



BEHAVIOR OF CREVICE CORROSION COUPLE AISI 420-316 IN FUNCTION OF SURFACE

Rogério Breganon
Gismar Schilive de Souza

Instituto Federal do Paraná – Câmpus Campo Largo. Rua Engenheiro Tourinho, 829, Vila Solene, CEP 83607-240, Campo Largo, Paraná, Brasil.
rogerio.breganon@ifpr.edu.br; gismar.souza@ifpr.edu.br

Ricardo Kertscher

Instituto Federal do Paraná – Câmpus Campo Largo. Rua Engenheiro Tourinho, 829, Vila Solene, CEP 83607-240, Campo Largo, Paraná, Brasil.
ricardo.kertscher@ifpr.edu.br

Anselmo Fabris

Instituto Federal do Paraná – Câmpus Campo Largo. Rua Engenheiro Tourinho, 829, Vila Solene, CEP 83607-240, Campo Largo, Paraná, Brasil.
anselmo.fabris@ifpr.edu.br

Abstract. *Although the stainless steel alloy has high chromium content, it is subject to the crevice corrosion process, mainly with the saline process. The stainless steel alloys has a wide industrial application in the petroleum area, justifying the research effort in order to optimize the use of these alloys. Although the Fe-C-Cr corrosion resistance, pitting processes and localized corrosion such as crevices due to stagnation of fluids between two surfaces lead to material failure. The study includes the mechanical characterization of surface hardness, surface roughness characterization by interferometry and by contact and estimation of corrosion rate by weighing. The experiments with crevice corrosion in stainless AISI 420-316 are performed with saline simulations moving closer to the actual condition. The mass loss per unit time caused by corrosion will be verified statistically correlated with the main variable, which is the surface finish for samples prepared in three different states.*

Keywords: *crevice corrosion, pitting, surface finishing, stainless steel, AISI420*

1. INTRODUCTION

The crevice corrosion phenomenon has been one of the most serious problems when using stainless steel in chloride containing environments, as in the case of actual use of the components in a marine environment. To minimize and prevent crevice corrosion, it is possible to take some preventive measures such as structural modification in design improvement, improving the environment and the material selection.

Taking material selection with minimum resistance to crevice corrosion in a given environment into consideration, it is known that an increase in the content of alloying elements such as Cr, Mo and N (except for ferritic steels) improves the crevice corrosion resistance. Some stainless steels with high content of Cr, Mo and N have been developed in order to minimize corrosion crevice (AZUMA et. Al, 2004).

According to the corrosive medium and material, different corrosion mechanisms can be presented to the corrosive processes, which can be detached chemical or electrochemical mechanisms. In electrochemical, corrosion in water or aqueous solutions, atmospheric corrosion, pitting corrosion in the ground and molten salts. In chemical, corrosion-free organic solvents in water and corrosion of non-metallic materials. For the case of the electrochemical mechanism, electrons are transferred in a given region and received on another, resulting in a pile of corrosion (Gentil, 1987).

The corrosion processes are heterogeneous chemical or electrochemical reactions occurring at the surface of the separation between the material and the medium. Corrosion can occur in different forms, the most frequent being uniform for plates, alveolar, pitting, intergranular, thready and exfoliation (Gentil, 1987). In the case of ad hoc type of corrosion, it is a very common problem for stainless steels and one of the main causes for this undesirable phenomenon which can be attributed to the presence of impurities. One way to quantify the resistance to localized corrosion is to use the number of pitting resistance equivalent (PREN), it can be used to Equations (1) and (2) in accordance with LO et al (2009).

$$PREN_{16} = \%Cr + 3.3 \times \%Mo + 16x \%N \quad (1)$$

$$PREN_{30} = \%Cr + 3.3 \times \%Mo + 30x \%N \quad (2)$$

Breganon, R.;Souza, G.;Kertscher, R.
Behavior of crevice corrosion couple AISI 420 – 316 in function of surface

Equation (3) PREN has been proposed as a new equation to consider the effect of the presence of the elements Mo and N jointly in the alloy. In general, the PREN can be considered an effective parameter for evaluating the behavior pitting and crevice.

$$\text{PREN} = \%Cr + 3.3\%Mo + 51\%N + 6\%Mo * \%N - 1.6(\%N)^2 \quad (3)$$

Due to the destructive nature of corrosion, it is needed to check the consequences and the selection of materials suitable for applications in various processing plants to piping and other equipment. Therefore, corrosion tests are used to better understand these effects. With the wide range of environments and test conditions that can be found and used in conducting laboratory tests, it is clear in the test by immersion, being an essay simple and easy to perform and can provide relevant results (BROSSIA, 2005).

