Technical Article

Pulse Periodic Reverse Plating— Possibilities for Electrodeposition of Metal Coatings with Improved Properties: Part 2

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In Part 1 of this paper¹ we discussed the cathodic and anodic processes that take place during pulse periodic reverse plating (PPRP) of metal coatings and found an appropriate way to combine the cathodic pulses of electrocrystallization with the anodic pulses of metal dissolution in order to obtain a positive commutative effect in respect to leveling and structural homogeneity. We established that at definite parameters of the forward current pulses and of the reverse voltage pulses, the leveling performance of the deposited metal coatings could be considerably improved in comparison to that of ones deposited by the unipolar pulse plating (UPP).

The second part of our paper presents the results of porosity and internal stress measurements of bright copper, nickel, gold and palladium coatings deposited by PPRP and UPP. The comparative analysis of the results obtained demonstrates indisputably the advantages of pulse periodic reverse techniques to unipolar pulse plating in regards to the deposition of metal coatings with improved properties. Thus, at those parameters of PPRP corresponding to the maximal leveling, we



Fig. 1—Metal dissolution by transfer of the structural elements A, B, C into electrolyte.

Nuts & Bolts: What This Paper Means to You

In the July 2002 issue, the authors presented the case for reverse pulse plating and its impact on manipulating all kinds of plated coating properties, including leveling and uniformity. This second installment shows how it can be applied to reduce porosity and ease internal stress. After many decades, the use of pulsing is at last coming into its own. can deposit high-quality metal coatings with reduced internal stresses and less porosity. We also offer a theoretical explanation of the process mechanisms in which the applied reverse (anodic) pulses in PPRP act as internal stress reliever and porosity reducer.

Theoretical Considerations

The active anodic dissolution of metals^{2,3} occurs when the application of potentials is more positive than the equilibrium potential in a given electrochemical system. Theoretically, the reaction of anodic dissolution, Me Me^{+z} + ze⁻, presents the reverse process of cathodic deposition of metals. In reality, however, metal dissolution is a more complex process including the disintegration of the crystal lattice, anion adsorption, ionization and the transportation of hydrated metal ions into the electrolyte:

$$Me + xH_2O \quad Me^{+z} \cdot xH_2O + ze^{-}, \tag{1}$$

$$Me + xH_2O + yA^- MeA_v^{z-y} \cdot xH_2O + ze^-.$$
 (2)

The active metal dissolution occurs only when the Tafel relationship between the anodic polarization, a_a and the anodic current density, i_a , is valid:

$$a = b_a \log \left(\frac{i_a}{i_a} \right) \tag{3}$$

The rate of anodic dissolution also depends on the presence of some anions and brightener species in the plating electrolyte. Their adsorption on the metal surface can play two opposite roles: as activators or inhibitors, respectively. The halide ions Cl⁻, Br⁻, I⁻, F⁻ and the hydroxide ion OH⁻ are anions with a strong catalytic action. The rates at which they are adsorbed depend on the nature of the metal, its electrode potential as well as the composition and pH of the electrolyte.

The energy needed to separate a given structural element from the lattice depends on its position on the crystal surface. Structural elements at the corners of the crystals require the least energy. They have the weakest bonds to the crystal because they are surrounded by only three other elements (Fig. 1), and, in addition, their transfer from the metal lattice into the electrolyte is made even easier by the fact that they attract high number catalytic anions. In order to leave the crystal edge, a structural unit has to overcome

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Table 1 **Plating Solution Compositions**

(a) Bright Acid Copper Deposition		
Copper sulfate (CuSO ₄ ·5H ₂ O)	70 g/L	
Sulfuric acid (H_2SO_4)	170 g/L	
Sodium chloride (NaCl)	0.06 g/L	
Brighteners	3 mL/L	
Hydrodynamically active agent	8 x 10 ⁻⁴ g/L	
(b) Bright Nickel Deposition	1	
Nickel sulfate (NiSO $_4$ ·7H $_2$ O)	250 g/L	
Nickel chloride (Ni $\dot{Cl}_2 \cdot 6\ddot{H_2O}_1$)	10 g/L	
Boric acid (H ₃ BO ₃)	10 g/L	
Complexer (Na Citrate)	60 g/L	
Hydrodynamically active agent	8 x 10 ⁻⁴ g/L	
Brightener	5 mL/L	
(c) Bright Gold Deposition		
Gold (as KAu(CN) ₂)	8 g/L	
Complexer (Na Citrate)	80 g/L	
Complexer (citric acid)	20 g/L	
Cobalt (as sulfate)	0.1 g/L	
Hydrodynamically active agent	8 x 10 ⁻⁴ g/L	
Brightener	0.2 g/L	
(d) Bright Palladium—Arsenic Dep	osition	
Palladium (as PdCl ₂)	11.0 g/L	
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Arsenic (as As_2O_3)	1.5 g/L	
Arsenic (as As_2O_{3}) Complexer: N-(2-hydroxyethyl)	1.5 g/L 90 g/L	
Arsenic (as As_2O_{3}) Complexer: N-(2-hydroxyethyl) -ethylenediamine	1.5 g/L 90 g/L	
Arsenic (as As ₂ O ₃₎ Complexer: N-(2-hydroxyethyl) -ethylenediamine Brightener	1.5 g/L 90 g/L 0.2 g/L	
Arsenic (as As ₂ O ₃) Complexer: N-(2-hydroxyethyl) -ethylenediamine Brightener Hydrodynamically active agent	1.5 g/L 90 g/L 0.2 g/L 8 x 10 ⁻⁴ g/L	

the interaction forces with the nearest four elements. In order to leave the flat surface of the crystal wall, the element has to break free from the bonds to its five neighbors.

According to Weil⁴ the two main causes of internal stresses in metal deposits are the coalescence of crystallites and hydrogen codeposition. It has been found that deposits in commercial plating solutions do not spread one atom layer at a time over the substrate. An atom layer spreads only a relatively short distance before it is stopped by foreign substances (brightener species and other addition agents) that attach themselves at the growth site. The atom layers on top of a stopped one cannot overtake it, resulting in the formation of three-dimensional crystallites.

A layer of deposit is formed by the joining of the crystallites, which have been found to have inclined side walls. The coalescence of such small grains or of crystallites can lead to tensile stresses if they are pulled together by surface tension before the spaces between them are filled. When the crystallites have smooth and planar side walls, they can be pulled together to a considerable degree resulting in large tensile stresses (+). Some additives such as saccharin used in nickel plating solutions can reduce tensile stress by roughening the sides of the crystallites and thus preventing them from coming too close to each other.

The crystallites are not pulled together to the same degree as in the absence of the asperities. The joining of only the asperities leads to tiny voids where the growth was stopped. When codeposited hydrogen diffuses into the voids and expands them, a compres-



Fig. 2—The internal stress meter—dilatometer.

sive stress develops. Thus, the addition agent can cause the stress to transform from tensile (+) to compressive (-).

Accordingly, pulse deposited metal coatings are expected to have greater internal stresses than DC-plated deposits because pulse current application leads to a considerable increase in the number of small crystallites and of tiny voids between them respectively.

As was mentioned above, anodic dissolution starts at the corners and edges of the crystal where the structural elements in position of the so-called half-crystal. The higher number of such half-crystal sites are found mainly in places where there are asperities of "misfit" crystallite boundaries adjacent, dislocation asperities and other surface defects on the metal lattice. During the short on-time of each anodic pulse, metal dissolution takes place predominantly on those sites of the metal surface where there is such an accumulation of sidewall asperities and crystal defects. Therefore, a desirable regime for the application of anodic voltage pulses would be one which leads to a smoothing of the crystallites sidewalls and hence to a reduction of compressive stresses. In our opinion, the pulse parameters of this regime of anodic dissolution should correspond to the ones of maximal levelling of PPRP deposited metal coatings.

Similar to internal stresses, the porosity of metal deposits is also largely dependent on the method and technology of deposition. In this case the presence of pores may be attributed to the inability of the plating process to adequately cover the surface through the conventional steps of nucleation and growth. If, for example, instead of outward growth, lateral growth of the deposit is promoted, coverage is faster and, therefore, more effective at lower thicknesses. In addition, the process of pore formation is controlled by the ratio of nucleation rate to the rate of grain growth, whereas the latter growth is related to the leveling mechanism. The above correlation between these two coating characteristics allows for the deposition of metal coatings with minimum porosity under the plating conditions that enable a maximum value of leveling power. Because of the use of reverse pulses of anodic dissolution, the maximum values of leveling power of PPR-deposited metal coatings are higher than those for UPP plating. Consequently, minimum coating porosity will be secured by the appropriate combination of forward pulses of metal deposition with the reverse pulses of metal dissolution at which the maximum value of leveling power is obtained.



Fig. 4—Schematic diagram of porosity measurement equipment.

Comparative Estimate of the Internal Stress of the Unipolar Pulse- & Pulse-Periodic-Reverse-Deposited Coatings

The internal stress measurements are based on the application of a dilatometric method.⁵ This method has proved accurate and easy to monitor, and, in addition, it is sufficiently sensitive to apply to all but the thinnest electrodeposits. What is 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.

The instrument used was specially designed and constructed for this study. As shown in Fig. 2, it consisted of a powder-coated steel frame (2). Within this frame a flat, uniform strip (4) of electrolytic copper [width = 12 mm (0.47 in.), working length = 80 mm (3.15 in.) and thickness = 0.03 mm (1.18 mil)] was mounted. The strip was pretensioned by a spring at its upper end.

Changes in length of the strip during plating were recorded by the movement of the pointer of a sensitive (\pm 0.5 micron) dilatometer (10), which was in contact with the tip of a shaft (9) connected to the top end of the strip. Tensile (+) and compressive (-) stresses were recorded with equal accuracy. Each strip was used once and kept for reference. The mean deposit thickness was calculated after plating using the same sensitive dilatometer. For a strip specimen, internal stress was simply calculated from the equation:

$$Stress = \frac{EdA}{21t} [kg/mm^2]$$
(4)

where:

- E = Young s modulus for copper, 1.15 x 10⁴ kg/mm² (16.4 x 10⁶ psi)
- l = length of the plated portion of the strip, mm
- t = thickness of the deposit, mm
- d = thickness of the substrate strip, mm
- A = strain recorded by dilatometer (elongation positive, compression negative), mm

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Fig. 3—Comparison between internal stress data (kg/mm²) of the metal coatings deposited by unipolar pulse- and pulse periodic reverse plating.

The plating solution compositions used in this work are given in Table 1.

The results of the internal stress measurements of bright nickel, gold, palladium-arsenic and copper, unipolar pulse- and pulse periodic reverse deposited are presented in Fig. 3. It is clear that the higher values of compressive stresses were valid for all four metal coatings deposited by unipolar pulse plating (UPP), whereas the lower compressive stresses corresponded to the same coatings deposited by pulse periodic reverse plating (PPRP). The greatest reduction of compressive stresses was recorded for nickel (from 26 to 12 kg/mm²; 37,000 to 17,100 psi) and palladium coatings (from 20 to 2.0 kg/mm²; 28,400 to 2,840 psi).

Comparative Estimate of Porosity of the Unipolar Pulse- & Pulse-Periodic-Reverse-Deposited Coatings

The electrochemical apparatus and the underlying principles of the porosity test used in the present investigations were described in our earlier publication.⁶ They are based on the method of linear polarization resistance (LPR), applied for example in the apparatus for corrosion monitoring.⁷ The well-known Stern-Geary expression⁸ was used to define the instantaneous corrosion rate of the metal in contact with liquid corrodent:

$$i_{corr} = \frac{b_a \cdot b_c}{2,3 \ (b_a + b_c)} \text{ or } i_{corr} = \frac{1}{R_p}$$
 (5)

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

Two flat metal-coated steel specimens were pressed into rubber O-rings closing the two identical axial openings located at the bases of the cylindrical electrochemical cell (Fig. 4). The electronic device measured the polarization conductance l/R_p by applying pulses of sign-changing polarizing voltage $E = \pm 10 \text{ mV}$ to a two-electrode assembly. The corresponding change in current *I* was automatically measured after eliminating the transition current occurring at the beginning of each polarizing pulse. The integral value $Q = (1/R_p)dt$ was calculated for a test period (0, t) and displayed by the 1/R-time integrator.

The porosity of metal coating could be considered proportional to the integral value Q provided the corrosion rate of the metaldeposit was negligibly low as compared to the dissolution rate of the metal-substrate through the pores. Therefore, when the goal was to provide the largest possible difference between the dissolution rates of the two metals, the most important problem with such porosity measurements was the accurate choice of a test electrolyte.

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The electrolyte used in the porosity measurements of nickel, palladium-arsenic, and gold deposits on mild steel substrate contained:

NaCl	18 g/L
Na-gluconate	8 g/L
NH₄F∙HF	2 g/L
$H_{3}PO_{4}(85\%)$	2 mL/L

When uncoated steel electrodes were in contact with the electrolyte for 5 min, the 1/R-time integrator displayed a value assumed to correspond to 100% porosity. For a two-nickel-electrode assembly, a two-palladium-electrode and a two-sheet specimen of pure gold in contact with the same test electrolyte, the obtained integral values of $Q = (1/R_p) dt$ were assumed to correspond to 0% porosity. The time for deposition for all coatings was the time required to obtain the same approximate thickness of 1.5 µm (59 µ-in.). The roughness of the steel substrate was the same in all cases and was equivalent to that obtained by treatment with #600 grit paper. Figure 5 represents the average values of a large number of measurements of the porosity of nickel, gold, and Pd-As coated steel samples.

