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CUANTIFICACIÓN FRACTAL DE LA CORROSIÓN DE ALUMINIO POR PICADURAS INDUCIDA POR EL CLIMA TROPICAL HÚMEDO

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Abstract
During three annual exposure periods, aluminum samples of wire, used for transmission of high voltage electricity, were exposed at outdoor atmospheric marine-coastal and rural environments, located in the humid tropical climate of Yucatan Peninsula, in the Mexican gulf. In atmospheric conditions the naturally formed aluminum oxide layer can be destroyed by the presence of chlorides, causing pitting localized corrosion attack, difficult for evaluation. The concepts of fractal geometry and self-similarity were used in this study for evaluation of the pitting corrosion as a function of time, making a statistics of the frequency of appearance of pits versus the area occupied by them. The data showed that the distribution of the pits follows a power law. The exponent of self-similarity varied between 1.7-1.9 and it is relatively stable with the progress of corrosion progress. The progress of pits in area and frequency is more pronounced in time in the marine-coastal atmosphere, compared to pitting developed in rural-urban one. The concepts of fractal geometry and self-similarity can quantify the extent of localized corrosion with time, as nondestructive form and rapid method.

Keywords: aluminum, fractal quantification, atmospheric corrosion, pitting corrosion, self-similarity.

1 Introduction
Aluminum is widely used metal for transmission of high voltage electricity and in construction industry. Thermodynamically it is very active and immediately corrodes when is produced (high level of free energy and high negative potential value -1.67 V) (Evans, 1965; Szklarska-Smialowska, 1971; Foley, 1986;
environment: Rural urban (RU) and Marine coastal (MC) test sites, located in humid tropical climate.

Table 1. Coefficients of $\sigma$ for different time of Aluminum corrosion progress and aggressivity of environment: Rural urban and Marine coastal areas (Veleva et al., 1997; Veleva and Kane, 2003; Corvo et al., 1997; Veleva and Maldonado, 1998; Santana-Rodriguez et al., 2003). The reports note that the humid tropical climate is extremely aggressive, according to ISO 9223:92 (1992), for the widely used standard metals (zinc, copper, low carbon steel and aluminum), compared to the aggressivity of different temperate climates.

Corrosion attack by pitting is difficult for evaluation. Different types of tests have been developed for pitting corrosion (ISO 11463-93, 1993; ASTM Guide G46-94, 2005; Kelly, 2005), based on physical and chemical methods. The exposures
of coupons to natural environments or solutions that simulate service conditions are extremely valuable tests, due to their direct applicability. However, mass loss measurement, which characterizes the rate of uniform metal corrosion, can be extremely misleading for pitting localized corrosion. Badly pitted specimens can exhibit negligible mass loss if the attack is extremely localized. There are several ways in which pitting can be described, giving a quantitative expression to indicate its significance, to predict the life of material. Some of the more commonly used methods for examination and evaluation of pitting corrosion are described in ISO 1146-93 (1993) and ASTM G 46 (1998) (Kelly, 2005), although for most cases no single method is sufficient by itself: (a) standard rating charts for pits in terms of density, size, and depth; (b) metal penetration expressed in terms of the maximum pit depth; (c) application of statistics to the analysis of corrosion pitting data; (d) loss in mechanical properties (tensile strength, elongation, fatigue strength, impact resistance and burst pressure), if pitting is the predominant form of corrosion and the density of pitting is relatively high. It should be stressed that some of the mentioned above methods are destructive as procedures.

While prediction of localized penetration rate remains a goal of electrochemical testing, recent applications of statistics to the corrosion process appear promising. Another technique which does not appear to have received much attention is the use of nondestructive image analysis of corroded metal surface morphology. Although the method is more time consuming than mass change measurements, this one has the potential of allowing the required data to be easily gathered and combined with statistical analysis of a sufficient number of images (sample area), deriving the progress of pit-size distribution in corrosion patterns or pitting penetration.

Nowadays fractal concepts have become increasingly popular when trying to quantitatively characterize apparently irregular or disordered objects (Mandelbrot, 1983; Vicsek, 1989; Gordon et al., 2001). Fractal geometry is finding many applications in material science. A preliminary account of fractal properties of steel corrosion pitting has been reported by Costa et al. (1991) and later the authors use a Monte Carlo simulation of localized corrosion (Reigada et al., 1994). An attempt is made to correlate the fractal dimensions of surface profiles measured on corroded aluminum specimens immersed in 3% NaCl, with results obtained with electrochemical impedance spectroscopy (EIS) (Roberge and Trethewey, 1995). Fractal characterization of two-dimensional aluminum foils corrosion fronts (in pH=12, 1M NaCl electrolyte), controlled pontentiostatically, was reported (Holten et al., 1994). The results show that the fronts (at the metal-electrolyte interface) can be described in terms of self-affine fractal geometry over a significant range of length scales.

