Theoretical and Practical Aspects of Electrodeposition Of Metal Coatings with Improved Properties (Part 1)

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The properties of electrodeposits, such as adhesion, corrosion and wear resistance, hardness, electrical conductivity and brightness, are important and even mandatory for a broad spectrum of applications. Many of these properties depend on the specific procedure for electrodeposition, because alternative procedures produce significantly different properties. In general, electrodeposited metal coatings with excellent properties must have fine-grained structure. A fine-grained structure, however, is only one of the conditions necessary for a metal coating with good decorative and functional properties. Leveling power is suggested as an additional adequate measure for quality estimation and as a criterion of discovering the best plating regime. Part 1 of this paper lays out the theoretical principles at work in the electrodeposition of metal coatings with fine-grained structure. It also offers a model for precise experimental determination of those plating parameters and hydrodynamic conditions under which fine-grained metal coatings with maximum leveling power are electrodeposited.

Theoretical Foundation for Fine-Grained Structure

The structure of electrodeposits determines their properties. Even minor structural differences often have a profound effect on the properties of electrodeposited metals. Four typical structures are encountered with electrodeposited metals: (1) columnar, (2) fibrous, (3) fine-grained and (4) laminar (or banded).[1] In general, fine-grained deposits are smoother, brighter, harder and stronger, but less ductile than columnar-grained deposits. Specific effects, such as the brightness of certain deposits, may be caused by the formation of successive bands in which the grains are extremely small. Consequently, to achieve electrodeposits with excellent properties, metal coatings must have fine-grained structure.

The crystal structure depends largely on the relative rates of formation of crystal nuclei as well as on the growth of existing crystals (Fig. 1). Conditions that favor crystal nuclei will yield finer-grained deposits, while conditions that favor the growth of existing crystals will result in fewer but larger crystals. According to the principles of electrocrystallization,[2] the rate of formation of new nuclei on the electrode surface increases exponentially as the cathodic polarization, η, increases:

$$\omega = B \exp\left\{ -\frac{K}{\eta^2} \right\} \qquad (1)$$

Here, the constants *B* and *K* are specific for a given metal and temperature. If all other conditions remain constant, the increase of cathodic polarization will result in a larger number of newly-formed nuclei and in a finer-grained structure of the electrodeposits.

Several types of polarization are distinguishable at an electrode, and the most important are the activation overpotential, η_a, and the concentration polarization, η_c.[3]

Activation Polarization

For an electrochemical reaction to proceed at an appreciable rate, activation energy is needed. If the cathode potential, E_c, is applied to an electrode with equilibrium potential, the difference (E_c - E_{eq}) represents the activation polarization, $\eta_{a,c}$. Then, the rate of the cathodic process is:

$$i_c = i = i_0 \exp\,[\alpha zF\eta_{a,c}/RT] \qquad (2)$$

For a given cathodic process at a given activity and temperature, α is constant and the Tafel equation is:

$$\eta_{a,c} = b_c \log(i_c/i_0) \qquad (3)$$

where

$$b_c = -2.3RT/\alpha zF \qquad (4)$$

The Tafel equation is valid when an electrode process is rate-determined by an activation energy hump situated inside the electric double layer. It then measures the extent of the interference with the equilibrium at the electrode.

Concentration Polarization

Concentration polarization results from concentration changes that arise at the electrode/solution interface because of the electrode reaction. When the cathodic reaction proceeds at an appreciable rate, there will be a decrease in the activity of the metal ions at the metal/solution interface. For example, at the electrodeposition of M^{+Z} ions at a bulk concentration C_b, if deposition is carried out at a current density i, then i/zF mol/sec are removed continuously from the double layer and discharged. Ions will be replaced by diffusion and migration until a concentration, C_e, is established at the metal/solution interface, that is, throughout a diffusion layer of thickness, δ, the metal ion concentration falls from the bulk value, C_b to C_e. Assuming that discharged ions are replenished only by diffusion (if migration is negligible), then, according to Fick's law, the number of gram ions transferred from the bulk

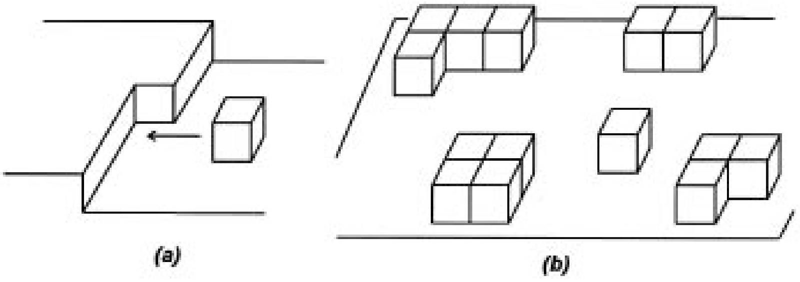

Fig. 1—Crystallization mechanisms: (a) build-up of existing crystals; (b) nucleation and formation of new crystals.

electrolyte to the electrode surface by this process is given by

$$\frac{i}{zF} = \frac{D}{\delta}(C_b - C_e) \qquad (5)$$

where D is the diffusion coefficient (cm^2/sec), and z is the charge of the cation. As i increases, C_e decreases and will eventually become zero at the limit $i = i_L$, so that

$$i_L = \frac{zFDC_b}{\delta} \qquad (6)$$

and

$$\frac{C_e}{C_b} = 1 - \frac{i}{i_L} \qquad (7)$$

Because the potentials corresponding to the concentrations C_b and C_e are

$$E_{eq} = E^0 + (RT/zF)\ln C_b, \text{ and } E_c = E^0 + (RT/zF)\ln C_e, \qquad (8)$$

it follows that the application of current i has produced a concentration overpotential of

$$\eta_c = E_c' - E_{eq} = \frac{RT}{zF}\ln\frac{C_e}{C_b} = \frac{RT}{zF}\ln(1 - \frac{i}{i_L}) \qquad (9)$$

This equation applies whenever the diffusion species is the potential-determining ion.

