

ANALYSIS OF PITTING CORROSION IN SUPER MARTENSITIC STAINLESS STEEL WITH DIFFERENT SURFACE ROUGHNESS IN SEAWATER

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ABSTRACT

Supermartensitic stainless steel (SMSS) has been used in the offshore oil and gas industry as a way to substitute the expensive duplex stainless steel, in some industrial activities that require good weldability and corrosion resistance. Therefore, in this present study, it was evaluated the pitting corrosion susceptibility of a super martensitic stainless steel, in a very corrosive environment, with different surface roughness. The pitting corrosion susceptibility of the steel, it was evaluated by electrochemical tests of cyclic potentiodynamic anodic polarization (CP) and electrochemical impedance spectroscopy (EIS), in an environment containing 190 g/L of NaCl and dissolved oxygen concentrations lower than 10 µg/L. It was also used the techniques of SEM-EDS (Scanning Electron Microscopy with Energy Dispersive Spectrometry) for superficial characterization of the steel. It was observed that the surface rough can influence, sometimes positively, in the pitting corrosion susceptibility of the studied stainless steel.

Keywords: super martensitic; stainless steel; pitting corrosion; surface roughness.

1.INTRODUCTION

The discovery of large oil and gas reserves in the Brazilian pre-salt layer caused a growing need for technological innovation in the industry. This need is stemmed from the necessity to develop materials that withstand an environment

characterized by high pressures, temperature variations, and especially severe corrosion. The corrosion process in deep water occurs due to the presence of dissolved gasses, such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S), low dissolved oxygen levels, and especially the high concentrations of chloride ions^(1,2).

In this context, to ensure better performance, have been introduced to the market a new generation of martensitic steels, called super martensitic stainless steel. The super martensitic stainless steel has been used in the offshore oil and gas industry as a way to substitute the conventional martensitic steel, providing better weldability and better resistance to corrosion than its predecessor. This characteristic is attributed to a lower carbon content and additions of molybdenum⁽²⁾. Kondo et al.⁽³⁾ (in Anselmo et al.⁽²⁾) observed a corrosion rate of around 0.1 mm/year in a super martensitic stainless steel, 10–20 times lower than the corrosion rate of conventional martensitic steel with a 13%Cr content.

Another factor favoring its use, it is the cost. The super martensitic stainless steel becomes a lower cost alternative to expensive super duplex stainless steels. Previous studies have reported the possibility of using this material in columns production and casing, saving in the cost of oil and gas production^(4,5). However, despite having better performance than conventional martensitic steel, super martensitic stainless steel suffers pitting corrosion when exposed to a high chloride ions concentration environment^(2,6). Besides the high concentration of chloride ions in solution, other factors such as surface roughness can influence the corrosive process in the material.

Combined with a high concentration of chloride ions, the surface roughness, stemmed from the manufacturing process of the steel, could act like a tension concentrator and therefore, accelerating the pitting corrosion rate of the stainless steel. In Hong and Nagumo⁽⁷⁾ study about the effect of surface roughness in pitting corrosion in Type 301 stainless steel wet-ground with different silicon carbide papers, the authors concluded that in more smooth surfaces, that is, less roughened, pits starting to grow on the surface becomes more difficult.

The analysis of the surface roughness influence in the pitting corrosion of the super martensitic stainless steel could be interesting because it is a parameter that could be monitored still in the manufacturing process. Gravalos et. al., previously studied the relation between parameters used in turning process and the pitting corrosion in a super austenitic stainless steel. The authors concluded that the lowest

formation of pitting sites was observed in the specimen with the lowest surface roughness⁽⁸⁾.

Therefore, the main goal of this study has studied the behavior against pitting corrosion of the super martensitic stainless steel with different surface roughness, in a high chloride ion and low oxygen concentration environment. In the consulted literature, there have been no studies correlating the influence of surface roughness in environments containing low dissolved oxygen concentrations ($\mu\text{g/L}$) and high concentrations of chloride ions, simulating similar conditions of the Brazilian pre-salt layer.

2. EXPERIMENTAL SECTION

2.1. Material

In this study was used samples of super martensitic stainless steel with 10 mm X 10 mm X 10 mm of dimensions taken from an offshore pipeline with 244.00 mm of diameter and 13.84 mm of thickness. The chemical composition of the material is according to the Table I.

