Electrochemical Formation of Nano-structured Metal Deposits and Anodic Oxide Coatings by Applying (DC+AC) Pulses and Using Drag Reducing Polymer Additives

Mois Aroyo

Two competing factors control the grain size of the electrodeposits: the nucleation of new crystals and the growth of existing crystals. Nanocrystal formation requires set of operating parameters that promote the nucleation of new crystals. If all other conditions stay the same, this process takes place when the concentration of the reacting species (metal and other ions) in the diffusion layer adjacent to the substrate is as high as that in the bulk solution. Therefore, thinner diffusion layers are related to faster rates of restoration by diffusion of the bulk concentration of ions consumed during the pulse on-time.

The present paper presents a new approach in the production of nano-structured metal electrodeposits and anodic oxide coatings that combines (DC+AC) pulse application with the addition in electrolytes small quantities of drag reducing polymers (DRP). Typically used to diminish the skin-friction drag of the turbulent flow, these polymers can be also added into flowing electrolytes to reduce the thickness of the boundary and diffusion layers. In support of the advantages and efficiency of the proposed electrochemical technology this paper offers three examples of (DC+AC) pulse formation: 1)nickel deposits, 2)aluminium, and 3)titanium anodic oxide coatings. In all three cases the coatings' nano-structure determines their excellent functional properties.

Key Words: *Nano-structured coatings, pulse plating, pulse anodizing, aluminum anodizing, titanium implant anodizing, drag reducing polymers*

Dr. Mois Aroyo
Sofia, BULGARIA
mmaroyo@abv.bg

Nanocrystalline materials form a new class of disordered solids with ultra-fine crystals, usually less than 100 nm in size.[1] The main structural characteristic of these materials is the large volume fraction of their interface atoms associated with grain boundaries and triple junctions. While this volume fraction is negligible in conventional polycrystalline materials, it becomes significant at grain sizes of less than 100 nm and it exceeds 50% for grain sizes of less than 10 nm. Consequently, nanocrystalline materials are expected to demonstrate considerable changes in many mechanical, physical, and chemical properties as a result of this large fraction of atoms located at the interfacial defect structure. The properties of even smaller nanocrystals (less than 10 nm) offer significant advantages over larger nanocrystals, particularly in the area of hardness, magnetic behavior, hydrogen storage, and wear resistance. Nanocrystalline materials can be obtained in several ways such as by sputtering, laser ablation, inert gas condensation, oven evaporation, spray conversion pyrolysis, high speed deposition, sol gel deposition, and electrodeposition. The major advantage of electrodeposition is that a large number of pure metals, alloys, and composites, can be electrochemically formed with grain sizes in the nanocrystalline range.

I start by laying out the electrochemical principles of formation of nano-structured cathodic deposits and anodic oxide coatings. The proposed practical method for the deposition of coatings with excellent functional properties is based on these theoretical principles.

THEORETICAL CONSIDERATIONS

As it is well known, 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. These two processes are in competition with each other and are influenced by different factors. 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. Therefore, nanocrystal formation requires set of operating parameters which promotes the nucleation of new crystals. According to Volmer's principles of electrocrystallization[2] the rate of formation of new nuclei on the electrode surface increases exponentially as the polarization, or overpotential η, grows up:

$$v = \mathrm{B}\ \exp\{-\frac{\mathrm{K}}{\eta^2}\} \qquad (1)$$

Here, the constants B and K are specific for given metal and temperature.

Cathodic deposition of metal coatings

Two types of overpotential control the rate of the cathodic reaction of metal deposition: the activation overpotential η_{act} and the concentration overpotential η_{conc}.

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, E_{eq} the difference $(E_c - E_{eq})$ represents the cathodic overpotential η_c. When the values of current are moderate, relatively low, the prevailing part of the cathodic overpotential, η_c constitutes the **activation overpotential** η_{act} that determines the rate of the cathodic process:

$$i_c = i_0 \exp\left[\alpha zF\ \eta_{act} / RT\right] \qquad (2)$$

After the application of a logarithm, we get the Tafel equation:

$$\eta_{act} = b_c \log\left(i_c / i_o\right) \qquad (3)$$

where $b_c = -2.3RT/\alpha zF$ is the slope of the tangent to the polarization curve (Fig. 1).

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. One immediate consequence of the Tafel equation is that the smaller the exchange current $\boldsymbol{i_o}$, the larger is overpotential η_c for a given net external cathodic current density $\boldsymbol{i_c}$. In fact, the adsorption of additives (brighteners and other organic species) on the electrode's surface can affect the deposit structure by blocking kink sites on the cathodic surface, thus increasing the activation overpotential of discharged metal ions. For example, saccharine, coumarin, thiourea and formic acid have all been successfully applied to achieve grain refinement of nickel electrodeposits.

