Formation of Anodic Aluminum Oxide Coatings with Excellent Corrosion Resistance by the Application of (DC+AC) Bi-polar Pulses

M. Aroyo, B. Tzaneva, N. Tzonev.
Technical University of Sofia, Bulgaria

The goal of the present paper is to prove the benefits of the (DC+AC) pulse reverse technique toward developing an environmentally-friendly technology for pre-paint treatment of aluminum and its alloys. This technique permits us to obtain anodic films that would present a better alternative to unsealed sulfuric and chromic acid anodized coatings. The method is based on aluminum anodizing in sulfuric/boric acid solution by the application of (DC+AC) bi-polar pulses. Due to the AC-component of the pulse current, both processes - of pore formation and of electrolytic deposition of the corrosion inhibiting substance (CIS) at the pore base of the anodic coating - are promoted. As a result the anodic oxide coatings filled with CIS provide an extremely high pitting corrosion resistance, several times greater than that of the anodic films formed at present time in sulfuric/boric acid, chromic acid or other anodizing electrolytes and technologies. Moreover, this exceptional result is obtained without etching of anodized aluminum alloys.

Keywords: Aluminum anodizing, pulse reverse waveforms, hexavalent chromate alternatives

Pulse reverse techniques and surface finishing processes

Industrial surface finishing of metals employs a diverse range of electrochemical processes. There is a wide variety of anodic and cathodic reactions that play an important role in metal finishing. For example, some selected electrode reactions relevant to metal finishing are listed in Table 1.

This dualistic electrochemical nature of the above processes based on the simultaneous and competitive reactions of oxidation and reduction, is the reason why we talk of binary sets of opposite process factors - growth/dissolution, adsorption/desorption, polarization/depolarization, acidity/alkalinity. In this context, pulse-reverse technologies have the largest potential in controlling of these processes. As we vary the parameters of cathodic and anodic pulses, we can change the relative influence of the above opposing factors and thus define the optimal process conditions. In our recently published work we have demonstrated the benefits of the (DC+AC) pulse reverse technique for cathodic deposition of metal coatings with improved properties.

The goal of the present paper is to prove the advantages of pulse anodizing by the application of (DC+AC) bi-polar pulses as a very effective and environmentally-friendly pre-paint treatment of aluminum and its alloys. This involves: (1) pulse anodizing of aluminum in sulfuric/boric acid solution by the application of (DC+AC) pulses with the appropriate parameters and (2) pulsed electrolytic deposition at the pore base of the oxide film of corrosion-inhibiting substances (CIS) obtained.

Pre-paint treatment for aluminum

Conversion coatings

The formation of conversion coatings is an artificially induced and controlled process of electrochemical corrosion producing on the metal surface a layer, firmly bonded to the base metal, increasing its corrosion resistance and simultaneously providing good paint adhesion. Irrespective of the types of metal substrate or conversion coating, there exists a common electrochemical mechanism involving two mutually linked reactions - anodic and cathodic. The anodic process of metal oxidation and proton and electron release is connected with the participation of precipitating ions (OH, CrO$_4^{2-}$, H$_2$PO$_4^-$):

$$\begin{align*}
xMe + yOH^- &= Me_xO_y \downarrow + yH^+ + ye^- \quad (1) \\
xMe + 2CrO_4^{2-} + yH_2O &= Cr_2O_3 + Me_xO_{y+5} + 2yH^+ + (2y-6)e^- \quad (2) \\
3Me + 2H_2PO_4^- &= Me_3(PO_4)_2 \downarrow + 4H^+ + 6e^- \quad (3)
\end{align*}$$

The oxidizing agents, so-called accelerators, depolarize at the microcathodes of the metal surface:

$$Ox_{(accel)} + H^+ + 2e^- = Red_{(accel)} + H_2O \quad (4)$$

* Corresponding author:
Dr. Mois Aroyo
Technical University of Sofia
Sofia 1756, Bulgaria
E-mail: mmaroyo@abv.bg
Table 1
Selected electrode reactions relevant to metal finishing

