Fractal Dimension Analysis of Aluminum Corrosion Roughness by Electrochemical and Optical Methods

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Abstract—Fractal dimension is a versatile method to study and evaluate corrosion from the point of view of metallic conditions, namely: surface roughness, electrochemical measurements and microscopy images. Aluminum corrodes at different rates, under different pH electrolytes with or without the presence of chloride ions. In this work, corrosion and the surface roughness for aluminum corrosion at different pH electrolytes: acid, with and without chlorides, neutral and basic solutions, were obtained. It was measured and obtained using electrochemical and optic techniques. The results of Electrochemical Impedance Spectroscopy (EIS) and Noise Measurements (ENM), Digital Holographic Microscopy (DHM), Scanning Electron Microscope (SEM) micrographs and their respective Fractal Dimension analysis were obtained. For the different experimental techniques and conditions, fractal dimension was obtained and presented, reflecting the surface condition of aluminum corrosion as a function of pH solution.

Index Terms—Fractal Dimension, Electrochemical Techniques, Holographic Microscopy, Aluminum.

I. INTRODUCTION

Euclidian geometry based on the properties of regular forms such as point, lines, surfaces and volumes classifies (ideal abstractions) them in dimensions shown by integer numbers: 0, 1, 2 and 3, respectively. Fractal geometry considers real dimensions as fractional numbers relating to the form to be treated, hence its name fractal geometry. A line may be spiky therefore the dimension should be between 1 and 2, a surface may be rough and dimension lies between 2 and 3 [1].

Corrosion is the gradual destruction of metallic materials by electrochemical reaction with their environment rendering the surface rough, porous or pitted, reducing the metal thickness and diminishing their mechanical properties. Surface roughness is the measure of physical surface topography, i.e., slight irregularities over the surface. The procedure to determine the surface roughness, is defining a height or depth that contains the profile information of the surface. This can be obtained either by measuring the surface with a profile meter, through atomic force microscopy (AFM) image, or by optical methods such as: optical interferometric measurements or light scattering [2, 9-13].

More recently other methods were developed and applied like: digital in-line holography [9, 10], digital speckle pattern interferometry [11], and structured light projection [9-13] to quantify the effects of metallic corrosion. In this latter work it was applied the concepts of digital interferometric and holographic microscopy were applied [9, 12-17].

A. EIS Fractal Analysis

Electrochemical impedance spectroscopy (EIS) evaluates corrosion, providing kinetic information about the corrosion process and particularly, about parameters like: polarization resistance (R_p), charge transfer resistance (R_{ct}), double-layer capacitance (C_{dl}), solution resistance (R_s), etc.

Sometimes Nyquist plot obtained at free corrosion presents the shape of a depressed semicircle. The equivalent electrical circuit to represent this is the Randles circuit corresponding to a combination of a capacitor and a resistance in parallel. For this circuit, under certain circumstances the ideal capacitor is replaced by a constant phase element (CPE) representing the double-layer capacitance C_{dl}. The complex impedance Z(jω), of a depressed semicircle is described as:

\[ Z = R_s + R_{ct} \left/ \left[ 1 + (j\omega C_{dl} R_{ct})^n \right] \right. \]  

(1)

For improved quality of electrical circuit fitting of experimental data for depressed semicircles, CPE substitutes the double-layer capacitance. The CPE is defined by the equation:

\[ Z_{CPE} = \frac{Z_{0}}{(j\omega)^n} = 1/Q(j\omega)^n \]  

(2)

where \( Z_{CPE} \) is the CPE impedance, Q is a proportionality factor, j is (-1)^{1/2}, ω is the angular frequency, and where n is related to the surface topographic calculation [18]. The CPE defines an electrode’s surface irregularities, promoting a Nyquist plot semicircle depression [19-23]. The reaction time constant (τ) and CPE element capacitance value are obtained through equations [5, 6]:

\[ Q = \tau^n R_c \]  

(3)

\[ C_{CPE} = [QR_c^{-1-n}]^{-1/n} \]  