Concentration overpotential, η_{conc} 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 metal ions M^{Z+} at a bulk concentration C_b, if deposition is carried out at a current density i_c, then i/zF mol/s are removed continuously from the layer, adjacent to the cathode surface 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 electrolyte to the electrode surface by this process is given by

$$\frac{i}{zF} = \frac{D}{\delta}(C_b - C_e) \tag{4}$$

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

$$i_L = \frac{zFDC_b}{\delta} \tag{5}$$

and

$$\frac{C_e}{C_b} = 1 - \frac{i}{i_L} \tag{6}$$

Because the potentials corresponding to the concentrations C_b and C_e are

$$E_{eq} = E^0 + (RT/zF)\ln C_b \quad \text{and} \quad E_c = E^0 + (RT/zF)\ln C_e \tag{7}$$

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

$$\eta_{conc} = E_c - E_{eq} = \frac{RT}{zF}\ln\left(1 - \frac{i}{i_L}\right) \tag{8}$$

From Eq.(8), it follows that $\eta_{conc} \to \infty$ when $i \to i_L$. In other words, when the applied current density increases and reaches values closed to i_L, the polarization of the electrodeposition process increases infinitely (Fig. 1).

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 practically applied current density of the electrodeposition process. This, together with high values of the cathodic overpotential, permits metal coatings with fine-grained structure.

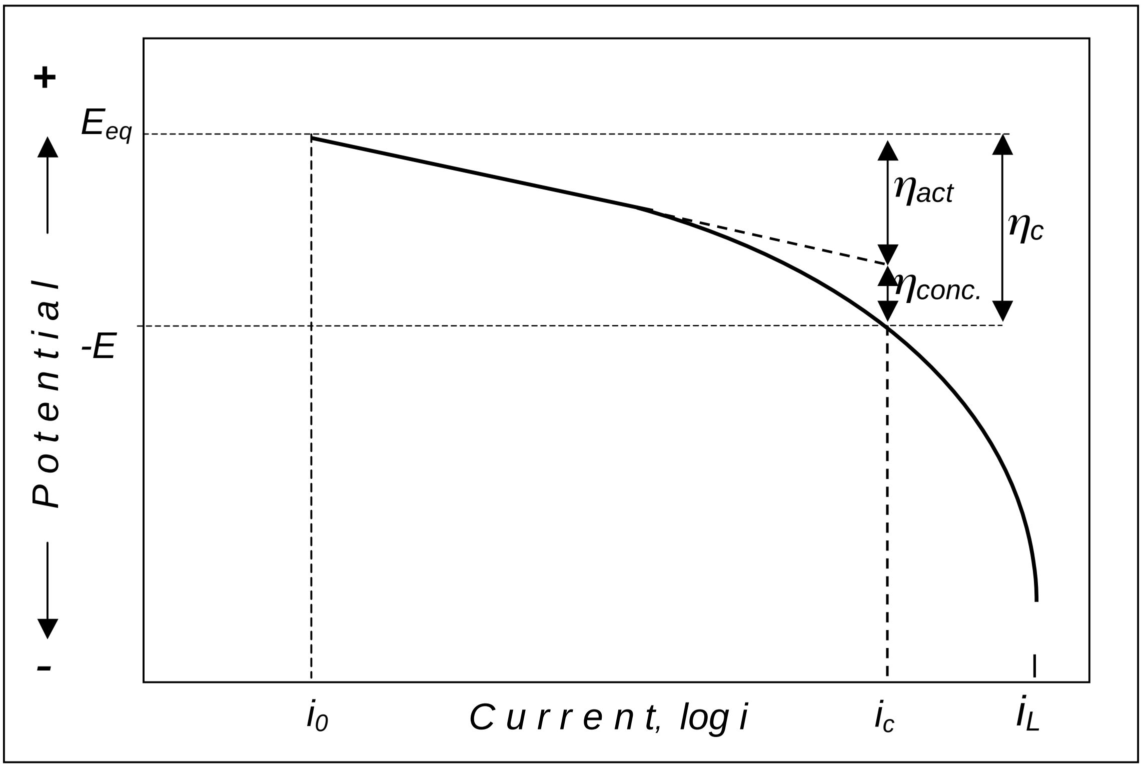

Fig. 1 - Cathodic polarization curve, showing increased values of cathodic overpotential *($\eta_c \rightarrow \infty$) at currents closed to the limiting current i_L*

How can the limiting current density, i_L be increased? According to equation (5), i_L grows when the thickness of the diffusion layer δ decreases. Two means are proposed to decrease the thickness of the diffusion layer δ:

1. Application of (AC +CD) pulses with very high current peaks

In pulse plating with short pulse durations two distinct cathodic diffusion layers can be defined instead of one, as in d-c operation (Fig.2). 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 intervals 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.[3,4]

The depletion of the cationic concentration in the pulsating diffusion layer δ_p limits the pulse current density, and the depletion of the cationic concentration in the outer diffusion layer δ_s limits the average current density The outer diffusion layer is essentially stationary. According to Fick's law for the pulse current density i_p and for the average current density i_m we can write:

$$i_p = zFD\,(C_e' - C_e)\ /\ \delta_p \qquad (9)$$

$$i_m = zFD\,(C_b - C_e')\ /\ \delta_s \qquad (10)$$

The pulse current density, i_p is proportional to the concentration gradient in the pulsating layer, whereas the average current density, i_m is proportional to the concentration gradient in the stationary outer diffusion layer.

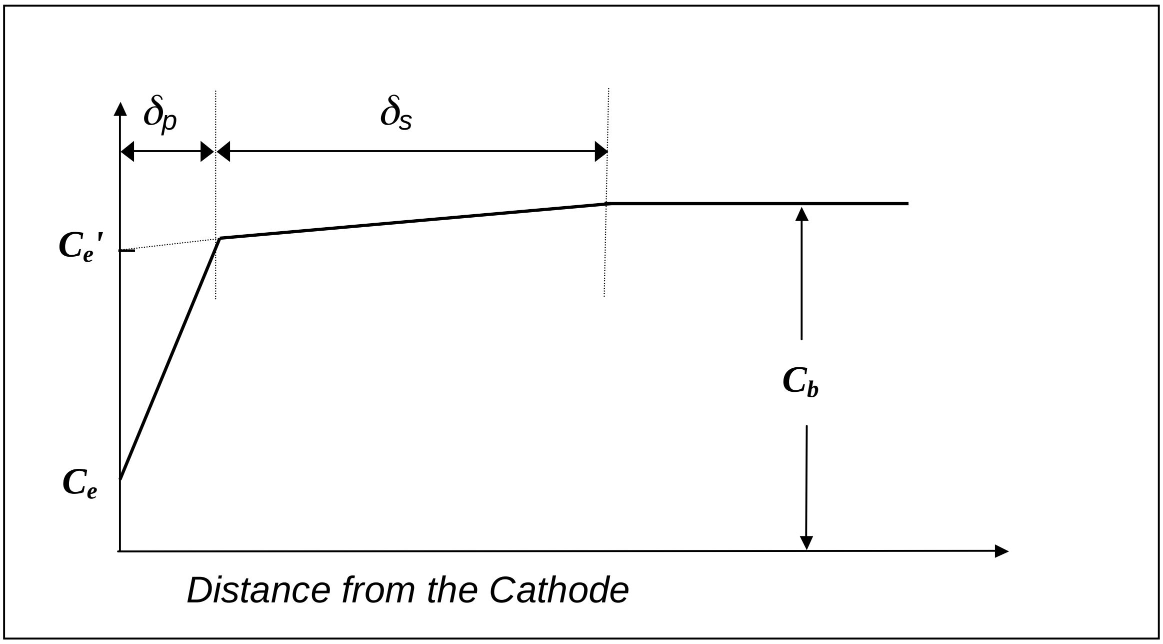

Fig. 2 - Concentration profiles of the two diffusion layers in pulse plating; δ_p *- thickness of the pulsating diffusion layer;* δ_s *- thickness of the stationary diffusion layer*

Because the concentration gradient in the stationary outer diffusion layer δ_s is considerably smaller than that in the pulsating diffusion layer δ_p, the latter becomes the main controlling factor for the plating process. According to equation (9), the higher pulse current density, i_p, rises, the thinner the diffusion layer becomes. Moreover, the thickness of the pulsating diffusion layer is defined, according to Ibl, by the following equation:

$$\delta_p = (2DT_{on})^{1/2} \qquad (11)$$

It is evident that δ_p depends also on the diffusion coefficient D of the cations and on the pulse length T_{on} . It follows, from equation (11), that the shorter the pulse length T_{on}, the smaller the thickness of the pulsating diffusion layer δ_p. Therefore, the higher peaks of the pulse current and the shorter pulse durations will result in finer-grained structures of the electrodeposits.

The comparison between pulse current peaks of the unipolar and bi-polar (DC+AC) pulses that can be found in our recently published study[5], demonstrates that for the same average current densities, the current peaks of (AC +CD) pulses are of 2.5 to 3 times higher than those of unipolar pulses (Fig. 7).

2. *Addition of drag reducing polymer (DRP) additives in flowing plating electrolyte*

The following theoretical considerations constitute the basis for the second means for thinning of diffusion layer δ.

