

Corrosion Behaviour of 304 Austenitic, 15-5PH and 17-4PH Passive Stainless Steels in acid solutions

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The objective of this work was to study is use electrochemical techniques to determinate the growth conditions, characteristics and resistance of passive layers of stainless steel (SS): 304 austenitic, 17-4PH (precipitation hardening) and 15-5PH. Passivation of the SS was performed in 15% citric acid at temperatures of 25 and 49 °C. The corrosion kinetics was obtained using the electrochemical technique as potentiodynamic polarization (PP), in a three-electrode system. The electrolytes used were sodium chloride (5 wt. % NaCl) and sulfuric acid (1 wt. % H₂SO₄). Passivation in citric acid allows obtain passive layers at temperatures of 49°C with immersion times of 30 minutes. In precipitation hardening steels, passive layers up to 360 mV in sodium chloride. Can be obtained. In sulfuric acid, there is a mechanism of passivation – transpassivation - secondary passivation, this due to the high electropositive values of potential.

Keywords: Stainless Steels, Precipitation Hardening, Corrosion, Passivation

1. INTRODUCTION

The use of stainless steels in the manufacture of helicopters, is limited due to its density, in comparison with other materials such as: aluminum (2.5 more dense), titanium (1.5 denser) and compounds (3.5 more dense). The properties of stainless steels have the advantage of resistance to wear, corrosion, costs and availability [1]. The corrosion that occurs in commercial, military and

private fuselages is considered an important problem that directly affects security, economic and logistical problems [2].

The protection corrosion in stainless steels is passivation, being one of the most common methods. Passivation is a term that is defined as "Treatment or coating generated to reduce the chemical reactivity of its surface" [3,4]. When a material has loss of passivity this can present a localized corrosion or pitting corrosion; this is due to a variety of different mechanisms: pitting, film breakage and adsorption of contaminants [5-6].

The passivation layer is a protection to reduce the damaging environmental impact of factors such as air or water. Consequently, this process requires a final product that is clean and free of iron and other contaminants [3-8].

The surface of a metal is considered passivated, even when it is exposed to ambient conditions, while the dissolution of the metal could be expected by thermodynamic considerations, this passive layer remains essentially unchanged over time [8-10].

Research has been carried out to obtain passive agents less toxic to the environment. In 2003 [11], the company Boeing evaluated the use of citric acid as alternative passivation of stainless steel aeronautical parts; Subsequently in 2008 [4] and 2011 [7], the National Aeronautics and Space Administration (NASA), continued with assessment of the use of citric acid as a passivating agent through stress and adhesion tests, and exposure in the salt spray chamber, making a recommendation to continue passive layer evaluation studies.

The objective of this work was to study by potentiodynamic polarization techniques, the temperature conditions and passivation times to obtain stable passive layers resistant to corrosion in precipitation hardening stainless steel, using a 5 wt % NaCl and 1 wt % H₂SO₄ as test solution.

2. EXPERIMENTAL

Materials used in this investigation were SS 304, 15-5PH and 17-4PH steels, whose chemical composition was determined by X-ray fluorescence.

Preparation of the electrodes: Each of the SS was prepared according to ASTM A380 [12] in order to obtain a surface without harshness, after that procedure a washing and rinsing was carried out to eliminate preparation impurities, thus obtaining the material to passivate.

The passivation process was carried under ASTM A967 [13], which consisted in the preparation of a 15% citric acid solution at a constant temperature of 25 and 49° C ($\pm 2^\circ\text{C}$). The material was introduced to passivate it for a time of 30 and 90 minutes, after which a rinsing was performed.

Electrochemical measurements: a conventional three-electrode cell was used for electrochemical studies, and the passivated specimen was used as the working electrode. A saturated calomel electrode (SCE) and a platinum mesh were used as reference and counter electrode, respectively. Electrochemical measurements were carried out using a Gill-AC potentiostat/galvanostat/ZRA from ACM Instruments. Potentiodynamic polarization was recorded at a

sweep rate of 60 mV/min, according to ASTM G5 standard [14]. A potential scan range was applied between -1000 and $+1200$ mV vs SCE.

