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Transient Analysis of Electrochemical Noise for 316 and Duplex 2205 Stainless Steels Under Pitting Corrosion

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The use of electrochemical noise (EN) technique for the investigation and monitoring of corrosion has allowed many interesting advances in the corrosion science in recent years. A special advantage of EN measurements includes the possibility to detect and analyses the early stages of localized corrosion. However, the understanding of the electrochemical information included in the EN signal is actually very limited. This work shows the results obtained from EN measurements for different materials that exhibit pitting corrosion. The obtained transients in potential and current time, correlates with the scanning electron microscopy (SEM) surface analysis. Electrochemical measurements were made at different exposure times in order to obtain any correlation. The used materials were austenitic 316 stainless steel and 2205 duplex alloy, immersed in ferric chloride ($FeCl_3$) and sodium chloride (NaCl) electrolytes. SEM analysis shows that the observed transients in the time series really correspond to the activity of pit nucleation developed on the surface of the electrodes.

Keywords: Pitting corrosion, electrochemical noise, electrochemical techniques

1. INTRODUCTION

Electrochemical noise technique for corrosion applications has gained popularity in the recent years and has emerged as a promising technique for corrosion analysis. Electrochemical noise describes the low level spontaneous fluctuations of potential and current that occurs during an electrochemical process. During a corrosion process, which is predominantly electrochemical in nature, the cathodic and the anodic reactions can cause small transients in the electrical charges on the electrode. These transients manifest in the form of potential and current noise, which can be exploited to map a corrosion event. Electrochemical noise can be measured in potentiostatically-polarized conditions and in freely corroding systems [1]. The instantaneous response to change in the conditions of a surface as it begins to corrode enables this method to be a powerful online corrosion-monitoring tool. High resistance to corrosion of stainless steels (SS) and nickel base alloys, aluminum, titanium, copper and other metals is mainly attributed to the passive oxide film formed on its surface. However, the passive film resistance is determined by environmental conditions is exposed to the material and the alloy composition [2].

The action of aggressive ions, especially chloride ions Cl^-, which by increasing its concentration increases the pitting [3], cause passive films are susceptible to localized breakdown, resulting in a rapid dissolution of the metal [4] mainly in places where there are heterogeneities, causing localized corrosion, mainly pitting corrosion as stainless steels. [2 - 5]

Electrochemical Noise is a nondestructive technique [6] to reflect the individual sum of random events of potential fluctuations and / or current of a material [7 - 12] subject to corrosive conditions and the value of the *Root Mean Square* (RMS) of amplitude of these events or standard deviation has been providing the *fingerprint* of the amount of dissolved metal, depending on the metal-environment combination [13]. The fluctuations appear to be linked to variations in the rates of anodic and cathodic reactions as a result of stochastic processes (breakdown and repassivation of passive film) and deterministic (formation and propagation of pitting) [14 - 16]. With this technique does not alter the state of the system under study, since it does not apply any external disturbance for measurement. The concept of electrochemical noise, it behaves inversely proportional to the frequency range of oscillations, lower the frequency higher amplitude [17], corrosion processes can be investigated by observation of electrochemical noise. In the case of pitting, which is a special case of localized corrosion, there are several methods to analyze noise data, and the most popular are the statistical methods as the pitting index and power density spectral or spectral analysis. These fluctuations are usually measured by a system of three electrodes [18].

Thus, the aim of the present work is to correlated the obtained transients of electrochemical noise in potential and current time series with the photomicrographs obtained by scanning electron microscopy (SEM) of 316 stainless steel and 2205 Duplex in aqueous solution of 3.5 wt.% NaCl and 6wt.% $FeCl_3$.

2.EXPERIMENTAL PROCEDURE

The chemical composition of type AISI 316 SS and AISI 2205 duplex austenitic – ferritic steel, used in the present study is given in Table1. The qualitative and quantitative chemical analysis was performed using the technique of Plasma Emission Spectrometry.

Table 1. Chemical composition of materials.

Material	Concentration of Elements, wt. %							
	C	Mn	Si	Cr	Mo	Ni	N	Fe
SS 316	0.08	1.47	0.69	16.65	2.094	10.45	***	Balance
Duplex 2205	0.028	1.6	0.44	23.012	2.973	5.876	0.165	Balance

The electrodes were cut from a bar of AISI 316 SS and AISI 2205 duplex of 1.13cm diameter, joined to a copper wire without insulation on the ends to make electrical contact at the time of the electrochemical tests and were encapsulated in epoxy resin. The exposure area of the steel samples in the test solutions was $1cm^2$. The samples were mechanically polished with grit paper up to grade 600. The samples were then degreased well with acetone and then rinsed with ethanol. After drying, the specimens were stored in desiccators for a period of 24h, before electrochemical testing. The electrolytes used in the study were ferric chloride (6 wt.% $FeCl_3$) and sodium chloride (3.5 wt.% NaCl); any solution was prepared with reagent grade chemicals and distilled water.