A liquid flow is possible if a force, ***F***, is applied. The changes in velocity then take place in a very thin layer adjacent to the electrode surface. (Fig.3). 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 distanceδ_{Pr} reaches the value U_0. That layer, in which the flow rate changes from $U = 0$ to U_0 is called boundary layer or Prandtl's layer, δ_{Pr}. 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. The diffusion layer δ is considerably thinner than the Prandell's layer,δ_{Pr}. In water solutions, δ is approximately ten times thinner than $\delta_{Pr.}$

The force, ***F,*** moving the liquid relative to the immovable metal surface is proportional to the contact surface area *A* and to the velocity gradient $dU/d\delta$

$$\mathbf{F} = A\ (dU/d\delta) \qquad (15)$$

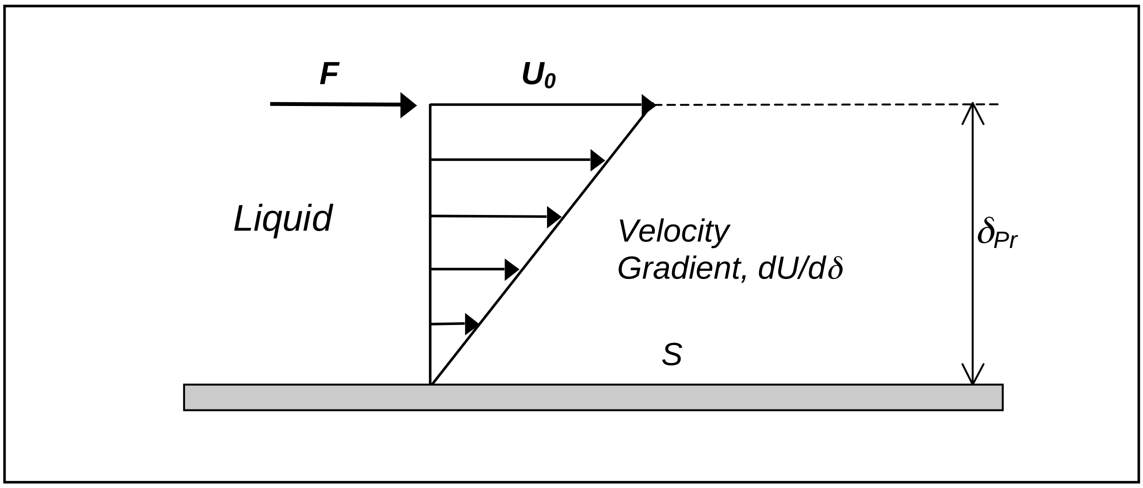

Fig.3 - Laminar liquid flow moving relative to the immovable metal surface S

For different kinds of liquids under equal conditions, the moving force, ***F***, grows proportionally to their viscosity. The higher the viscosity of the liquid requires a greater moving force ***F*** in order to achieve a given velocity U_0. This relationship can be expressed by the coefficient of proportionality or viscosity coefficient, μ

$$F = \mu\ A\ (dU/d\delta) \qquad (16)$$

Thus, the liquid viscosity can be expressed by the following formula:

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

As can be seen from eq.(17) the viscosity is reversibly proportional to the velocity gradient, $dU/d\delta$. Accordingly, reduction of viscosity coefficient, μ, will make the diffusion layer, δ, thinner.

How can we then decrease the viscosity of the electrolyte in order to decrease the thickness of the diffusion layer? In reality, this can be accomplished by adding small amounts of drag reducing polymers (DRP) to the plating electrolytes. Even minuscule quantities (few parts per million) of such water soluble additives with high moleculse weight in the order 2.10^5 to 3.10^6 decrease the hydrodynamic drag of the turbulence flow and increase considerably its velocity without altering the driving pressure. This effect is related to these polymers' linear macromolecule: polyacrylamide and poly-ethilenoxide (known under the trade name POLYOX) act like soft rubber bands that suppress flow disturbances and laminate the fluid structure by stretching and aligning themselves parallel to the axis of flow.[6,7,8] This behavior of these linear macromolecules eases the flow by reducing the internal friction (viscosity) among liquid layers. Consequently, according to the equation (17), the velocity gradient increases and the boundary layer's thickness decreases (Fig. 4).

