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Electrochemical Noise Analysis of Nickel Based Superalloys in Acid Solutions

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In this paper we study the corrosion behavior of nickel-based superalloys (Inconel 690, Inconel 718, Incoloy 800, Incoloy 825), compared with commercial steels (carbon Steel 1018 and stainless steel 304), in acid (10% H_2SO_4 and 10 % CH_3COOH) and H_2O at room temperature, by electrochemical noise technique, with sampling 1024 points per second. Statistical analysis of electrochemical noise technique yielded LI localization index, the type of corrosion and the noise resistance as well as the corrosion rate. The corrosion rates of 304 stainless steel and carbon steel where much higher than nickel base alloys. Current noise time series indicate superalloy have mostly noble potentials, but depends on the electrolyte. Nickel base superalloys have good response to low temperature corrosion, but tend to localized corrosion in the electrolyte tested.

Keywords: nickel-based superalloys, corrosion, electrochemical noise, localization index.

1. INTRODUCTION

Modern technology demands efficient and effective components to work in increasingly hostile environments. Each technological advance forces overcome complicated problems such as corrosion. By the great economic impact on environmental safety, which can cause failure of metal components in service, currently a correct selection of materials is a key factor in the success of industrial processes [1,2].

To improve substantially the corrosive properties, formerly resorted to complex and costly metal alloys. Fortunately, however, modern technology has superalloys.

Of the different kinds of materials that are currently on the market, nickel-based alloys have been well accepted in industries such as chemical, petrochemical, and nuclear, among others, because they offer excellent mechanical properties, high resistance in corrosive environments and high temperatures, and combination of these factors [2,3]. It has been observed that metallurgical condition of these alloys is a key parameter which benefit greatly its resistance to localized corrosion.

Nickel-based superalloys, unlike the iron-base, don't depend on micro-structural changes associated with carbon, to obtain the desired mechanical properties. Nickel is an austenite stabilizer (γ ') in stainless steels, so that both in pure nickel as in the family of alloys with high nickel content, does not occur any allotropic transformation. These alloys are austenitic type since the melting temperature to absolute zero, so are not subject to the ductile-brittle transition experienced by most of alloys with bcc crystal structure. Although some intermetallics can be formed such as hardening gamma prime phase (γ ') and the carbides, these don’t change the basic structure of the matrix, austenite type, because nickel is found in nature in the form of nickel sulphide minerals and nickel oxide, so it has a natural tendency to combine with sulfur and oxygen. The above is one of the important factors to consider when nickel or nickel based alloys are taken into account for industrial applications where may be exposed to aggressive medium containing sulfur compounds, either in solid form, such as lubricants, in the aqueous medium containing thiosulfate, as well as in gaseous form such as sulfur dioxide or hydrogen sulfide.

Operating conditions, the welding method used the inappropriate heat treatment and operating temperatures between 482 and 816 ° C, promotes the precipitation of chromium carbides and the subsequent depletion of chromium in grain boundaries, inducing thus the sensitization of the metal structure.

Searching for materials that have greater resistance to corrosion and provide greater and better integrity of the equipment and processes, the petrochemical industry for the transport and disposal of hazardous waste chlorinated, uses 304 stainless steel containers, which unfortunately is susceptible to pitting corrosion.

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 [4].

The electrochemical noise (EN) is a nondestructive technique [4] which reflects the sum of the individual random events of fluctuations in potential and / or current of a material subjected to corrosive conditions, and the value of the root mean square (RMS) of the amplitude of these events, or standard deviation, has been providing a "fingerprint" of the amount of dissolved metal, depending on the combination of metal and the environment. The fluctuations appear to be linked to variations in the anodic and cathodic reactions as a result of stochastic processes (breakdown and repassivation of the passive film) and deterministic (formation and propagation of pitting) [5-7]. This technique does not alter the state of the system under study, already not apply any external disturbance measurement. The concept of electrochemical noise, behaves inversely proportional to the frequency range of the oscillations, the lower amplitude higher frequency [8]. 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 spectral density analysis, or spectral analysis . These fluctuations are generally measured by a three electrode system [9].

The objective of this research was to characterize the electrochemical behavior of nickel-based super alloys in acid media using electrochemical noise technique.