(4)

where, C_{CPE} is the obtained double layer capacitance from the CPE, and α is the semicircle’s depression angle:

\[ \alpha = (1-n) \times 90^\circ \]  

(5)

where the n parameter is equal to 1 for an ideal capacitor. In real systems, capacitive behavior is hardly observed because of odd current distribution over the metal surface [24]. In the case when \( n = 1 \), the term \((j\omega C_{dl} R_{ct})^n\) reduces to \( j\omega C_{dl} R_{ct} \). This is an indication of the level of heterogeneity.
over the electrode [24, 25]. When the n value is higher than 0.5, it is related to a severe roughness of the metal surface, but when n is equal to 1, the surface is considered totally smooth.

The degree of surface heterogeneity or roughness is related to the fractal dimension [26]. A “fractal” is an object with complex structure, that reveals novel details as long as its magnification degree is increased, it remains equal or similar (self-similar) at different magnifications [27-29]. Metals, with a fracture or surface heterogeneities could be described through fractal geometry, by fractal dimension (Dfs).

Taking into consideration the degree of the Nyquist diagram semicircle’s depression, and to obtain the fractal dimension of the metal surface the following equation is utilized [21, 22]:

\[ n = 1 / (D_{fs} - 1) \]  

(6)

where Dfs is the fractal dimension, taking values close to 2 for a smooth, or to 3 for a very rough surface. The fractal dimension of an electrode obtained through electrochemical impedance spectroscopy correlates with atomic force microscopy or other optical techniques [9-11].

Electrochemical noise (ENM) technique is utilized to determine the type of corrosion attack under different corrosion conditions and its protection [30]. Data are collected as a series of potential and/or current vs. time of sufficient length. Data analysis include: visual, statistical or spectral analysis of time-records [31-35]. When localized attack is present, the EN signal presents high-frequency transients of varying amplitudes.

Spectral analysis of (ENM), has been used to determine the periodicity of the structure of EN signals [30, 31, 35]. The power spectrum is a plot of the spectral amplitude against frequency of the electrochemical noise variable. Two types of behavior are commonly observed in the spectra: white noise (random) independent of frequency, and 1/fβ behavior, related to the slope of the spectral density function (SDF) at higher frequencies. Different values of β exponent have been obtained for specific processes [36].

Mandelbrot [26, 27] fractal geometry and mathematics provide the resources for analysis and characteristics of the variable in the time domain. The connection between the structure and scaling exponents of the EN time series, the spectral density function (characterized by Dr and β), and oxidation reactions responsible for corrosion, can be thus obtained. For this case, the fractal dimension is defined as:

\[ D_r = (5 - \beta) / 2 \]  

(7)

B. ENM Fractal Analysis

The ENM time records can be characterized by the Rescaled Range or Hurst analysis and its Hurst exponent H; being the variable time record a “random” fractal sharing the same statistical properties and the level of details. The fractal geometry and its dimension Dr, describes the structure roughness of an EN time record and the explanation for Dr, H, and β values observed for the EN time-series spectra parameters.

The Hurst exponent related to β, shows the long-term time dependence on the time-series and is the result of alterations that occurs in the data obtained. A time series is a fractal when variations in the time data set over a specific time interval known as the lag time are proportional to the lag time increased to the power H. According to Hurst’s empirical law proposed [27]:

\[ R / S = (\tau / 2)^H \]  

(8)

R is the difference between the maximum and minimum values of the variable, S is the standard deviation of the time series; τ is the period of time measured and H is the Hurst exponent. Parameter H shows the appearance ("roughness") of the time-series: when 0.5 < H < 1 represents an undulating signal and “persistency” of the processed signal that is concerned; when 0 < H < 0.5 is a ‘zig-zagged’ signal that indicates “anti-persistency”. When H is equal to 0.5 the process is random, independent of time lags. These characteristics are associated to the physicochemical corrosion process [20-23].