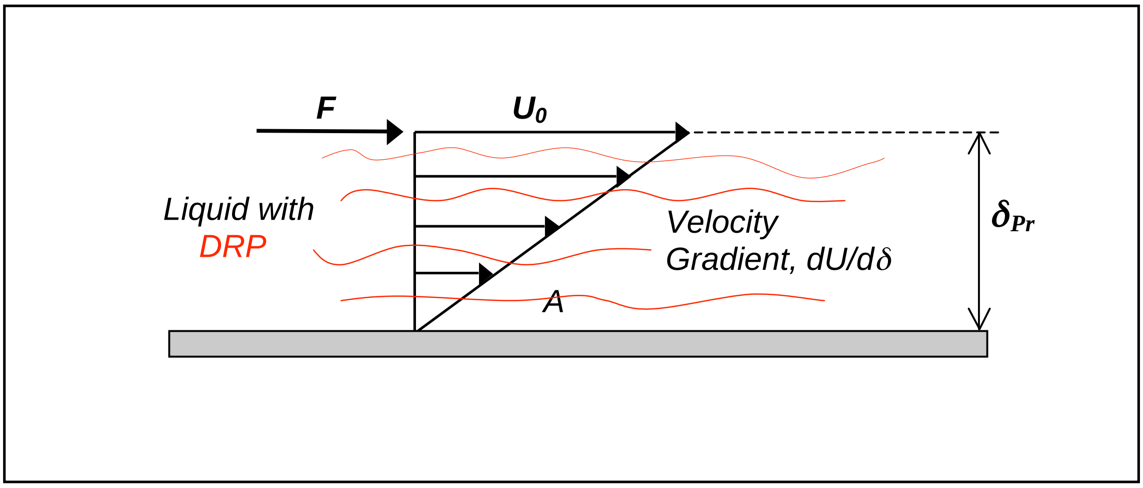

Fig. 4 - The addition of DRP to the flowing solution results in increased velocity gradient $dU/d\delta$ and to a decreased thickness of the boundary layer

Anodic formation of oxide coatings

Anodic oxidation is a commonly applied surface treatment of metals that enhances corrosion protection, electrical insulation, and adhesion to polymers. Depending on the metal substrate and electrochemical forming conditions, the anodic oxide films may exhibit compact or porous structure. Each one of these overall amorphous structures has its advantages for given applications. The formation of porous oxides is considered an important surface preparation aimed at improving the organic coatings' adhesion and strengthening the environmental behaviour of metals such as aluminium and titanium alloys.

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

- Active dissolution through metal ion transport from a bare metal surface into the electrolyte (line AB)
- Passivation or formation of anodic oxide films on the metal surface (line CH)
- Transpassivation (line DJ) and/or oxygen evolution (line FG)

Each one of the above processes occurs in a distinct potential zone of the anodic polarization curve *E vs. log i* obtained as the resulting current is recorded while the applied anodic potential is gradually increased (Fig.5). The zone of active metal dissolution is located at the beginning of the curve where the anodic current and, hence, the dissolution rate increase exponentially as the potential is made more positive than the stationary corrosion potential. A further increase of the potential is accompanied by the partial formation of an oxide or a hydroxide film on the surface:

$$xM + yH_2O = M_xO_y + 2yH^+ + 2ye^- \qquad (18)$$

When the potential $E_{M/MxOy}$ is reached, the anodic current of active metal dissolution starts to divert from the linear Tafel line passing through a maximum value, $i_{crit.}$. The formation of an oxide film acts as a barrier to further dissolution and the current suddenly falls. Within this region the rise of anodic potential to point D causes a small increase in current density because of the electrical resistance of progressively thickening passivating film. A **resistance polarizarion** η_R equal to the ohmic potential drop occurs:

$$\eta_R = R.i_{pass} \qquad (19)$$

where R is the film's ohmic resistance(Ω).

