Technical Article

Pulse Periodic Reverse Plating—New Possibilities for Electrodeposition of Metal Coatings with Improved Properties: Part 1

By M. Aroyo & N. Tzonev

The main objective of this work is to explore using the potential of pulse periodic reverse plating for the deposition of high-quality metal coatings. Our research is based on the fact that the fine-grained metal coatings deposited by unipolar pulse plating at frequencies yielding maximum leveling exhibit a higher degree of structural homogeneity and, consequently, possess superb functional properties. In the case of pulse periodic reverse plating, an even larger effect can be achieved when a sequence of cathodic (forward) pulses is applied, followed by anodic (reverse) pulses, where both series of pulses are arranged by frequency of maximum leveling power. The application of anodic pulses, however, is likely to cause oxidation of the metal surface and the leveling characteristics of the deposits will deteriorate. In order to avoid this oxide formation, we have studied the precise role of a variety of factors favoring the oxidation process.

Pulse periodic reverse plating (PPRP) offers considerable advantages in achieving superior leveling and structural uniformity in the resulting deposits. In this work, we describe the systematic procedure used to find the optimum set of PPRP parameters for the best leveling of nickel, copper and gold deposits. The maximum values of leveling power of the metal coatings deposited by unipolar pulse plating (UPP) and by pulse periodic reverse plating (PPRP) were compared. We found that under certain conditions, PPRP ensures the deposition of metal coatings with better leveling characteristics and, consequently, higher quality than the best of the unipolar pulse-deposited metal coatings.

Nuts & Bolts: What This Paper Means to You

Pulse plating has been making inroads like never before. First there was unipolar cathode-only pulse plating, which produced fine-grained, leveling layers with superb properties. Recently, pulse-reverse plating, with a series of anodic pulses thrown in, has been shown to provide even better quality deposits. The anodic pulses shake up the chemical boundary layers around the part. Here, the authors delve deeply into the process, including one concern ... avoiding the chance of forming oxides while the anodic pulses are applied.







Fig. 2—Pulse periodic reverse waveform.

Theoretical Considerations Unipolar Pulse Plating (UPP)

Pulse plating has emerged as an electrochemical technique for depositing metal coatings with improved properties. In conventional direct-current (DC) deposition, there is only one parameter, current density, that can be varied. In classical unipolar pulse plating, however, there are three independent electrical parameters: pulse current density, i_p , pulse length, T_{on} and pulse frequency, $f = (T_{on} + T_{off})^{-1}$, where T_{off} is the time interval between two pulses. Typical UPP waveforms include a cathodic pulse followed by a period without current. The sum of the times T_{on} and T_{off} constitute one pulse cycle. Some important relationships used in unipolar pulse plating are:

duty cycle, $t_d = T_{on} / (T_{on} + T_{off})$ and average current density, $i_a = i_p \times t_d$.

The average current density is similar to that used in DC plating. We experimented with multiple combinations of



Fig. 4—Schematic drawing of a galvanostatic anodic polarization curve.

 Fig. 3—Schematic drawing of a typical potentiostatic anodic polarization curve.
 Fig. 4—S

these parameters to establish the best pulse plating conditions to produce high-quality metal coatings.

As is well known, in order to produce electrodeposits with optimum properties, such as porosity, ductility, hardness, roughness, electrical conductivity, corrosion or wear resistance, they must have a fine-grained structure. In general, fine-grained metal coatings are smoother, brighter, harder and stronger than columnar-grained deposits.¹ Pulse plating has emerged as an indispensable electrochemical technique for producing fine-grained electrodeposits.

The crystal structure largely depends on the relative rates of formation of crystal nuclei, as well as on the growth of existing crystals. Conditions that favor crystal nuclei will yield finer-grained deposits, while conditions encouraging the growth of existing crystals will lead to the formation of fewer but larger crystals.²

According to the principles of electrocrystallization, the rate of formation of new nuclei on the electrode surface increases exponentially as the cathodic polarization _______ increases:³

$$\operatorname{tr} = \left(\frac{\partial \theta}{\partial t} \exp\left(- \frac{\partial \theta}{\partial t} \right) \right)$$

 η_L
(1)

Here, the constants B and K are specific for a given metal at a given temperature. If all other conditions remain constant, the increase of cathodic polarization will result in a larger number of newly formed nuclei and, therefore, a finer-grained deposit structure. Also, from the kinetic equation for the cathodic process, it follows that c when i i_t (the limiting current):

$$\eta_{k'} = \frac{RT}{xF} \ln(1 - \frac{i}{J_L}). \quad (2)$$

In other words, when the applied current density increases to values approaching the limiting current density i_L , the polarization of the electrodeposition process increases infinitely (Fig. 1). It seems that in order to obtain metal coatings with a fine-grained structure, the cathodic current should be very close to i_L , where