2. EXPERIMENTAL

2.1 Sampling

The materials used in this research were: Carbon Steel (CS) 1018, stainless steel (SS) 304, Inconel 690, Inconel 718, Incoloy 800 and Incoloy 825.

2.2. Electrodes preparation

Electrodes were cut from different steel bar. A section of 1.13 cm in diameter, joined to a 13 cm copper wire, to make electrical contact, allowing the flow of electrons, and thus to obtain the readings of the electrochemical tests. Samples were encapsulated in epoxy resin. The exposure area of the sample was 1cm^2.

Subsequently electrodes were grinding to grade 600 with silicon carbide abrasive, rinsed with distilled water and alcohol, and dried with forced hot air. The electrodes were stored in a desiccator for a period of 24 hrs.

The electrolytes used in this work were:

Table 1. Concentration of Electrolytes.

Solution	Formule	% w
Sulfuric acid	H_2SO_4	10
Acetic Acid	CH_3COOH	10
water	H_2O	100

2.3. Electrochemical system

The experiments were performed by immersion in a corrosion cell with an arrangement of three electrodes (two identical working electrodes [11, 12]) at a temperature of 25 °C. The reference electrode was calomel (SCE).

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 noise was monitored with respect to time for the particular electrode–electrolyte combination, under open-circuit condition [12]. The electrochemical current noise series–time records were thus obtained using a potentiostat / galvanostat / ZRA "Solartron 1285". The number of points for each measured using 1024 points at a rate of 1 point per second.

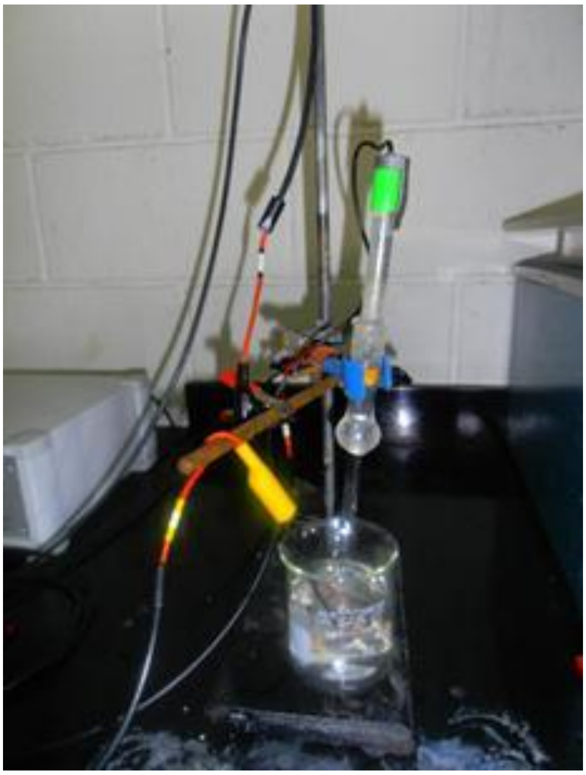

Figure 1. Experimental setup used for electrochemical noise.

3. RESULTS AND DISCUSSION

3.1. Microstucture.

In Figure 2 we can observe the microstructure of the alloys in study: a) shows the microstructure of a typical carbon steel composed of ferrite and pearlite, b) 304 stainless steel has an austenitic structure and the presence of twins, typical of this material, c) on inconel 718 is observed precipitation of carbides in grain boundaries, d) in the inconel 690 were observed equiaxed grains with precipitation of carbides at the grain boundaries and in the matrix, e) incoloy 800 showing a finer grain structure, but at higher magnification shows precipitation of carbides in grain boundaries, and f) the incoly 825, as 800, showing a finer grain structure, less precipitation of carbides and regular grains.