Therefore, fractal dimension Df, for signals as a function of time is:

\[ D_f = 2 - H = (5 - \beta) / 2 \]  

(9)

C. Phase-Shifting Digital Holographic Microscopy

Optical methods are widely used; one of such techniques known as optical interferometry is able to measure surface characteristics under 0.1 μm without physical contact [37]. Also light scattering techniques have been used for superficial roughness measuring at 0.1-3 μm range [38-43]. More recently, laser speckle techniques were applied on different science and engineering areas [44-52]; the spectral speckle correlation being the most commonly used technique for surface evaluations at 1.6-50 μm interval [53-55].

K. Habib was probably the first in using holographic interferometric principles to monitor metallic electrodes immersed in saline solutions [56, 57]. Michelson interferometry was applied to perform optical monitoring of corrosion processes on metallic samples under similar conditions [58]. Some other optical methods have been used and reported to quantify the effects of corrosion on metallic surfaces. Digital holographic microscopy (DHM) is a relatively new technique based on the concepts of optical holography, introduced by Dennis Gabor in 1948 [59].

Digital Holography (DH) can be performed when an interference pattern is accomplished by superposition of an object and reference beam, by digital sampling of a CCD sensor and is finally sent to a computer as a numbers array, preventing the need for chemical development utilized in conventional holography. It also allows numerical information access to the amplitude and the phase data, related to the object wave field [60-62]. Quantitative physical measurements of analyzed samples, like surface shape or optical thickness, are embedded in the phase distribution Δφ, of the digital hologram sampled by the CCD. As such phase distributions suffer from module 2π ambiguities, phase unwrapping algorithms are necessary in order to obtain a 3D reconstruction of the samples [63].

During a DH process the zero-order and the twin-image
terms that are always present, can be removed in a three steps stages during the computational numerical reconstruction, when the phase of a reference beam is changed with a mirror installed on a piezoelectric transducer system. This method known as Phase-Shifting Digital Holographic Microscopy (PSDHM), applies digital holographic concepts to microscopy allowing a direct calculation of $\Delta \varphi$ (phase shift) from three or more subsequent interferograms with phase-shifts among them, introduced by a piezoelectric transducer [64-66].

Regarding surface roughness characterization, the statistical data processing has been used for determination of certain parameters such as RMS roughness ($R_{\text{rms}}$) and average roughness ($R_a$) where: $L$, $R_a$ and $R_{\text{rms}}$ represent sampling length, arithmetic average of the absolute values of heights $z(x)$, and quadratic shifts average value with respect to average height, respectively. However, as such values depend on the analyzed characteristic length, it is necessary to follow another method to avoid this dependence such as the self-affinity analysis. This method is usually used for interface roughness and material surface studies, and involves determining the Hurst exponent ($H$), also known as roughness exponent (mentioned above).

Unlike former $R_a$ and $R_{\text{rms}}$ parameters, $H$ is ideally independent from sampling size with $H = 1$ for a fully smooth profile (straight line). On the other hand, Hurst coefficient $H$ is a quite versatile and simple concept, as it has been used as a control parameter in roughness studies using speckle digital patterns obtained in return from the laser beam scattering on a metallic rough surface [67], as well as surface roughness determination on polymers [66, 67]. Therefore, within this work, the analysis of DHM is focused on determination of the method’s sensitivity for different roughness scales, where Hurst coefficient is obtained from optical profiles and digital holographic patterns acquired from scattered light coming from a known rough surface. A detailed description of the method can be found on specialized literature [64].

Fractal analysis is commonly used during the analysis of digital images demonstrating analogous structures at different ranges. Various approaches to calculate the fractal dimension $D$ of objects recorded in these images have been utilized in different scientific fields. Although a direct comparison between these different procedures has not been performed, however, reasonable outcomes have been demonstrated. Even though, improvements in digital imaging, enhanced resolution and $D$ calculation have been attained, algorithms have not been thoroughly evaluated with their application to high resolution imaging. Nevertheless, these methods are close to or already included in end-user applications that should provide quick and trusted results.