Experiments were performed by immersion in a glass of precipitate to a temperature of 25 °C. Electrochemical tests were performed in a three-electrode electrochemical cell system, two nominally identical working electrodes [19, 20], one as a working electrode 1 and the other as working electrode 2, the reference electrode used was saturated calomel (SCE), the arrangement used is shown in Figure 1.

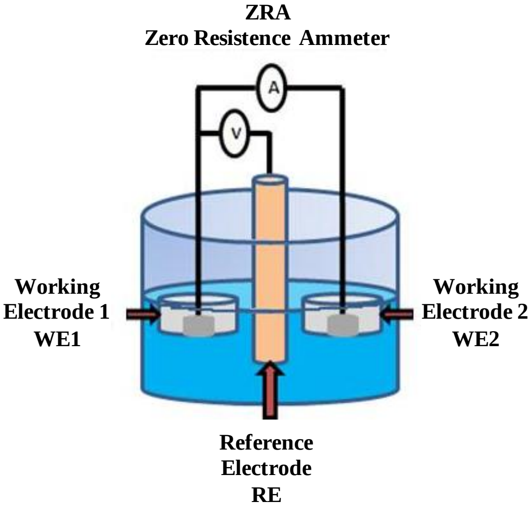

Figure 1. Experimental setup used for electrochemical testing.

Electrochemical current noise was measured between the two working electrodes. Simultaneously, the electrochemical potential noise was measured between one of the working electrodes and the reference electrode. The electrochemical current and potential noise was monitored with respect to time for the particular electrode–electrolyte combination, under open-circuit condition. The electrochemical potential and current noise series–time records were thus obtained using a potentiostat / galvanostat / ZRA mark "Solartron 1285" the number of points for each measured block sample varied and were 500, 1000, 2500 and 4096 points at a rate of 1 point per second. After electrochemical testing, the samples were dried with alcohol and pressurized hot air and stored in a desiccator and subsequently making the analysis by scanning electron microscopy (SEM). The SEM analysis was carried out on the entire sample surface to identify the nucleation or pits.

3. RESULTS AND DISCUSSION

Figure 2 shows the current and potential time series for electrochemical noise measurements recorded in blocks of 500, 1000, 2500 and 4096 points, each point measurement was made every 1s, for type 2205 duplex stainless steel in 6 wt.% $FeCl_3$. In the time-series in potential is a trend towards more noble potentials, and thus the passivation of the material under study. Figure 2b, shows the electrochemical current time-series, it was observed high frequency fluctuations in a short time period, such noise signals have also been obtained for uniform, passivation and localized corrosion processes by Legat and Dolcek [13, 21].

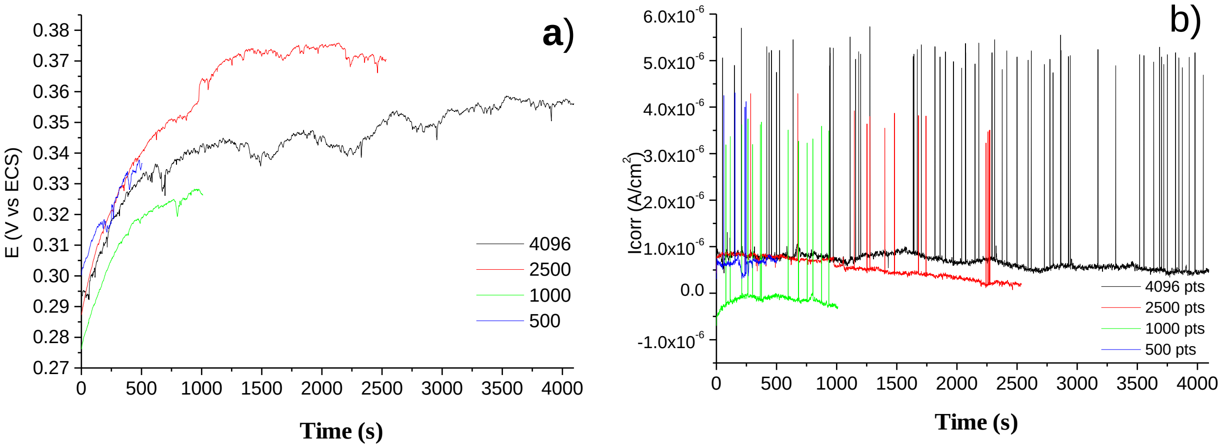

Figure 2. (a) Potential noise and (b) current noise series obtained for 2205 Duplex steel after several times of immersion in 6 wt.% $FeCl_3$ solution.

Figure 3 shows the current time series for electrochemical noise measurements recorded in blocks of 500, 1000, 2500 and 4096 points, and their micrographs respectively for type 2205 duplex stainless steel in 6 wt.% $FeCl_3$. Regardless the number of measured block data, the trend of the fluctuations is similar. Also, there are anodic current transients in time-series clearly identify whit high frequency and very short durations with low intensities of 4 x 10^{-6} A/cm^2, which is characteristic of the nucleation of pitting [22-25] in corrosive media such as $FeCl_3$, although stainless steels present a passive oxide films. Visual examination of the surface showed well-developed pits.

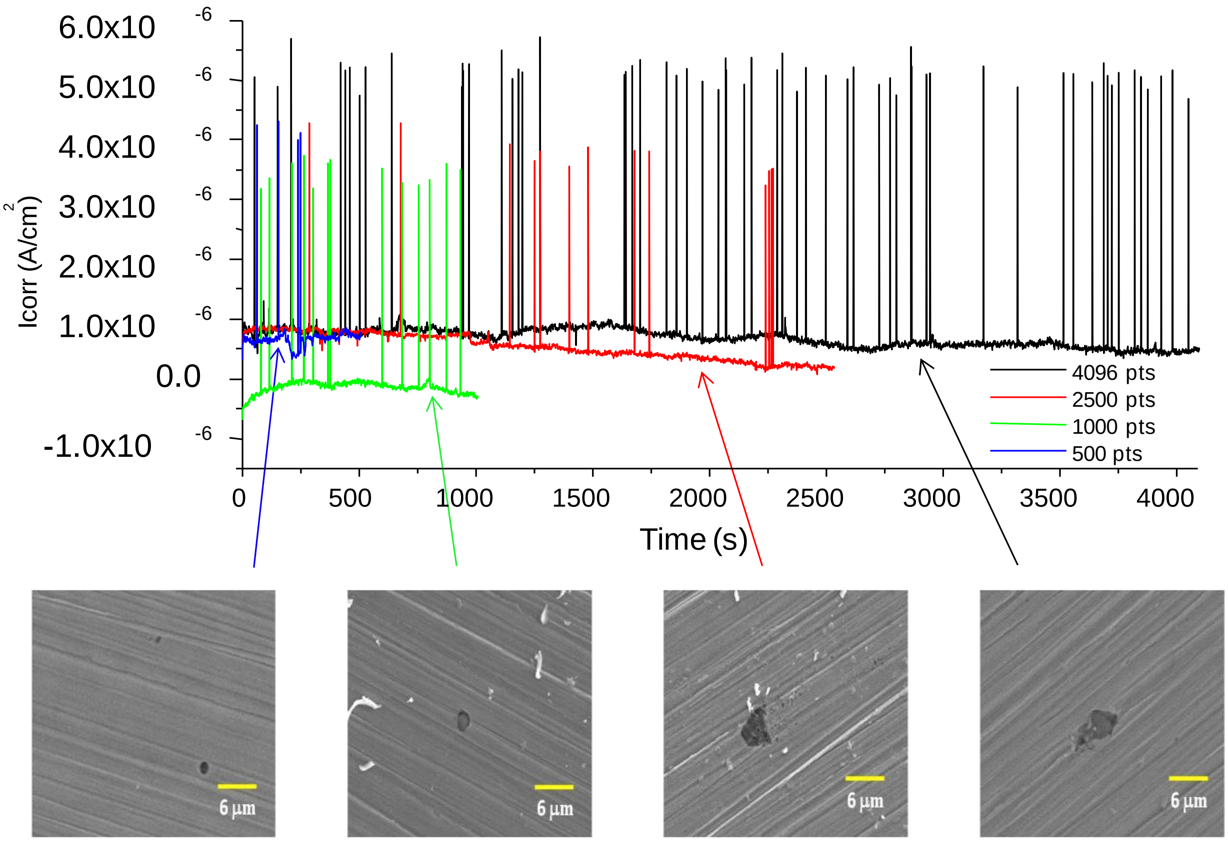

Figure 3. Electrochemical noise current time-series for steel in 2205 Duplex in 6 wt.% $FeCl_3$ solution in blocks of 500, 1000, 2500 and 4096 data, with corresponding SEM photomicrographs taken at 3500X.