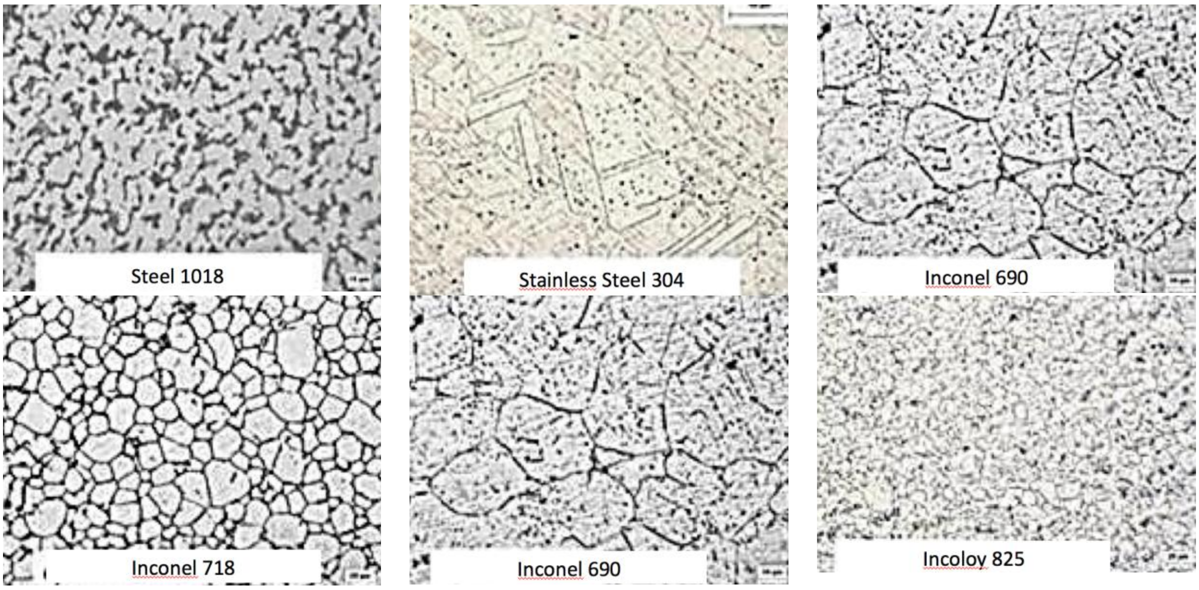

Figure 2. Alloys microstructures

3.2. Electrochemical Noise

The results obtained in the corrosion study, by acid solutions on alloys 600, 718 and 800 respectively, come from analyzing the time series of current noise, to determine the electrochemical noise resistance (Rn) and the corrosion current density (Icorr).

In Figures 3 to 5 are presented the time series of electrochemical current noise for all alloys studied and in all environments tested. In Figure 3, the current time series has very low current demands, which are of the order of $1x10^{-5}$ and $1x10^{-6}$ mA/cm^2. There are some transients (uninterrupted sequence of values characterized by a run-up and followed by a run-down), which cause the material has a type of localized corrosion. Current transients have been observed on many metals and alloys, and the analysis of time records show two types of current transients, the Type I is distinguished by a slow initial growth, followed by sudden decrease, but the Type II displays a sudden increase followed by a smooth decrease. Both transients, characterized by a sudden birth or sudden death, generate 1/f 2 noise in the high frequency range [13].

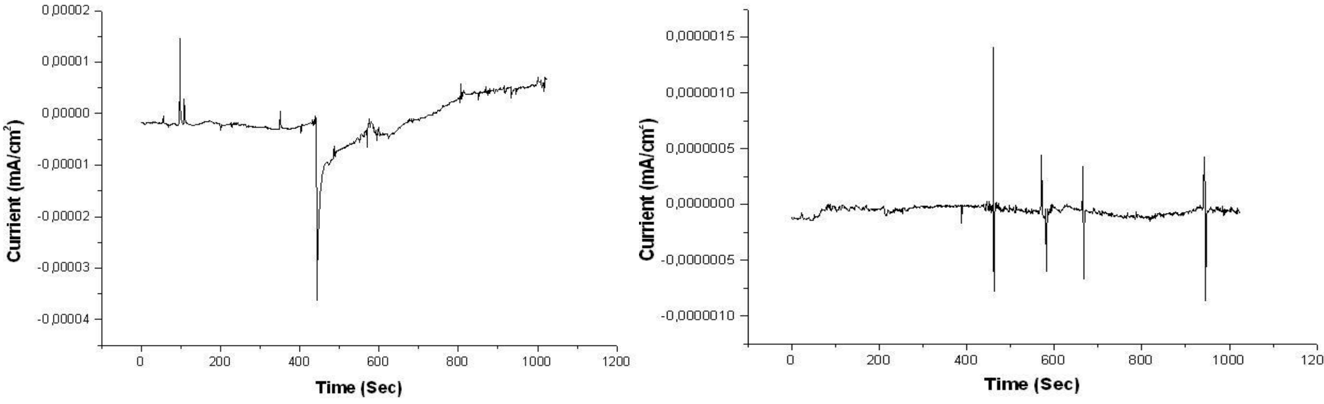

Figure 3. Current noise time series for alloys in H_2O.

The time series of Figure 4 correspond to 10% sulfuric acid (H_2SO_4). The current demands are around $1x10^{-2}$ and $1x10^{-3}$ mA/cm^2. There is a greater increase in amplitude and frequency of transients, and localized corrosion still occurs. The high frequency fluctuations in a short time period have also been obtained for uniform, passivation and localized corrosion processes [14, 15]. The transients that have a very short life time and are in both anodic and cathodic directions indicate that there is a breakdown of the passive films in localized areas.

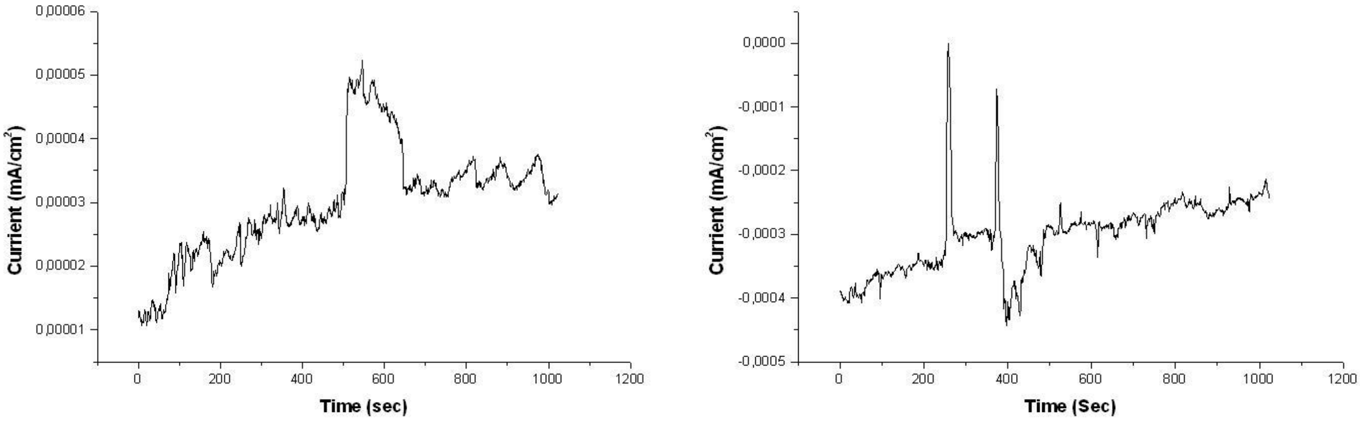

Figure 4. Current noise time series for alloys in 10% H_2SO_4**.**

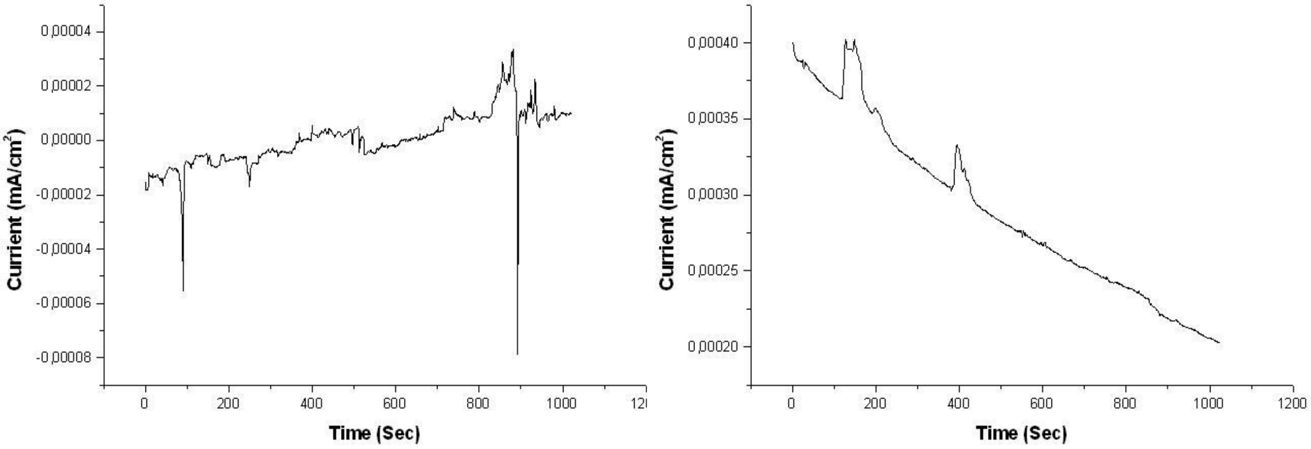

Figure 5. Current noise time series for alloys in 10% CH_3COOH.

Figure 5 shows the time series of current noise for alloys exposed in acetic acid (CH_3COOH). It has very low current demands, which are the order of $1x10^{-4}$ and $1x10^{-6}$ mA/cm^2. There are some high frequencies and low amplitude transients, causing that the material have a type of localized corrosion. The generic term ‘localized corrosion’ implies any corrosion process that is not uniformly distributed over a metal surface, and these processes are associated with large fluctuations in the corrosion current, when compared to uniform corrosion. The current transients in time records are known to be closely associated with the initiation and repassivation of metastable pit, which provides useful information on the initial process of pitting corrosion. The amplitude of the transient characteristic of nucleation has an average of 2.5 A/cm^2.

In Tables 2 to 4 are the results of the electrochemical parameters obtained by the alloys under consideration in the different environments, and these parameters are: electrochemical noise resistance (Rn), corrosion current density (Icorr), corrosion rate and localization index (LI), reporting the corrosion type for each alloy.

The electrochemical characterization results indicate that the corrosion type that occurred in the nickel based alloys is located, in the majority of all cases. The comparison of nickel base alloys was with 304 stainless steel and carbon steels, where its corrosion rates are much greater than for superalloys, as expected. The corrosion rate behavior can be observed in figures 6 to 8, for each electrolyte.

Table 2. Electrochemical test results in H_2O.

Electrochemical parameters					
Material	Rn (mΩ-cm^2)	Icorr (mA/ cm^2)	Corrosion rate (mm/year)	Localization Index (LI)	Corrosion type
CS1018	6302.84	0.0030	0.03490	0.277	Localized
SS304	1398073	0.0009	0.015612	0.965	Localized
Inconel 690	1999541	0.00001	0.000188	0.150	Localized
Inconel 718	999326	.00009	.0000997	0.493	Localized
Inconel 800	104917	0.0001	0.001613	0.811	Localized
Inconel 825	650762	0.00124	0.013177	0.712	Localized

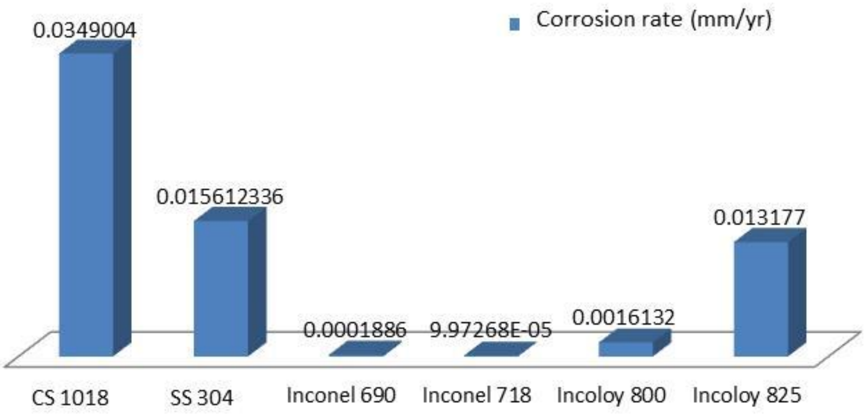

Figure 6. Corrosion rate for alloys in H_2O.