<table>
<thead>
<tr>
<th>Type of electrode reaction</th>
<th>Cathodic reaction ( \text{Ox} + n\text{e}^- \rightarrow \text{Red} )</th>
<th>Anodic reaction ( \text{Red} - n\text{e}^- \rightarrow \text{Ox} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal / metal ion</td>
<td>( \text{Me}^{\text{aq}} + n\text{e}^- \rightarrow \text{Me} )</td>
<td>( \text{Me} - n\text{e}^- \rightarrow \text{Me}^{\text{aq}} )</td>
</tr>
<tr>
<td>Metal / gas</td>
<td>( 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 )</td>
<td>( 2\text{H}_2\text{O} - 4\text{e}^- \rightarrow 4\text{H}^+ + \text{O}_2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} )</td>
<td>( 4\text{OH}^- - 4\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} )</td>
</tr>
<tr>
<td>Metal / conversion coating</td>
<td>( \text{Ox}_\text{accel} + 2\text{H}^+ + n\text{e}^- \rightarrow \text{H}<em>2\text{O} + \text{Red}</em>\text{accel} )</td>
<td>( \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- )</td>
</tr>
<tr>
<td>Metal / metal oxide</td>
<td>( \text{Cu}_3\text{O} + 2\text{H}^+ + 2n\text{e}^- \rightarrow 2\text{Cu} )</td>
<td>( 2\text{Al} + 3\text{H}_2\text{O} - 6\text{e}^- \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 2\text{Cu} - 2\text{e}^- \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ )</td>
</tr>
<tr>
<td>Metal / redox species</td>
<td>( \text{Fe}^{3+} + n\text{e}^- \rightarrow \text{Fe}^{2+} )</td>
<td>( \text{Fe}^{2+} - n\text{e}^- \rightarrow \text{Fe}^{3+} )</td>
</tr>
<tr>
<td></td>
<td>( \text{Cu}^{2+} + n\text{e}^- \rightarrow \text{Cu}^{+} )</td>
<td>( \text{Cu}^{+} - n\text{e}^- \rightarrow \text{Cu}^{2+} )</td>
</tr>
</tbody>
</table>

Aluminum very quickly forms a natural oxide layer that is not uniform, and unfortunately localized corrosion can occur. Also, the oxide is not stable at elevated pH and its solubility creates problems under paint. One way to improve the corrosion resistance of a painted aluminum surface is to treat it chemically or electrochemically in order to make it more passive. This treatment results in converting the natural surface oxide layer into a homogeneous and relatively inert film. The chemical treatment for aluminum is acidic and takes advantage of the low pH solubility of aluminum and its oxide. The formation of a chromate conversion coating on aluminum by immersion in solutions containing chromic acid, phosphate ions and fluoride ions is a common way to enhance corrosion resistance and prepare the metal to accept paint. The fresh chromate conversion coating, however, is heat-sensitive. Heat destroys its effectiveness by altering the chemical composition of the film by expelling the waters of hydration in the crystal structure. Because chromium (VI) is a confirmed human carcinogen, there has been growing concern in recent years about pollution of waterways, and attention has been directed to reducing or eliminating this harmful agent.

For non-chromate pre-paint applications, fluoracid chemistry is the dominant approach. The treatment solutions contain zirconium and/or titanium as complex fluoride ions, phosphates and water-soluble resin. Although the absence of hexavalent chromium is an advantage of the non-chromate treatment solutions, this type of treatment solution nevertheless suffers from a corrosion resistance and paint adherence inferior to those for chromate-type treatments.

**Anodic coatings**

Another type of conversion coating can be obtained by anodizing, which is an electrochemical process of oxide film formation on the aluminum surface by the application of anodic polarization. Anodic oxide coatings in their unsealed condition are an excellent base for paints, lacquers, resins, etc. The chemical conversion treatments do not compare with anodizing either for quality of finish or application in industry. The coatings obtained by electrolytic means are not only superior mechanically, but can also be produced with much higher corrosion and abrasion resistance. The environmentally-acceptable anodizing solutions are based on sulfuric and phosphoric acids. Although chromic acid anodizing is a valuable base for paint, this process is recommended only for severe and long-term service conditions because of the environmental and health problems posed by hexavalent chromium.

In the process of anodizing, the aluminum part is made the anode. When a current is passed through the electrolyte, the negatively-charged anions migrate to the anode where they are discharged each with a loss of one or more electrons. In an aqueous solution, the anion partially consists of oxygen, which unites chemically with the aluminum (see eq. 1 and eq. 2). The result of the reaction depends on a number of factors, particularly the nature of the electrolyte, the consequent reaction products that are formed and the operating conditions. In simple terms, the following oxidation reactions at the anode can occur:

(a) The reaction products may be almost insoluble in the electrolyte and form a strongly adherent and practically non-conducting, barrier film on the anode. Films formed in this way are extremely thin, and dielectrically compact. They can be formed in a number of electrolytes of which borate or tartrate solutions are the most common examples.

(b) The reaction products may be sparingly soluble in the electrolyte. In this case, film growth takes place as above but is accompanied by localized dissolution of the film and thus pores are formed in the coating (Fig. 1). Porous oxide films are formed in sulfuric, oxalic, phosphoric and chromic acid solutions. When anodizing is performed at a constant potential \( E_s \), the current decreases exponentially with time as the film grows thicker and electrical resistance increases. When the rate of film growth becomes equal to the rate of dissolution of the film in the electrolyte, the film thickness remains constant. The maximum film
Moreover and most probably for the same reason - the presence of an AC-voltage component - the use of a (DC+AC) pulse regime permits a simpler and more reliable mode than any other pulse method to anodize copper bearing aluminum alloys without etching.

The apparatus used for (DC+AC) pulse anodizing of aluminum schematically consisted of a generator for the potentiostatic application of (DC+AC) bi-polar pulses on a two-electrode electrolytic cell. With the help of a two-channel oscilloscope, the current and voltage peaks of the pulses were measured. The average current was measured by an ammeter. The waveform of the (DC+AC) pulses is shown in Fig. 2. There are three pulse parameters of bi-polar (DC+AC) anodizing which have the most significant influence on the property performance of deposited metal coatings and which we vary in order to establish the optimum pulse-reverse conditions:

- Pulse frequency, \( f_p \) (Hz)
- Alternating voltage frequency, \( f_{a-v} \) (kHz)
- Pulse duration, \( T_{on} \) (msec)

The anodic voltage amplitude controls the anodic pulse current density \( I_{a} \) and the average current density. They are varied in order to maintain the same values of average current densities for all the anodizing operating conditions used. The optimal values of the above parameters are established experimentally through leveling power measurements. On the basis of our previous investigations of pulsed electrodeposition of metal coatings, we can assume that in the present case of pulse anodizing the above mentioned optimal balance between the rates of opposite processes can be

---

**Experimental techniques and methodology**

**Pulse anodizing**

Pulse anodizing of aluminum is applied to obtained uniform oxide film without powdering or burning. On the continuous (DC) anodizing with high current density or high voltage, the surface temperature rises locally and this has detrimental effect on the oxide film. A periodic drop of the voltage can prevent the accumulation of heat and assist it to diffuse evenly. Another advantage of pulse anodizing is related to the possibility of establishing the pulse parameters for an optimum balance between the rate of coating formation and the rate of film dissolution. In the case of (DC+AC) pulse anodizing in particular, due to the high frequency of superimposed AC-voltage (up to 5 kHz), the reactive resistance,

\[
X = \frac{1}{\omega C}
\]

is reduced which in turn results in an additional increase in peak pulse current. The benefit of this is that both processes of pore formation and electrolytic deposition at the pore base of corrosion-inhibiting substance are considerably promoted.

---

**Figure 1—Pore structure of anodic coatings on the aluminum substrate.**

**Figure 2—The waveform of the (DC+AC) pulses.**
achieved at a definite pulse frequency corresponding to the maximum value of the leveling power.

**Leveling**

Leveling can be qualitatively characterized as the ability to diminish the difference in heights between protrusion peaks and recesses of the microprofile as a result of electrochemical treatment of electrode surface. Our quantitative estimations included the roughness measurements of both the initial metal substrate $R_0$ and of the anodized surface after pulse plating $R_d$ in order to determine the leveling power using the following expression:

$$LP\% = \frac{(R_d - R_0)}{R_0} \times 100$$  \hspace{1cm} (5)

The initial roughness $R_0$ was obtained by grinding an electrode in one direction only with grade 280 emery paper. Half of the surface of the rotating disc electrode (0.5 cm$^2$) had been previously insulated with a thin film of photo-resist lacquer. After pulse anodizing on the other half, this film was removed with the help of an organic solvent. Thus, it was possible to determine directly from a single electrode the roughness changes due to the anodic treatment of the aluminum surface. The speed of rotation was maintained at a constant 300 rpm. From these graphs we could determine the leveling maximum and the corresponding pulse parameters at which it occurred.

From the graphical relationship between leveling power, $LP\%$ and pulse frequency $f_p$, it can be seen that the maximum values of leveling power were obtained at 6 Hz (Fig. 3). This value was 40% higher than the values obtained by DC anodizing. The other pulse parameters affecting the leveling maximum include: pulse duration $T_{on} = 60$ msec, and alternating voltage frequency $f_{a-v} = 4.0$ kHz.

These parameters of these applied (DC+AC) pulses were actually of relevance to pulse anodizing of aluminum samples. The rectangular samples (10 × 60 mm) were made from thin aluminum (99%) sheets.

**Pitting corrosion measurements.**

The present corrosion study chose the susceptibility to pitting corrosion as the basis for semi-quantitative comparative evaluations of the corrosion resistance of anodized aluminum in different aqueous solutions and under different operating conditions.

It is well known that pitting is a localized attack on an oxide-covered metal surface, which occurs at a number of points in the oxide film where it is less thick, less strong or more permeable. Attack is confined to these very small areas of the metal surface whereas the bulk remains intact. When the remaining film is comparatively inert, corrosion will continue to this point alone with the cathodic reaction taking place on the outside of the residual film. Active metals such as aluminum are most susceptible to this form of attack.

A pit is initiated by the adsorption of activating anions, particularly chloride ions, on certain defective sites in the oxide film. In the electric field induced by these ions, metal cations are pulled outwards through the film, whereupon they dissolve as anion complex. As it might be expected, the breakdown process is potential-dependent. Only when the electric field in the passivating film is sufficiently great, will the cations be pulled through the film. Such a high field may either be applied externally or introduced by the adsorbed chloride ions. In order for a pitting to occur on a metal, a certain minimum potential, the so-called pitting or breakdown potential, $E_b$ must be attained (Fig. 4). This potential is lower than the transpassive potential and is situated within the passive range of the metal. As indicated in Fig. 4, $E_b$ depends on the chloride ion concentration and the breakdown potentials $E_b^A$, $E_b^B$, $E_b^C$ cor-

![Figure 3—The relationship between leveling power and pulse frequency in (DC+AC) pulse anodizing of aluminum in a dilute sulfuric acid solution.](image)

![Figure 4—Schematic diagram of polarization curves exhibiting film breakdown.](image)
respond to their increasing concentration (A > B > C). Since the strength of the induced field will be greater at higher concentration, a lower applied potential needs to be superimposed to break down the film. In other words, the more negative the breakdown potential, the greater the susceptibility to pitting corrosion of the oxide coated metals (Fig. 5). And conversely, the increased pitting corrosion resistance is rated to the shift of the breakdown potential in the positive direction.

The aluminum samples were anodized by using the following three solutions:

1. 150 g/L H$_2$SO$_4$; DC anodizing 10V
2. 60 g/L CrO$_3$; DC anodizing 40V
3. H$_2$SO$_4$/H$_3$BO$_3$ solution; (DC+AC) pulse anodizing and filling the pores with CIS.