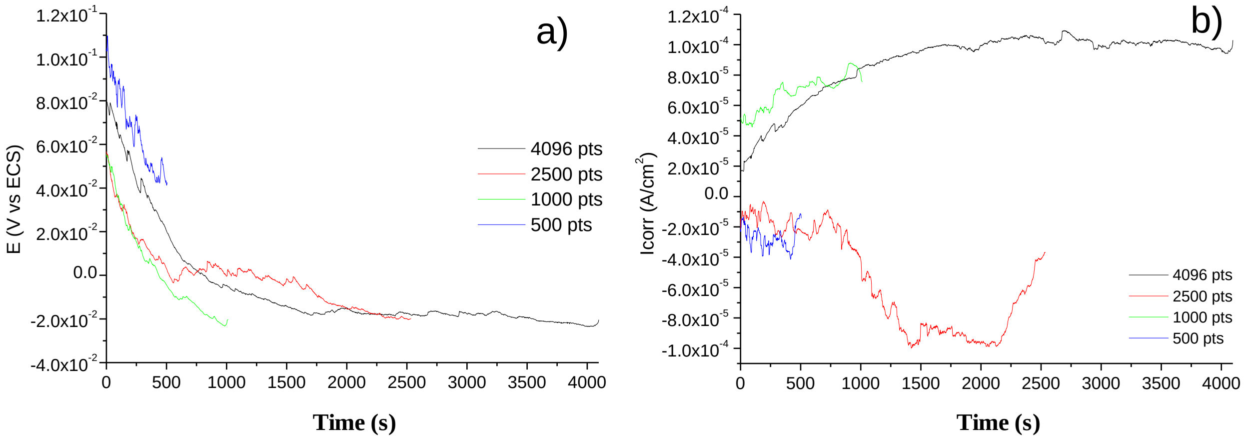

Figure 4. (a) Potential noise and (b) current noise series obtained for type 316 stainless steel after several times of immersion in 6 wt.% $FeCl_3$ solution.

Micrographs taken in the scanning electron microscope shows the way that nucleation occurs and the growing of the pits. In block of 500 s, pits have a size approximately of 1 µm. Also, when the exposure time of the sample increase the size of the pits increases. In block of 4096 s, pits have a size approximately of 4 µm. All those pits were correlated with transients observed in their time-series for electrochemical noise measurements recorded in blocks of 500, 1000, 2500 and 4096 points.

Figure 4, shows the current and potential time series for electrochemical noise measurements recorded in blocks of 500, 1000, 2500 and 4096 points, each point measurement was made every 1s, for type 316 stainless steel in 6 wt.% $FeCl_3$.

Unlike the 2205 duplex steel in the same solution of $FeCl_3$, in this material can not be observed any transient. Figure 4 (a), shows that ENC fluctuations started in the noble potential values then decrease to active potential, contrary to the previous case. Regardless of the number of sampled data, they all follow the same trend. However, fig.4b shows that the reading of 4096 data, for type 316 stainless steel begin to stabilize its potential, which indicates that this material, start passivation. For electrochemical noise current measurements recorded in blocks of 500, 1000 and 4096 points. Data shows an increase which corresponds to dissolution of the passive film of stainless steel with a tendency to repassivation as can be seen in block of 4096 data, where current consumption is not increasing and tends to stabilize.