. The use of such high current densities without producing burned, rough, "treed" or spongy coatings is possible only by the application of very short square-wave cathodic pulses (T_{on} very small). In theory, the on-times can be shortened and the applied pulse current density can be very high. The relationship between T_{on} and i_p for the pulse deposition of finer-grained coatings should be such that the current between the electrodes is consumed entirely during a single pulse. Therefore, there would be a complete reduction of metal ions. In practice however, if the pulse current density is very high while the on-times are very short (on the order

of μ sec), the desired effect cannot be achieved. There would be a strong damping effect on the Faradaic current at such high pulse frequencies. Further, duty cycle values would be too small.⁴ Therefore, the on- and off- times should vary within the range of 5 to 100 msec, which corresponds to the time needed for diffusion transport, adsorption and desorption of metal ions, brightener molecules and other species participating in processes of electrocrystallization.

A fine-grained structure is necessary to achieve a metal coating with better decorative and functional properties. Yet this structure alone is not sufficient to guarantee it. Among numerous pulsedeposited metal coatings with fine crystal structures, there are really only a few with the desired properties. As shown in our recently published work,⁵ there is a correlation between leveling performance of bright metal deposits and their properties. Therefore, leveling power can be used as an objective criterion for estimating the properties of DC- 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 deposits on the one hand, and pulse frequency, f, on the other. Fine-grained metal coatings deposited at pulse frequencies associated with maximum leveling should demonstrate superb qualities because of the high degree of uniform distribution of dislocations, tiny voids and other crystal defects within the deposit. Conversely, an irregular distribution of these crystal imperfections was found to occur at a minimum value of leveling power. By varying the pulse frequency, we can find those pulse parameters that enable maximum leveling and thereby create the plating conditions required to obtain the improved deposit properties.

The main objective of the current work has been to seek even higher-quality metal coatings by using pulse periodic forwardreverse systems. Our expectation was that if we could find an appropriate way to combine the trains of cathodic pulses of electrocrystallization with the trains of pulses of metal dissolution, we could obtain a positive commutative effect with respect to leveling and structural homogeneity of the metal deposits.

Pulse Periodic Reverse Plating (PPRP)

As shown in Fig. 2, the pulse periodic reverse waveform features a train of cathodic pulses, followed by a train of anodic pulses. The parameters of the forward and reverse pulses can be separately and independently controlled.

The current investigations apply the same method as that used with unipolar cathodic pulse plating. We looked at the relation-



Fig. 6—The relationship between leveling power, LP% and the pulse frequency of the anodic pulses, f in pulse periodic reverse plating of nickel deposits.

ship between leveling power (LP%) and the anodic pulse parameters to determine the conditions under which maximum leveling occurred.⁵

The process of anodic metal dissolution is often accompanied by oxide formation on the electrode surface. Under such passivation conditions, it is difficult to establish a correlation between the leveling performance of the deposits and the anodic pulse parameters. Therefore, an important question first had to be answered: What application regime of anodic polarization should be chosen so that the leveling performance depends only on the metal dissolution process?

The following theoretical considerations about the anodic behavior of the metal-electrolyte system help us to answer this question and to clarify the role of anodic polarization in the reverse portion of PPRP. They also serve as a basis for the experimental determination of the conditions required for maximum leveling power.

Active-passive Transition

The application of anodic polarization in a metal-electrolyte system results in a DC current that may be related to one of following electrochemical reactions:

- Active dissolution through metal ion transport from the bare metal surface into the electrolyte,
- Passivation, the formation of conversion oxide films or salt layers on the metal surface, or
- · Transpassivation and/or oxygen evolution.