In our study we present the progress of pitting corrosion attack on aluminum after exposure to humid tropical climate (marine and rural environments) during one year, as a function of time, making a statistics of the frequency of appearance of pits versus the area occupied by them. The degree of corrosion damage manifests itself in the severity of corrosion and aggressivity of the environment. Since corrosion results in texture changes of a metal surface, it changes its fractal dimension as well. The concept of fractals and self-similarity were applied for the study of the phenomena of localized corrosion of aluminum.

2 Materials and methods

2.1 Sampling and field exposure

Wire samples (1 m and 3.1 mm of diameter) of electrolytic aluminum (99, 999%), used for electricity transmission of high voltage, were prepared as open helix specimens (exposed vertically). Their surface encompasses all exposure angles and is oriented equally with respect to all wind directions, which usually determine the principal pollutants (ISO 9223:92, 1992). Therefore it is recommended that preference be given to the comparison of metal corrosion rates obtained with open helix specimens when exposures are conducted in different climates and at different geographical latitudes (ISO 9223:92, 1992; Veleva and Maldonado, 1998). After exposure at tropical climate, the samples where chemically treated according to ISO 8407 (1993), removing the corrosion products on the aluminum surface.

2.2 Test site characterization

During three annual exposure periods, aluminum open helix specimens were exposed in accordance with ISO 9226 (1992) at outdoor atmospheric corrosion in two test sites located in the humid tropical climate of the Yucatan Peninsula (Southeastern Mexico, in the Caribbean area): marine-coastal (MC) environment (at Progreso Port, 21°18’N, 89°39’W), 30 m from the seashore and a rural-urban (RU) site at Merida, 30 km far from the sea (Fig. 3).
Periodically, at 1, 3, 6, 9, and 12 months, three replicate open helix specimens were evaluated. Time of wetness (TOW) values was calculated using a statistical analysis of temperature-relative humidity (T-RH) complex. Despite the close distance between both test sites, the difference in their daily T-RH complex makes them interesting to study, because they show how variable the tropical climate can be [18]. For example, the RU zone is hotter that the MC one, however, the MC zone is more humid than the RU environment, but the MC shows less fluctuation in T-RH values during the year. We believe that the described differences are due to the influence of the permanent thermodynamic buffering effect of the sea on T and RH for the MC atmosphere. On RU zones, this effect is not present and T and RH show much larger fluctuation during the night and day, interrupting corrosion process and introducing internal stress in corrosion metal products. Besides, the annual TOW values (4,800 h in RU-site and 8,400 h in MC one) have very different distribution of TOW in temperature regions. In the RU site a larger percentage of TOW (54-66%) occurs in the 20-25°C range, but in the MC site 64-73% of TOW is in the 25-30°C.

The airborne salinity (chlorides) and SO$_2$ were monitored monthly, according to ISO 9225 (1992), using the wet candle and sulphation plate methods, respectively. The MC site presents high concentration of airborne salinity (annual average of chlorides $\approx$ 362 mg m$^{-2}$ d$^{-1}$), while the RU atmosphere salinity is very low (10.21 mg m$^{-2}$ d$^{-1}$) and insignificant from the point of view of corrosive attack. Both test sites present low and very low annual categories of SO$_2$ aggressiveness, according to ISO 9223 (1992).

### 2.3 Fractal quantification of pitting corrosion

A fractal is defined as “a set for which the Hausdorff dimension strictly exceeds the topological dimension” and is less than the embedding dimension (Vicsek, 1999; Gordon et al., 2001; Costa et al., 1991; Bunde and Havlin, 1991). The fact that the pits cover a finite area on the metal surface, give the reason to study their distribution using the concept of fat fractal (Mandelbrot, 1983; Vicsek, 1999). The characterization analysis consists in obtaining black and white images of pitted regions on the metal surface. This is done in order to obtain data on pit density and pit size, during the time of corrosion progress, distinguishing the influence of atmosphere corrosive aggressively (pollution) of both test sites. After elimination of corrosion products, 33 samples were cut (1 cm of length of wire) from helix specimens that have been exposed at different period to corrosion in MC and RU test sites. Scanning Electron Microscope (SEM), Phillips XL-30 ESEM (at 0.3 Torr and work distance of 7.7-12.5 mm), was used for morphology analysis of aluminum corroded surface.

The collected 174 images where characterized with the Image J program, defining conversion factor of pixels to area ($\mu$m$^2$) and running the program for statistical analysis of pitted areas for one base threshold and for thresholds moved to $\pm$5%.

The cumulative frequency for pit area was calculated for each time and site of exposure. The analyzed data show power-law decay, whose coefficient and exponent can be finding from log-log graphs. Therefore, it is clear that we can use the Korcak’s exponent of self-similarity ($s$), as exponent of fat fractal ($\beta$) (Vicsek, 1999).

