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Electrochemical noise evaluation of anodized aluminum. Comparative study against corrosion behaviour in the atmosphere

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Abstract The present work reports the evaluation of aluminum and anodized aluminum by electrochemical noise, as a part of the PATINA/CYTED project of the working group Nº 5. A visual examination is also made. The samples were exposed at several Ibero-American atmospheres up to 2 years of exposure. Different thickness of anodized aluminum were evaluated. The electrochemical potential noise of the 5 µm unexposed sample (pattern) showed a different behaviour to that showed by the other anodized specimens. This could be due to a slower sealed of the samples of higher thickness. The same behaviour was observed on the samples exposed at the rural station El Pardo. According to the visual examination, the samples of bare aluminum and those of anodized 5 µm thickness were the most affected by pitting corrosion in the highly polluted atmospheres. A good correlation between corrosion behaviour determined by visual examination and EN was obtained.

Keywords Aluminum. Corrosion. Electrochemical noise. Anodized aluminum. Atmospheric corrosion.

Evaluación de probetas de aluminio anodizado mediante ruido electroquímico. Comparación con su comportamiento frente a la corrosión en la atmósfera

Resumen Como parte de las investigaciones de la Red PATINA el grupo de trabajo Nº 5 dedicó su atención al comportamiento del aluminio desnudo y anodizado con diferentes espesores en diferentes atmósferas de Iberoamérica. En el presente trabajo se presenta una evaluación de patrones de aluminio 99,5 % de pureza desnudo y anodizado con espesores de 15 y 25 µm, mediante ruido electroquímico. Los resultados obtenidos se comparan con el comportamiento determinado en diferentes atmósferas durante un período de 2 años. El ruido de voltaje del patrón de 5 µm de espesor presenta un comportamiento diferente al de los restantes espesores, lo que coincide con una mayor susceptibilidad a la corrosión picadura de este primer anodizado. Se reportan también algunas diferencias en el ruido de corriente. Se concluye que mediante la utilización del ruido electroquímico es posible caracterizar el aluminio con respecto a su sensibilidad a la corrosión picadura en condiciones atmosféricas.

Palabras clave Aluminio. Corrosión. Ruido electroquímico. Aluminio anodizado. Corrosión atmosférica.

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1. INTRODUCTION

It is well known that aluminum in contact with the atmosphere forms a passive layer of aluminum oxide. In spite of its amphoteric behaviour this thin layer protects aluminum from further corrosion. However, the presence of aggressive species, such as chloride ions, can provoke the film breakdown in localized sites, giving rise to pitting corrosion.

An effective protection method against atmospheric corrosion is the anodization of aluminum, which consists in increasing the thickness of the natural layer of oxide by means of an electrochemical method.

In the last years, several authors have tried to explain the mechanism of the atmospheric corrosion of aluminum by chloride ions, by means of electrochemical techniques, mainly because of the traditional methods of analysis do not allow to reflect the localized character of pitting corrosion.

One of the techniques employed is the electrochemical noise which offers the possibility to obtain information without the need of introducing any signal strange to the system. This is limited to register the spontaneous oscillation of the potential and/or of the current of the electrochemical reactions as function of time. These signals can be transformed to the frequency domain by FFT.

From the analysis of the potential and current fluctuations it is possible to obtain information about the mechanism of corrosion and the intensity of the attack. Different methods have been proposed to register these signals. The interpretation and the conclusions obtained by different researchers when relating the electrochemical noise with the rate of the process have sometimes turned out to be seemingly opposite[1].

The present work reports the evaluation of aluminum and anodized aluminum by electrochemical noise, as a part of the PATINA/CYTED project of the working group Nº 5. For this purpose, samples of bare aluminum and of aluminum with different thickness of anodized were exposed at several Ibero-American atmospheres up to 2 years.

2. EXPERIMENTAL PROCEDURE

Specimens of bare aluminum and anodized aluminum were exposed in tenth test stations located at different Iberoamerican countries (Table I).

The specimens were anodized in solution of sulfuric acid 18 % in weight at 20 ºC and current density of 1.5 A/dm^2 with thickness of 5, 15 and 25 µm, were sealed during 60 min in distilled boiling water.

The specimens were evaluated during periods of 1 and 2 years. They were evaluated by visual observation[2]. To conversion of chart rating designation into percentage area of the significant surface covered by corrosion pits is indicated in table II[2].