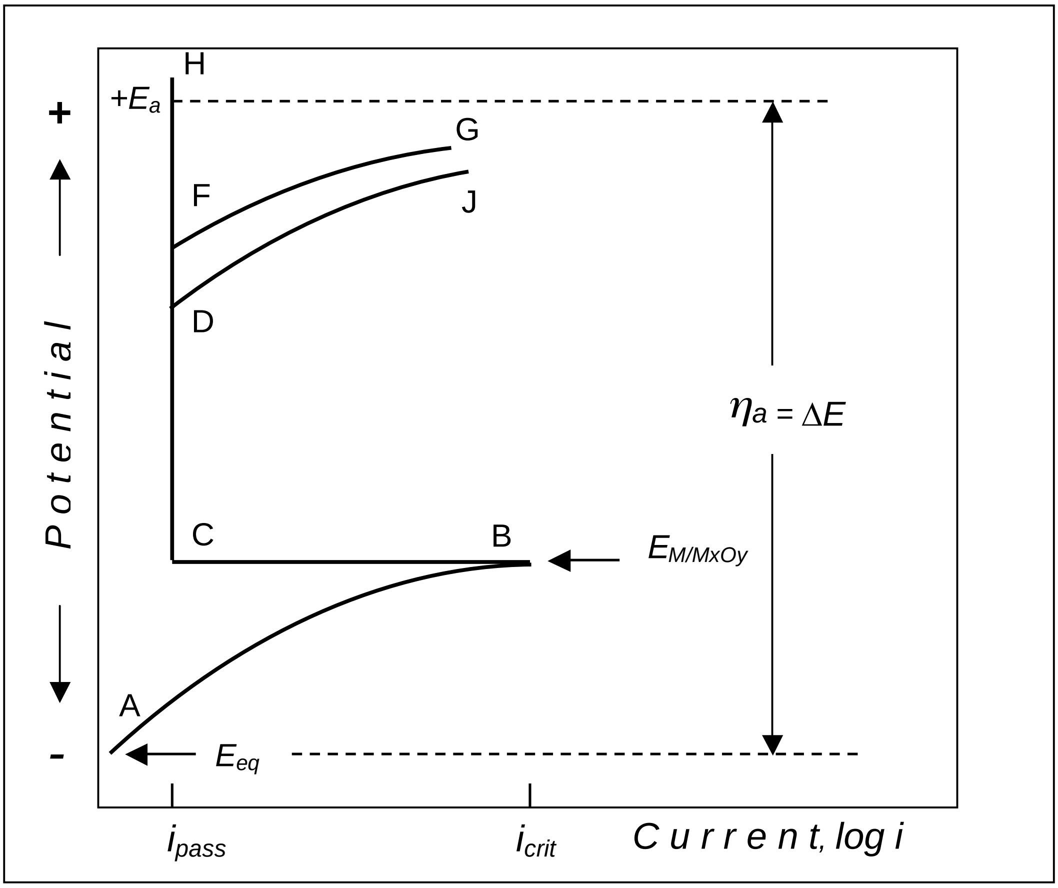

Fig. 5 - Schematic anodic polarization curve

At even higher potentials there are two possibilities:

1) If the film is a good electronic conductor then it may be oxidised to a soluble oxide species and dissolution recommences along D-J. In this region metal is in the transpassive state. Alternatively oxygen may be evolved along F-G according to the equation:

$$4OH^- = O_2 + 2H_2O + 4e^- \qquad (20)$$

2) If the film is a poor electronic but a good ionic conductor, then anodic oxidation or anodizing may take place (FH) under high field strengths at high anodic potentials. This occurs with metals like aluminum, titanium and other so-called vent metals. The thickening of the oxide film along F-H line proceeds by transport of metal cations, M^{z+} outwards and their combination with O^{2-} or OH^- ions at the film/solution interface (equation 18). Thus, by anodizing it is possible to convert the metal surface to the oxide coating which is an integral part of the metal. This way the metal properties of like resistance to corrosion and abrasion, hardness, adhesion, appearance, etc. may be altered and improved.

Fig. 5 shows that anodizing requires the application of high anodic polarization η_a that, according to principles of electrocrystallization (eq. (1), favors the grain refinement of coatings. The application of high overvoltage is a necessary yet not sufficient pre-condition for fine-grained crystallization. Nanoscale coatings' formation is possible only when the application of high overvoltage is related to high current density, which corresponds to the increased rate (velocity) of formation of new nuclei on the electrode surface (please see Fig. 1). In the case of d-c anodizing, however, because of the great ohmic resistance of the oxide film, the passivity current density, i_{pass} remains very low even at high applied voltages.

One should note that (DC+AC) pulse anodizing demonstrates an advantage related to the structure and hence, to the properties of the obtained porous oxide coatings. Due to 1) the depolarization action[5] of the AC component of voltage pulse, and to 2) very short pulse duration, the current in passive state, i_{pass}, reaches relatively high values - three to five times greater then that in DC anodizing. This means that during the (DC+AC) pulse, both processes of anodizing - a) transport of the metal ions, M^{z+} through the oxide layer and b) chemical reaction between M^{z+} and O^{2-} or OH^- ions at the film/solution interface - proceeds with a greater velocity. Thus, by the application of very high but short (DC+AC) voltage pulses we can ensure the formation of nanoscale anodic oxide coatings with improved functional properties while at the same time avoiding the risk of film breakdown.

EXPERIMENTAL ACHIVEMENTS

Three examples are given below to illustrate the formation of high quality nano-structured coatings by the combined use of (DC+AC) pulses and flowing electrolytes containing small quantities of DRP-additives.

Example 1: Electrodeposition of bright nickel coatings

The authors of the US patent[9] claim that the application of high pulse current densities (2 to 3 A/cm^2) in combination with stress relievers and grain refining additives in electrolyte (10 g/l saccharin) is sufficient to produce nanocrystaline nickel deposits with grain size smaller than 11 nm.