Digital image figures are used for investigation, because they are readily available for the purpose of storing, processing and analysis. Various procedures to calculate fractal dimension $D$ of objects in digital imaging are used in medicine, geology, geography or astronomy. The commonest algorithm is the box-counting method (BCM), because it straightforwardly implements the measurement of object counts based on box size and number, representing the pixel grid of digital images, as proposed [27, 28]. The initially binary (b/w) images established methodologies during the last decades, include applications to different tones of grey images, and the box-counting method can be applied using free software such as DFRAC. Scanning electron microscope (SEM) micrographs were obtained from different grey value images for fractal dimension $D$ estimation, with an efficient application of converted binary object [67].

Aluminum is an active metal, but develops a very stable and protective passive film, decreasing corrosion for many environs. The oxide is stable in neutral and some acid solutions, but is affected severely by alkali solutions. Corrosion rates in acid media depend on the nature of anions; and its corrosion characteristics make it particularly suitable in seawater and other chloride containing environments [68, 69].

Pure aluminum is soft and weak, alloying and heat treatment of it improves the mechanical properties. Corrosion resistance and other characteristics that contribute to its wide application are: its colorless appearance, nontoxic corrosion products, electric and thermal conduction, reflection, and good strength to weight ratio. All these properties make it attractive for new technological applications in aerospace, energy, etc. Nowadays, with scarce resources, low budgets, care of the environment and sustainable development, aluminum is fully recyclable which makes it a very useful material.

Several investigations have been reported [70-75] where fractal analysis methods using different techniques were used, related to metallic corrosion degradation. Corrosion damage on the surface of an aluminum alloy used in the aircraft industry was characterized by applying fractal dimension. Identification and classification of the type of corrosion damage were carried out through the fractal dimensions obtained. Also reports on the use of fractal dimension to evaluate surface corrosion and inhibitors efficiency can be found [21, 22]. Another interesting application is the prediction and evaluation of general or localized corrosion such as: pitting, inter-granular stress and fatigue cracks, with fractal dimensions being different for each case. This is especially in the case of the corrosion resistant aluminum alloys and steels, although no direct relationship has been found between the corrosion rate and fractal dimension.

D. Objective

The aims of the present work was to show the possibility of fractal dimension relations obtained and compared from different electrochemical techniques, of the corrosion performance of aluminum samples. To determine the metal surface characteristics shown as the surface fractal dimension, calculated from EIS measurements and compared with the one obtained through the $H$ exponent calculated from EN measurements, and evidenced by digital holographic and SEM images and their fractal dimensions obtained. The purpose was to evaluate surface corrosion attack and corrosion resistance characteristics in different solutions.
II. EXPERIMENTAL PROCEDURE

A. Materials

Aluminum cylindrical samples with 2 cm in length and 6 mm in diameter encapsulated in a commercial epoxy resin with an exposed surface of 1.13 cm² to the solution. All samples abraded with 600 SiC emery paper were rinsed with distilled water followed by ethanol (C₂H₅OH). Different pH solutions were prepared and used for the electrochemical tests namely: sulfuric (pH 2 and 3) and hydrochloric (pH 5) acids, potassium hydroxide and distilled water solutions.

B. Electrochemical Measurements

Measurement of the electrochemical free corrosion potential of the working electrode, $E_{corr}$, was performed using a silver/silver chloride reference electrode. EIS measurements were performed with a Gamry 300 EIS equipment in the frequency interval of 0.010 Hz to 10,000 Hz with an amplitude of ±10 mV at the free corrosion potential after reaching stability under immersion in the solution, and a graphite rod was used as auxiliary electrode. Afterwards, the depression angles from the Nyquist plots analysis were obtained. Micrographs at different magnifications were obtained from FESEM Jeol JSM-7600 model, to observe the corrosion attack over the metal surface, and fractal analysis over the images were performed and obtained.

The electrochemical noise measurements (ENM) were made gathering simultaneously the potential and current oscillations using two ‘identical’ working electrodes and the reference electrode, at a sample rate of 0.5 second per read during a period of 1024 seconds. A computer controlled ACM zero-resistance ammeter (ZRA) was used. DC signal trend was removed from the raw noise data was through a least-squares fitting method. The noise resistance ($R_n$) was obtained as the ratio of the potential noise standard deviation over the current noise standard deviation ($R_n = \sigma_E/\sigma_I$). From the EN time records, the Hurst coefficient and the fractal dimension of the electrochemical noise signals from the R/S analysis, were obtained [77-79].