Corrosion experiments were performed by immersion of the passivated specimens, with an exposed surface area of 1.0 cm^2 , in a 5 wt % NaCl and 1% H_2SO_4 solution, at $25\text{ }^\circ\text{C}$ temperature.

3. RESULTS AND DISCUSSION

The chemical composition obtained by X-ray fluorescence of the Stainless Steels used in the present study is given in table 1.

Table 1. Chemical composition of stainless steels (wt %)

Stainless Steel	Elements					
	Cr	Ni	Mn	Cu	Si	Fe
304	18.06	07.96	01.63	00.36	00.60	Balance
15-5PH	15.04	04.12	00.80	03.25	00.59	Balance
17-4 PH	15.03	04.53	00.74	03.49	00.48	Balance

3.1 Stainless Steel in NaCl solution.

The Potentiodynamic polarization behavior obtained in 304, 17-4PH and 15-5PH Stainless Steel; Passivated in citric acid and exposed in a sodium chloride (5 wt % NaCl) medium at room temperature ($25\text{ }^\circ\text{C}$) are shown in Figures 2-4.

The SS 304 passivated at 25 and $49\text{ }^\circ\text{C}$, with 30 and 90 min of immersion, all the cathodic and anodic polarization curves exhibit a mixed control by activation. In the graph at $25\text{ }^\circ\text{C}/90$ min occurs activation in the anodic reaction, followed by a pseudo-passivation, but with 30 min of immersion, the anodic reaction curve indicates passive layer formation with subsequent breakdown, caused by the dissolution of the metal. The corrosion potential was -298 mV (figure 1).

The Potentiodynamic polarization curve at temperature $49\text{ }^\circ\text{C}/30$ min shows the same behavior at $25\text{ }^\circ\text{C}/30$ min with a corrosion potential of -318 mV. With passivation temperature of $49\text{ }^\circ\text{C}/90$ min with a corrosion potential of -352 mV where passive layer formation and dissolution are observed, similar behavior that indicated by the polarization curves of $25\text{ }^\circ\text{C}/30$ min and $49\text{ }^\circ\text{C}/30$ min. It is observed that the $25\text{ }^\circ\text{C}/90$ min curve shows an order of magnitude difference in the corrosion current density with respect to the curves of $25\text{ }^\circ\text{C}/30$ min and $49\text{ }^\circ\text{C}/30$ min and 90 min which have a passivation zone of 150 mV. The cathode region in all curves shows activation [15].

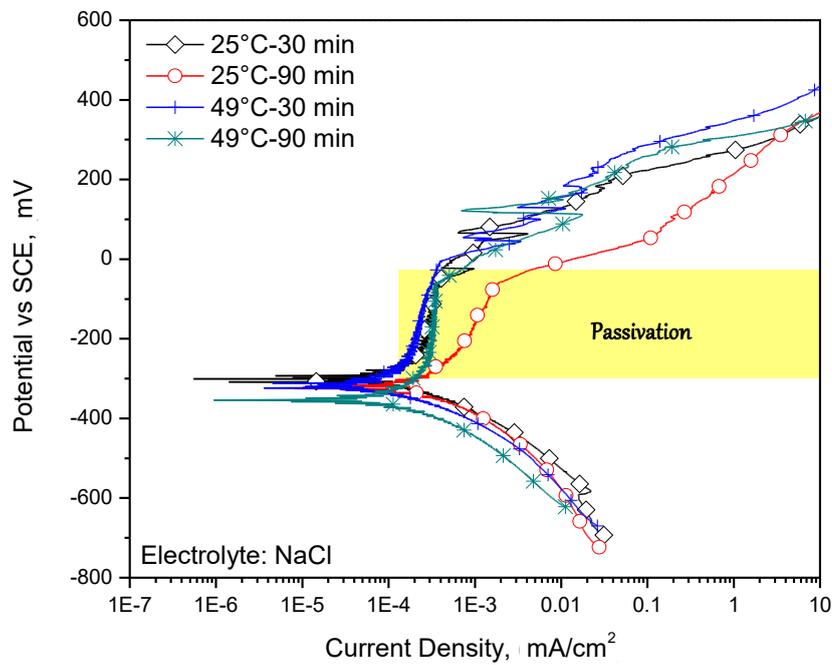


Figure 1. Potentiodynamic polarization of passivated 304 SS, in 5 wt % NaCl solution [15].