The possibility for application of such high pulse current densities in (DC+AC) pulse plating is demonstrated graphically in Fig. 6. Obviously, the applied pulse current densities in (DC+AC) plating are of 2.5 to 3 times higher than those in UPP for the corresponding pulse frequency and the same average current density. In addition, using cathionic polyacrylamide as a DRP-additive in flowing electrolyte, we can obtain the same result with a concentration of brighteners and other organic compounds that is two to three times lower.

The comparative porosity measurements[5] of bright nickel deposits obtained by using both pulse plating regimes prove the advantages of the application of (DC+AC) pulses for deposition nanocrystal metal coatings: bright nickel coatings obtained by unipolar pulses have higher porosity (11%) than those deposited by the application of (DC+AC) bi-polar pulses (6% porosity).

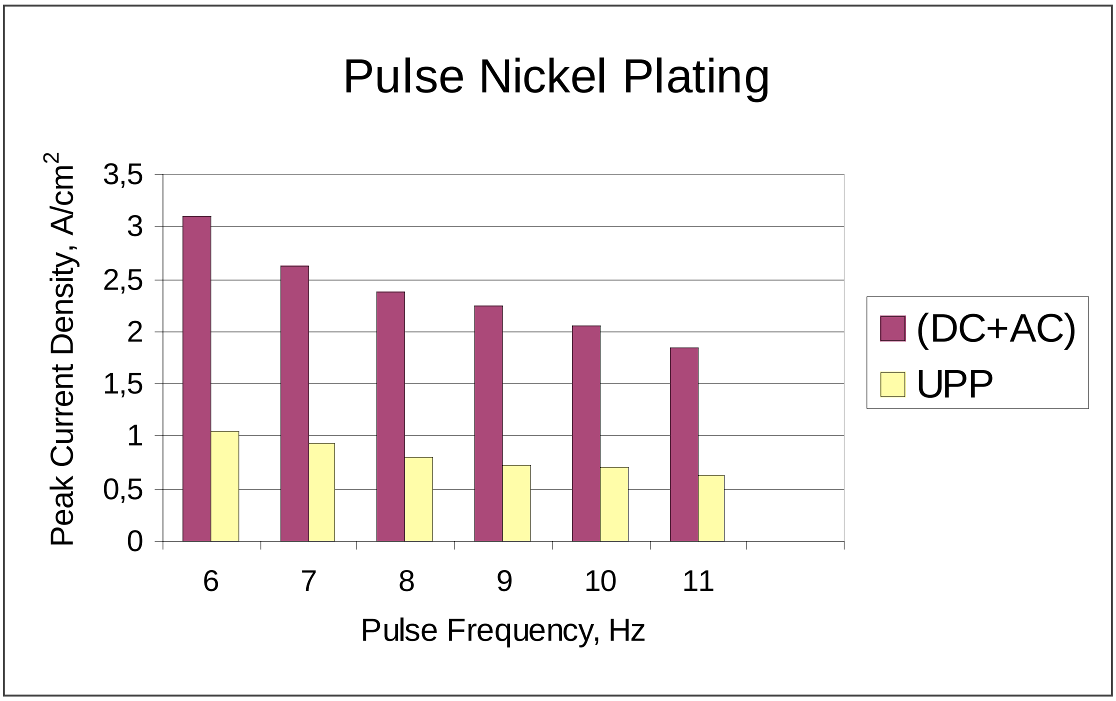

Fig. 6 - Peak current densities in bright nickel deposition by unipolar DC- & bi-polar (DC+AC) pulses

Example 2: *Aluminium anodizing*

This example proves the benefits of the (DC+AC) pulse technique for developing an environmentally friendly technology for pre-paint treatment of aluminum and its alloys. The proposed mode of anodizing and consequent electrolytic deposition of the corrosion inhibiting substance (CIS) at the pore of the anodic coating permits us to obtain the anodic films that would present a better alternative to the chromic acid anodized coatings. The method is based on aluminum (DC+AC) pulse anodizing in sulfuric/boric acid solution, containing drag reducing polymers (DRP).The electrochemical treatment of rotating aluminum samples (99% Al) proceeds over two stages:

1) (DC+AC) pulse anodizing at forming voltage up to 25 V.
2) Electrolytic deposition (filling) the pores of the anodic coating with corrosion inhibiting species (CIS)

For quantitative and comparative evaluations of the anodic oxide coatings, we have developed an electrochemical test for speedy and precise determination of corrosion resistance, especially of the coatings' susceptibility to pitting corrosion. This test is based on the measurement of the quantity of electricity, Q (in coulombs) needed to break through the anodic film when the above treated aluminium samples immersed in 0.1 M NaCl are anodically polarized. Within the galvanostatic regime of polarization (anodic current density = 0.3 A/dm^2) the quantity of electricity related to the unit area of the anodized aluminium samples is proportional to the time (in seconds) necessary to achieve the same value of potential situated in the pitting potential region. The greater Q,the higher the pitting corrosion resistance. The average Q-value of (DC+AC) pulse anodized aluminium and electrolytically filled with corrosion-inhibiting species is 220 A.sec/dm^2. This value is more than seven times greater than in the case of aluminium samples that are DC anodized and then electrolytically filled with CIS.

