# A-C modified Pulsed Pulse Reverse (PPR) Techniques - Effective Means for the Deposition of High-Quality Metal and Conversion Coatings

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Our goals are to advance and unify the PPR techniques for deposition high-quality metals and to improve conversion coating. Previous work demonstrates that via definitive PPR deposition, a commutative effect of forward and reverse pulse trains improves leveling and structural homogeneity. Application of anodic pulses may cause surface oxidation and diminish leveling. With the use of commutated anodic AV (alternating voltage) pulses, amplitude and frequency are selected for greatest metal deposition efficiency. Optimizing the PPR technique for high-quality metal coatings is facilitated.

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Dr. Mois Aroyo Dept. Chemistry, Technical University of Sofia Sofia 1797, "Kl.Ohridski" 8 Bulgaria e-mail: msaroyo@ecad4sun.vmei.acad.bg The results of our recently completed work<sup>1</sup> have demonstrated that at the definite parameters of pulsed pulse reverse (PPR) plating, a large positive effect in terms of leveling performance and structural homogeneity of the obtained metal deposits can be achieved. In order to deposit high-quality metal coatings by using PPR techniques, two very important electrochemical principles must be applied:

- 1. The electrocrystalization of metal coatings during the forward period should take place under the conditions of highest possible cathodic polarization.
- 2. The dissolution of metal coatings during the reverse period should take place under the conditions of lowest possible anodic polarization.

In the following, we provide a theoretical explanation for the necessity to apply the above electrochemical principles in PPR plating.

## THEORETICAL CONSIDERATIONS Cathodic deposition of metal coatings

As it is well known, one of the necessary conditions for cathodic deposition of highquality metal coatings is that the deposits must have fine-grained structure. The size of the crystal grains depends largely on the relative rates of formation of crystal nuclei as well as on the growth of existing crystals. Such conditions that favor the creation of new crystal nuclei would yield finer-grained deposits, while conditions encouraging the growth of existing crystals would lead to the formation of fewer but larger crystals. The rate of formation of new nuclei on the electrode surface increases exponentially as the cathodic polarization  $\mathbf{I}_{e}$  grows according to the expression<sup>2</sup>:

$$w = B \exp\{-\frac{K}{h_c^2}\}$$

Here, the constants B and K are specific for a given metal at a given temperature. The increase of cathodic polarization  $\mathbf{L}_{\mathbf{k}}$  will result in a larger number of newly formed nuclei and thus, in a finer-grained structure of the electrodeposits.

Also, from the kinetic equation of cathodic process 
$$\mathbf{h}_{c} = \frac{RT}{zF} \ln(1 - \frac{i}{i_{L}})$$

follows that  $\mathbf{h}_c \to \mathbf{Y}$  when  $i \to i_L$ . In other words, when the applied current density  $i_p$  increases reaching values close to the limiting current density  $i_L$ , the polarization  $\mathbf{h}_c$  of the electrodeposition process increases infinitely (Fig. 1). It seems that in order to obtain metal coatings with fine-grained structure, the cathodic current should be very close to  $i_L$ , where  $\mathbf{h}_c \to$  $\mathbf{Y}$  However, if under certain plating conditions the metal ions in the diffusion layer are consumed and the potential of hydrogen evolution is reached fairly quickly, the deposits became burned, excessively rough or spongy. High current densities can be reached without the risk of ruining the deposits, only if square-wave current pulses with very small duration  $T_{on}$  (5 – 10 msec) are applied. When short pulses are applied, a potential hydrogen evolution cannot be reached even if very high current densities are used. Also, during the relatively long pause between two short pulses, the bulk concentration of the metal ion in the diffusion layer is renewed quickly and a new cycle can resume.





**Fig. 1** *Cathodic and anodic (active-passive) polarization curves of metal-electrolyte electrochemical systems.* 

The presence of a fine-grained structure is a necessary but not a sufficient condition for the deposition of a metal coating with better decorative and functional properties. Among numerous pulse deposited metal coatings with fine crystal structure obtained by multiple combinations of the three independent variables there are only a few with the desired properties. As it has been proved in our previously published work<sup>3</sup>, there is a correlation between leveling performance of bright metal deposits and their properties, and therefore, the leveling power could be used as an objective criterion for property estimation of d-c or pulse deposited metal coatings. We have also described the leveling mechanism at work and focused on the relationship between the rates of diffusion, adsorption and incorporation of brightener species into the deposite on the one hand, and the pulse frequency on the other. Fine-grained metal coatings deposited at pulse frequency that guarantees maximum leveling should demonstrate superb qualities because of the high degree of structural homogeneity. Conversely, an irregular distribution of the crystal imperfections occurs at minimum value of leveling power.