In fact, the usage of additives (brighteners and other organic species) can affect the deposit structure by blocking kink sites on the cathodic surface, thus increasing the activation polarization, η_a, of discharged metal ions. Also, from Eq. (9), it follows that $\eta_c \rightarrow \infty$ when $i \rightarrow I_L$. In other words, when the applied current density increases and reaches values close to I_L, the polarization of the electrodeposition process increases infinitely (Fig. 2).

It seems that to obtain metal coatings with fine-grained structure, the cathodic current should be very close to the limiting current density, i_L, where $\eta_c \rightarrow \infty$. Under such conditions, however, the deposits become burned, excessively rough, “treed” or spongy.

Evidently, the value of i_L is a factor limiting the practical application of high current density. The higher the value of i_L, the higher the value of the practical applied current density of the electrodeposition process. This, together with higher values of the cathodic polarization, permits metal coatings with fine-grained structure.

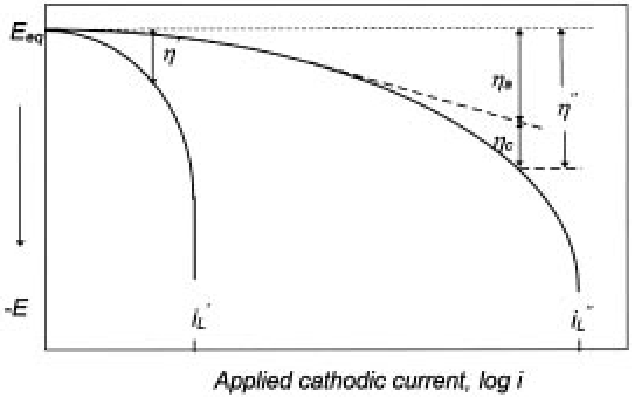

Fig. 2—Cathodic polarization curves showing increased values of polarization, h≤, and limiting current, i_L≤, as a result of vigorous agitation, addition of brighteners and a hydrodynamically active agent.

How then to increase the limiting current density, i_L? According to Eq. (6), i_L grows when the thickness of the diffusion layer, δ, decreases. Three means are proposed to decrease the thickness of the diffusion layer:

♦ *Through increasing the rate of the laminar flow of the electrolyte around the cathodic surface*

In a flowing electrolyte during electrolysis, the changes in concentration take place in a very thin layer adjacent to the electrode surface. Nernst’s presumption that the diffusion layer is static does not seem possible, because the intermolecular bonding forces prevent the layer that is 10^{-2} to 10^{-3} cm thick from assuming a stable position on the surface of the electrode. Levich’s theory of convection diffusion takes into consideration liquid movement in the diffusion layer and enables a more precise assessment of the various factors with an influence on the diffusion flow in stirred electrolytes.[4,5] If the flow is laminar, the thickness of the diffusion layer, δ, is a function of the flow rate, and, when the rate is unchanging, (U_0) then δ is constant. The rate of the flow immediately adjacent to the electrode surface is U = 0, whereas, at a certain distance, the rate reaches the same value of the flow rate, which is U_0. That layer in the electrolyte, in which the flow rate changes from U = 0 to U_0, is called Prandtl’s layer, δ_{Pr} (Fig. 3). The diffusion layer, δ, (the layer in which the concentration of discharged ions changes from C_b to C_e,) is positioned within Prandtl’s layer, δ_{Pr}.

The thickness of δ_{Pr} depends on the flow rate, U_0, and on the kinematic viscosity of the electrolyte, ν, (ν = δ/d). Because the units of the coefficient of viscosity, η, are kg m^{-1}sec^{-1}, and the units of density, d, are kg/m^3, ν has units of m^{2}sec^{-1} (the same units as a diffusion coefficient). The thickness of δ_{Pr} also increases with the growth of the distance, x, from the beginning of the flow:

$$\delta_{Pr} = \sqrt{\frac{\nu . x}{U_O}} \qquad (10)$$

The diffusion layer, δ, is considerably thinner than the Prandtl’s layer, δ_{Pr}. In water solutions, δ is approximately ten times thinner than δ_{Pr}:

$$\frac{\delta}{\delta_{Pr}} = (\frac{D}{\nu})^{1/3} \qquad (11)$$

The combination of Eqs. (10) and (11) results in the following expression:

$$\delta = D^{1/3}\nu^{1/6}x^{1/2}U^{-1/2} \qquad (12)$$

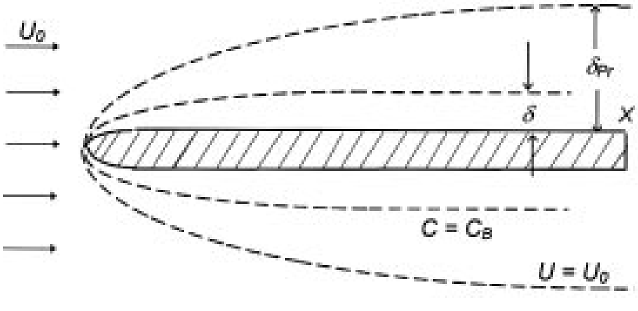

Fig. 3—Changes of the thickness of Prandtl’s layer and the diffusion layer along the surface exposed to the flow.