The above data presents indisputable evidence that in comparison to the structure of the anodic films obtained by d-c anodizing the nano-porous structure of the oxide coatings obtained by (DC+AC) pulse anodizing promotes to a greater degree the subsequent process of electrolytic deposition of CIS.

Example 3: *Titanium alloy anodizing*

The titanium alloy Ti6Al4V is widely used for medical implants. The review of recent literature suggests that there is a variety of electrolytes and electric regimes employed in the anodic formation of nanoscale oxide films on titan or on the Ti-6Al-4V alloy.[10,11]

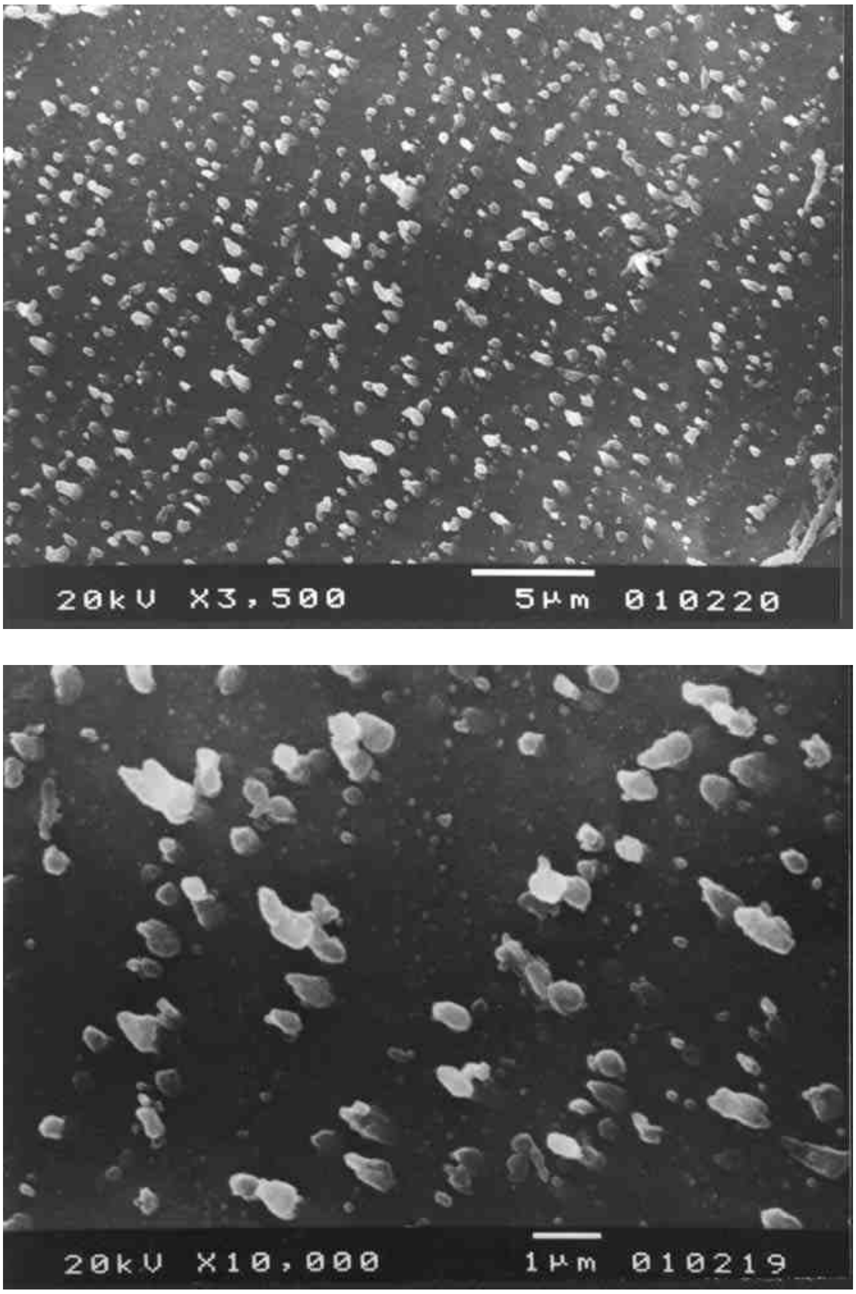

Fig. 7 - SEM top-view image of (DC+AC)-pulse anodizied titanium rotating electrodes under the following conditions: