and the current range of active anodic dissolution expands considerably, which allows for the use of higher current densities without the risk of oxide film formation. This is the case of depolarization of the anodic reaction, due to the decrease of the impedance (complex resistance) when AC-voltage is applied.

• There is a considerable reduction of internal stresses and porosity of the deposits.

This benefit appears as a result of the previous one. Pulse deposited metal coatings have greater internal stresses than DC plated deposits because of the increased number of smaller crystallites and of the larger contact surface between them. According to Weil⁸, internal stresses are caused by 1) the coalescence of crystallites and 2) the hydrogen co-deposition. A layer of deposit is formed by the joining of the crystallites. The coalescence of such small grains of crystallites can lead to *tensile stresses* if the grains are pulled together by surface tension before the spaces between them are filled. The joining of only the asperities leads to tiny voids where co-deposited hydrogen atoms diffuse into the voids and expand them and, as a result, *a compressive stress* develops.

Since the applied AC voltage has a depolarization effect on the reaction of anodic dissolution of metal coatings, the application of bi-polar (DC+AC) pulses enables an anodic dissolution of the crystallites' asperities, and thus reduces the opportunity for the formation of tiny voids to be filled by adsorbed hydrogen atoms. Ultimately, this microleveling and grain-refining action of the alternating current leads to a considerable decrease of the compressive stress.

The presence of pores, micro-cracks and other defects disrupting the continuity of metal coatings also is related to the method of their deposition. In the case of electrodeposition of metal coatings, the porosity is largely dependent on whether the surface can be adequately covered through the conventional steps of nucleation and growth. If instead of outward growth of the deposit the lateral growth can be promoted, coverage is faster and therefore more effective at lower thickness. The ratio of the nucleation rate to the rate of grain growth, in turn, controls the average grain size of the deposit at any given thickness. Obviously, the mechanism of pore formation is related to the leveling mechanism of DC or unipolar pulse plating. In practice, there is a correlation between these two coating characteristics. As it was previously established, the maximum leveling corresponds to minimum porosity, and vice versa.⁹

The improved effectiveness of an active anodic dissolution by the applied AC-voltage reduces the risk of partial passivation of the electrode surface and enhances the levelling. In result, (DC+AC) bipolar pulse plating increases leveling power by 20% to 30% compared to that of unipolar pulse plating, which means that the porosity of metal deposits will decrease correspondingly.

Experiments: Techniques and Methodology

The main goal of the present investigations is to demonstrate the advantages of bi-polar (DC+AC) electrodeposition of metal coatings in comparison to the unipolar pulse and/or other pulse reverse plating techniques. Fig.6 shows schematically the apparatus for (DC+AC) pulse-reverse deposition of metal coatings. It consists of a generator **G** for potentiostatic application of bi-polar (DC+AC) pulses, electrolysis cell with rotation cathode **W.E.**, and two-channel oscilloscope **Osc.** The latter measures the current and voltage peaks of the applied bi-polar (DC+AC) pulses. The average current is measured by the ampermeter A. The presence of the quick-pulse diod D ensures the elimination of reverse capacitive anodic current from the double layer discharging so that, if needed, the bi-polar (DC+AC) pulse plating regime could be transformed into a unipolar one.

As we have established in previous research, the above electrolytes used in pulse plating require a concentration of commercially available brighteners that is three to four times lower than the one recommended for DC plating. Moreover, the pulse reverse deposition of bright nickel coatings was conducted by using Watt's electrolyte, modified by a complexing agent. The latter facilitates the process of metal dissolution during the reverse anodic polarization and thus reduces the risk of partial passivation of the electrode surface.

There are two pulse parameters of bi-polar (DC+AC) plating that have the most significant influence on the property performance of deposited metal coatings and that we vary in order to establish the optimal pulse-reverse plating conditions:

- Pulse Frequency, f_p , Hz
- Frequency of Alternating Voltage, $f_{av} kHz$

The pulse duration T_{on} was set constant at 5 ms. This is the optimal time for the cathodic process of crystal growth as well as for the anodic process of metal dissolution. This time is not sufficient for the metal ions to be depleted completely in the diffusion layer during the forward cathode polarization. Also, the period of 5 ms is too short for even the most intensive metal dissolution during the reverse process to cause etching and roughening of the metal coating. The cathodic voltage amplitude U_c is varied in order to maintain the same defined values of the average current densities for all used pulse frequencies. The applied anodic voltage U_a controls the anodic pulse current density $i_{p,a}$ whose optimal value is established experimentally through leveling power measurements.