Each of the above processes occurs in a distinct potential zone on the anodic polarization curve, E vs. log *i*. The graphic form of the anodic polarization curve depends on whether it is obtained by applying controlled potential (potentiostatic curve) or controlled current (galvanostatic curve).^{6,7}

Figure 3 schematically shows a potentiostatic polarization curve E vs. log *i* obtained while the applied anodic potential was gradually increased. Here, the region of active metal dissolution is located at the beginning of the curve, where the anodic current and, therefore, the dissolution rate, increase exponentially as the potential is made more positive than the equilibrium potential. Under conditions of active metal dissolution, the relationship between anodic polarization, E_a and the logarithm of current density, i_a is linear. A further increase of the potential is accompanied by partial formation of an oxide or a hydroxide film on the surface,

$$xM + yH_2O = M_vO_v + 2yH^+ + 2ye$$

The expression of the corresponding standard metal/metal oxide potential is:

$$E_{MMx0y} = E^{0}_{MMx0y} - 0.059 \text{ pH}$$
(3)

For any potential more noble than $E_{M/MxOy}$, the preferred state of the metal surface is one covered with oxide and this potential

Table 1Bath Composition for Bright Nickel Deposition

NISO 7H O	250 g/I
$HISO_4 \cdot / H_2O$	250 g/L
NICI ₂ ·6H ₂ O	10 g/L
H ₃ BO ₃	10 g/L
Sodium citrate (complexing agent)	60 g/L
Hydrodynamically active agent	0.8 mg/L
Proprietary brightener	5 mL/L

is progressively lowered with the increasing pH. When the potential $E_{M/MxOy}$ is reached, the active metal dissolution and the anodic current start to divert from the linear Tafel line, passing through a maximum value—the so-called critical passivating current density, i_{crit} . What follows is a sudden drop of current, corresponding to the onset of full passivity. The potential at which the minimum current density is reached is called the Flade potential, $E_{\rm F'}$. A further rise in anodic potential to point c causes little increase in current density, and metal dissolution occurs at a constant rate through the progressive thickening of the passivate film. This thickening usually proceeds by transport of cations outwards and the combination of these M^{+Z} with O⁻² or OH⁻ ions at the film/solution interface.

At even higher potentials, a transpassivity condition (dotted line) and/or an oxygen evolution may occur from the outside of the oxide film according to the equation:

$$4OH^{-} = O_{2} + 2H_{2}O + 4e^{-}$$

provided that the film is electronically conducting.

Figure 4 shows the galvanostatic anodic polarization curve, E vs. log *i*. Anodic dissolution takes place along with some oxide film formation, as the potential jumps discontinuously from a to d and *vice versa*. Mathematically speaking, there is an equivocal relationship between the potential as a function and the current density as an argument. In other words, several resulting potentials in the active, passive, or transpassive regions of the anodic polarization curve may simultaneously correspond to a specific current value. Thus, the controlled value of external current could simultaneously cause dissolution, oxide film formation and/or oxygen evolution.

Conversely, in the potentiostatic regime each value of applied potential corresponds to only one current density (Fig. 3). Therefore, in order to ensure the conditions that preclude oxide film formation on the electrode surface, we should work in a regime of *potentiostatic* application of anodic pulses with small voltage amplitudes,

E. For example, anodic polarization in the range of 50mV to 250mV would cause the net electrical current to be consumed mainly for active metal dissolution.

In many cases, however, because of the chemical nature of the metals, pH and the plating electrolyte compositions, the potential region of active anodic dissolution of the metal coating is too narrow. The application of even a very small anodic polarization can displace the electrochemical system from the region of active anodic dissolution into the zone of passivation, roughening the deposit microprofile.

As Fig. 5 shows, the zone of active anodic dissolution is limited by the potentials E_{MM} +z and E_{MMxOy} . The potential of metals in equilibrium with solutions of their ions, E_{MM} +z depends on the concentration of metal ions [M^{+z}] according to the Nernst equation:

$$E_{MM} + z = E^0 + 0.059 \ln [M^{+z}]$$
(4)

The lower concentration of metal ions, the more negative the potential E_{MM} +z will be, and *vice versa*.

The potential region of active anodic dissolution can be considerably expanded by the addition of complexing agents like those used in electroless plating solutions. Such agents combine the free metal ions in a chelated complex and, according to Nernst equation (4), displace the potential E_{M/M}+z in the negative direction. Also, the presence of complexing agents in the plating bath keeps the concentration of the free metal ions at the electrode/electrolyte interface under the level sufficient for its precipitation as an oxide layer.

Table 2—Influence of Applied Anodic Polarization,	Ε,
on Leveling Power, LP%, for Bright Nickel Deposit	s*

		$F O R W A R D$ $T_{on} = 10 msec$		I			
Sample No.	Pulse Frequency	Avg. Current density	Period Duration	Pulse Frequency	Anodic Polarization	Period Duration	LP%
	f_{for} , Hz	A/dm ²	T_{for} , sec	f_{rev} , Hz	<i>E</i> , mV	T_{rev} , sec	
01	10	2.4	10	7	100	2	6
02	10	2.4	10	7	150	2	10
03	10	2.4	10	7	200	2	8
04	10	2.4	10	7	250	2	-2
05	10	2.4	10	7	300	2	-6
06	10	2.4	10	7	350	2	-18
07	10	2.4	10	7	400	2	-32
*Reverse	e dutv cvcle =	16.6%.					