Measurements of electrochemical noise were made after the first and second year of exposition with an ACM Instruments AUTO AC DSP. The oscillations of the potential and the current were registered simultaneously, the time of measurement was 0.5 seg being obtained 2048 data. The values

Table I. Environmental characteristics of test sites

Tabla I. Características ambientales de las estaciones de ensayo

Station	Country	Type of atmosphere	Agressivity according ISO	[Cl] mg/m^2d	[SO_2] mg/m^2d	Corros.[3] g/m^2a
Esmeraldas	Ecuador	Marine-industrial	C3	2.7	16.5	0.38
El Pardo	Spain	Rural	C1	3.9	6.4	0.13
Cubatao	Brazil	Industrial	C3	8.1	54.5	
Panamá	Panama	Urban	C2	9.8	21.7	0.36
Lumiar	Portugal	Urban	C2	26.7	22.6	–
El Tablazo	Venezuela	Marine	C3	53.7	6.0	0.65
Lima	Peru	Urban	C5	4.9	14.0	5.20
Punta del Este	Uruguay	Marine	C5	143.5	3.9	–
La Voz	Venezuela	Coastal	C5	567.7	9.5	1.31
Viriato	Cuba	Coastal	C4	919.3	42.4	2.42

Table II. Conversion of chart rating designation into porcentage area covered by corrosion pits

Tabla II. Conversión de la tasa de evaluación en % de área cubierta por corrosión picadura

Rating						Porcentage of area of defects
A						No defect
B1	B2	B3	B4	B5	B6	< 0.02
C1	C2	C3	C4	C5	C6	> 0.02 and < 0.05
D1	D2	D3	D4	D5	D6	> 0.05 and < 0.07
E1	E2	E3	E4	E5	E6	> 0.07 and < 0.10
F1	F2	F3	F4	F5	F6	> 0.10 and < 0.25
G1	G2	G3	G4	G5	G6	> 0.25 and < 0.5
H1	H2	H3	H4	H5	H6	> 0.50

were transferred to the field of the frequencies by means of the FFT.

Noise data were obtained using two equals samples, placing and sealing a PVC tube above each specimens and joining them with saline bridge. The solution used was NaCl 0.5 mol/L and calomel electrode was used as reference.

3. RESULTS

Figure 1 shows the behaviour of the EN potential for aluminum and anodized aluminum where the numbers 1, 2 and 3 correspond respectively to 5, 15 and 25 μm of thickness.

It has been observed that the aluminum (Pattern 0) has the more negative value as it was expected. This fact even is better reflected for current (Fig. 2) where the values of Pattern I with smaller thickness has a behaviour slightly less active than the rest, that present curves practically superimposed, that indicate that beginning from 15

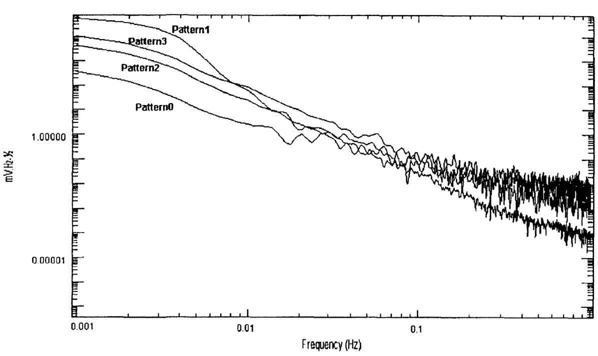

Figure 1. Potential EN spectra of patterns.

Figura 1. Espectros de RE en potencial de los patrones.

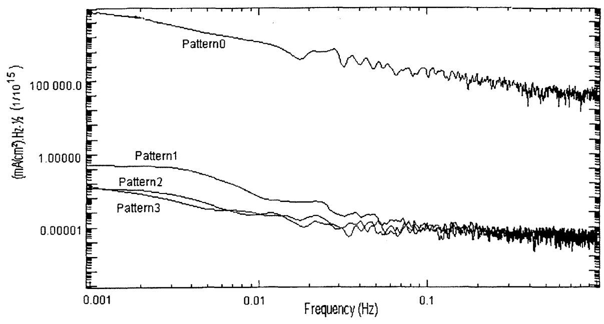

Figure 2. Current EN spectra of patterns.

Figura 2. Espectros de RE en corriente de los patrones.

μm there are not significant increments of protection of the anodic layer.

This same behaviour can be observed in the samples exposed in the stations of El Pardo and Viriato during 1 year (Figs. 3 and 4) with minimum and maximum values of contamination respectively, where the differences between the

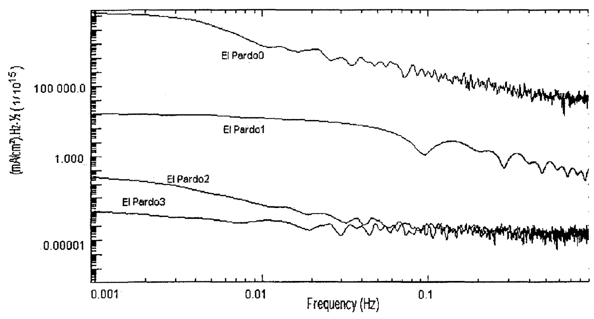

Figure 3. Current EN spectra after a year of exposure in the rural station (El Pardo).

Figura 3. Espectros de ruido en corriente después de un año de exposición en una estación rural (El Pardo).