The immersion test consists by wrapping a material interest in an environment of immersion condition. The main advantage is that with minimum effort and equipment, a wide range of conditions and materials can be evaluated simultaneously. As the immersion tests are common, there are a number of standardized procedures which have been developed and published and are often used to quantify the effects of corrosion. The most widely used criteria are appearance (such as the sample appearance before and after the test) and weight change. The methods used are appearance (such as the sample appears before and after the test) and weight change. For the most part, the standard method used for testing also includes information on evaluation and pass/ fail criteria. In addition, there are a number of procedures for evaluating relevant standard, including ASTM G46 and ASTM G1 (BROSSIA, 2005).

Some evaluation processes tend to be specific to a type of corrosion. For example, the ASTM G31 (change or weight loss) which may be applicable to any mode or type of corrosion and the corrosion rate converted to mass per time (mm/ year) via Equation (4) (BROSSIA 2005).

$$CR \left(\frac{mm}{y} \right) = \frac{8.76 \times 10^4 W}{At\rho} \quad (4)$$

Where CR= corrosion rate in mm/y
W = mass loss in g
A = exposed area in cm²
t = time in hours
ρ= material density in g/cm³

However, the measurement of the weight loss will lead to an underestimation of the corrosion rate of localized corrosion is true is the dominant mechanism of corrosion. This arises because of a localized corrosion rate tends to be higher than the rest of the material surface. These situations result in negligible change in the weight of the sample, making it difficult to interpret and extrapolate performance data. To overcome this, ASTM G31 recommends a minimum duration for the test, given by Equation (5), the corrosion rate in mass per time (BROSSIA, 2005).

$$\text{TestTime}(h) \approx \frac{787.4}{CR \left(\frac{mm}{yr} \right)} \quad (5)$$

Thus, taking the corrosion rate (CR) obtained in mm/year and considering the minimum recommended test of 787 hours or approximately 32 days may calculate the minimum test. Corrosion rates are generally small, requiring longer times of testing to verify its accuracy (BROSSIA, 2005).

In the case of alloy steels, the chromium addition considerably increases the resistance to oxidation and corrosion. Steels with levels above 12% chromium are called stainless steels, which are of great interest for engineering, depending on their oxidation resistance, mechanical properties at elevated temperatures and tenacity. The composition most common stainless steels have, for example, are 12% to 18% Cr and 8% Ni.

For purposes of classification and discussion of its properties, stainless steels are grouped into five categories: martensitic, ferritic, austenitic, ferritic - austenitic (duplex) and precipitation hardening. The martensitic steels are alloys of iron and chromium (11-18%) with a carbon content above 0.1%, where high chromium content produces very high hardenability and increasing the temper softening resistance, while the alloy is austenitic iron chromium (16-30%) and nickel (8-35%) after predominantly austenitic heat treatment, characterized by good corrosion resistance, high toughness and good weldability.

The aim of this study is to investigate the behavior of crevice corrosion pair of stainless steel AISI 420-316 as a function of surface finish, using test environments of total immersion in seawater with a flow forced by a small centrifugal pump. Surface finishes used in the samples were: sanding, polishing and machining state as obtained by turning. The effect of oxide formation at the interface (between the sample surfaces) after the test time is checked by measuring the weight loss.

2. MATERIALS AND METHODS

In this study we used two steel representatives of two families of stainless steel, and austenitic stainless steel AISI 316 and AISI420 martensitic with standardized chemical compositions shown in Table (1). After microhardness Vickers measurement using a load of 300gf 10s top indentation in the samples, an average value was obtained for the AISI 316 $269 \pm 3.2\text{HV}_{0.3}$ and the AISI 420 $273 \pm 2.0\text{HV}_{0.3}$, both the delivery condition.

Table 1. Chemical composition of stainless steels used, AISI 316 and AISI 420.

	Chemical Composition			
	% C	% Cr	% Ni	% Mo
AISI 316	0.08 max.	19	10	2.50
AISI 420	0.20	13	-	-

For this study, we used samples with 12.7 mm diameter and a length of 15mm cut using cutoff Fortel CF I, following preparations with three different surface finishes after hot inlay. The first sample was machined by turning conventional carbide tools, after which the sample was embeddable cut, the first condition resulting surface finish analysis.