Then another question arises: Why is it that we should apply anodic pulses? Isn t it possible to use DC anodic polarization? In this case, pulsed anodic polarization has several advantages over DC polarization:

The duration of anodic pulses is 5 to 10 msec, and this time is too short to allow for partial formation of an oxide film on the metal surface, even if the potential of the electrode leaves the Tafel region of active anodic dissolution and comes close to the critical potential of passivation. Even if an oxide layer is formed during the pulse, it could be dissolved in the acid electrolyte during the pause between the two pulses. By varying the pulse frequency of the anodic pulses, we can find those pulse parameters that enable a maximum value of leveling power.

Experimental Procedure

Determination of Pulse Parameters for Best Leveling

For the purposes of the present investigation into the pulse periodic reverse plating of metal coatings, a special electronic device was constructed. It consisted of two electronic units that were interconnected:

1. An electronic unit for galvanostatic application of the forward train of cathodic pulses, whose parameters can be varied within the following ranges:

0 – 50 mA; 0 – 500 mA;
0 –5 A; 0 – 50 A
1 – 99 msec
2 – 22 Hz
1 – 99 sec
1 – 6 sec

2. An electronic unit for potentiostatic application of the reverse train of anodic pulses, whose parameters can be varied within the following ranges:

Amplitude of Potentiostatic Pulses,	E:	0-2000 mV
Pulse Duration, T _{an}		1 – 99 msec
Pulse Frequency, f :		1 – 10 Hz;
Reverse Period Duration, T_{Ray} :		1 – 99 sec
Switching Time:		1 – 6 sec

Leveling can be qualitatively characterized as the ability to diminish the difference in heights between protrusion peaks and recesses of the microprofile via electrochemical treatment of the electrode surface. Characterization of leveling includes roughness measurements of both the initial metal substrate, R_0 and of the deposit surface after pulse periodic reverse plating, R_d on a rotating disk electrode. In order to determine the leveling power (LP%), the following expression is used:

$$LP \uparrow = \frac{(R_0 - R_d)}{R_0} * 100$$
(6)

The initial roughness R_0 is obtained by grinding an electrode in one direction only, with grade 220-emery paper. Half of the surface of the rotating disc electrode (0.5 cm²) was previously insulated with a thin film of photo-resist lacquer. After a metal coating was deposited by pulse periodic reverse plating on the other half, the film was removed with an organic solvent. Therefore, it was possible to determine the change in roughness arising from metal deposition directly from a single electrode. The speed of rotation was maintained at a constant 250 rpm.

The following pulse reverse parameters had the most significant influence on the leveling performance of metal coatings:

- Frequency of the reverse pulses, f_{rev} (Hz)
- Value of applied anodic polarization, *E* (mV)
- Reverse duty cycle, T_{rev}/(T_{rev} + T_{for}) (%)
 Reverse pulse duration, T_{on} (msec)

In order to determine the PPRP parameters corresponding to the maximum values of leveling power, we propose the following approach:

- 1. It is first necessary to establish the graphical relationship between the frequency of reverse (anodic) pulses, f_{rev} (Hz), and the leveling power, LP%, of the metal coatings deposited by pulse periodic reverse plating. The experiments used the same methodology used in the studies of unipolar pulse plating. We varied the frequency of anodic pulses to determine the pulse frequency at which the leveling maximum occurred. At the same time, the frequency of the forward (cathodic) pulses was maintained at a constant value corresponding to the pulse frequency of the leveling maximum for unipolar pulse plating.
- 2. It is then necessary to determine the voltage amplitude of the anodic pulses E, (mV), which corresponds to the maximum value of the leveling power derived from the relationship between E and LP%. The values of anodic polarization varied within certain limits, whereas frequency and other parameters of the cathodic and anodic pulses were maintained at a constant value.