C. Phase-Shifting Digital Holographic Microscopy

The experimental PSDHM setup is shown at Fig. 1. An optical beam emission from a He-Ne laser of $\lambda=633$ nm wavelength and $P_e=35$ mW output power, is firstly amplified and collimated by means of a 25 $\mu$m pinhole, 20X microscopic objective and a 50 mm focal length lens (Lens 1). After being reflected from mirrors 1 and 2, light is passed through a second 50 mm focal length lens (Lens 2) and a beam splitter; this divides our beam in an object and a reference beams with mutually orthogonal trajectories. The object beam is focused on the metallic sample by lens 2 and its reflection is focused on a CCD sensor by a 4X microscopic objective and another 50 mm focal length lens (Lens 3). The reference beam is reflected from mirror 3 and focused on the CCD sensor by another 4X microscopic objective and Lens 3, where interferes with the object beam. The third mirror is fixed onto a piezoelectric transducer set on a moving platform, which operates as the mechanical phase-shifting system in a $\Delta Z=5 \mu m$ range.

Resulting holographic interferometric patterns, i.e. interferograms (HI), obtained by the object and reference coherent optical beams superposition on the plane of the CCD sensor, are digitally stored in a PC where the CCD is connected, for further 3D numerical reconstruction of the samples. The fractal dimension of these images was calculated using the box counting method applied to the obtained pixel matrix [80].

III. RESULTS

Fractal analysis from the corroded metal holograms were performed and obtained, using the box counting method [27]. Reactive aluminum can develop a passive film protecting it from electrochemical corrosion in neutral and some solutions but it is attacked in basic electrolytes [69]. According to the Pourbaix diagram [76], aluminum dissolves actively in acid or basic solutions while in neutral media corrodes, forming a stable and protective corrosion products or passive film over the metal substrate. From Fig. 2 the free corrosion potential of aluminum immersed in different pH solutions can be observed, presenting different values aligned accordingly, as a function of pH: nobler or less negative potentials for acid and active or more negative for basic conditions. For neutral (pH 7) conditions, the free corrosion potential starts as active potential (~700 mV) reaching the steady state at more positive values (~450 mV) and above, probably reflecting the growth of the passive film over the metal surface. For pH 10 and 11, values are very similar and overlap in the active potential region.

Fig. 3 presents some electrochemical impedance (EIS) results obtained, for different pH’s. From the Nyquist plots (Fig. 3) capacitive semicircles can be observed, from which electrochemical parameters were calculated including
charge transfer resistance and the depression angle, used for the surface fractal dimension. Solution resistance varies for different electrolytes as expected, but is not involved for direct calculations of fractal dimensions.

Table I presents the electrochemical parameters obtained from EIS measurements, in which the effect of the solution pH can be clearly observed. Smaller charge transfers resistances for lower and higher pH values, being the highest for neutral solution and the smallest for the alkaline pH 12 solution [76].

<table>
<thead>
<tr>
<th>pH</th>
<th>n</th>
<th>Depresión angle Θ</th>
<th>Rct</th>
<th>Cdl</th>
<th>Df</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.80</td>
<td>17.34</td>
<td>1.23E+02</td>
<td>1.02E-03</td>
<td>2.23</td>
</tr>
<tr>
<td>3</td>
<td>0.92</td>
<td>7.02</td>
<td>3.88E+03</td>
<td>7.96E-02</td>
<td>2.08</td>
</tr>
<tr>
<td>5</td>
<td>0.94</td>
<td>4.76</td>
<td>7.50E+03</td>
<td>5.35E-02</td>
<td>2.05</td>
</tr>
<tr>
<td>7</td>
<td>0.67</td>
<td>29.21</td>
<td>1.31E+04</td>
<td>1.18E-01</td>
<td>2.48</td>
</tr>
<tr>
<td>10</td>
<td>0.85</td>
<td>13.03</td>
<td>9.77E+02</td>
<td>1.10E-02</td>
<td>2.17</td>
</tr>
<tr>
<td>11</td>
<td>0.81</td>
<td>16.55</td>
<td>9.84E+02</td>
<td>1.10E-02</td>
<td>2.22</td>
</tr>
<tr>
<td>12</td>
<td>0.92</td>
<td>6.55</td>
<td>3.57E+01</td>
<td>8.36E-04</td>
<td>2.07</td>
</tr>
</tbody>
</table>