Comparing the porosity of UPP deposits to that of the coatings deposited by PPRP demonstrates the advantages of deposition by pulse periodic reverse plating, which ensures lower porosity of nickel and gold coatings. In this case we can clearly see that the increase of the leveling power value led to decreased porosity.

This correlation was not valid in the case of pulse periodic reverse plating of metal alloy deposits such as Pd-As. The Pd-As coatings deposited by PPRP had higher porosity than those deposited by UPP. Most probably this is because of the relatively higher anodic dissolution rate of the alloy component arsenic when compared to the anodic dissolution rate of the palladium matrix during the reverse period. As a result, tiny pits were formed and they could not be filled during the following period of cathodic deposition. Therefore, the plating conditions of PPRP enabling a maximum value of leveling power did not necessarily guarantee Pd-As coatings with minimum porosity. This specific case of pulse periodic reverse plating of metal alloy coatings containing components with very different anodic dissolution rates can be considered as an exception in which the plating conditions of PPRP do not necessarily guarantee a deposition of metal alloy coatings with the lowest porosity.

Why should arsenic be used as an alloy element in palladium coating and what is its role in the cathodic process of deposition? The answer to this question is based upon the following considerations.

Table 2Approximate Values of the ExchangeCurrent Densities for the HydrogenEvolution Reaction on Various Metals

Metal	Exchange Current Density I _{O,H} , A/cm ²
Pb, Hg	10-13
As	10-12
Sn, Al, Be	10-10
Ni, Ag, Au, Cd	10-7
Fe, Au, Mo	10-6
Co, Ta	10-5
Pd, Rh	10-4
Pt	10-2

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According to the Tafel equation for the cathodic process

$$= b_c \log (i_c/i_o), \tag{6}$$

at a given rate i_c , the larger the exchange current i_o , the smaller the overpotential c_c . Since hydrogen ions are invariably present in aqueous plating solutions, the reduction of hydrogen ions at the cathode is the usual alternative metal electrodeposition process. The rate of hydrogen reduction will depend on the values for $i_{o,H}$ for hydrogen on the electrodeposited metal.

The approximate values of the exchange current densities for the hydrogen evolution reaction on different metal are given in Table 2.⁹ The immediate consequence of the wide differences in $i_{o,H}$ was that for a given rate of hydrogen evolution i_c at a few mA/ cm², the overpotential on lead was many times greater than that on platinum. For iron and copper an intermediate value was observed. Similarly, at a given overpotential $_{H}$ the rate of hydrogen evolution from lead was smaller than that for iron, copper or platinum.

Evidently, the very high values of $i_{o,H}$ for hydrogen evolution on some precious metals (Rh, Pd, Pt) account for electrodeposited coatings that are prone to hydrogen adsorption and inclusion of it into the deposit. In order to effectively solve this problem, one could cathodically deposit these metals in combination with metals on which the $i_{o,H}$ for hydrogen is 10,000 times lower (*e.g.*, Pb, Hg, As). In their work, J. Abys and H. Straschil¹⁰ have included some telling examples in this respect.

Indeed, the porosity measurements of palladium coatings pulsedeposited from the electrolyte with no arsenic content have demonstrated that the porosity is considerably greater (67%) than that for Pd-As coatings of equivalent thickness deposited by both UPP and PPRP from electrolyte containing 1.5 g/L As (Fig. 5).

Conclusions

The internal stress and porosity measurements have yielded results that warrant the following conclusions:

- Because of the deposition mechanism of unipolar pulse plating (UPP) the fine-grained metal coatings obtained exhibited higher internal stresses. Therefore, UPP is not a suitable method for the deposition of nickel and palladium electroforms.
- The anodic dissolution of crystallite asperities during the reverse period of PPRP leads to a smoothing of the sidewalls and hence to a considerable reduction in compressive stresses of the metal coatings. This makes PPRP the preferred pulse method for the deposition of nickel, palladium and other electroforms.
- Suitable combinations of forward pulses of metal deposition with the reverse pulses of metal dissolution result in a positive



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Fig. 5—Comparison of the porosity data for metal coatings deposited by unipolar pulse- and pulse periodic reverse plating.

commutative effect with respect to leveling and the structural homogeneity of deposits. Given that the leveling maximum corresponds to the minimum porosity, when it comes to the deposition of fine-grained metal coatings with lower porosity (*e.g.*, for higher corrosion and wear resistance), priority should be given to pulse periodic reverse plating as well.

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