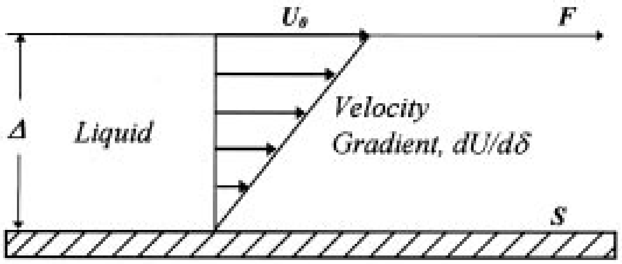

Fig. 4—Laminar liquid flow moving relative to the immovable metal surface, S.

Obviously, δ decreases with increasing fluid velocity, U_0. It must be noted, however, that U_0 cannot rise indefinitely, but only to values at which the fluid flow remains laminar. This limitation is related to the Reynolds number, Re, and the condition, $Re = (U_0x/\nu) \leq 10^4$. If $Re > 10^4$, the flow is turbulent and the principles of convection diffusion are no longer valid.

It is apparent, also, that the thickness of the diffusion layer, δ, is not constant, and its value depends on the distance, x. Because the value of x in the different sites of the electrode is different, the thickness of the diffusion layer will be different on the various sites of the surface. This problem of the experiment can be solved if a rotating disc electrode is used. When the disc is rotating, the electrolyte flows as a result of the centrifugal forces pointing away from the center of the disc. The thickness of the diffusion layer, δ, is expected to increase from the center to the periphery of the disc because the distance, x, is rising. At the same time, however, the rate of the laminar flow, U_0, is increasing proportionally to the distance, x. According to Eq. (12), the ratio between x and U_0 remains constant, so the thickness of the diffusion layer will remain even and will depend only on the angular velocity, ω, of the rotating disc electrode:

$$\delta = 1.62\ D^{1/3}\ \nu^{1/6}\omega^{1/2} \qquad (13)$$

Equation (13) is known as Levich's equation. The combination of Eqs. (13) and (6) results in

$$i_L = 0,62\ zFD^{2/3}\ \nu^{1/6}\omega^{1/2}C_b \qquad (14)$$

For example,[6] substituting in Eq. (13), we can estimate the diffusion layer thickness for a one-electron reduction of O at a rotating disk electrode for $D_0 = 10^{-9}$ m^{2}sec^{-1}, $\nu = 10^{-6}$ m^{2}sec^{-1}, as ω increases from 10 to 1000 rad/sec (from 100 to 10,000 rpm). The diffusion layer thickness is $(1.62 \times 10^{-4}\ \text{m} \cdot \text{sec}^{-1})\omega^{-1/2}$ so that as ω increases from 10 to 1000 rad/sec, δ decreases from 51 µm to 5.1 µm. The limiting current for an electrode of one mm diameter and C_b = 1 mM is, from Eq. (14),

$$i_L = (3.03 \times 10^{-10}\ \text{A-m})/\delta$$

Therefore, over the dynamic range (10 < ω < 1000 rad/sec), the limiting current ranges from 6 to 60 µA.

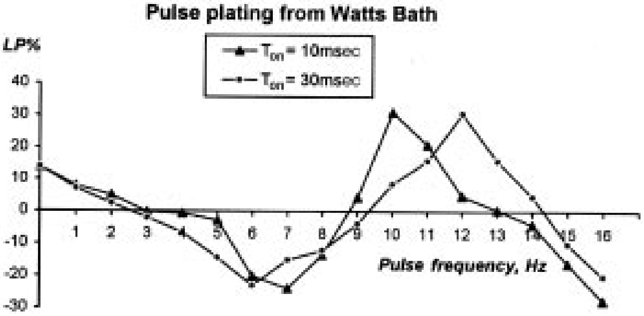

Fig. 6—Leveling power (LP) dependence on pulse frequency for nickel coatings deposited from a Watts solution.

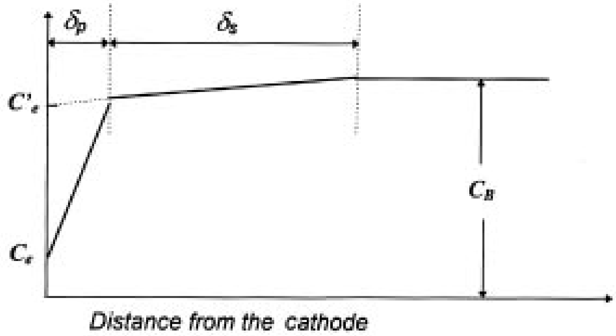

Fig. 5—Concentration profiles of the two diffusion layers in pulse plating: δ_p - thickness of the pulsating diffusion layer; δ_s - thickness of the stationary diffusion layer.

♦ *Through addition of hydrodynamically active agents in plating solutions*

Hydrodynamically active agents are special substances that, added to plating baths, even in minuscule quantities, can reduce by several times the value of kinematic viscosity of the electrolyte. The viscosity is caused by internal friction among liquid layers during their movement.[7] This is the reason that a flow is possible only if a force, F, is applied (Fig. 4). The velocity of the layer immediately adjacent to the immovable surface, S, equals zero. The velocity of the liquid layers increases proportionally to their distance from the surface, S, and at distance, Δ, reaches the value U_0.

The force, F, moving the liquid relative to the immovable metal surface, S, is proportional to the surface area, A, and to the flow velocity, U, and is reversibly proportional to the distance Δ to S:

$$F = A\ (dU/d\Delta) \qquad (15)$$

where dU/dΔ is a velocity gradient.