The measurements obtained from spontaneous fluctuations of potential and current, generated by variations in the kinetics of corrosion reactions; include monitoring of potential and current. The electrochemical noise measurements are influenced by the nature of the corrosion process, and several parameters have been suggested as indicators of localized corrosion. Among the statistical methods that use these parameters together, is the standard deviation σ (Eq. 1):

$$\sigma^2 = \frac{1}{n}\sum_{i=1}^{n}(x_i - x^{-})^2 \qquad (1)$$

Calculate the noise resistance (eq. 2) was performed by ratio of the standard deviation of the measured potential and current noise [14,16]:

$$R_n = \frac{\sigma_E}{\sigma_i} \qquad (2)$$

Rn data was used to calculate the corrosion rate (eq. 3), in analogy with the equation of Stern - Geary [17]:

$$I_{corr} = \frac{B}{R_n} \qquad (3)$$

The location index, IL (eq. 4), 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 [18]. This parameter is a direct relationship between these two parameters, and its values are expected between 0 and 1.

$$IL = \frac{\sigma_I}{\sqrt{I^2}} \qquad (4)$$

Table 3. Electrochemical test results in 10% H_2SO_4

Electrochemical parameters					
Material	Rn ($m\Omega$-cm^2)	Icorr (mA/ cm^2)	Corrosion rate (mm/year)	Localization index	Corrosion type
CS1018	40.714	6.3581	71.593	0.129	Localized
SS304	1133.40	3.0608	39.979	0.157	Localized
Inconel 690	3599.14	2.3083	32.855	0.150	Localized
Inconel 718	359902.44	0.3437	5.723	0.283	Localized
Inconel 800	4919.22	2.8623	38.756	0.281	Localized
Inconel 825	9767.37	0.0477	0.506	0.187	Localized

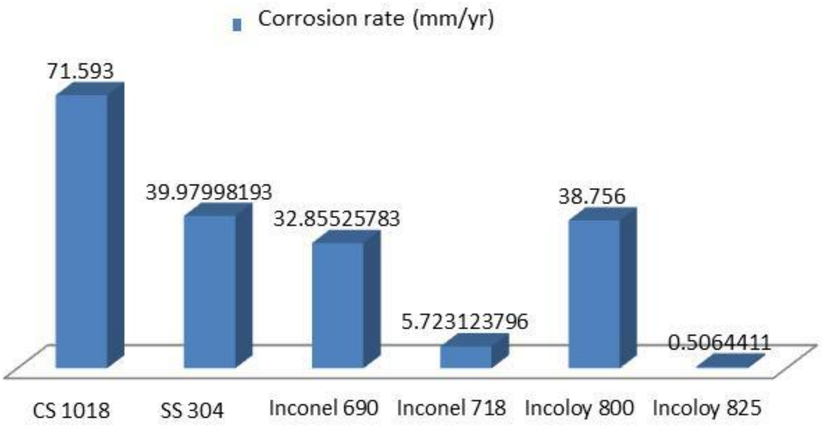

Figure 7. Corrosion rate for alloys in 10% H_2SO_4 .

Table 4. Electrochemical test results in 10% CH_3COOH.

Electrochemical parameters					
Material	Rn (mΩ-cm^2)	Icorr (mA/ cm^2)	Corrosion rate (mm/year)	Localization index	Corrosion type
CS1018	350.69	0.1741502	1.9609	0.891	Localized
SS304	471816.91	0.1122299	1.9438328	0.275	Localized
Inconel 690	124096.64	0.0000725	0.0007790	0.192	Localized
Inconel 718	524562.26	0.015557	0.2590247	0.059	Mix
Inconel 800	1340655.14	0.0077412	0.104816	0.999	Localized
Inconel 825	632703.43	0.0062909	0.066683	0.001	Mix

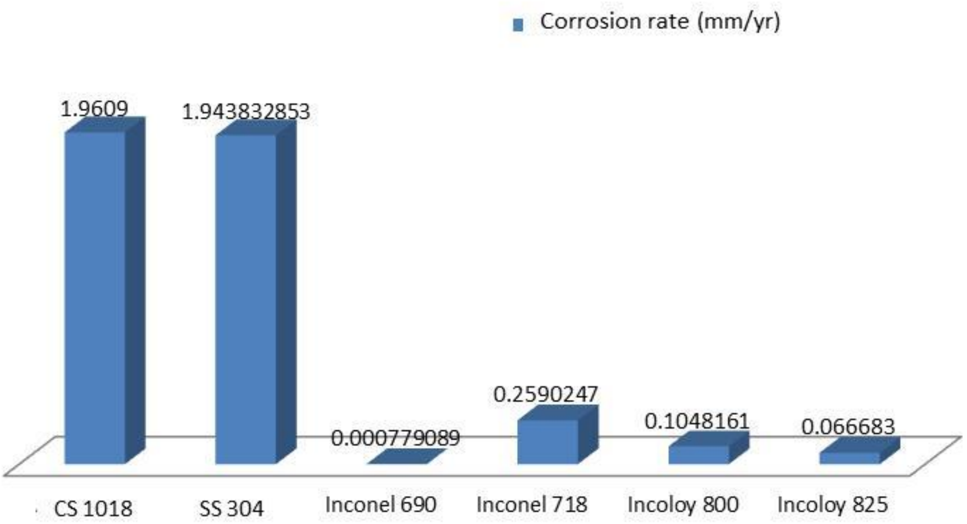

Figure 8. Corrosion rate for alloys in 10% CH_3COOH.

Regarding the corrosion resistance, there are practically no studies applying the technique of electrochemical noise, let alone, a comparison made between the response of various types of alloys. In fact, there aren't many previous works on the corrosion behavior of superalloys, and even less using electrochemical noise technique, some of them we summarize here: Tirdad and Akram [19], developed a study to evaluate the electrochemical bahaviour of incoloy 800 in sulphate solutions containing H_2O_2. They used OCP anodic and cathodic polarizations, and EIS to characterize it, and found that an increase in temperature and a lowering in the pH would lead to a higher corrosion rate. Kup [20], analyzed the effect of alloying on the corrosion behavior of several superalloys with Mo, Ni and Al. They used potentiodynaminc polarization technique and NaCl 3% like electrolyte. Their conclusions were the percentage of Mo, Al and Ni play an important role in inhibiting corrosion. In the linear sweep voltammograms shown that the free corrosion potentials become more negative as de Mo content increases.

Recently, Ting [21], applied an aging treatment to a 718 nickel-base alloy with previous finishing treatments, and find that the pitting corrosion resistance is modified by the finishing process, because affects the surface and the stresses condition. In 2012, Mohammadi [22] performed a study of corrosion behavior of alloy 625 in molten salt at different temperatures, utilizing OCP, potentiodynamic polarization, EIS and weight-loss measurement techniques. In the conclusions stablished that The alloy 625 presented the active dissolution behavior and an anodic film was formed on the surface of the alloy, which was characterized as a non-protective porous corrosion product layer. In an electrochemical study, Batista [23], found that the anodic behavior of the incoloy 800 and 304 SS, depended essentially on the chloride concentration and pH of the solution. The techniques used were OCP and potential-dynamic anodic polarization curves. The oldest is from 1983, of Bogaerts [24], who made electrochemical corrosion tests on 304 SS, incoloy 800 and inconel 600 for determine the influence of solution temperature and composition, on the pitting corrosion behaviour

4. CONCLUSIONS

- Based on the results obtained it was found that the electrochemical noise technique allows to characterize the behavior of localized corrosion in nickel-base superalloys.
- These measurements are possible without disturbing the surface by imposing current or potential, which appears as a significant advantage over other electrochemical techniques.
- The electrochemical characterization results indicate that the type of corrosion that occurred in the nickel based alloys is located in the majority of all cases, with the criterion of the location index.
- The corrosion rates of nickel base alloys were much lower than those obtained for 304 stainless steel and carbon steel 1018.
- The most aggressive environment was the ammonia, which presented current demands from $1\text{x}10^{-3}$ to $1\text{x}10^{-5}$ mA/cm^2.
- Nickel-based superalloys have good response to low temperature corrosion, but tend to exhibit localized corrosion depending on the electrolyte to which they were exposed.
- Suffered localized corrosion superalloys is due to the precipitation of carbides on grain boundaries.

- In the case of Inconel 690 in 10% H_2SO_4, higher corrosion rate may be due to the formation of carbides throughout the matrix of the structure.

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