The second after cut sample passed by manual sanding with three different grits, and 220/400/600, sequentially, with an inclination of 90 each. The third after sample cut went through the process of manual sanding with grits described above, and then polished mechanically with alumina 1μ for 15 min with rotation 400 rpm. This entire process was repeated for a batch of samples distributed according to the requisites addressed in the study, taking into account the homogeneity of the sample.

To check the surface finish, we utilized primarily a contact profilometer portable 2D model TR200 TIME, followed by characterization by interferometry in 3D profilometer Talysurf CCI Robson Taylor for mapping the surface for a sample area of 0.8 mm^2 at the center of each sample. It is an important mapping morphological surface, since the study of the behavior correlates crevice corrosion due to processing, and therefore the roughness to different sample pairs, considering the loss in mass.

For the immersion corrosion test, we used a galvanic cell constructed of polycarbonate 170 x 280.5 x 180.7 mm (width x length x height), with 9.06 liters of seawater from the coast of Paraná. It is important to stress, and as can be seen in Figure (1) an overview of the corrosion cell, which was used using a small centrifugal pump 12V DC engine to maintain a constant flow and movement of the test solution, avoiding the difference in oxygen concentration in the solution.

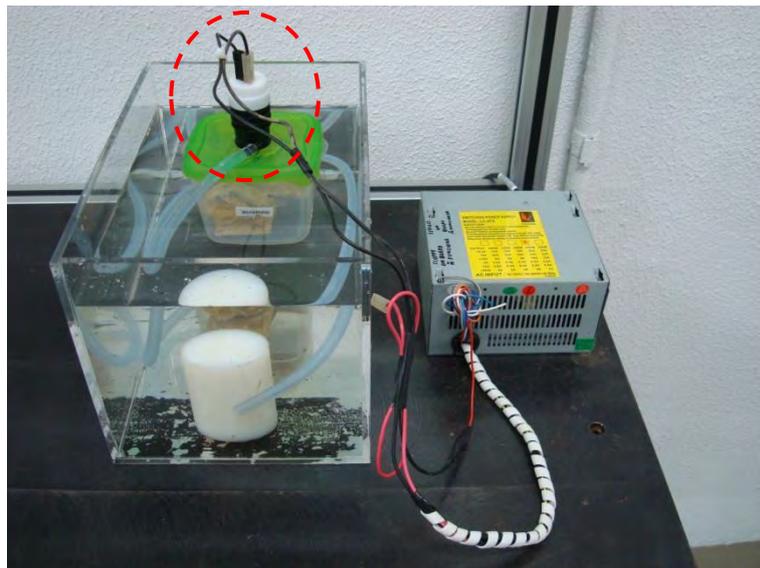


Figure 1. Corrosion cell in overview, highlighted the centrifugal pump circulating electrolyte.

The distribution of the immersion test in galvanic cell with a replica thereof is mounted between pairs of alloys, AISI 316 and AISI 420, forming pairs for lifting mass loss after crevice corrosion process. Then there is the following:

- 1) machined surfaces: 316/316, 316/420, 420/420;
- 2) sanded surfaces: 316/316, 316/420, 420/420;
- 3) polished surfaces: 316/316, 316/420, 420/420;

Breganon, R.;Souza, G.;Kertscher, R.
Behavior of crevice corrosion couple AISI 420 – 316 in function of surface

Under pre-test assuming a critical situation finishing state as sectioned assaying for the time recommended by ASTM G31, 32 days. There was a test shorter than 8 days in the case, leading to a satisfactory quantitative results, this fact can be attributed to the constant movement of the solution during the entire time of the test.

For verification of mass loss, we used JKI an analytical balance, making measurements of the mass of oxide of respective pairs after the process of mechanical removal by scraping manually with the aid of a blade.

3. RESULTS AND DISCUSSION

The results obtained are correlated to surface morphology as a function of the finishing process and the etch rate due to loss of mass. Additionally, roughness is considered 2D and 3D surfaces in the macro aspect of the form of corrosion of alloys pairs.

3.1 Loss of mass

The results of weighing the oxides removed using an analytical balance of the pairs is shown in Table (2) as a function of surface finish.

Table 2. Loss of weight average three measurements as a function of the roughness of the samples.

Finish	AISI 420-AISI 420 (g)	AISI 420-AISI 316 (g)	AISI 316-AISI 316 (g)
Turning	0.035	0.078	0.015
Sanding	0.033	0.044	0.015
Polish	0.078	0.043	0.013

3.2 2D roughness

The results of the measurement of surface roughness by contact on line 2D is shown in Table (3) as a function of the roughness of each alloy.

Table 3. Surface roughness of the samples of AISI 316 and AISI 420, cutoff of 0.8mm and RC filter. ISO standard.

Alloy	Finish	Ra (μm)	Rq (μm)	Rz (μm)	Rt (μm)	Rsm (μm)
AISI 316	Sanding	0.111	0.158	0.848	1.700	0.118
	Polish	0.383	0.511	2.180	3.859	0.571
	Turning	0.833	0.973	3.372	5.679	0.500
AISI 420	Sanding	0.143	0.183	0.976	1.240	0.032
	Polish	0.054	0.067	0.207	0.379	0.500
	Turning	3.770	4.440	17.070	25.280	0.333

3.3 3D roughness

The results of the 3D roughness measurement by interferometry are shown in Table (4).

Table 4. 3D surface roughness of the samples of AISI 316 and AISI 420 for an area of 0.8 mm².

Alloy	Finish	Sq (μm)	Sz (μm)	Sa (μm)	Sds (μm)
AISI 316	Sanding	0.2199	1.7590	0.1677	12377
	Polish	0.0736	0.4234	0.0598	13633
	Turning	1.1970	10.260	0.8523	14126
AISI 420	Sanding	0.3358	2.3510	0.2611	14533
	Polish	0.0799	0.4570	0.0632	13433
	Turning	8.680	42.710	7.1070	14456

The result of mass loss for the pairs tested showed some dependence on surface finish, this can be due to some outstanding images of 3D surface topography for the most critical cases, which occurred for the couple AISI 316-AISI 420, in finish by sanding and turning.

As the result of the topographic surface produced by lathing depends on the process parameters, and they may have not been optimally selected, the resulting surface shown in Figure (2) demonstrates that the surface was left with deep

22nd International Congress of Mechanical Engineering (COBEM 2013)
November 3-7, 2013, Ribeirão Preto, SP, Brazil

grooves, in which crevice corrosion conditions aggravate the situation, because it would create microslot with the ideal plan of the interface region of stagnant electrolyte.

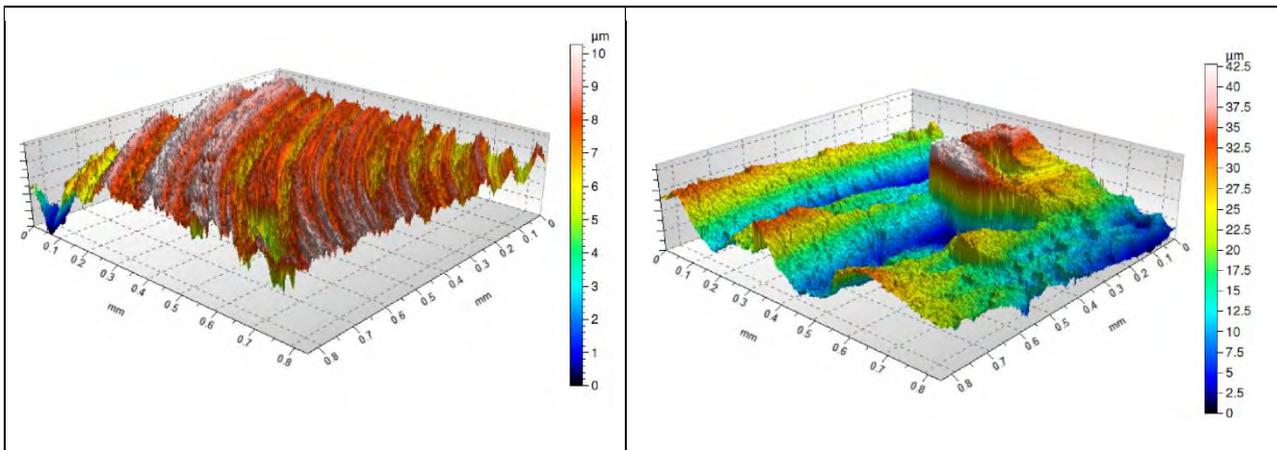


Figure 2. The left surface topography of AISI 316 and AISI 420 right, both turned.

The result obtained by sanding the surface in terms of surface finish parameters, has values close to those produced by the polished surface. In Figure (3) it is possible to observe the surface topography resulting from sanding performed on the samples.

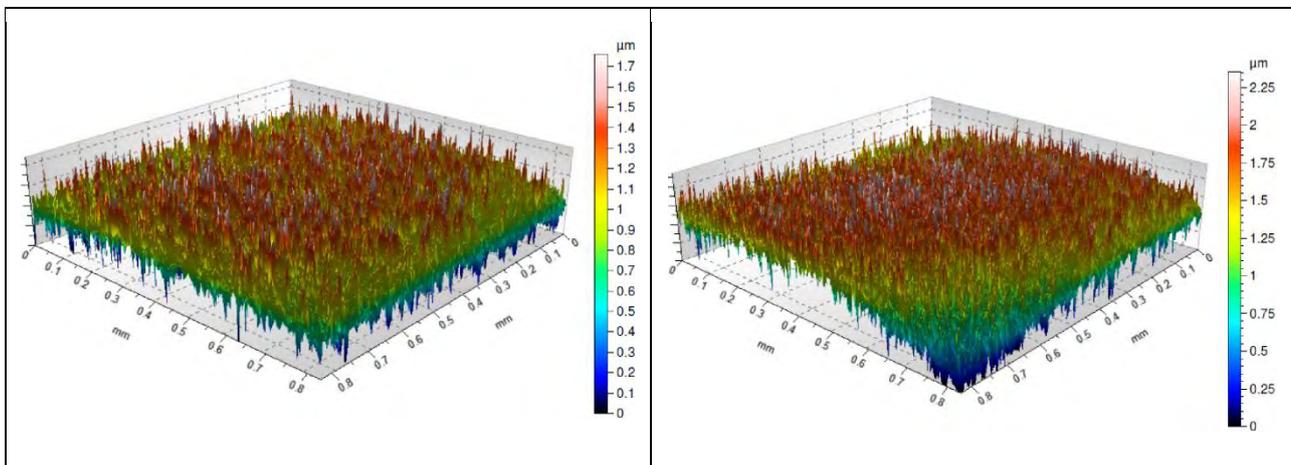


Figure 3. The left surface topography of AISI316 and AISI420 right, both sanded.

Regarding the surfaces obtained by polishing, it is possible to observe in Figure (4), which was the best result proven by the parameter values of root mean square deviation 3D (S_q) Table (4).

Performing a quick interpretation of Figures (2) and (3), it can be seen that there is a large difference in distances between the peaks and valleys of the asperities between the condition of turning and the condition sanded, indicating that regardless of the electrolyte, there is a greater gap in pairs obtained by turning than those obtained by sanding.

Breganon, R.;Souza, G.;Kertscher, R.
 Behavior of crevice corrosion couple AISI 420 – 316 in function of surface

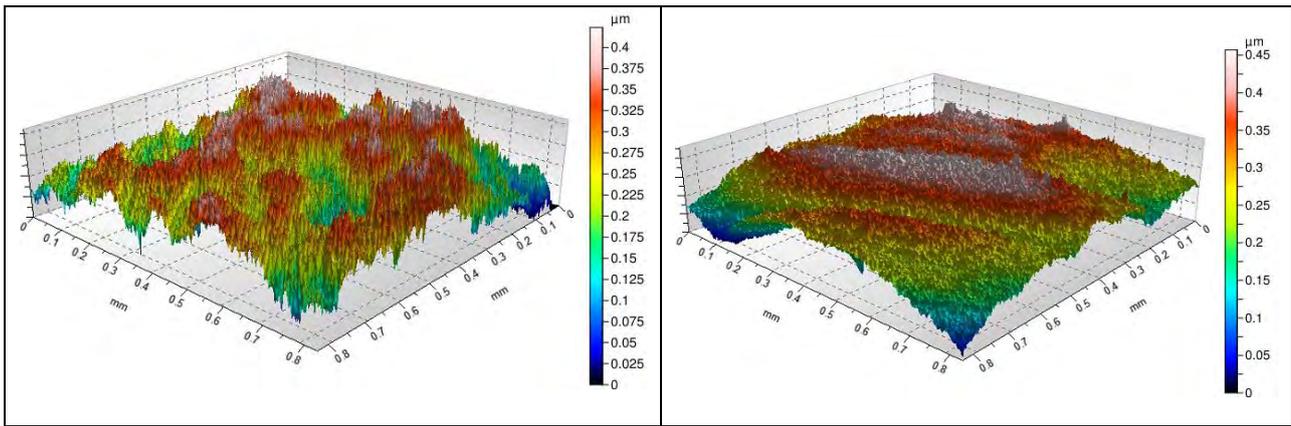


Figure 4. The left surface topography of AISI316 and AISI420 right, both polished.