Table I. The nominal chemical composition of the studied super martensitic stainless steel.

Chemical Composition (wt %)									
C	Cr	Ni	Mo	Ti	Si	Mn	P	S	Fe
<0,03	11,50	5,50	1,50	0,15	0,10	0,30	<0,025	0,010	Bal.

The specimens were wet-ground with 600 grit paper, welded in a covered Ni wire and after embedded in cold epoxy resin.

2.2. Electrochemical Tests Environment

To the electrochemical test, was used an electrolyte containing 190 g/L of NaCl, 0.66 g/L sodium acetate trihydrate and dissolved oxygen concentrations of $<10 \mu\text{g/L}$. Levels of oxygen dissolved in the solution have been achieved if bubbling nitrogen gas (N_2) in the electrolyte and measuring their concentration with an oxygen sensor. Finally, pH was adjusted using acetic acid (CH_3COOH) until the pH 4.00 ± 0.1 .

2.3. Surface Roughness

To measure the superficial roughness was utilized a rugosimeter with tapered tip probe and three specimens, one for each surface finish. The specimen was wet-ground with silicon carbide paper ranged from 180 grit to 360 and 600 grit and then, was realized three analyses in each specimen.

2.4. Cyclic Potentiodynamic Anodic Polarization

The tests were conducted in an electrochemical cell with three electrodes arrangement, using an Ag/AgCl (KCl 3 mol/L) electrode as a reference electrode and a platinum auxiliary electrode (Pt).

Firstly, prepared the electrolyte in a tank of work, to achieve the desired dissolved oxygen values. Subsequently, sanded the specimens with silicon carbide paper to obtain the desired surface finish. To obtain different values of surface roughness, in order to simulate roughness that can be obtained in the manufacturing processes of the studied steel, was used silicon carbide paper ranged from 180 grit to 360 and 600 grit in the surface finish of the specimens. Transferred the electrolyte from a work tank to the electrochemical cell, under a continuous flow of N₂ to keep an inert atmosphere in the electrochemical cells interior.

Before the start of sweep potential, the specimen was left submerged in the electrolyte by one-hour period, to measure the value of the open circuit potential (OCP). The analyses were performed at a sweep rate of 0.5 mV/s starting from the OCP to a potential corresponding to the current density of $5 \times 10^4 \mu\text{A}/\text{cm}^2$. The analyses were performed at a temperature of $24 \pm 3 \text{ }^\circ\text{C}$.

After the CP tests, the specimen was observed in SEM-EDS, to analyze the surface morphology of the specimens.

2.5. Electrochemical Impedance Spectroscopy Results (EIS)

In the analysis of electrochemical impedance spectroscopy, was used the same preparation processes of the electrolyte, electrochemical cell, and specimens used in the CP technique. The tests were performed at frequencies range 2 mHz to 5 kHz applying a perturbation AC potential of amplitude 10 mV, starting from the OCP value. The analyses were performed at a temperature of $24 \pm 3 \text{ }^\circ\text{C}$.

3. RESULTS AND DISCUSSION

3.1. Roughness Characterization

The values found for the superficial roughness were R_a 0.70 for 180 sandpaper grit, R_a 0.20 for 360 grit and R_a 0.04 for 600 grit.

3.2. Cyclic Potentiodynamic Anodic Polarization Results (CP)

The cyclic polarization curves obtained for the super martensitic stainless steel for each roughness is shown in Figure 1. Through the cyclic polarization curves, is possible analyze some parameters that could indicate the pitting corrosion behavior of the studied material, in each condition of surface finish utilized. In a first moment, it's possible clearly observe that the surface roughness interferes directly in the material behavior in the evaluated conditions. It can be seen that with decreasing surface roughness value, there is an improvement in the behavior of the material front to pitting corrosion. This improvement in the behavior of the material is perceived, between the analyzed parameters, an increase in E_p (the pitting potential was defined in this paper as an inflection point where a sharp increase in current density occurs) value with maintenance near values on the E_{corr} . The increase in the E_p agree that decreasing the roughness was shown also in Figure 1. Similar results for Type 301 and 304 stainless steel were obtained for other authors^(7,10,11). Furthermore, was observed an increase in the extension of the passive layer as long reduces the superficial roughness.

This behavior may be associated that the fact the superficial roughness may act like a tension concentrator, which can destabilize and accelerates the passive film breakdown. The roughness could have a strong effect on the number of sites available for metastable pitting that subsequently can keep growing⁽⁷⁾. According to the work of Burstein and Pistorius⁽¹¹⁾, a smoother surface can reduce the number of metastable pitting, in this way, the total number of sites that could become a stable/growing pitting reduces agree that reduces the superficial roughness.

The values of the analyzed parameters are shown in Table III.

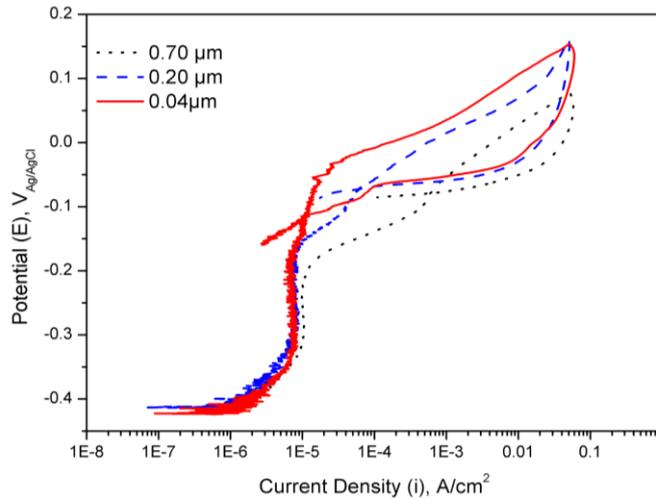


Figure 1. Polarization curves obtained for each surface finish in 190 g/L NaCl and dissolved oxygen <10 µg/L

Table III. Analyzed parameters obtained in the cyclic polarization curves for each surface finish in 190 g/L NaCl and dissolved oxygen <10 µg/.

Roughness R_a (μm)	E_{corr} (mVAg/AgCl)	E_p (mVAg/AgCl)	E_{rp} (mVAg/AgCl)	i_{pass} ($\mu\text{A}/\text{cm}^2$)
0.70	-415±4	-187±4	-	8.94±0.93
0.20	-413±3	-165±2	-	7.8±0.69
0.04	-422±4	-68±18	-114±48	7.52±0.95

It is observed in Figure 1, to the higher surface roughness R_a 0.7 μm and 0.2 μm , when the potential scan direction was reversed, the forward and backward curves crossed each other in a region above the E_p and in a high current density region above the passivation current density (i_{pass}). Some authors portray the area above the pitting potential as an active corrosion zone, where new pitting are nucleated and remain growing⁽¹²⁾. Besides, this hypothesis can be sustained for an approach with the E_{rp} (repassivation potential). The E_{rp} can be determined as a cross-over potential, which the forward and the backward curves cross each other⁽¹³⁾, and be defined as a potential which the current density returns to the passive value⁽¹⁴⁾. Næss⁽¹⁵⁾ define the E_{rp} as the potential where the material comes back to a passive state after pits have been formed. Therefore, it is suggested that for these rough surface finish, there was no repassivation of the analyzed material, considering that the forward and the backward curves do not cross in the passivation current density region. For this reason, there is not possible to determinate the E_{rp} value for this surface finish in Table III.

The same behavior is not observed in the cyclic anodic polarization curve for the specimen with a surface roughness R_a 0.04 μm . In this surface finish, when the

potential scan direction was reversed, the forward and backward curves crossed each other in the passive region of the polarization curve, a fact that characterizes the repassivation of the material and the possibility to determinate the E_{rp} . Some author portrays the region between the E_{rp} and the E_{corr} , as a region where pits will neither initiate and propagate^(12,14). The cyclic potentiodynamic anodic polarization results suggest that super martensitic stainless steel showed improved corrosion resistance when tested with a surface roughness R_a 0.04 μm .

After the end of each test the specimens were observed in the SEM (scanning electron microscopy) to verify the existence of pitting in the surface. Was observed pitting on the surface of all specimens after the CP, as shown in Figure 3.

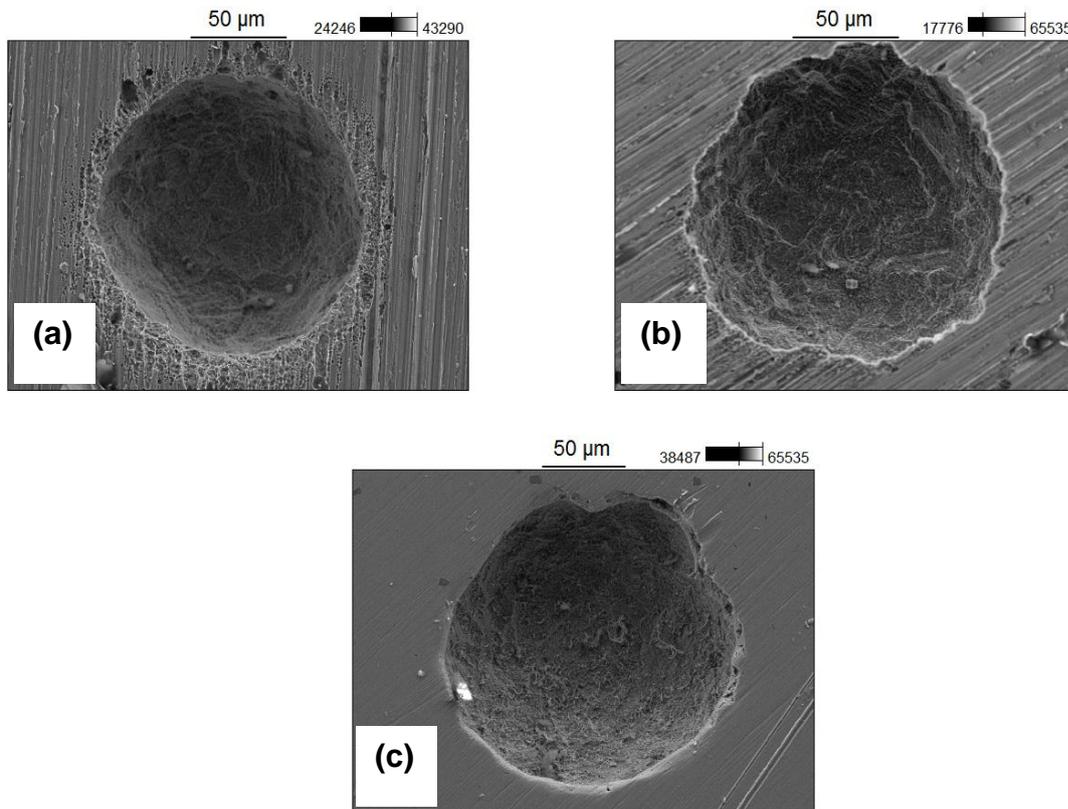


Figure 3. SEM image of the super martensitic stainless steel after the cyclic anodic polarization in 190 g/L NaCl and dissolved oxygen <10 $\mu\text{g/L}$. (a) 0.70 μm . (b) 0.20 μm . (c) 0.04 μm

It was still observed through the EDS (energy dispersive spectrometry) the presence of titanium precipitates in the periphery (Figure 4 (a)) and inside (Figure 4 (b)) the most of the analyzed pitting.

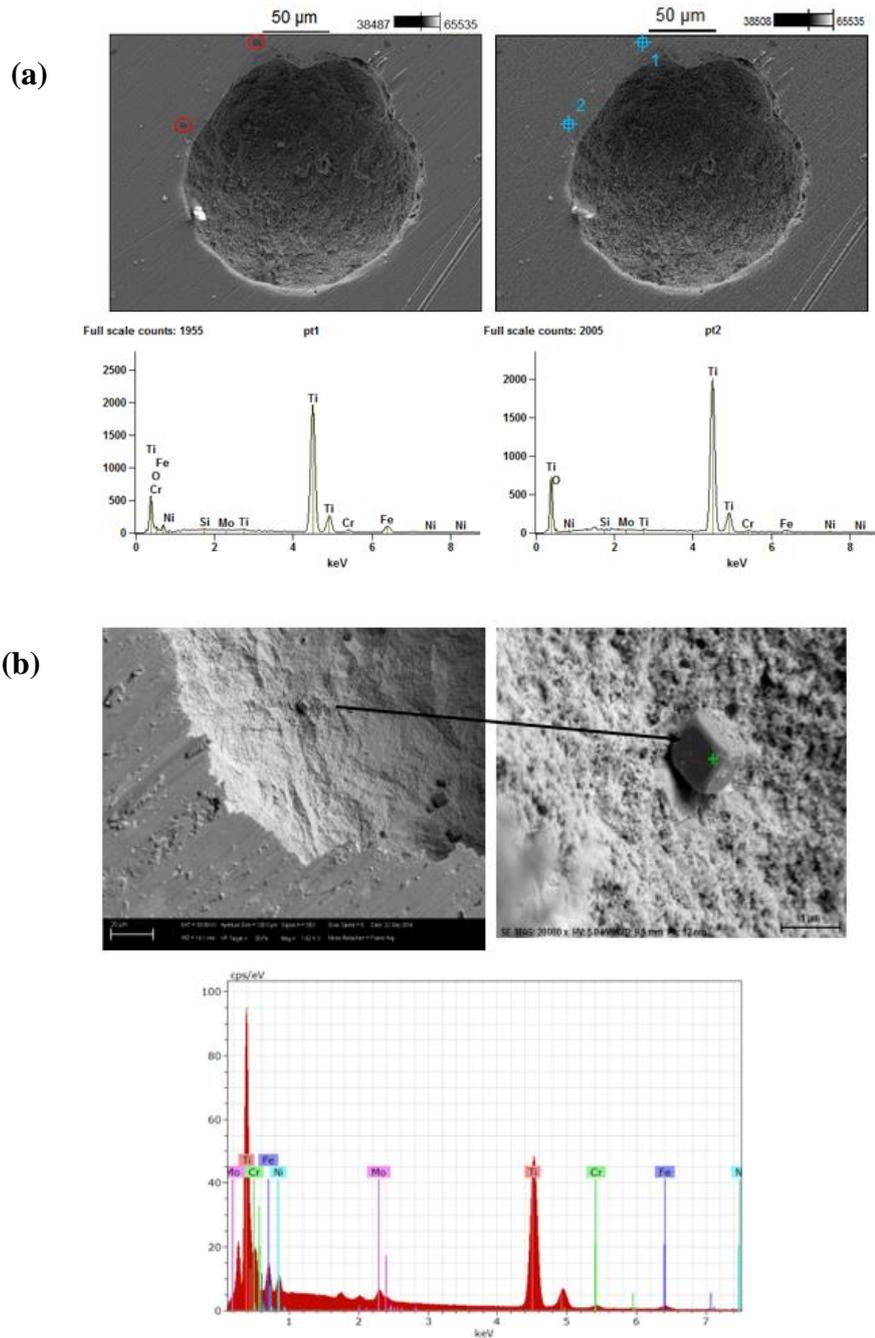


Figure 4. SEM-EDS analysis of the titanium precipitated on the surface of the super martensitic stainless steel after the cyclic anodic polarization in 190 g/L NaCl and dissolved oxygen <math>< 10 \mu\text{g/L}</math>. (a) the periphery of pitting. (b) inside pitting.

This behavior was also reported by Leban and Tisu⁽¹⁶⁾. The authors concluded in their study that probably the initiation of pitting occurred in areas with the presence of titanium precipitated on the surface of the material analyzed. Such precipitates would act as a cathode compared to steel and therefore accelerating the breakdown of the protective passive film.

3.3. Electrochemical Impedance Spectroscopy Results (EIS)

It is shown in Figure 5 a comparison between the Nyquist diagram results obtained for the super martensitic stainless steel for each roughness, and the fitting results simulated computationally through the equivalent circuit. The equivalent circuit obtained in the computational fitting is shown in Figure 6.

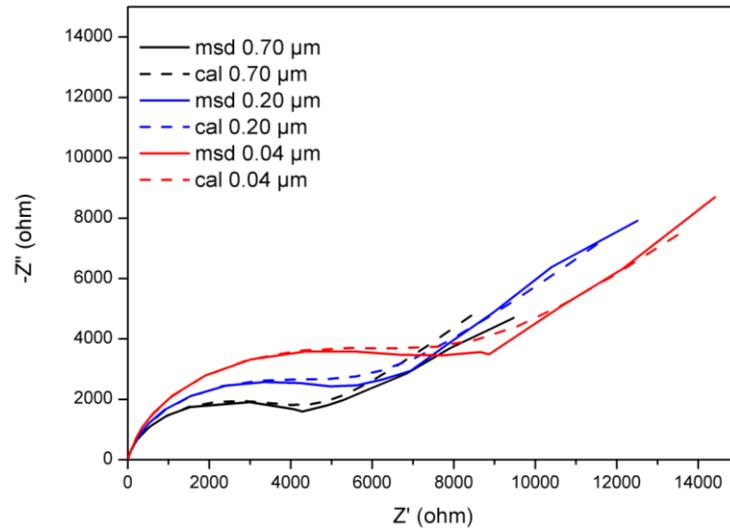


Figure 5. Comparison between the Nyquist diagram results obtained in the EIS analysis, and the fitting results simulated computationally in 190 g/L NaCl and dissolved oxygen <math><10 \mu\text{g/L}</math>. msd = measured; cal = fitting

It is observed in the equivalent circuit (Figure 6) the presence of some elements. The “Q” element as named constant phase element. This element has the function to compensate the inhomogeneity of the corrosive system. The “W” element is called the Warburg impedance and he is related to mass transfer by diffusion in the corrosive process. In the Nyquist diagram, this element is characterized by a rectilinear stretch, forming an angle of 45° with the real axis. The R_e (electrolyte resistance) is associated with resistance to current flow in the electrolyte, while the R_{tc} (charge transfer resistance) is associated with the load passage resistance at the electrode/electrolyte interface, which determines the rate of reaction corrosion⁽¹⁷⁻¹⁹⁾.

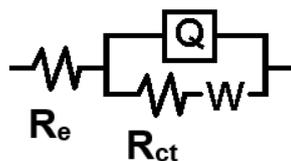


Figure 6. Equivalent circuit obtained fitting the EIS results computationally.

In the Table IV are shown the main parameters obtained after the simulation of the equivalent circuit.

Table IV. Analyzed parameters obtained in the fitting of the EIS results for each surface finish in 190 g/L NaCl and dissolved oxygen <10 µg/.

Roughness R_a (µm)	OCP Ag/AgCl (mV)	R_e (Ohm.cm ²)	CPE (mΩ ⁻¹ .cm ⁻² .s ^α)	α	R_{ct} (Ohm.cm ²)	W (mΩ ⁻¹ .s ^{1/2} .cm ⁻²)
0.7	-417	4.00	0.150	0.886	4046	1.34
0.2	-419	4.00	0.142	0.887	5123	0.87
0.04	-410	4.00	0.114	0.887	7237	0.69

Through the fitting results shown in Table IV, it is observed that the capacitance values of the CPE, which would be the electric potential energy stored in a capacitor, decrease agree that it decreases the surface roughness. According to Alves et al.⁽²⁰⁾, the corrosive process can be associated with the system capacitance. Higher capacitance values of the electrode/electrolyte interface, indicate a higher electric charging of the electric double layer formed, coming from charge exchange with the metal surface. This behavior indicates that for higher values of capacitance, the corrosive process on the surface of the analyzed material occurs with greater speed and, therefore, smaller capacitance values indicate that the surface has suffered a less aggressive corrosive attack. It also observes that the decreasing in the superficial roughness value caused an increase in the charge transfer resistance value (R_{ct}) of the metal surface. The charge transfer resistance is associated with resistance to charge passage at the interface electrode/electrolyte, which determines the corrosion rate of reaction and, according to Wolyne⁽¹⁷⁾, the increase in value means that the corrosive process decreases. Therefore, the parameters obtained in the simulation of the equivalent circuits one more time suggest that super martensitic stainless steel showed improved corrosion resistance when tested with a surface roughness R_a 0:04 µm, confirming what had been previously observed in cyclic potentiodynamic anodic polarization tests.

4. CONCLUSIONS

In summary, this study sought to evaluate the surface roughness influence in the pitting corrosion of a super martensitic stainless steel in a high chloride ion and

low oxygen concentration environment. In general lines, it was possible to verify the clear influence of the variation of surface roughness in pitting corrosion behavior of the material studied.

Was verified that the decrease in the surface roughness value, makes the studied steel less prone to pitting corrosion. It was observed that the studied super martensitic stainless steel, with surface roughness Ra 0:04 μm , showed lower susceptibility to pitting corrosion in all conditions studied. It was also observed that for this surface roughness was the only condition in which, after the formation of pitting, occurred the repassivation, i.e., there was the formation of a new passive layer inside the pitting.

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