Fig.6 Scheme of the apparatus for (DC+AC) pulse reverse deposition of metal coatings

PULSE CURRENT MEASUREMENTS

The possibility for application of higher pulse current densities in (DC+AC) plating than in unipolar pulsed deposition has been demonstrated experimentally by using bright copper and nickel electrodeposition. The values compared are obtained under the same plating conditions related to the pulse frequency and average current density. Fig. 7 and Fig.8 show the peak current densities of bright copper and nickel coatings. In both cases of metal coatings deposition, the peak current densities applied in (DC+AC) plating are 2.5 to 3 times greater than in UPP for the corresponding pulse frequency and at the same average current density $i_m = 0,032$ A/cm². As it was already emphasized, the possibility for application of 2 - 3 times higher pulse current densities is due to two factors:

- the effective time used for cathodic polarization during the pulse in UPP plating is exactly twice as long as the one of (DC+AC) pulses
- the high frequency (up to 5.0 kHz) of the applied alternating voltage ω reduces the faradaic

impedance as it decreases the reactive component $X_s = \frac{1}{\omega C_s}$ of the complex resistance.

It can be seen that the depolarization effect occurs when AC-polarization of 2.0 kHz frequency is

applied (Table 2). For example, the values of the polarization resistance $R^{"} = \frac{U_{c}^{"}}{I_{n}^{"}}$ ohms, in bi-

polar (DC+AC) copper plating are by 40% to 50% lower that ones $R' = \frac{U_c}{I_p}$ ohms, of UPP

deposition. It should be noted that the greatest reduction of R^* is observed within the close range of those pulse frequency values that are related to the maximum values of leveling power.

The authors of the already cited patent⁴, claim that the application of high pulse current densities (2 to 3 A/cm²) in combination with stress relievers and grain refining additives in the electrolyte (10 g/l saccharin) is sufficient to produce nanocrystalline nickel deposits with grain size smaller than 11 nm. Fig.7 and Fig.8 demonstrate that in our case such high pulse current densities can be easily reached. In addition, we can obtain the same result with two to three times lower concentration rates of brighteners and other organic compounds in the plating electrolyte. Moreover, in our cases of (DC+AC) pulse-reverse deposition, the pulse duration of 5 milliseconds is two times longer than the one stipulated in the patent as the optimal duration of 2.5 ms.

Pulse	Copper plating			Nickel plating		
Frequency,	R',ohm	R ["] ,ohm	$R' - R''_{,\%}$	R',ohm	R ["] ,ohm	R' - R''', %
Hz			R			Ŕ
6	3.1	1.8	41.9	8.0	7.0	12.5
7	3.4	1.8	47.0	9.1	7.8	14.3
8	3.8	1.9	50.0	9.5	7.5	21.0
9	4.0	1.9	52.5	10.6	8.0	24.5
10	4.0	2.1	47.5	10.6	8.3	21.7
11	4.0	2.3	42.5	10.7	8.5	20.5

Table 2 Relative reduction of polarization resistance R" in (DC+AC) plating(compared to polarization resistance R' in UPP plating)

LEVELING MEASURMENTS

Leveling can be qualitatively characterized as the ability to diminish the difference in heights between protrusion peaks and recesses of the microprofile in result of electrochemical treatment of electrode surface. Our quantitative estimations include roughness measurements of both the initial metal substrate R_0 and of the deposit surface after pulse plating R_d in order to determine the leveling power using the following expression:

$$E \ \% = \frac{(R_0 - R_d)}{R_0} \times 100$$

The initial roughness R_0 is obtained by grinding an electrode in one direction only with grade 280-emery paper. Half of the surface of the rotation disc electrode (0.5 cm²) has been previously insulated with a thin film of photo-resist lacquer. After pulse plating of metal coating on the other half, this film is removed with the help of an organic solvent. Thus, it is possible to determine directly from a single electrode the roughness changes due to the metal deposition. The speed of rotation is maintained constant - 300 rpm. Pulse duration in both cases of pulse plating is the same: 5 msec.