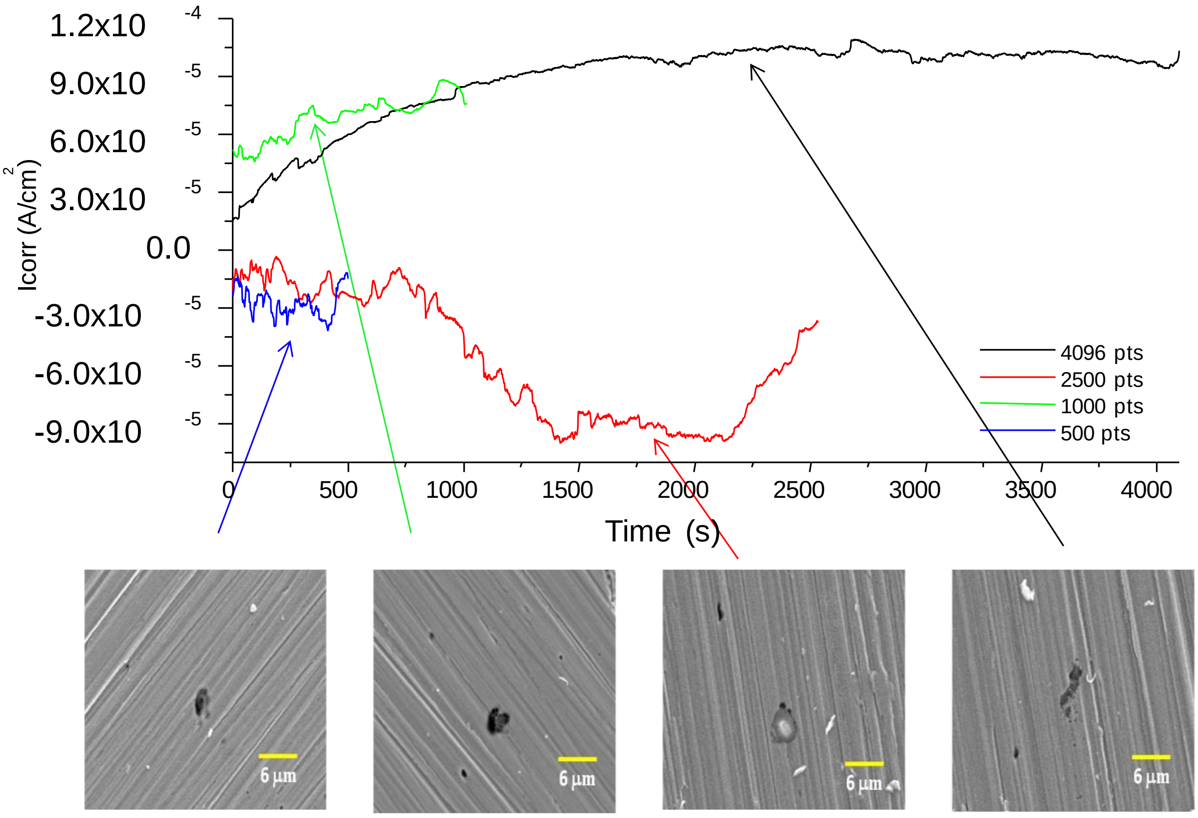

Figure 5. Electrochemical noise current time-series for type 316 stainless steel in 6 wt.% $FeCl_3$ solution in blocks of 500, 1000, 2500 and 4096 data, with corresponding SEM photomicrographs taken at 3500X.

Figure 5, shows the current and potential time series for electrochemical noise measurements recorded in blocks of 500, 1000, 2500 and 4096 points, each point measurement was made every 1s, for type 316 stainless steel in 6 wt.% $FeCl_3$. Unlike the 2205 duplex steel in the same solution of $FeCl_3$, in this material can not be observed any transient. However, current increases are identified followed by a decrease in it. In the micrograph corresponding to 500 data is shown one pit and around a series of nucleation, or metastable pits which not all go on to develop as seen in the photomicrographs for 1000, 2500 and 4096 data. A growth of pit up to 6 µm long and 3 µm wide approximately, presenting irregularly shape that growing along the rough marks as can be seen in block of 4096 data.

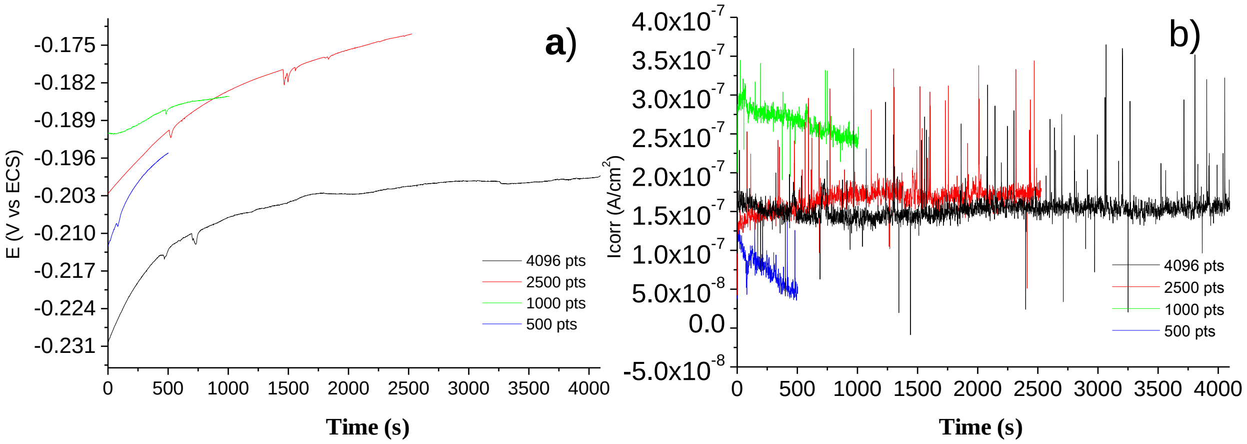

Figure 6. (a) Potential noise and (b) current noise series obtained for 2205 Duplex steel after several times of immersion in 3.5 wt.% NaCl solution.

Figure 6 shows the time series of potential (a) and current (b) without a trend for 2205 duplex stainless steel in 3.5 wt.% NaCl which is manifested in localized corrosion activity, specifically a number of nucleation pits. Figure 6 (a) shows a tendency to noble potential values and a state of passivation, the trend is clearly identified in the reading of 4096 data, It can be seen that at a time between 500 and 800 *s* of sampling there is a small drop in the potential, which has a correspondence with the fluctuations observed in the current time series, Figure 6 (b), suggesting the development of metastable pitting.