**Results**

The comparative study of the susceptibility to pitting corrosion of aluminum samples anodized in above three electrolytes was performed in 0.1M NaCl. The breakdown (pitting) potential determination was done through galvanostatically obtained current-potential polarization curves (Fig. 6). In fact, the curves in Fig. 6 represent the final result of the preliminary recorded changes of electrode potential while a definite anodic polarization current is maintained constant. To every point of the curves there is a corresponding average value of the potential, obtained from five to six individual measurements of aluminum samples anodized at the same operating conditions. The established stationary value of the potential was recorded at the end of each test period (20 to 30 min). In this way, the experimental data obtained enabled us to determine the breakdown potential, $E_b$, as the potential corresponding to the extreme point of the $E$-$i$ curves, shown in Fig. 6. The values of $E_b$ for the different cases of aluminum anodizing in the three aqueous solutions can be seen in Table 2.

One can see from the table that the $E_b$ values for aluminum samples anodized in solutions #2 and #3 were very close, and that they were situated in the region of more positive potentials than the value for aluminum anodized in solution #1. This fact, as well as the almost complete convergence of their identical $E$-$i$ curves, supports the thesis that both anodic oxide films have the same corrosion protective properties. This conclusion, however, is based on the comparisons of pitting potentials, which by itself is an intensive value. Therefore the evaluation of the corrosion resistance of anodized aluminum samples primarily provides an orientation for the change of trend.

The quantitative comparative evaluations are possible only if the extensive values of electric current are determined. In order to conduct quantitative evaluations of the corrosion resistance, we have developed an electrochemical test for speedy and precise determination of their 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 anodized aluminum samples immersed in 0.1 M NaCl are anodically polarized. Within the galvanostatic regime of polarization (anodic current density, A/dm$^2$ = constant) the quantity of electricity related to the unit area of the anodized aluminum samples is proportional to the time (in seconds) necessary to achieve the same value of potential situated in the pitting potential region. The greater the time, or the greater $Q$, the higher the pitting corrosion resistance. The average $Q$-value of (DC+AC) pulse anodized aluminum, electrolytically filled with corrosion-inhibiting species is 220 A·sec/dm$^2$. This value is more than seven times greater than that of the ordinary

### Table 2

<table>
<thead>
<tr>
<th>Anodizing solution</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150 g/L H$_2$SO$_4$</td>
<td>60 g/L CrO$_3$</td>
<td>H$_2$SO$_4$/H$_3$BO$_3$</td>
</tr>
<tr>
<td>$E_b$, mV$_{SCE}$</td>
<td>-520</td>
<td>-310</td>
<td>-330</td>
</tr>
</tbody>
</table>

Figure 5—Schematic galvanostatic polar.

Figure 6—Galvanostatic $E$ vs. $i$ relationship for aluminum, anodized from a solution containing: (□) 150 g/L H$_2$SO$_4$; (•) 60 g/L CrO$_3$; (+) H$_2$SO$_4$/H$_3$BO$_3$ + CIS.
DC-anodized aluminum samples in the same sulfuric/boric acid solution or in chromic acid electrolyte ($Q = 30 \text{ A·sec/dm}^2$).

The above data presents indisputable evidence that the anodic oxide coatings formed and filled with a corrosion-inhibiting substance (CIS) by the application of (DC+AC) bi-polar pulses have a very high pitting corrosion resistance, several times greater than that of the anodic films formed at present time in sulfuric acid, chromic acid or other anodizing electrolytes and technologies. On the basis of these results we can conclude that this method of (DC+AC) pulse anodizing and electrolytic deposition of corrosion-inhibiting species can be developed as a very effective and environmentally-friendly technology for pre-paint treatment of aluminum and its alloys. Moreover, the use of (DC+AC) pulses permits the anodization of copper-bearing aluminum alloys without etching.

References

About the Authors
Dr. Mois Aroyo is 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.

Dr. B. Tzaneva is Assistant Professor in the Department of Chemistry at the Technical University, Sofia, Bulgaria. Her scientific interests cover chemical resistance of metals, different forms of localized corrosion, electroplating and metals oxidation. She has several publications on the topic of corrosion.

Dr. Nikola Tzonev is Associate Professor in the Department of Mechanical Engineering at the Technical University of Sofia, Bulgaria. For over ten years he has conducted intensive research the field of surface analysis systems and mechanical measurement devices. He has published more than 25 papers.