For different kinds of liquids under equal conditions, the moving force, F, grows proportionally to their viscosity. This relationship can be expressed by the coefficient of proportionality, η (viscosity coefficient):

$$F = \eta A\ (dU/d\Delta) \qquad (16)$$

When the distance, Δ, is comparable to the thickness of the diffusion layer, δ, the liquid viscosity can be expressed by the following formula:

$$\eta = F.A\ \frac{1}{dU/d\delta} \qquad (17)$$

As can be seen from Eq. (17), the viscosity is reversibly proportional to the velocity gradient, dU/dδ. Accordingly, reduction of viscosity coefficient η will make the diffusion layer, δ, thinner.

In the case of the rotating disc electrode, the relation between the thickness of the diffusion layer and the solution's kinematic viscosity is demonstrated by the Levich equation (13). According to this equation, the diffusion layer thickness, δ, is proportional to the 1/6 power of the kinematic viscosity, ν. For example, if the viscosity is decreased by a factor of four, the thickness of the diffusion layer will decrease by a factor of six.

♦ *Through the application of pulsed current*

In pulse plating with short pulse durations, two distinct cathodic diffusion layers can be defined instead of one, as in d-c operation (Fig. 5). In the immediate vicinity of the cathode, the concentration pulsates with the frequency of the pulsating current—decreasing during the pulses and relaxing in the interval between them. Consequently, a pulsating diffusion layer formed close to the cathode does not have time to extend very far into the solution; it does not reach the region where convection takes over the mass transport.[8,9]

In terms of the double diffusion layer model, the two distinct layers are related to two kinds of limitations. The depletion of the cationic concentration in the pulsating diffusion layer limits the pulse current density, and the depletion of the cationic concentration in the outer diffusion layer limits the average current density. The outer diffusion layer is essentially stationary. According to Fick's law for the pulse current density and for the average current density i_m, we can write:

$$i_p = zFD\,(C_e' - C_e)/\delta_p \qquad (18)$$

$$i_m = zFD\,(C_b - C_e')/\delta_s \qquad (19)$$

The current density, i_p, during a pulse is proportional to the concentration gradient in the pulsating layer, whereas the average current density is proportional to the concentration gradient in the stationary outer diffusion layer. The thickness of the pulsating diffusion layer is defined, according to Ibl, by the following equation:

$$\delta_p = (2DT_{on})^{1/2} \qquad (20)$$

It is evident that δ_p depends only on the diffusion coefficient D of the cations and on the pulse length T_{on}, and is proportional to the square root of the product of these two quantities. It follows, from Eq. (20), that the shorter the pulse length, the smaller the thickness of the pulsating diffusion layer, δ_p. The decrease of T_{on} is constrained by the time required to charge the electrical double layer; this time period should be much shorter than the pulse duration. When the charging time is longer than the pulse length, a capacitive effect occurs—the metal deposition current is more or less strongly damped and d-c conditions are imminent. In this case, the potential benefit of pulse plating for the structure of coatings is lost.

The experimental part of this study is based on the combined application of the above three approaches to decrease the thickness of the diffusion layer, δ, and, respectively, to increase the limiting current density, i_L, and cathodic polarization, η_c, which results in deposition of metal coatings with very fine-grained structure. This is the reason that the experimental conditions for leveling measurements of metal coatings include motion of the cathode (rotating-disk electrode), addition of hydrodynamically active agents and the application of pulsed current.

Leveling Performance of Bright D-C and Pulse-Plated Coatings

A fine-grained structure is a necessary, but not sufficient, condition for deposition of a metal coating with good decorative and functional properties. Among numerous pulse-electrodeposited metal coatings with fine crystal structure (obtained under a variety of plating conditions corresponding to a vast number of combinations involving the three parameters, T_{on}, T_{off} and i_p), there are only a few with the desired properties. It is necessary, therefore, to find an objective criterion for those pulse plating conditions under which electrodeposits with the best properties are obtained. The leveling (microthrowing) power could be such a criterion.

Leveling can be qualitatively characterized as the ability to diminish the difference in height between protrusion peaks and recesses in a surface microprofile. The greater this ability, the thinner the coating with the same functional properties. For quantitative leveling estimation, a reliable and precise method has been developed.[10] This method includes roughness measurements of both the uncoated substrate, $R_{a,0}$, and the coated surface, $R_{a,c}$. The following expression determines the leveling power (LP) of metal coating electrodeposited on half of the surface of the disc electrode under given plating conditions:

$$LP = \frac{(R_{a,o} - R_{a,c})}{R_{a,o}} \qquad (21)$$

It should be noted that all experiments have been performed in a *galvanostatic regime* of electrodeposition, satisfying the requirement that $i_p \cdot T_{on}$ = const. and with the supply of a constant amount of electricity necessary for nuclei formation during a single pulse. Therefore, the relationship between average current density, i_m, and pulse current density i_p

$$i_m = \frac{i_p \cdot T_{on}}{T_{on} + T_{off}} \qquad (22)$$

is transformed as follows:

$$i_m = f \cdot const. \qquad (23)$$

Expression (23) also shows that the cumulative number of nuclei formed for a fixed time period is proportional to the pulse frequency, f. Plating time is precisely defined to ensure a constant number of pulses for each value of pulse frequency used. The metal coatings were deposited on a rotating disk electrode (0.5 cm^2) under the following conditions: (a) constant speed of rotation, 250 rpm; and (b) combined motion, consisting of rotation at 50 rpm and vibration at 600 cpm.

Table 1
Bath Composition for Bright Watts & Sulfamate Nickel Deposition

Watts		**Sulfamate**	
$NiSO_4 \cdot 7H_2O$	250 g/L	Ni-sulfamate	80 g/L
$NiCl_2 \cdot 6H_2O$	30 g/L	$NiCl_2 \cdot 6H_2O$	4 g/L
H_3BO_3	40 g/L	H_3BO_3	30 g/L
Brightener	5 mL/L	Brightener CHT*	0.07 g/L
Hydrodynamically active additive (SA-LFPP)	4 x 10^{-4} g/L	Hydrodynamically active additive (SA-LFPP)	4 x 10^{-4} g/L
Bath temp	50 °C	Bath temp	50 °C
pH	3.5	pH	4.0

* Bulgarian patent 54663 (1981); US patent 4,585,531 (1988).

Leveling Performance of Bright Nickel, Palladium & Gold Coatings

Nickel coatings for engineering purposes are usually electrodeposited from standard Watts and sulfamate electrolytes containing commercially available brighteners. Bath compositions and operating conditions are shown in Table 1. Because of the presence of a hydrodynamically active additive

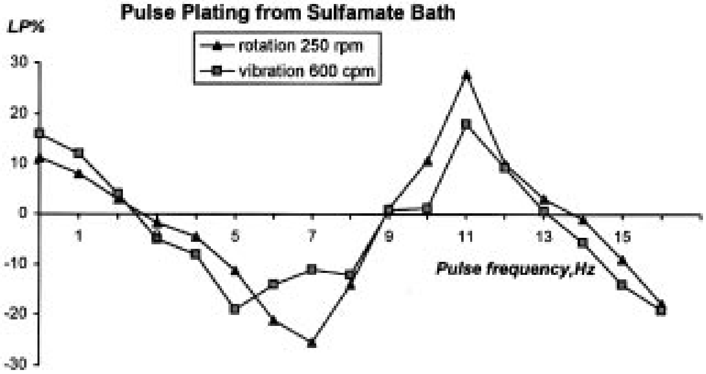

Fig. 7—Leveling power (LP) dependence on pulse frequency for nickel coatings deposited from sulfamate solution.

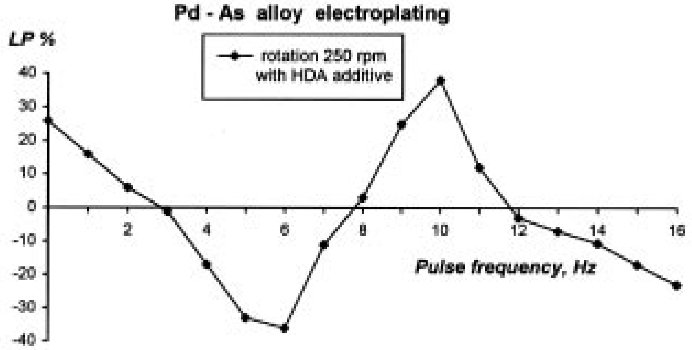

Fig. 8—Leveling power (LP) dependence on pulse frequency for Pd-As electrodeposits.

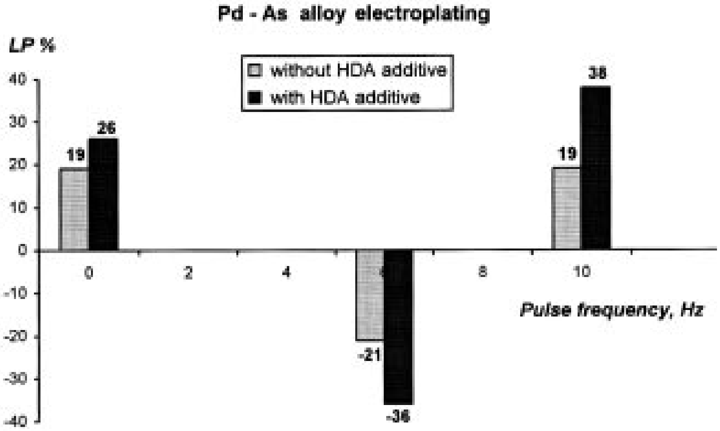

Fig. 9—Influence of a hydrodynamically active (HDA) additive on the leveling power of Pd-As alloy deposits.

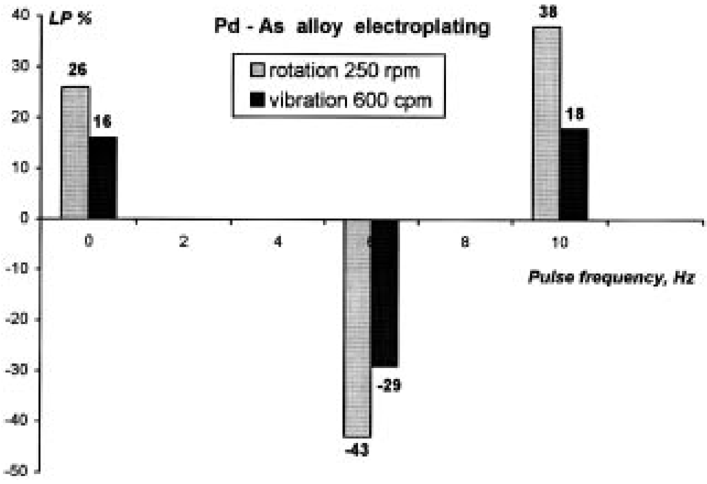

Fig. 10—Influence of vibration on the leveling power of Pd-As alloy deposits.

in the plating solutions, the concentration of the brighteners is 3-4 times lower than that recommended for d-c plating.

The leveling power dependence on pulse frequency in Watts nickel plating shows the roughening tendency of the pulse-electrodeposited nickel coating in the beginning of the frequency range (Fig. 6). At 7 Hz, the leveling power begins to increase gradually and reaches its maximum value at 10 Hz. With the increase of pulse duration (up to 30 msec), the roughening maximum is reached at 6 Hz, and the leveling maximum at 12 Hz. Here, the maximum value of leveling power is twice as large as that in d-c plating.

The same leveling performance is also characteristic of the semi-bright nickel coatings deposited from a sulfamate bath. In Fig. 7, a comparison of leveling power dependences on pulse frequency is depicted by using: (a) rotation speed of 250 rpm; and (b) frequency of vibration 600 cpm for the rotating disk electrodes. It was observed that, on the one hand, the vibration doesn't change the character of the leveling performance (as in Fig. 6). On the other hand, however, the vibration decreases both roughening and leveling over nearly the whole frequency range.

Electroplated palladium and palladium alloys are used in a variety of applications, including deposition of protective coatings on decorative articles such as jewelry and watches, and of electrical-contact coatings on electronic devices. The use of palladium or palladium alloys in these applications is preferred because of their lower cost compared to traditionally used metals, such as gold and platinum. The electroplated palladium, however, is frequently not adherent, tends to be porous, often develops cracks and is generally quite brittle. Investigations into the reason why electroplated palladium layers exhibit such poor quality reveal that this is the result of incorporation of hydrogen into the electroplated palladium layers.

Because of very high values of the exchange current, $i_{0,H}$, for hydrogen evolution on Pd, those electrodeposits are prone to hydrogen adsorption and incorporation. To solve effectively this detrimental problem, cathodic deposition can be employed in combination with alloying metals for which $i_{0,H}$ is ten thousand times lower (Pb, As, Sb).

The developed bright Pd-As alloy electroplating process works even at acidic pH (5.5-6.5). This promotes adhesion of palladium alloy coatings on base metals and, correspondingly, no preliminary use of pure palladium strikes is needed for high-quality deposition of these coatings. Bath compositions and operating conditions are listed in Table 2.

The leveling power dependence on pulse frequency of Pd-As plating processes, shown in Fig. 8, is similar to those of Watts or sulfamate-nickel electrodeposition. As can be seen, a roughening tendency occurs in the beginning of the frequency range (0-6 Hz). Above 6 Hz, the leveling power begins increasing gradually, and, at 10 Hz, it reaches its maximum value, which is higher than that in d-c plating. Further increase of the pulse frequency leads to a steep decrease of the leveling power (LP) percentage, the values of which become negative at 12 Hz. Beyond this frequency, the palladium coatings become increasingly rougher.

Table 2
Bath Composition for Pd-As Alloy Deposition

Pd (added as $PdCl_2$)	9.0 g/L
Complexing agent (aliphatic polyamine)	40 g/L
As (added as As_2O_3)	2.0 g/L
Brightener CHT	0.07 g/L
Hydrodynamically active (HDA) agent	0.4 mg/L
Bath temp	45 °C
pH	6.0

Fig. 9 shows the influence of a hydrodynamically active (HDA) additive on the leveling performance of bright Pd-As alloy deposits for pulse frequencies 0, 6, and 10 Hz, at which the extreme LP% values are obtained. The addition of an HDA agent to the plating bath enhances the leveling or roughening effects of the cathode surface over the whole pulse frequency range. This fact can be explained if it is assumed that the HDA agent reduces the thickness of the diffusion layer by several times and therefore increases the concentration gradients and rates of brightener diffusion flows. It is worth noting that the maximum LP value (38%) of bright Pd-As alloy coatings, electrodeposited at 10 Hz with an HDA agent, is exactly twice as great as the d-c plating value (19%) without an HDA agent.

Gold electroplating is used in many industries to confer good electrical properties and corrosion resistance on finished components. Pure gold has poor wear characteristics, however, and this problem can be overcome by developing gold alloy plating processes operating at acidic pH. All the acid electrolytes currently in use are alloy plating baths from which gold is co-deposited with nickel, cobalt or iron. The composition of a gold plating bath is shown in Table 3.

The leveling performance of cobalt-hardened gold coatings, d-c or pulse deposited from this acid bath, exhibit a character identical to those of the nickel and palladium-arsenic alloy coatings. As can be seen, the only differences are manifested in those values of the pulse frequency at which minimum and maximum values of LP% are obtained. It is worth noting that the maximum LP value (33%) of a gold coating electrodeposited at 11 Hz with an HDA agent is nearly twice as great as the d-c plating value (19%) without an HDA agent.

Leveling Mechanism

The results of the precise experimental determination of leveling power dependence on pulse frequency in nickel, palladium and gold bright plating form the basis of the current considerations. The same leveling performances of the above plating processes are obviously based on a common leveling mechanism that makes possible its application in any other low-frequency pulsed electrodeposition. This leveling mechanism can be clearly described by using the schematic pictures shown in Figs. 14 and 15.

The following principles, based on the adsorption-diffusion mechanism, explain the leveling per-

Table 3
Bath Composition for Hard Gold Alloy Deposition

Gold (as $KAu(CN)_2$)	8.0 g/L
Citric acid	80 g/L
Sodium citrate	40 g/L
K_2HPO_4	40 g/L
Cobalt (as sulfate)	0.1 g/L
Brightener CHT	0.08 g/L
Hydrodynamically active (HDA) agent	0.4 mg/L
Bath temp,	38 °C
pH	3.5

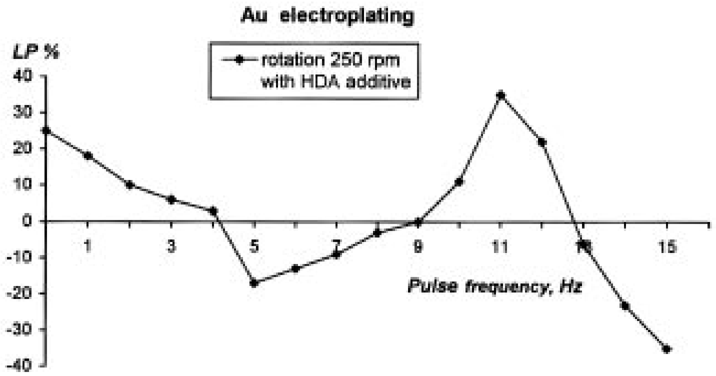

Fig. 11—Leveling power (LP) dependence on pulse frequency for gold electrodeposits.

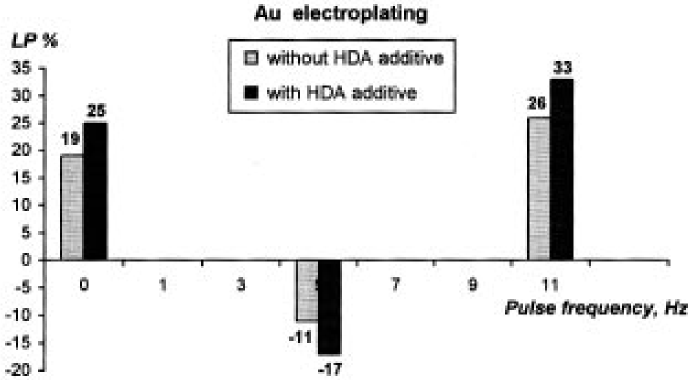

Fig. 12—Influence of a hydrodynamically active (HDA) additive on the leveling performance of gold deposits.

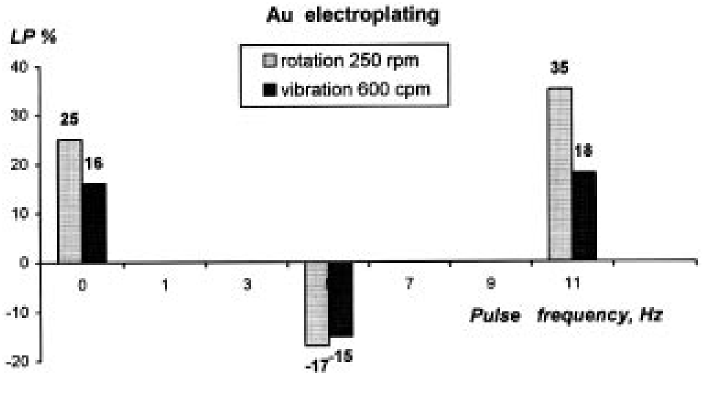

Fig. 13—Influence of vibration on the leveling performance of gold deposits.

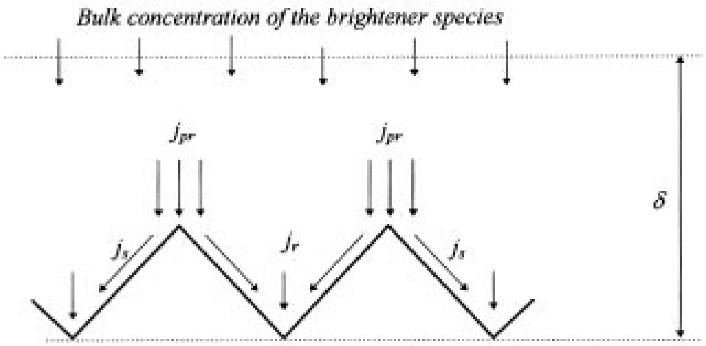

Fig. 14—Brightener diffusion flows toward the cathode surface with regular V-groove microprofile.

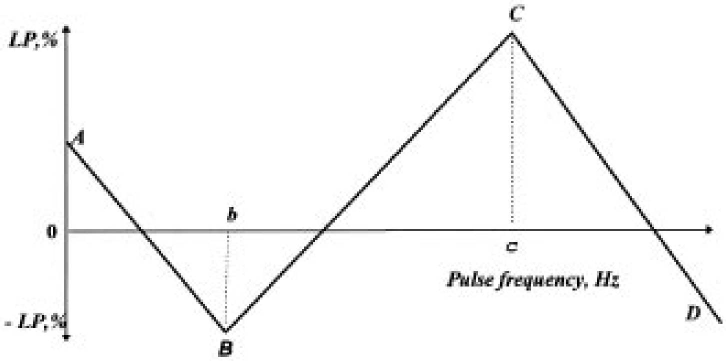

Fig. 15—Scheme of the experimental leveling power (LP) dependences on pulse frequency.

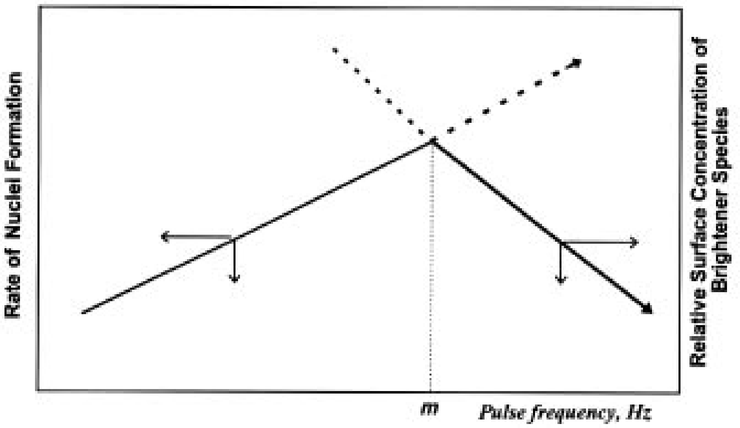

*Fig. 16—"Limiting" pulse frequency **m**, at which the leveling maximum occurs.*

formances of metal coatings deposited in low-frequency pulse plating with brightener additives and hydrodynamically active agents:

♦ The participation and consumption of various species s_1, s_2, s_3 ..., such as metal ions, organic molecules of additives, etc. in cathodic reactions, create diffusion layers with respective thicknesses of δ_1, δ_2, δ_3 ... Each species consumed at the cathode has its own concentration gradient representing the driving force of the different flows.