In Figure 7, corresponding to steel 2205 Duplex in NaCl solution shows the current time series together with micrographs taken by SEM. The amplitude of the transients in time series 500, 1000, 2500 and 4096 is the same, clearly identified the background noise and distinguished transients of amplitude of approximately 2.5 x 10^{-7} A/cm^2, the transients have a very short life time and are in both anodic and cathodic directions, indicating that there is a breakdown of the passive film in localized areas caused by the concentration of chloride ions as identified in the analysis by energy dispersive X-ray spectroscopy (EDS) in SEM. The analysis by SEM, in block of 500 data, was observed few nucleation pits, and those detected were quite superficially on the sample. Compared with the results obtained in the solution $FeCl_3$ for this material, the intensity in the current transients are smaller (2.5 x

10^{-7} A/cm^2), which can be verified in the previous micrographs to any number of data, which are smaller and were superficial ones.

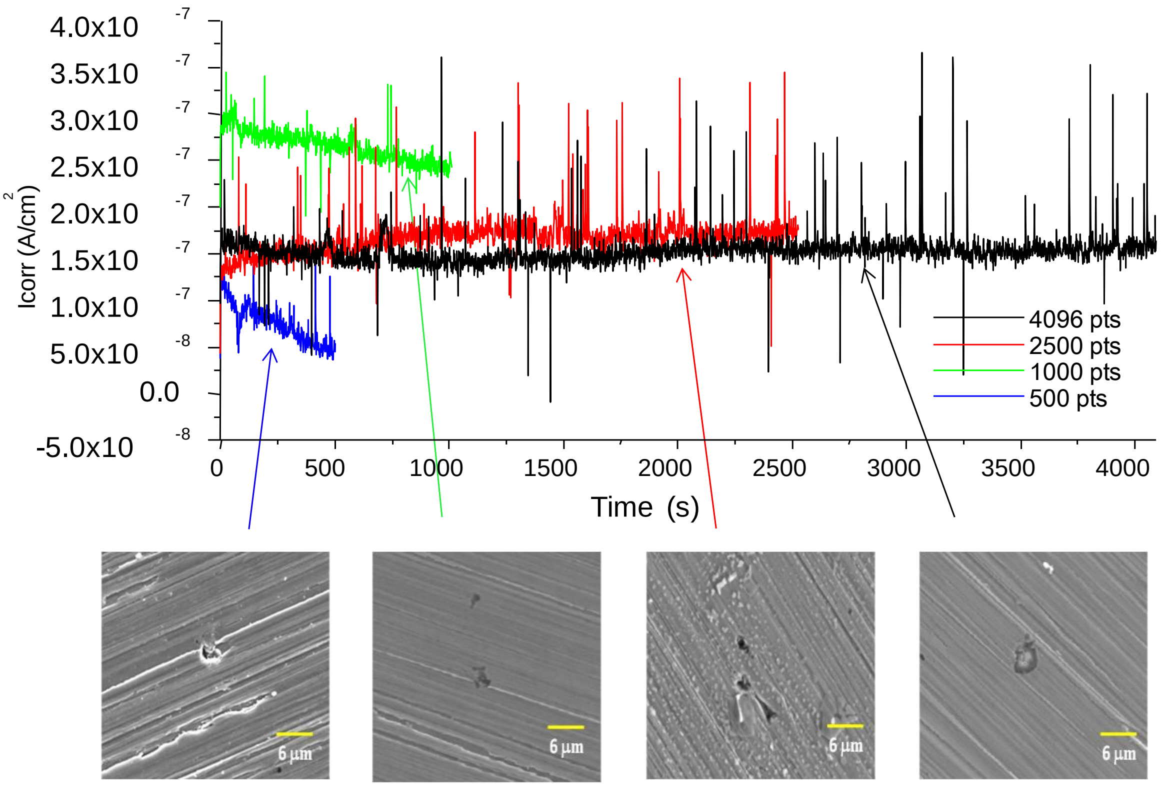

Figure 7. Electrochemical noise current time-series for type 2205 Duplex stainless steel in 3.5 wt.% NaCl solution in blocks of 500, 1000, 2500 and 4096 data, with corresponding SEM photomicrographs taken at 3500X.