	Reverse Duty Cycle	FORWARD $T_{on} = 10$ msec				$R E V E R S E$ $T_{on} = 5 msec$			
Sample No.		Pulse Frequency	Avg. Current density A/dm ²	Period Duration	Pulse Frequency	Anodic Polarization E. mV	Period Duration	LP%	
01	,,,	10	24	10	J_{rev} , 12	150	2	6	
02	16	10	24	10	5	150	2	16	
03		10	24	10	6	150	2	10	
04		10	24	10	4	150	3	8	
05	23	10	24	10	5	150	3	20	
06		10	24	10	6	150	3	16	
07		10	24	10	4	150	4	18	
08	28	10	24	10	5	150	4	25	
09		10	24	10	6	150	4	23	
10		10	24	10	4	150	5	15	
11	33	10	24	10	5	150	5	24	
12		10	24	10	6	150	5	20	
13	-	10	24	-	-	-	-	19	

Table 3—Influence of Reverse Duty Cycle on Leveling Power, *LP*%, for Bright Nickel Coatings Deposited by Pulse Periodic Reverse Plating

3. Last, we need to estimate the influence of the reverse duty cycle, $T_{rev}/(T_{rev} + T_{for})$ (%) on the leveling performance of metal coatings deposited at constant forward and reverse pulse parameters corresponding to the leveling maximum (as determined in Steps 1 and 2 above).

The duration of the anodic pulses, T_{on} was set at 5 msec. Within the 5-msec interval, there is a minimal chance for the oxide film to form, even if the anodic polarization comes close to the critical passivation potential. Even if an oxide layer is formed during the pulse, it likely will be dissolved in the acid electrolyte during the long pause between the two short pulses.

The following example illustrates how our systematic method is actually used to find the pulse parameters for optimum leveling. Here, we considered bright nickel deposition using a modified Watt s bath, modified with a complexing agent. The bath composition is shown in Table 1.

The frequency of the forward (cathodic) pulses was maintained at a constant value of 10 Hz, corresponding to the pulse frequency of the leveling maximum in unipolar pulse plating. At the same time, the frequency of the anodic (reverse) pulses was varied. The relationship between leveling power (*LP%*) and anodic pulse frequency f is shown in Fig. 6. From this graph, we can determine the leveling maximum and the corresponding frequency of reverse pulses (5 Hz) at which the maximum occurs.

From Table 2 we can define the value of voltage amplitude (E = 150 mV) that ensures maximum leveling.

The influence of reverse duty cycle on the leveling power of the bright nickel coatings produced by pulse periodic reverse plating (PPRP) is shown in Table 3. Sample No. 13 provides a comparative measurement for unipolar pulse plating (UPP).

The highest values of leveling power were obtained at an anodic pulse frequency of around 5 Hz. The reverse duty cycle value was 28.5%. Under these plating conditions, the maximum value of leveling power obtained with PPRP (*i.e.*, 25%—Sample No. 08) was about 30% greater than the maximum value of leveling power for bright nickel deposited by UPP (*i.e.*, 19%—Sample No. 13).

Similarly, our procedure was applied to determine the optimum PPRP pulse parameters for copper and gold deposits. The maximum values of leveling power for bright copper and gold coatings deposited by unipolar pulse plating (UPP) and pulse periodic reverse plating (PPRP) are compared in Table 4. This comparison shows the advantages of deposition by pulse periodic reverse plating, where the maximum values of leveling power of copper and gold deposits are correspondingly 27 percent and 20 percent greater than that ones of the same metal coatings deposited by unipolar pulse plating.

Leveling Mechanism & Pulsed Anodic Polarization

According to the leveling mechanism of unipolar pulse plating (UPP) with brightener additives, which we have already presented,⁵ for every bright pulse deposition process, a definite pulse frequency of optimal coordination of both the rates of nuclei formation and adsorption of brightener species can be found. This frequency coincides exactly with the frequency of cathodic pulses at which maximum leveling occurs.

The electrochemical symmetry between both processes—of cathodic deposition (crystal growth) and of active anodic dissolution of the metal coating—presupposes a similar interpretation of the leveling mechanism at work during the reverse period of PPRP. This is why most of the principles explaining the leveling performances of UPP deposits are also valid for the PPRP regime. Here is a brief exposition of the principles we take into consideration:

- The brightener molecules inhibit anodic dissolution at the sites of their adsorption. The adsorption is preferential on the peaks of the microprofile (*i.e.*, those portions of the electrode surface that are more accessible to these agents by diffusion).
- The difference between the quantities of brightener species adsorbed on protrusions and recesses, respectively, creates a concentration gradient dc_s/dx_s of the surface diffusion flow $j_{s,j}$ forcing the transportation of inhibiting agents from the protruding areas to the recesses during the off-time T_{off} between two anodic pulses.
- When T_{off} is sufficiently long (*i.e.*, at lower frequencies), the surface diffusion flow j_s spreads the adsorbed brightener species evenly over the entire microprofile surface. When the brightener concentration is evenly distributed, the local current density at the protrusions is greater than that at the recesses because of the lateral accessibility of current flow lines to the peaks.⁸