♦ The brighteners act as inhibitors of crystal growth at the sites of their adsorption. In pulsed electrodeposition, such sites of adsorption are the new nuclei formed by each pulse (Fig. 1b). The higher the pulse frequency, the more active sites available for adsorption.

♦ Electrodeposition is preferentially inhibited on those portions of the electrode surface that are more accessible to these agents by diffusion (Fig. 14). As a result, there occurs a considerably greater polarization than that in the recessed or valley areas. This means that the number of new nuclei on protrusions formed per pulse will be much greater than that in recesses.

♦ The difference between the quantities of brightener species adsorbed on protrusions and in recesses creates a concentration gradient of the surface diffusion flow, j_s, forcing the transportation of inhibiting agents from protruding areas to the recesses during the time interval T_{off} between two pulses. This causes increased coating roughness in the beginning of the frequency range (this corresponds to the line AB in Fig. 15). At pulse frequency b, the surface roughness reaches its maximum value, B. At frequencies higher than b, T_{off} becomes progressively shorter and the influence of j_s as a roughness factor gradually decreases (this corresponds to line BC).

♦ The pulse frequency c, at which the leveling power reaches its maximum value, C, is called the "limiting" frequency. Above it, the rate of brightener diffusion flow towards the microprofile surface becomes lower in comparison to the ever increasing rate of nuclei formation. The crystallization process takes place under conditions of brightener deficit. As a result, the leveling power gradually decreases (line CD).

♦ In accordance with the definition of surface diffusion flow j_s, as a roughness factor, low rates of this flow should correspond to high values of leveling power and vice-versa. If the interval between pulses is sufficiently long, the flow rate will be defined solely by the surface concentration gradient, dc_s/dx_s. In d-c bright plating, this gradient is small because of the low concentration difference, dc_s, of the brightener species adsorbed onto microprofile protrusions and recesses. In this case, the leveling power is a positive quantity. At the "limiting" pulse frequency, c, j_s is zero because T_{off} becomes much shorter than the time needed for the transportation of brightener species over the surface from peaks toward valley areas. The increase in frequency, however, also leads to a larger difference, $(j_{Pr} - j_r)$, and at c, the leveling maximum is achieved. This maximum could be several times greater than the LP% in d-c plating.

♦ From the condition $i_p T_{on}$ = const., valid for all the experiments, it can be concluded that increasing the pulse duration, T_{on}, leads to a decrease in pulse current density (*i.e.*, the higher the T_{on} value, the smaller the number of nuclei formed per pulse). This is the reason that the "limiting" frequency, c, is displaced toward a higher frequency value (see Fig. 6). From the expression for pulse frequency, $f = (T_{on} + T_{off})^{-1}$, it is clear that an increase in T_{on} reduces T_{off}. Therefore, the "critical" time, T_{off}, needed for the transportation of brightener species by the surface diffusion flow, j_s, is reached at a lower frequency, b.

♦ The addition of a hydrodynamically active (HDA) agent to plating baths reduces by several times the diffusion layer thickness, which increases the concentration gradients of brightener diffusion flows, j_{pr}, j_r, and j_s. This leads to enhancement of the roughening or leveling effects.

♦ The effect of vibration (600 cpm) on the leveling performances of pulse-electrodeposited coatings is opposite to the influence of an HDA agent. The vibration causes turbulent flows, interfering with the brightener diffusion and adsorption. This results in a lower degree of roughening or leveling of the coatings in comparison to the leveling performance of the coatings deposited in a plating regime of laminar electrolyte flow.

Conclusions

The interpretation of the results obtained justifies the following generalizations and conclusions, which are valid for any bright pulse-plating process:

1. The combined application of (1) the pulsed current, (2) the addition of hydrodynamically active agents into bright plating baths, and (3) the solution agitation, creates a synergistic effect manifested in an efficient decrease of the thickness, d, of the diffusion layer, which results in electrodeposition of metal coatings with very fine-grained structure.
2. The presence of a fine-grained structure, however, is only one of the conditions for deposition of a metal coating with good decorative and functional properties. In this respect, the leveling power can be used as an additional criterion for discovery of the best plating regime.
3. Pulse frequency is the major rate-controlling factor of leveling performance in bright electrodeposition when a galvanostatic regime of pulse plating is used. By varying pulse frequency, *every bright pulsed electrodeposition process* could be schematically divided into two simultaneous and related processes—nuclei formation and adsorption of brightener species (Fig. 16). Increase of pulse frequency leads to a rising number of new nuclei, and to decrease of the relative surface concentration of adsorbed brightener species. At a definite pulse frequency, m, the rate of brightener diffusion flow reaches the limiting value, above which crystal growth takes place under the condition of brightener deficit. This value of the pulse frequency, providing the optimal coordination of the rate of both processes, coincides exactly with the "limiting" frequency, c, at which the leveling maximum occurs.
4. The theoretical model of pulsed plating with brighteners and hydrodynamically active additive appears appropriate, especially for industrial reel-to-reel plating of nickel, gold, palladium and tin-lead on wires, strips, and other objects with a simple shape and profile. These industrial applications can meet the hydrodynamical conditions under which there is a practical possibility to achieve a diffusion layer that is evenly thick over the entire surface of the cathodic substrate.

Editor's note: *This paper is based on AESF Research Project 97. Part 2 contains the experimental data to support the thesis of Part 1 and will appear in P&SF next month.*

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