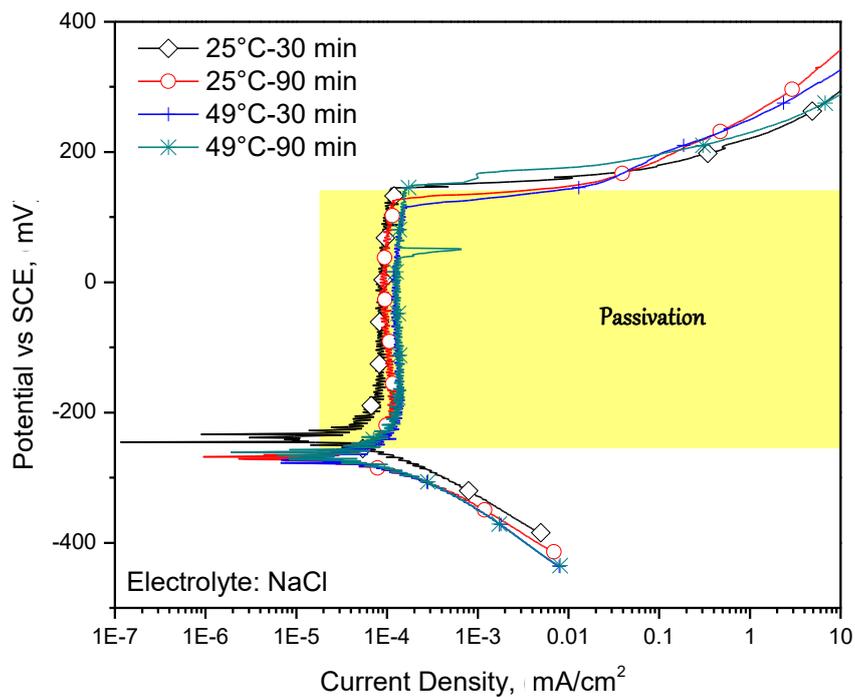


Figure 2. Potentiodynamic polarization of passivated 15-5PH SS, in 5 wt% NaCl solution[15].

The PP for steel 15-5PH at 25 and 49°C with passivation times of 30 and 90 min, in all the curves a mixed control is observed in the anodic and cathodic part. At temperature of 25 °C/90 min and 49 °C with 30 and 90 min, there is a displacement of the curves to more active potentials. The steel at 49 °C/90min shows a breakdown of the passive layer; this same curve has the best passive layers of 240 mV followed by the curve at 25 °C/90 min with 360 mV. At 25 °C/90 min and 49 °C/30 min there is transpassivity of the material followed by activation, whereas at 49 °C/90 min and 25 °C/30 min there is a stepped increase in the corrosion current density (figure 2).

At 25 °C/30 min and 90 min of passivation, Anodic control is observed in the PP of 17-4PH steel (Figure 3); in both cases, the cathodic region in both cases is limited by the reduction process. In both curves there are pitting and regeneration of the passive layer, followed by transpassivity accompanied by dissolution of the material. At 90 min, there is a greater stability of the passive layer of 750 m. At temperature of 49 °C/30 and 90 min there is a displacement of the curves towards less active potentials, around -360 to -240 mV. The Passivation of steel at 90 min presents there is an abrupt change in anodic region that causes pitting and breakdown of passive layer, caused by the dissolution of the material, there is passive layer stability of 180mV. In both cases a process of transpassivation is followed.

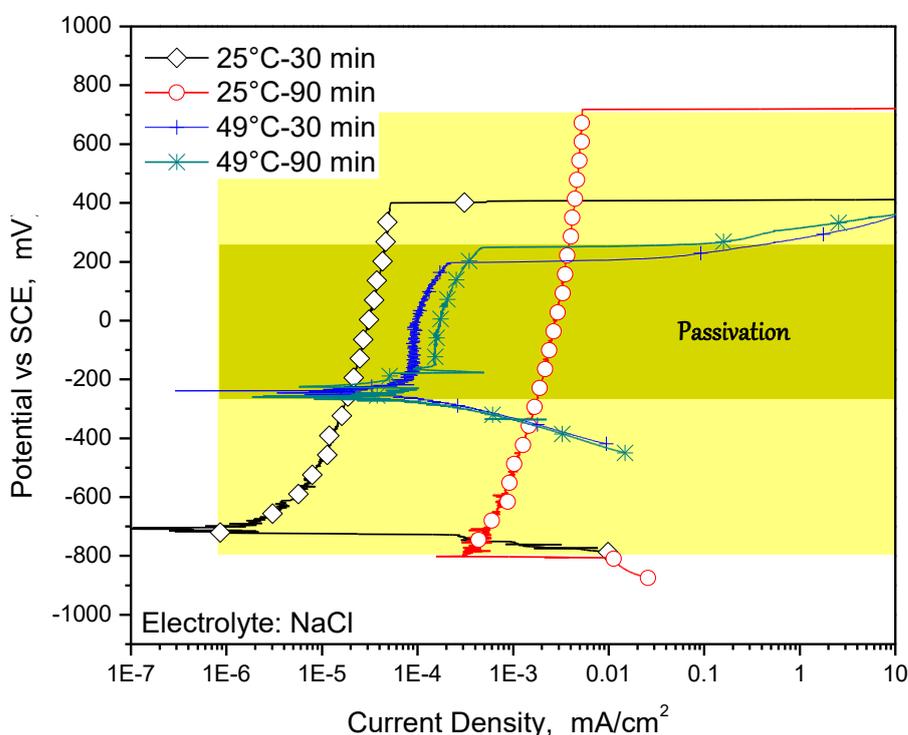


Figure 3. Potentiodynamic polarization of passivated 17-4PH SS, in 5 wt% NaCl solution[15].

The result of potentiodynamic polarization for stainless steel 304 in sodium chloride (NaCl) at temperature of 49 °C has small passive layer formation of 150 mV. Above -100 mV there is breakdown of layer with system activation. The 15-5PH presents a good response to the polarization generating passive layers of up to 360 mV, followed by a transpassivity; In this material the

passivation temperature can be 25 °C but with immersion times of up to 90 min. Steel 17-4PH exhibits passive layer formation of 180 mV at temperatures of 49 °C, at ambient temperature the material exhibits passivity but at active corrosion potentials.

3.2 Stainless Steel in Sulfuric Acid Solution

The Potentiodynamic polarization behaviour obtained in 304, 17-4PH and 15-5PH Stainless Steel, passivated in citric acid and exposed in a sulfuric acid (H₂SO₄) solution at room temperature (25 °C), is shown in Figures 4-6.

Figure 4 shows the results obtained for steel 304 with a mixed polarization control, and a cathodic region with the reduction of hydrogen ions. The anodic region exhibits critical passivation corrosion current densities of 10^{-3} - 10^{-2} mA/cm², later exhibit a transition where the passivating film begins to form and causes an abrupt fall of the i_{corr} . The increase of potential to electropositive values generates a pseudo-passive layer up to 375 mV, potential from which the decomposition of the film takes place generating a transpassive region and the oxidation of the material. Above 1000 mV dissolution is made giving the beginning of a region of secondary passivity (49 °C/90 min). At 49 °C/30 min and 25 °C (30 and 90 min), a secondary pseudo-passivation occurs.

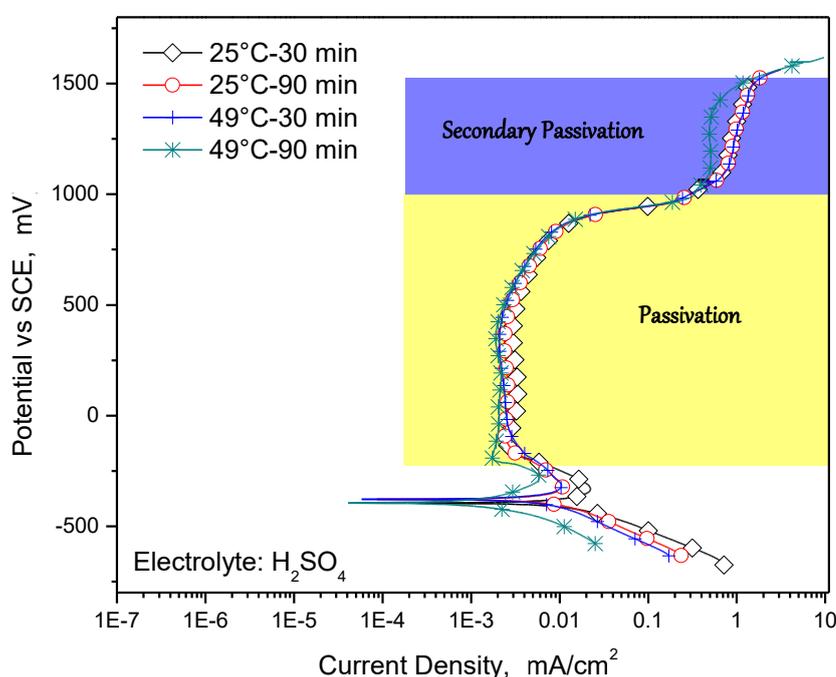


Figure 4. Potentiodynamic polarization of 304 SS passivated, in 1 wt. % H₂SO₄ solution [15].

In 15-5PH (figure 5) a mixed control with corrosion potentials of around -320 mV is observed in polarization curves for the different temperatures and passivation times. With the exception of curve at 49 °C/90 min, the others have an anodic behavior with critical passivation current densities of order 10^{-2} mA/cm², with a current density drop at potentials of -250 mV, potential in which there is an active solution of the material and initiation of the formation of the protective film. This process generate decrease of the current density followed by a passive state of -125 to 440 mV. Above this latter

potential, decomposition of the film occurs with an increase in the anodic current density, generating oxidation of the material and producing insoluble ions, giving rise to the transpassivity. A secondary pseudo-passivation is presented above a potential of +900 mV until secondary passivation occurs in potentials around 1200 mV and an i_{corr} of the order of 10^{-1} mA/cm².

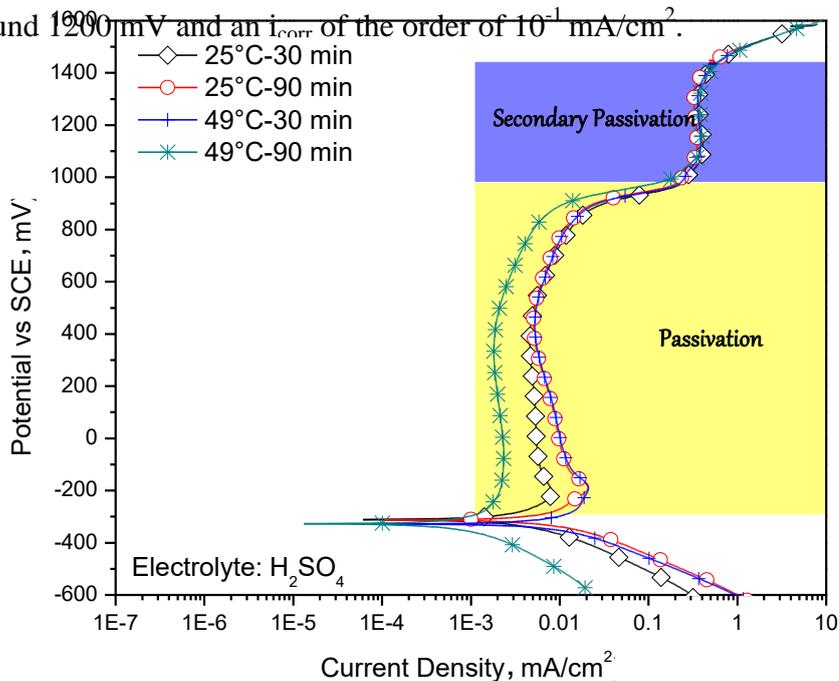


Figure 5. Potentiodynamic polarization of 15-5PH SS passivated, in 1 wt% H₂SO₄ solution [15].

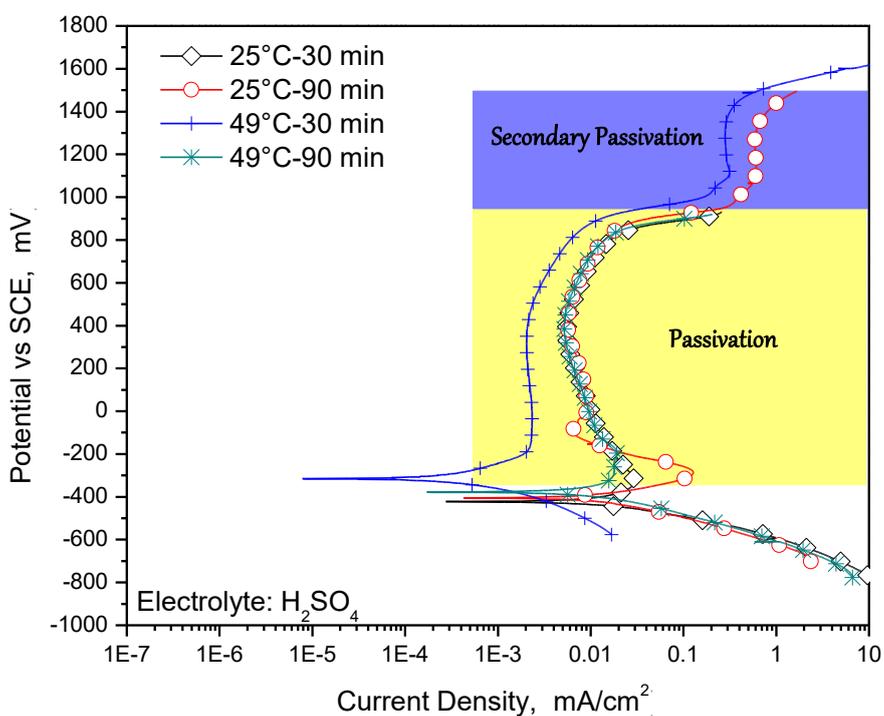


Figure 6. Potentiodynamic polarization of 17-4PH SS passivated, in 1 wt% H₂SO₄ solution [15].

In the PP of the figure 6 a mixed control for 17-4PH stainless steel is observed. The cathode region is activated and the anode region exhibits displacement to electropositive potentials as the passivation temperature increases from 25 to 49 °C. The corrosion potential for the 49 °C/30 min curve is -318 mV with a passive layer of 600 mV, followed by transpassive interval from 420 to 1000 mV; potential in which the degradation of the film is observed and an increasing of the i_{corr} . At a potential above 1000 mV, a secondary pseudo-passivation is observed and when achieves values of 1100 mV there is presence of secondary passivation. A similar behavior occurs in the curves at 49 °C/60 min and 25 °C/30 min. In the 25 °C/90 min curve is present an abrupt drop of the i_{corr} after the beginning the formation of the passive layer.

PP performed on SS 17-4PH passivated in citric acid at different temperatures and times, and exposed in sulfuric acid (H₂SO₄) presented a critical current density at potentials of -330 mV, with the beginning of passive layer formation, followed by an activating that generates transpassivity and formation of a secondary passivation region. Only precipitated hardening stainless steel at 49°C shows passive layer formation with lower current demand.