Fig. 4 presents the electrochemical current noise (ECN) time series results obtained, for different pH solutions. Some ECN time series (Fig. 4) present distinctive stochastic behavior namely: random noise (pH-11), low frequency (pH-5) or transient oscillations (pH-7) associated to film rupture-repassivation events; or a mixture of them. These different oscillations relate to uniform, mixed, passive or localized events over the metal surface [30].

As an example, Fig. 6 presents the fractal dimension analysis using the FDim software, for the SEM 500X sample immersed in a solution pH 2, showing the graph to obtain the Hurst coefficient and surface fractal dimension.
Fig. 6. SEM micrograph 500X for the sample immersed in a pH 2 solution, and the FDIM software graph to obtain the Hurst coefficient to calculate the fractal dimension.

Fig. 7 presents some SEM micrographs (500X) for aluminum samples immersed at acid, neutral and basic pH solutions. It can be observed the different surface conditions obtained after the samples were removed from the solution.

Using FDim free software, micrographs analysis was performed and from the scale of grays, the fractal dimension was calculated. Also, micrographs for different (1kX, 2kX and 4kX) magnifications were also obtained.

It can be seen in Fig. 8(a and b), that for acid or alkaline solutions the fractal dimension changes slightly as a function of SEM micrograph magnifications obtained for different pH solutions. Being 2 for completely smooth and 3 for totally rough, for acid solutions the fractal dimension diminishes for increased magnification. The opposite is true for alkaline solutions where the fractal dimension increases for increments in magnification. These could be due to the formation of corrosion products and slower corrosion rates in acid media, while faster dissolution rates render the surface more uniform in alkaline conditions, being necessary greater magnification to observe changes in the surface roughness. Nevertheless, fractal dimension values suggest more or less smooth surfaces, reflecting the corrosion attack and state of the surface [80].

Some examples (Fig. 9 a and b) of fractal dimensions obtained for SEM micrographs (500X), of samples immersed in different pH solutions and compared to EIS and ECN time series fractal dimensions calculated. SEM fractal dimensions registered, suggest the surfaces being somewhat smooth, presenting a direct relation obtained comparing with EIS fractal dimensions obtained, using DFrac free software. As for ECN time series, the trends are similar but showing an inverse relation was obtained, being the difference greater for neutral solutions. The highest value obtained was for the pH 5 solution showing the effect of chlorides. In all cases low fractal dimensions were obtained, suggesting an apparent smoothness surface conditions. SEM fractal dimension obtained seems to be underrated, maybe
due to the quality of the micrographs.

Fig. 9. Fractal dimension of SEM micrograph (500X) obtained for different pH solutions compared to a) EIS and, b) ECN time series fractal dimensions

As an example, Fig. 10(a) presents microscopic image of a corrosion pit produced on the metallic surface of the sample which was previously immersed in a hydrochloric acid solution (pH 5); Fig. 10(b) obtained by the PSDHM technique shows the 3D mesh plot representation of the unwrapped phase map calculated for the sample. Fig. 10(c-d) show corresponding x-y pixel profiles of Fig. 10(b).