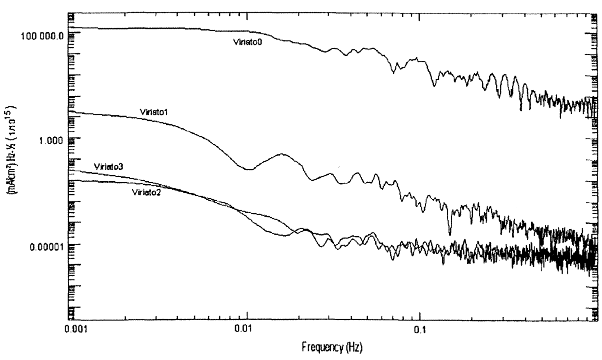

Figure 4. Current EN spectra after a year of exposure in the coastal station (Viriato).

Figura 4. Espectros de RE en corriente después de un año de exposición en una estación costera (Viriato).

smaller thickness and the rest can be better observed.

In the figures at frequencies greater than 10^{-2} Hz there are fluctuations in the spectra that can be suppose to be related to localized corrosion. It can be observed that Viriato has the highest fluctuations. It can be deduced that when passive layer breaks (zone of low frequencies without practically change of the spectrum) an increase of the signal width in the zone is produced.

In figure 1 it can be noted that spectrum of Pattern I at low frequencies is over Pattern 3. This fact was also observed at El Pardo (minimum levels of contamination) although in this case it remains the same in all range of frequencies studied (Fig. 5). The same behaviour is observed up to 2 years of exposure. This fact could be due because after sealing the samples with greater thickness need more aging time for pores hydration[4].

Let us analyze now the results obtained of the visual evaluation reported in the table III. The samples of the station El Pardo, didn't have apparent affectation during all the exposure period; however, samples of bare aluminum from Viriato station are already affected to the maximum level at the first year of exposure and the samples having smallest thickness present affectation in the second year of exposition. In general, anodized aluminum of 15 and 25 μm thickness do not show visible pits in the evaluated period. A difference is presented in the case of Lima corrosion station. Instead to the existence of a low contamination at this station, a high corrosion affectation is reported, coinciding with data reported previously (Table I).

Samples were completely covered by dust, perhaps under this conditions aluminum corrosion notably increases. Current EN spectra of this station shows also a very active behaviour.

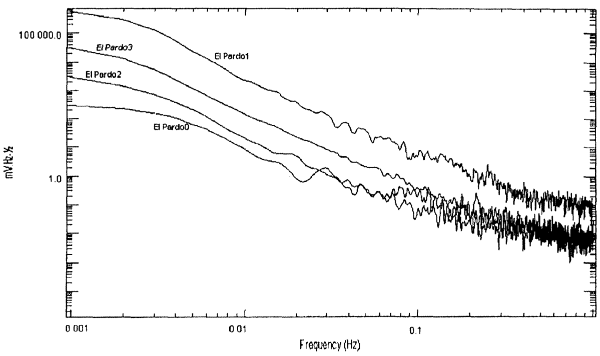

Figure 5. EN Spectra after a year in the rural station, El Pardo.

Figura 5. Espectros de ruido en potencial después de un año de exposición en una estación rural (El Pardo).

Table III. Visual evaluation according to Norma ISO by 1 year of exposure

Tabla III. Evaluación visual de acuerdo a la Norma ISO después de 1 año de exposición

Specimens	Rating 1 year	Rating 2 years	Specimens	Rating 1 year	Rating 2 years
Esmeraldas			Lima		
0	E2/A	E2/F4	0	>H1/>H1	>H1/>H1
1	B5/A	B5/A	1	B1/B2	D1/C1
2	B5/A	A/A	2	A/A	A/A
3	B5/A	A/A	3	A/A	A/A
El Pardo			El Tablazo		
0	A/A	A/A	0	–	Out of limit
1	A/A	A/A	1	–	B4/A
2	A/A	A/A	2	–	A/A
3	A/A	A/A	3	–	A/A
Cubatao			La Voz		
0	H6/E6	>H3/H3	0	–	H6/H6
1	G6/B4	E2/B1	1	–	A/A
2	F6/A	A/A	2	–	F3/A
3	F6/A	A/A	3	–	–
Panamá			Viriato		
0	B6/F5	B4/F6	0	>H1/>H1	Out of limit
1	A/A	A/A	1	A/A	C2/D1
2	A/A	A/A	2	A/A	A/A
3	A/A	A/A	3	A/A	A/A
Lumiar					
0	H6/H3	H6/H3			
1	A/A	A/A			
2	A/A	A/A			
3	A/A	A/A			

4. CONCLUSIONS

- The EN technique has been useful to study atmospheric corrosion of bare and anodized aluminum. Current EN can be used to compare corrosion behaviour of these samples exposed to the atmosphere.
- The electrochemical potential noise of the 5 μm pattern showed a different behaviour to the rest of the pattern specimens.
- According to the visual examination, the samples of bare aluminum and those with 5 μm of anodized exposed in the high polluted atmospheres were more appreciably affected by pitting corrosion.

– There is correspondence between corrosion behaviour determined by visual examination and EN.

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