The electrochemical parameters obtained from the PP are presented in Table 2. Corrosion rates of 10⁻⁷ mm/yr are observed for sodium chloride (NaCl) solution, while corrosion rate of 10⁻⁴ mm/yr for sulfuric acid is obtained.

Table 2. Electrochemical parameters obtained by PP for passivated stainless steels.

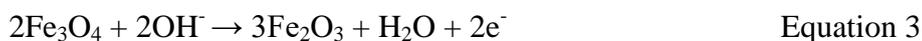
Solution	Temperature (°C)	time (s)	Stainless Steel / Corrosion Rate (mm/yr)		
			304	15-5PH	17-4PH
5wt% Sodium chloride	25	30	8.70E-07	3.50E-07	4.68E-08
		90	1.42E-06	4.46E-07	9.12E-07
	49	30	6.38E-07	5.26E-07	3.38E-07
		90	6.56E-07	4.75E-07	5.63E-07
1wt% Sulfuric acid	25	30	1.06E-04	3.41E-05	1.16E-04
		90	5.29E-05	6.41E-05	1.12E-04
	49	30	5.65E-05	8.15E-05	3.31E-06
		90	1.39E-05	6.90E-06	9.00E-05

The results indicate that the electrochemical mechanisms obtained independently of the passivating agent, temperatures and time, was mixed activation in the anodic and cathodic reactions in all systems, as well as a passivation followed by a transpassivation or secondary passivation. Cheng Man et al in 2018 [16], mentions that passivation films in stainless steels commonly have primary and secondary passive films, which are formed before and after transpassivation. These primary and secondary passive films, which are formed before and after transpassivation. The transpassivation is the phenomenon in which a passivated metal or alloy begins to dissolve rapidly if the electrode potential

becomes too noble [17-18]. The transpassive region is limited by the newly formed oxide film on the surface in stainless steel [19]; this is called secondary passivation. The investigations into passive films of stainless steels have focused mainly on the film formed in the main passive region, but little attention has been paid to the passive second film [18-21].

The dissolution of the passive layer in the anodic region gives rise to the start of transpassivation [20]. The chromium oxidation solution results from the transformation of the primary passive film to a second passive film [21-24].

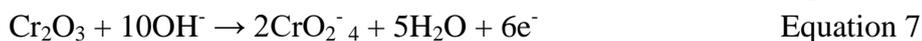
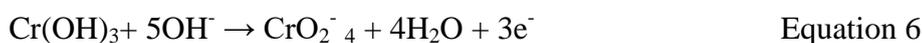
In stainless steel, the compositions of the primary and secondary passive films formed are anodic reactions during the growth of the film (oxidation of iron and chromium) [16]. The reactions of oxidation of iron in the two passive regions are similar, see equations 1 to 3 [25].



The electrochemical reactions of chromium (in the primary passive region) can be as equations 4 and 5. [25-26].



When the applied potential is in the secondary passive region, the transpassive solution of chromium is carried out according to equations 6 and 7 [17]:



The results obtained from the potentiodynamic polarization for 15-5PH and 17-4 PH stainless steels passivated in citric acid indicate a pure passive behavior.

4. CONCLUSIONS

- The electrochemical study of passivated stainless steels, has allowed to identify the formation of resistant passivation layers that were presented in the evaluation of potentiodynamic polarization in the presence of corrosive environments.
- Stable passivation layer are presented in 15-5PH stainless steel up to 360 mV. The passivation temperature is a determining factor to obtain the passive layer at 49 ° C, where a better layer is

obtained with an immersion time of 30 min in the acidic critic.

- The evaluation in sodium chloride of 15-5PH SS, presents passivation followed by a zone of transpassivity, while in sulfuric acid there is passivity-transpassivity-process of secondary passivity.
- The 17-4PH steel presented a corrosion rate of 10^{-8} mm/year, in sodium chloride at temperatures of 25 °C/30 min, having a stable passive layer at 800 mV.
- Austenitic stainless steel 304, in the different passivation conditions, presents in the electrochemical evaluation pseudo-passivation and passive degradation of the layer, having unstable passive layers.

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