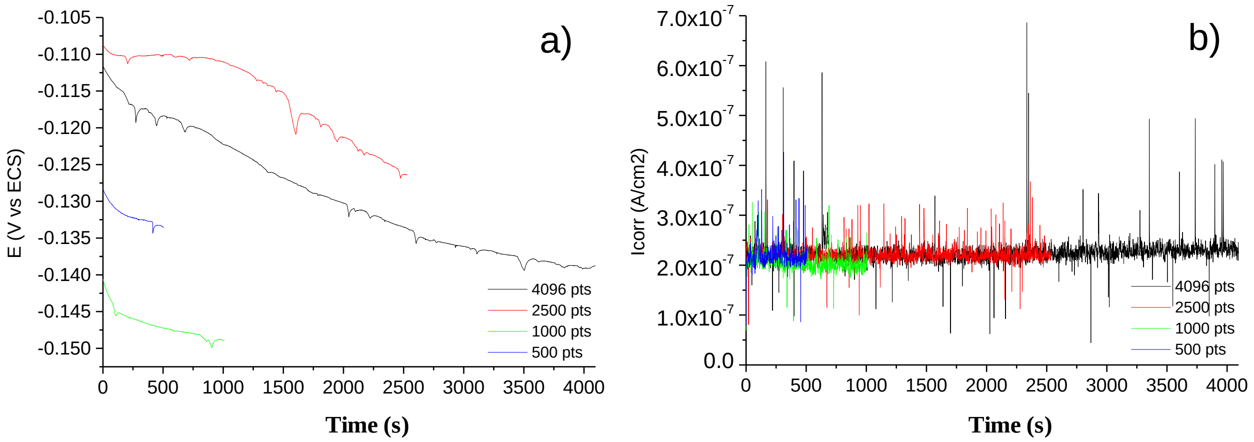

Figure 8. (a) Potential noise and (b) current noise series obtained for type 316 stainless steel after several times of immersion in 3.5 wt.% NaCl solution.

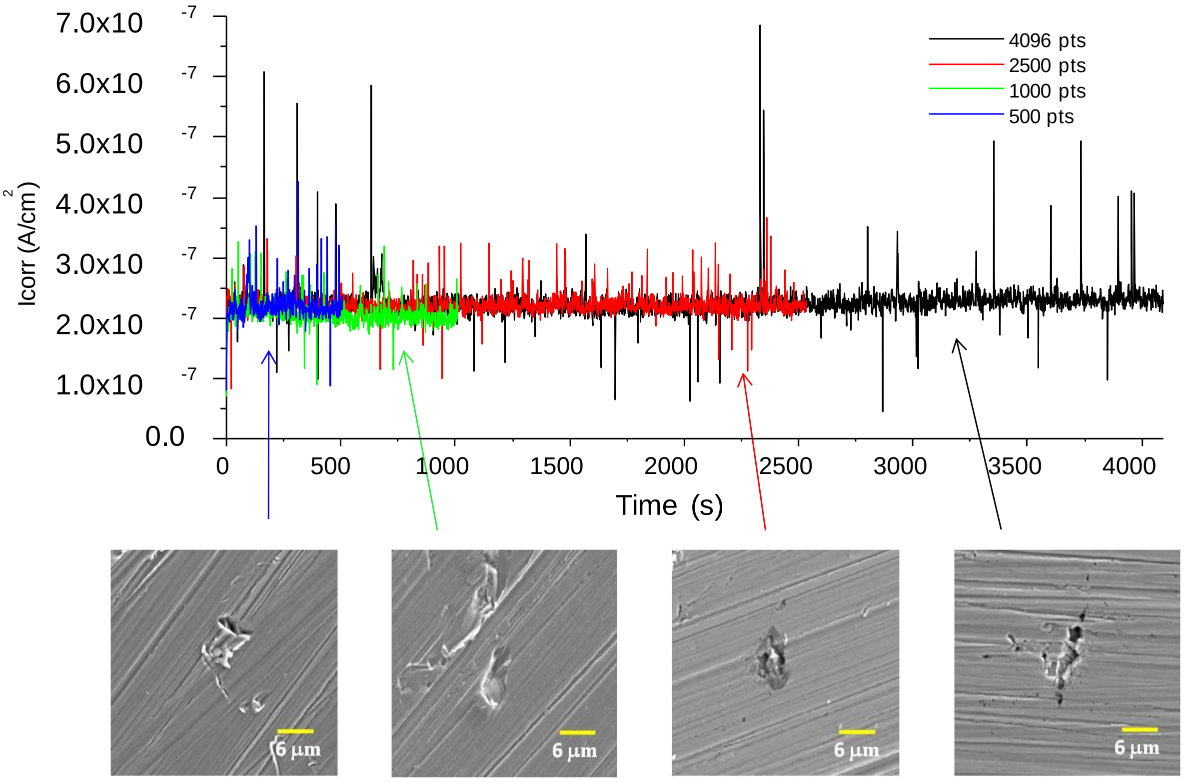

Figure 9. Electrochemical noise current time-series for type 316 stainless steel in 3.5 wt.% NaCl solution in blocks of 500, 1000, 2500 and 4096 data, with corresponding SEM photomicrographs taken at 3500X.

Figure 8, shows the current and potential time series for electrochemical noise measurements recorded in blocks of 500, 1000, 2500 and 4096 points, each point measurement was made every 1s, for type 316 stainless steel in 3.5 wt.% NaCl. Figure 8 (a), shows a few drops of potential fluctuations for any recorded block of sample data. In the same way as in the $FeCl_3$ solution for stainless steel 316, the trend is to active potential. Identifies some decreases in the course of the experiment to 4096 *s*, followed by a recovery potential and its behavior corresponds to the fluctuations present at the current time series, Figure 8 (b), in which was observed a negligible increase in current.

Figure 9, analyzed together the time-series of current and micrographs, for type 316 stainless steel in 3.5 wt.% NaCl. Regardless the number of measured block data, the trend of the fluctuations is similar. It was observed the typical current transients, characterized by a quick rise followed by a slow recovery, are believed to reflect the metastable pitting process: initiation, growth and repassivation of metastable pits. The amplitude of the transient characteristic of nucleation has an average of 2.5 A/cm^2. However, there are some that can reach amplitude up to 4 A/cm^2, compared with those observed in the solution of $FeCl_3$ in the current time series analyzed by SEM. There was a lower pit nucleation density. The nucleation of pits were found superficially in the sample with an irregular shape of approximately 6 μm long and 2 μm wide for the experiment in block of 4096 s.

Table 2 shows the results of the parameters obtained (resistance to noise, location index, corrosion current density and corrosion rate) from electrochemical tests, in which confirm those obtained by SEM analysis. To obtain the electrochemical parameters were used to statistical method least squares, calculated for the experiment to 4096 data.

Table 2. Electrochemical Parameters Calculated from Equations 1-3. [27]*.

Material	Solution	Electrochemical parameters			
		Rn (Ω-cm^2)	Icorr (A/cm^2)	IL	*Corrosion Type
Duplex 2205	$FeCl_3$	7965.6	3.26 x 10^{-6}	0.6017	Localized
	NaCl	54768	4.7473 x 10^{-7}	0.1118	Localized
SS 316	$FeCl_3$	1582	1.64 x 10^{-5}	0.2855	Localized
	NaCl	21307	1.2202 x 10^{-6}	0.1013	Localized

Calculate the noise resistance (eq. 1) was performed by ratio of the standard deviation of the measured potential and current noise [22 - 24]:

$$Rn = \frac{\sigma E}{\sigma I} \qquad (1)$$

Rn data was used to calculate the corrosion rate (eq. 2), in analogy with the equation of Stern - Geary [25]:

$$I_{corr} = \frac{B}{Rn} \qquad (2)$$

The location index (eq. 3), which is a parameter that evaluates the variation of current noise and compares the average value was calculated by the ratio of the current standard deviation and root mean square current according to [26].

$$IL = \frac{\sigma I}{I_{RMS}} \qquad (3)$$

4.CONCLUSIONS

The transients presented in all time series of potential and current show repeatability and are characteristic of pitting nucleation or metastable pitting. These transients are independent of the number of sampled data and are reaffirmed by the SEM analysis, which showed a correlation between the pitting nucleation density and the number of transients in the time series for each experiment.

The amplitude of the transients is related to the size of the nucleation of the pit, for the 2205 duplex steel in the solution of $FeCl_3$ were identified transient with an average size of 4 x 10^{-6} A/cm^2 and interacting with a 1 micron nucleation. In the austenitic stainless steel in the solution of $FeCl_3$ was observed amplitudes of 4.3 x 10^{-6} cm^2 on average with a correspondence in the nucleation size of 1.5 microns. In NaCl solutions for both steels are presented amplitudes with one order of magnitude smaller than those observed in the solution of $FeCl_3$ and the nucleation of pitting was found on a sample surface in contrast to those found in solutions of $FeCl_3$ which were deeper in the steel. In the case of 2205 duplex steel in NaCl solution the average of the amplitudes is 1.5 x 10^{-7} cm^2 and corresponds to 1 micron in size for nucleation and Type 316 stainless steel in NaCl solution were also observed amplitudes of 1.5 x 10^{-7} but with size of 1.5 microns.

AISI Type 2205 duplex steel had a higher noise resistance (54768Ω-cm^2) in the NaCl solution. AISI Type 316 SS presented the lowest resistance and it was 1582 Ω-cm^2 in the solution of $FeCl_3$. The location index for duplex stainless steels 316 and 2205 in both $FeCl_3$ and NaCl solutions corresponds to a type of localized corrosion, showing the highest IL in 2205 duplex $FeCl_3$ solution and the lower 316 stainless steel in NaCl solution.

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