Fig. 2 Pulsed pulse reverse waveforme

By varying the pulse frequency we can find those cathodic pulse parameters that enable a maximum value of leveling power and thus create the plating conditions for electrodeposition of metal coatings with improved properties.

#### Anodic dissolution of the metal deposits by reverse pulses

If we find an appropriate way to combine the trains of cathodic pulses of electrocrystalization with the trains of anodic pulses of metal dissolution, we can obtain a positive commutative effect in respect to leveling and structural homogeneity. The exact determination of the parameters of reverse pulses can be based on the anodic behavior of the electrochemical system metal-electrolyte in general, and on the mechanism of active anodic dissolution, in particular.

As it is shown schematically in Fig. 3, the energy needed for the separation of a given structural element in the metal crystal from the lattice depends on its position on the crystal surface. Structural elements A at the corners of the crystals require the least energy, because they are surrounded by only three other elements, and, in addition, their transfer from the metal lattice into the electrolyte is helped along by the high number catalytic anions attracted by them. In order to leave the crystal edge a structural unit B has to overcome the interaction forces with the nearest four elements. And in order to leave the flat surface of the crystal wall the element C has to break free from the bonds with five neighbours.

The application of pulsed anodic polarization would result in metal dissolution starting first at the corners and edges of the crystal where the structural elements in position of so-called halfcrystal. Such sites of half-crystal are mainly are found in places where there is "misfit" crystallite boundary adjacent to the dislocation asperities and other surface defects on the metal lattice. Therefore, at definite reverse parameters of the applied anodic pulses a superior leveling performance and structural homogeneity of metal deposit can be obtained.

In previous works we have already discussed the theoretical considerations that determine the choice of parameters for the reverse anodic pulses in the process of pulsed pulse reverse plating.<sup>1,4</sup> We have established that the leveling performance of PPR deposited metal coatings depends strongly on the active-passive polarization characteristics of the electrochemical system metal deposit//plating electrolyte.



Fig. 3 - Metal dissolution by transfer of the structural elements A, B, C into electrolyte

Also, we have observed that even the partial formation of thin anodic oxide films leads to a considerable deterioration of the leveling performance of metal coatings. In order to reduce the possibility of passivation of the metal surface during the reverse period, the rectangular anodic pulses must be **potentiostatic** with relatively small voltage amplitude  $\mathbf{IDE}$  (150 - 300 mV) and a very short pulse duration  $T_{on}$  (5 ms). Nevertheless, oxide formation and passivation during the reverse period remain a practical possibility, since the process of anodic dissolution goes through various stages – disintegration of the crystal lattice, anion adsorption, ionisation, and the transportation of hydrated metal ions into the electrolyte – and each of these stages may, by itself or in combination with the other, contribute the partial or complete passivation of the metal coating surface.

#### How then to diminish the risk of anodic passivation?

In order to answer this question, we must give consideration to the following theoretical premises.



Fig. 4 A-C modified pulsed pulse reverse waveforme

An anodic dissolution of metals occurs when the applied potentials are more positive than the equilibrium potential of a given electrochemical system. Under the conditions of active metal dissolution, the following relationship between anodic polarization  $h_a$  and current density,  $i_a$  is valid:

$$\mathbf{h}_a = b \log i_a / i_0$$

where  $b = tg \mathbf{b}$  is the Tafel's slope of the linear relationship  $\mathbf{h}_a - log i_a$  (see Fig.1). The anodic polarization,  $\mathbf{h}_a$  can be associated with a retardation in one or more of the above mentioned process stages – destruction of the crystal lattice, ionisation, or transportation. For example, a slow diffusion of metal ions from the electrode surface to the bulk solution is the reason for their accumulation near to metal-electrolyte interface and, hence, for the increased anodic polarization. Similarly, retardation in the other stages of the process gives rise to the electrode potential in a positive direction. In other words, the higher the anodic polarization the steeper Tafel's slope. Therefore, the potential of passivation  $E_{MxOy}$  is reached at a lower level current  $i_{crit}$ . Conversely, when the anodic polarization is small, the Tafel's slope is flatter and the current range of active anodic dissolution expands considerably, which allows for the use of higher current densities of metal dissolution without the risk of oxidation.

An effective way to reduce the anodic polarization of metal dissolution, and thus to expand the current range of active metal dissolution, can be found in the application of asymmetrical sinusoidal AV pulses with anodic d-c component. The waveform of the A-C modified PPR techniques is shown in Fig. 4.