An underlying principle in the experiments was to vary pulse frequency while the average current density and other pulse parameters have been maintained at a constant value. The relationship between leveling power *LP*% and pulse frequency, $f_p Hz$ in unipolar pulse plating and bipolar (DC+AC) pulse plating of bright copper and nickel deposits is shown in Fig.9 and Fig.10. From these graphs we can determine the leveling maximum and the corresponding pulse frequency at which it occurs. It can be seen that the maximum values of leveling power obtained in (DC+AC) pulse plating are 30% to 40% higher than those of bright copper and nickel coatings deposited by unipolar pulse plating.



Fig. 7 Peak current densities in bright copper deposition by unipolar DC- & bi-polar (DC+AC) pulses



Fig. 8 Peak current densities in bright nickel deposition by unipolar DC- & bi-polar (DC+AC) pulses



Fig. 9 *The relationships between leveling power and pulse frequency in UPP plating and (DC+AC) plating of bright copper*



Fig. 10 *The relationships between leveling power and pulse frequency in UPP plating and (DC+AC) plating of bright copper*

The similar graphical relationships between leveling power and pulse frequency of the metal coatings deposited by UPP and bi-polar (DC+AC) pulse reverse plating point to a common leveling adsorption-diffusion mechanism. That leads to conclude that similarly as in UPP, in the case of (DC+AC) deposition the pulse frequency is the major controlling factor of leveling performance. For every bright (DC+AC) pulse plating process a definite pulse frequency can be found so that the rates of both simultaneous and related processes – nuclei formation and adsorption of brightener species - can reach the optimal coordination. This frequency of cathodic pulses coincides exactly with the frequency at which the leveling maximum occurs. Moreover, the lower rates of surface diffusion flow of brightener species towards recesses of the microprofile correspond to the higher values of the leveling power. This means that the slower the surface diffusion of brightener species, the higher is the leveling power value. The application of bi-polar (DC+AC) pulses, obviously, can slow down this surface diffusion flow, and thus increase the leveling power values in comparison to that ones of the obtained in UPP metal deposits for the same pulse frequencies (see Fig.9 and Fig.10). The retardation effect of surface diffusion is at it highest at 2000 Hz frequency of alternating voltage. It was at this frequency that (DC+AC) depositions were performed.

INTERNAL STRESS MEASUREMENTS

The present internal stress measurements are based on the application of a dilatometric method¹⁰. This method has proved accurate and easy to operate, and, in addition, it is sufficiently sensitive to apply to all but the thinnest electrodeposits. What has been measured is the elastic expansion or contraction of a pre-stressed copper strip, brought about by the force developed along its axis by the tensile or compressive stress in the deposit grown on its two surfaces. Changes in length of the strip during plating are recorded by the movement of the pointer of a sensitive (\pm 0.5 micron) dilatometer, which is in contact with the tip of a shaft connected to the top end of the strip. Tensile and compressive stresses are recorded with equal accuracy. Each strip is used once, and may then be kept for reference. Mean deposit thickness is calculated after plating using the same sensitive dilatometer.



Fig. 11 *Comparison between compressive stress data (with negative sign) of nickel coatings deposited by unipolar pulse-, (DC+AC) pulse reverse- and DC plating*

The results of the internal stress measurements of bright nickel coatings DC and pulse deposited are shown in Fig.11. Comparing the values of internal stress of bright nickel coatings deposited at pulse frequency of maximum leveling power, we can conclude that the bi-polar (DC+AC) pulse reverse plating regime demonstrates an obvious advantage. In this case, the effective anodic dissolution during the reverse period leads to the considerable reduction of the compressive stress values. The latter, nevertheless, remain sufficiently high in comparison with these of DC deposited nickel coatings.