Table II presents the Hurst exponent and fractal dimensions from the surface reconstructions, calculated for the samples immersed at different solutions. The lowest fractal dimension obtained corresponds to the pH 3 and the highest at pH 10 solutions, contrary to the SEM micrographs fractal dimensions

<table>
<thead>
<tr>
<th>pH</th>
<th>D_f</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.048</td>
<td>0.952</td>
</tr>
<tr>
<td>3</td>
<td>2.020</td>
<td>0.980</td>
</tr>
<tr>
<td>5</td>
<td>2.038</td>
<td>0.962</td>
</tr>
<tr>
<td>7</td>
<td>2.042</td>
<td>0.958</td>
</tr>
<tr>
<td>10</td>
<td>2.063</td>
<td>0.937</td>
</tr>
<tr>
<td>11</td>
<td>2.042</td>
<td>0.958</td>
</tr>
<tr>
<td>12</td>
<td>2.033</td>
<td>0.967</td>
</tr>
</tbody>
</table>

Comparison can be seen in Fig. 11 where both fractal dimensions for different solutions can be observed. DHM fractal dimensions obtained as a function of pH are similar.
presenting slightly lower values than the ones obtained using SEM micrographs, that shows values related to relatively smooth surfaces, but with an inverse trend. Bear in mind that surface dimension analysis was larger for SEM micrographs than DHM reconstruction, being the possible explanation for the results observed.

Fig. 11. Fractal dimensions as a function of pH for DHM and SEM

Pure aluminum commonly presents an air formed passive film over the surface protecting it from corrosion. This passive film (Al2O3) is stable between pH 5 and 8, according to the Pourbaix [76] diagram. Below and above active dissolution may occur at free corrosion conditions. Fractal dimensions obtained from the different techniques at neutral conditions corroborates this rough surface condition presenting the highest values since the passive film is formed over the finished abraded surface.

Activation is the transition from passivity to the active state after removal of the passive film, under the influence of a more negative electrode potential than the passive film formation potential, or subject to acid or basic solutions due to cathodic currents [25, 31, 32]. Under acid conditions, general corrosion proceeds and the corrosion rate diminishes as the pH increases. In general, the fractal dimensions obtained reflects this, observing lower values for more acidic conditions. At neutral conditions (pH 7) the protective film is formed, and in alkaline condition generalized corrosion proceeds with an increasing rate as pH becomes more basic, being corrosion rates greater than in acidic solutions [82]. The smallest fractal dimensions were obtained at pH 12 suggesting a smooth surface. In the presence of chlorides (hydrochloric acid pH 5) pitting corrosion may proceed by disruption of the passive film at local sites [32, 83], where fractal dimensions are relatively high probably due to mixed corrosion showing the effect of chlorides over the unstable film.

The analysis of the fractal characteristics of the material’s surface subjected to corrosion reflects these conditions. The calculated values of fractal dimension D through electrochemical and optical measurements provide evidence for the possible formation of a fractal structure of the surface during the corrosion attack. It also provides direct evidence on the relation of corrosion rates and fractal dimension, and compares favorably with the reported literature [76, 82, 83].

IV. CONCLUSIONS

Fractal dimensions obtained using different techniques present low values for acid or basic conditions, being the lowest (smooth surface) for the more basic the solution is. The highest fractal dimension value belongs to the neutral condition for the EIS and SEM techniques, and the effect of chlorides can be observed in the hydrochloric acid solution. However, ECM and DHM showed an opposite trend due to the fact that in the former is the surface while in the latter methods refer to the signal structure rather than the surface itself, showing an inverse trend relation.

The aluminum surface roughness appears to depend on the surface finishing of the metallic sample and the solution condition, showing correlation at a macro-scale, through the fractal dimension Df. In general terms the fractal dimension, which is related to the statistical behavior of a measured parameter, reflects the corrosion rate and attack condition.

V. CURRENT AND FUTURE DEVELOPMENTS

Fractal analysis has proved to be a relatively simple and useful analysis to characterize metal surface under different conditions. Another advantage is the application for different experimental techniques results obtained, namely: electrochemical, optics and image analysis. These may reveal general, localized corrosion and fracture conditions and morphology. Future developments into the incorporation of these techniques and analysis to practical working and in-service conditions is necessary from non-destructive corrosion monitoring and routine inspection instrumentation to correlate the fractal dimension to service and failure events.

VI. CONFLICT OF INTERESTS

The authors confirm that this article content has no conflict of interest

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REFERENCES

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