Fig. 5 Equivalent circuit of electrode - electrolyte electrochemical system

In order to explain how the depolarization action of the applied sinusoidal voltage  $U_{av}$  affects the electrode processes, we present the real plating cell as an equivalent circuit of resistors and capacitors<sup>5</sup> as it is shown in Fig. 5. The total resulting current through the working interface is the sum of distinct contributions from the faradic process  $i_f$  and double-layer charging  $i_c$ . The double-layer capacitance resembles closely a pure capacitance; hence it is represented in the equivalent circuit by the element  $C_d$ . The rate of the net electrochemical electrode process  $i_f$  is in inverse proportion to the faradaic impedance  $Z_f$ . The later can be presented as a combination of the series resistance  $R_s$  and the pseudocapacity  $C_s$ . In contrast to  $C_d$ , which is a nearly ideal circuit element, the components of the faradaic impedance are not ideal because they

change with frequency  $\mathbf{w}$  From the frequency dependencies of  $R_s$  and  $C_s$  it follows that we can determine experimentally such a frequency of the applied voltage  $U_{av}$  at which the faradaic impedance  $Z_f = R_s(\mathbf{v}) + \frac{1}{\mathbf{w}C_s}$  is minimal and, correspondingly, the faradaic current  $i_f$  is at its maximum

maximum.

## EXPERIMENTAL PROCEDURE

## Leveling performance of bright nickel coatings, deposited by A-C modified PPR plating

In the case of A-C modified pulsed pulse reverse techniques, PPR parameters include additional four parameters characterizing the applied AV polarization: anodic peak of the sinusoidal voltage  $U_a$ , cathodic peak of the sinusoidal voltage  $U_c$ , frequency of AV polarization

 $f_{AV}$ , and symmetry coefficient  $K_{sym} = \frac{U_c}{U_m}$ , where  $U_m$  is the amplitude of the sinusoidal voltage.

All parameters used in A-C modified PPR plating are shown in Table 2.

For the study of the leveling performance of bright nickel coatings deposited by A-C modified PPR techniques we have used Watt's electrolyte modified with a complexing agent.

Table 1.	Bath (	Composition	<i>i</i> for	<b>Bright</b>	Nickel .	Deposition
		· · · · · · · · · · · · · · · · · ·	J			<b>r</b>

NiSO <sub>4</sub> .7H <sub>2</sub> O	250 g/l
NiCh_6H2O	10 g/l
H <sub>3</sub> BO <sub>3</sub>	10 g/l
Complexing agent: Na – citrate	60 g/l
Brightener: TS - 55	5 ml/l
Hydrodynamically active agent	4 mg/l

PLATING MODE		PULSE PLATING PARRAMETERS						
		Forward	Reverse					
		Pulse Current Density $i_p$ , $mA/cm^2$	Pulsed Voltage <b>DE</b> , <i>mV</i>					
keverse	Reverse	Pulse Duration $T_{on}$ , ms	Pulse Duration, $T_{on}$ , ms					
	Pulse I	Pulse Frequency $f_{for}$ , $Hz$	Pulse Frequency $f_{rev}$ , $Hz$					
Pulse ]	Pulsed	Forward Period Duration $T_{for}$ , sec.	Reverse Period Duration $T_{rev}$ , sec.					
Julsed		-	Peak of Anodic Voltage $U_a$ , $mV$					
fied ]		-	Peak of Cathodic Voltage $U_c$ , $mV$					
C modi		-	Coefficient of Symmetry, $K_{sym} = \frac{U_c}{U_m}$					
A.		-	Frequency of Altern.Voltage $f_{AV}$ , $kHz$					

 Table 2 Pulse plating parameters of PPR and A-C modified PPR techniques

The parameters of the forward pulses have been maintained at a constant value corresponding to the pulse frequency of the leveling maximum in unipolar pulse plating. At the same time, the parameters of A-C modified reverse pulses were varied.

	"Duty Reverse	FORWARD								
		$i_p A/cm^2$		$T_{on, j} ms$		$f_{fo}$	ffor, Hz		T <sub>for</sub> sec	
Sample		2,6		10			10		10	
ш	Cycle"	REVERSE								
#	%									
		∎E, mV	T <sub>on</sub> , ms	frev , Hz	T <sub>rev</sub> , sec.	U <sub>a</sub> , mV	$U_c$ , mV	K <sub>sym</sub>	<b>f</b> a-v , kHz	
01		-	5	4	3	150	11	0,13	2,0	21,7
02	23,0	-	5	5	3	150	11	0,13	2,0	24,7
03		-	5	6	3	150	11	0,13	2,0	22,5
04		-	5	4	4	150	11	0,13	2,0	22,7
05	28,5	-	5	5	4	150	11	0,13	2,0	27,1
06		-	5	6	4	150	11	0,13	2,0	19,0
07		-	5	4	5	150	11	0,13	2,0	26,3
08	33,3	-	5	5	5	150	11	0,13	2,0	27,5
09		-	5	6	5	150	11	0,13	2,0	24,5
10	37,0	-	5	4	6	150	11	0,13	2,0	24,7
11		-	5	5	6	150	11	0,13	2,0	25,0
12		-	5	6	6	150	11	0,13	2,0	21,0
13	28,5	150	5	5	4	-	-	-	-	23,2