POROSITY MEASURMENTS

The electrochemical apparatus for the porosity test used in the present investigations is described in our earlier publication¹⁰. It is designed for comparative estimation of the porosity of thin metal coatings (up to 2 μ m) deposited on the substrate of different metals. This porosity test is based on the method of linear polarization resistance (LPR) applied for example in devices for corrosion monitoring. The well-known Stern and Geary's expression is used to define the instantaneous corrosion rate of the metal in contact with liquid corrodent:

$$i_{corr} = \frac{b_c \cdot b_a}{2,3(b_c + b_a)}$$
 or $i_{corr} = \frac{B}{R_p}$

where R_p is the polarization resistance of the metal-electrolyte system and b_a and b_c are Tafel slopes of anodic and cathodic polarization curves, respectively.

The two flat metal-coated specimens are pressed to rubber O-rings closing the two identical axial openings located at the bases of the cylindrical electrochemical cell. The electronic device measures the polarization conductance $1/R_p$ which represents the ratio between the resulting current ΔI , mA, and the voltage $\Delta E = \pm 10 \text{ mV}$ of the applied sign-changing pulses. The current ΔI is automatically measured after eliminating the transition current is occurring at the beginning of each pulse. The integral value $Q = \int (1/R_p) dt$ is calculated for a definite test period of 5 or 10 minutes and displayed by the 1/R-time integrator.

The porosity of the metal coating could be considered proportional to the integral value Q, provided that the corrosion rate of the metal-deposit is negligibly low in comparison to the dissolution rate of metal-substrate through the pores. Therefore, when the goal is to provide the largest possible difference between the dissolution rates of the two metals, the most important problem with such porosity measurements is the accurate choice of a test electrolyte. The electrolyte used in the porosity measurements of nickel deposits on mild steel substrate contains NaCl, Nagluconate, NH₄ F. HF, and H₃ PO₄. When uncoated steel electrodes are in contact with the electrolyte for 5 *min*, the 1/R-time integrator displays a value assumed as 100% porosity. For a two-pure nickel-electrode assembly in contact with the same test electrolyte, the obtained integral values $Q = \int (1/R_p) dt$ are assumed as 0 % porosity. The time for deposition for all nickel coatings is the time required to obtain the same approximate thickness of 1.5 μ m. The roughness of the steel substrate is the same in all cases and was equivalent to that obtained by treatment with # 600 grit paper. The average porosity values are obtained from the large number of measurements. The nickel coatings were deposited at pulse frequencies corresponding to the maximum leveling power – 8 Hz, and at the average current density– 2 A/dm². The frequency of alternating voltage was 2500 Hz.

The comparison between the porosity of the coatings deposited by UPP and (DC+AC) plating demonstrates the advantages of the pulse-reverse plating technique. Bright nickel coatings deposited by UPP plating have higher porosity (11%) than that of coatings deposited by the application of (DC+AC) pulses (6% porosity).

Conclusions

The present investigations have yielded results that warrant the following conclusions:

- The application of bi-polar (DC+AC) pulses obtained by a superimposition of an alternating current (AC) on direct current (DC) presents a new pulse-reverse technique; this technique offers a simple and effective electrodeposition of metal coatings with improved properties.
- The (DC+AC) plating makes it possible to apply cathodic pulse current densities that are two to three times higher than these of unipolar pulse plating (both at the same average current density); as a result, (DC+AC) plating enhances the creation of new nuclei and promotes deposition of nanocrystalline metal coatings.
- The presence of *off-time* between two (DC+AC) pulses determines the same leveling mechanism as in the unipolar pulse plating. It is focused on the relationship between the adsorption and surface diffusion of adatoms, and brightener species during T_{off} on the one hand, and the pulse frequency on the other. The fine-grained metal coatings deposited at a pulse frequency that guarantees maximum leveling power should demonstrate superb qualities because of the high degree of structural homogeneity.
- The forward (cathodic) AC-polarization slows down the surface diffusion rates of brightener species and thus, increases the leveling power by 30% to 40% (in comparison to unipolar pulse plating) for the all pulse frequencies in investigated range. Given that the better leveling corresponds to the minimum porosity, when it comes to the deposition of very fine-grained metal coatings with lower porosity, e.g. with higher corrosion and wear resistance, priority should be given to (DC+AC) pulse reverse plating.
- The reverse (anodic) AC-polarization improves the effectiveness of the active metal dissolution and decreases the risk of partial passivation. This additionally enhances the leveling and results in a considerable reduction of the compressive stress of metal deposits.

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