The fractal characteristic more important is that the fractal has a d lower dimension value than need include the object. However, there is structures that $D_f = d$, but show a fractal behavior [Mandelbrot Benoit B., (2004)]. In these cases, when the volume $V(l)$ was compute, usually called fat fractal, using spheres the decrease size $l$, this converge a finite value whiten a exponent no whole. In fat fractal $V_0 = V(0)$, but $V(l) = f(l)$, show a power law with an exponent, which is just a rescale structure value. This can be expressed in Farmer (1986) form in the Eq. (1):

$$V(L) \approx V_0 + A L^{\beta}$$

where $A$ is a constant and $\beta$ is an exponent that quantify the fractal properties.
Figure 4. Menger sponge to tree iterations with $D_F = 1.8927$, [Bunde Armin, Havlin Shlomo. (1995)].

An example for these fractals is the Menger sponge (Bunde and Havlin, 1991), as shown in Fig. 4.

3 Results and discussion

Figures (5a)-(5b) present SEM images of aluminum surface of samples, corroded in MC and RU environments during different exposure times. It can be seen that the intensity of pits formed in the marine atmosphere (Fig. 5b) is more pronounced than in the rural-urban test site (Fig. 5a), because of the more accelerated corrosion progress, due to the very high salinity (chloride) contamination. After 6 months of corrosion, the pitting attack is more extended on the surface and the pits penetrate deeper into the metal structure. However, the formed corrosion products also can act as physical barrier between the metal surface and the environment, and due to this fact the corrosion progress goes slowly. This effect is observed in the MC zone, where the corrosion progress is more accelerated, compared to that in the RU one, and the samples show less pitting formation in 9 months, compared to that in 6 months, for example.

After analyzing all collected SEM images of pitting attack, graphs presenting the frequency of pitting events as a function of their area ($\mu m^2$) were constructed, following the methodology described above in the experimental part of this study. The graphs exhibited a good fitting to the power law, therefore can be presented the log-log form of these graphs (Fig. 6). The graphs show only the central part of the respective curves. For very small pits there are difficulties with the resolution limit of the images. On the other hand, the frequency for very large pits is quite low, giving rise to large statistical fluctuations. The accumulated frequency had be show in the Eq. (2):

$$\sigma(a) = \frac{\text{number of pits with area larger than } a}{\text{total area of the sample}}$$

Fig. 5. SEM images of localized corrosion (pitting) formed on aluminum surface after 1, 3 and 6 months of exposure in rural-urban (a) and marine-coastal (b) tropical climate.
shows well defined power law scaling and a similarity to Eq. (1), that is:

\[ \tau(a) = \sigma_0 a^{-\sigma} \]  \hspace{1cm} (3)

for any length of exposure, in both environments. Here \( \sigma \) is the exponent of self-similarity and \( \sigma_0 \) is a constant.

The parameters \( \sigma_0 \) and \( \tau \) can be obtained using the logarithmic form of Eq. (3):

\[ \log \tau(a) = \log \sigma_0 - \sigma \log a \]  \hspace{1cm} (4)

The value of \( \sigma_0 \) can represent and reflect the corrosive aggressivity of test site and the changes of the density of pits with corrosion progress (see Eq. 4). The results show that the values of exponent of self-similarity vary between 1.7 and 1.9 during the annual corrosion period of aluminum exposed in both test sites, part of tropical humid climate: some values for \( \sigma \) are shown in Table 1. These results indicate that \( \sigma \) change (dependency) is a function of time of metal corrosion progress and aggressively of environments.

<table>
<thead>
<tr>
<th>Exposition time</th>
<th>RU ( \sigma (\mu m^{-2}) )</th>
<th>MC ( \sigma (\mu m^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 months</td>
<td>0.0422</td>
<td>0.170</td>
</tr>
<tr>
<td>9 months</td>
<td>0.0259</td>
<td>0.0336</td>
</tr>
<tr>
<td>12 months</td>
<td>0.0243</td>
<td>0.0289</td>
</tr>
</tbody>
</table>

**Conclusions**

The development of pitting has been studied as a function of time, making a statistics of the frequency of appearance of pits versus the area occupied by them. The data show that the distribution of the pits follows a power law. Even the corrosion pitting appears chaotically (depending of the anodic sites location, excess of Gibbs energy, etc. factors, the nature of aluminum obeys all the time the principal corrosion law - a power law. Therefore, the concept of self-similarity can be applied for the study of the phenomenon of localized corrosion, describing their development with time.

The exponent of self-similarity varies between 1.7 and 1.9 and it is relatively stable with the progress of corrosion progress on aluminum surface. The corrosion progress is more accelerated in marine-coastal environment, due to its high salinity (chloride) contamination. Due to this fact the progress of pits in area and frequency is more pronounced in time, compared to pitting developed in rural-urban atmosphere. The humid tropical climate induces accelerated progress of pitting, that affect the aluminum surface in very short period of time (months), extending the attack to the dept of the metal.

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References