**Table 3.** The influence of "duty reverse cycle" & frequency of reverse pulses  $(f_{rev}, Hz)$ on leveling power (LP%) of bright nickel deposits

	$i_p$ , $A/cm^2$		$T_{on}$ , $m_{s}$	s f <sub>f</sub>	ffor, Hz		, sec.	
	2,	6	10		10		.0	
Sample #	REVERSE						Ι	LP%
	T <sub>on</sub> , ms	f <sub>rev</sub> , Hz	T <sub>rev</sub> , sec.	U <sub>a</sub> , mV	$U_c$ , mV	K <sub>sym</sub>	fa-v, kHz	
01	5	5	5	150	0	0	0,6	21,0
02	5	5	5	150	8	0,1	0,6	19,5
03	5	5	5	150	17	0,2	0,6	24,5
04	5	5	5	150	26	0,3	0,6	20,7
05	5	5	5	150	37	0,4	0,6	20,6
06	5	5	5	150	0	0	1,0	21,1
07	5	5	5	150	8	0,1	1,0	21,0
08	5	5	5	150	17	0,2	1,0	25,4
09	5	5	5	150	26	0,3	1,0	23,4
10	5	5	5	150	37	0,4	1,0	20,9
11	5	5	5	150	0	0	1,5	22,0
12	5	5	5	150	8	0,1	1,5	23,3
13	5	5	5	150	17	0,2	1,5	27,0
14	5	5	5	150	26	0,3	1,5	26,8
15	5	5	5	150	37	0,4	1,5	25,0
16	5	5	5	150	0	0	2,0	21,7
17	5	5	5	150	8	0,1	2,0	27,7
18	5	5	5	150	17	0,2	2,0	30,5
19	5	5	5	150	26	0,3	2,0	29,1
20	5	5	5	150	37	0,4	2,0	25,0

**Table 4.** The influence of  $K_{sym}$  & frequency of AV reverse pulses( $f_{av}$ , kHz) on leveling power (LP%) of bright nickel deposits

The influence of a "duty reverse cycle" and the frequency of reverse pulses on the leveling power (*LP*) of bright nickel coatings deposited by A-C modified PPRP is shown in Table 3. The highest values of leveling power are obtained at frequency of the anodic pulses around 5 Hz and the "duty reverse cycle" at 33,3%. Under these plating conditions (sample # 08), the maximum value of leveling power is 17% greater than the maximum value of leveling power of bright nickel coatings deposited by PPR techniques with rectangular anodic pulses (sample # 13). One can see that the "duty reverse cycle" exerts a minimal little influence on *LP* values; *LP* values remain high within a relatively wide range of values for this parameter.

Similar the experimental results are summarized in Table 4. The high values of leveling power of bright nickel deposits obtained by varying definite ranges of symmetry coefficient  $K_{sym}$  and AV frequency ( $f_{av}$ , kHz) serve as an evidence that the depolarization effect of asymmetric sinusoidal voltage is also accompanied by a stabilization of the electrochemical system and by an unification of the plating conditions related to surface diffusion and adsorption of metal ions and brightener species within a wide diapason of changing of pulse parameters.

As one can see from the Table 4, in each of the fourth series of experiments corresponding to the fourth used AV frequency, the maximum value of leveling power is obtained when the symmetry coefficient  $K_{sym}$  is 0,2. The highest value of LP - 30,5% is obtained when the AV frequency is 2,0 kHz (sample #18). This LP value is 31% greater than LP of bright nickel coatings deposited by PPR techniques with rectangular anodic pulses (sample # 13, Table 3).

### **Conclusions**

The present investigations have confirmed the expected depolarization effect of asymmetric sinusoidal voltage on the processes of anodic dissolution of metal coatings deposited by A-C modified pulsed pulse reverse techniques. This effect favours the deposition of metal coatings with very good leveling performance within a wide range of varying of pulse plating parameters.

As we take into consideration the previously proven correlation between leveling power and some coating's properties (porosity, tensile strength, ductility, internal stresses), we can state with certainty that in such regime of A-C modified pulsed pulse reverse plating that guarantee maximum value of leveling power the metal deposits will possess the best properties.

#### References

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