Sample No.	Reverse Duty Cycle	FORWARD $T_{on} = 10$ msec			$\mathbf{R} \mathbf{E} \mathbf{V} \mathbf{E} \mathbf{R} \mathbf{S} \mathbf{E}$ $T_{on} = 5 \operatorname{msec}$			
		Pulse Frequency	Avg. Current density	Period Duration	Pulse Frequency	Anodic Polarization	Period Duration	LP%
	%	f_{for} , Hz	A/dm ²	T_{for} , sec	f_{rev} , Hz	<i>E</i> , mV	T_{rev} , sec	
Cu (PPRP)	16	6	24	10	6	300	2	2
Cu (PP)	-	6	24	-	-	-	-	2
Au (PPRP)	23	11	12	10	6	200	3	2
Au (PP)	-	11	12	-	-	-	-	2

Table 4—Pulse Parameters of the PPRP & UPP of Bright Copper& Gold Deposits with Maximum Values of LP%

According to the expression,

$$i_m = i_n \cdot T_{on} \cdot f$$

the average current density i_m increases as the pulse frequency is increased. Consequently, with the pulse frequency increasing, the metal dissolution rate at the protrusions becomes higher than that at the recesses. In that frequency interval, the tendency toward leveling will increase.

- As the frequency of anodic pulses further increases, the time between two anodic pulses T_{off} becomes shorter and shorter. This maintains preferential adsorption of the inhibiting species on the protrusions of the microprofile. Beyond a certain value of pulse frequency, the anodic dissolution rate at the protrusions becomes lower than that at the recesses and, consequently, there will be a stronger tendency toward roughening in this frequency range.
- The point of intersection between the above two tendency lines determines the frequency of the reverse anodic pulses at which the maximum value of leveling power occurs. (see Fig. 6)

Finally, it is noteworthy that, unlike unipolar pulse plating (where cathodic polarization can be realized by galvanostatic, as well as by potentiostatic pulses), the leveling mechanism described above is at work only during the potentiostatic application of anodic pulses. In order to exclude the possibility of passivation of metal deposits during the reverse period of the pulse periodic reverse plating, the anodic pulses should have a small voltage amplitude within the potential zone of active metal dissolution.

Given the correlation already established between leveling performance and deposit properties, we can also conclude that for the deposition of metal coatings with improved functional properties (*i.e.*, minimal internal stresses, excellent electrical conductivity, high resistance to corrosion, wear or abrasion) priority should be given to pulse periodic reverse plating (PPRP) over unipolar pulse plating (UPP) and DC plating.

The experimental data supporting this thesis will be given in the Part II of the current work.

References

- J. Dini, Electrodeposition: The Materials Science of Coatings & Substrates, Noyes Publications, Park Ridge, NJ, 1992; p.141.
- J.Cl. Puippe & F. Leaman, Eds., *Theory & Practice of Pulse Plating*, AESF, Orlando, FL, 1986; pp.1-12.
- 3. V. Scorchillety, *Theoretical Electrochemistry*, Mir, Moscow (1974); p.476. (in Russian).
- J.Cl. Puippe & F. Leaman, Eds., *Theory & Practice of Pulse Plating*, AESF, Orlando, FL, 1986; pp. 41-54.

- M. Aroyo, *Plating & Surface Finishing*, **85**, 53 (August 1998); **85**, 92, (September 1998).
- J.M. West, *Electrodeposition & Corrosion Processes*, 2nd Ed., Van Nostrand-Reinhold, New York, NY, 1971; p. 86.
- J.T.N. Atkinson & H. Van Droffelaar, Corrosion & Its Control, NACE, Houston, TX, 1982; p.34.
- 8. O. Kardos, Plating, 61, 129 (1974).

About the Authors



Dr. Mois Aroyo is an associate professor in the Department of Chemistry at the Technical University, Sofia, Bulgaria. His research interests include electrochemical corrosion, pulse plating of metal deposits, conversion coating applications and related fields. He has published numerous technical papers.

Nikola Tzonev is an

assistant professor in the Department of Mechanical Engineering at the Technical University of Sofia, Bulgaria. For more than 10 years, he has conducted intensive research the field of surface analysis systems and mechanical measurement devices. He has published more than 25 papers.