3.4 Appearance Corrosion

The macro pairs set in the corrosion cell may be seen in Figures (5) and (6), and Figure (5) on the samples finished by turning, and Figure (6) on the sanded and polished samples.

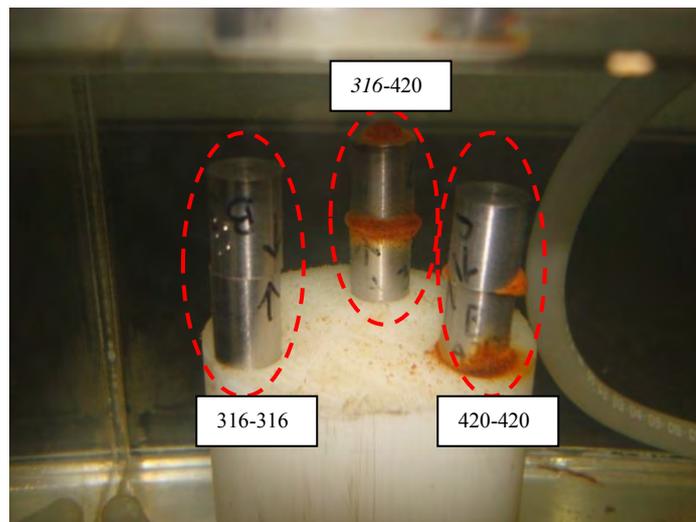


Figure 5. Corrosion cell with peers and finish by turning.

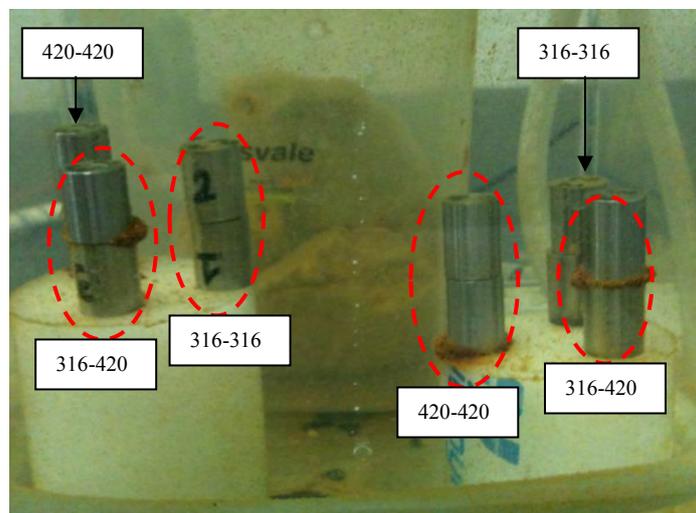


Figure 6. Corrosion cell with pairs of samples. Finish by sanding and polishing left image, right image.

It is possible to see in Figures (5) and (6), pairs of AISI 316-AISI 316, regardless of the state of the surface finish, do not form metal oxide-metal interface. The only traces of corrosion were found in the interface of AISI 316 alloy billet with the polymer, which values are shown in Table 2, for the case of polishing a loss of 0.013g, and machined and polished to 0.015g loss.

In Figure 7 it can be seen for the case of AISI 316, AISI 316 that after completion of the test and complete drying of the sample, by separating the two surfaces samples show no apparent corrosion.

The non-occurrence of corrosion at the interface AISI 316, AISI 316 comes from meeting with the measure of pitting resistance equivalent obtained by calculating the PREN for alloys as a function of alloying elements. Performing the calculation for the two alloys used in the assay using Equation (1) more conservative, based on the values of Table (1), was obtained for a value of AISI 420 PREN= 13.0 and the value for the AISI 316 of PREN=29.01. It is found that the value of PREN for AISI 316 is more than double the value of AISI 420, indicating that he has great ability to withstand localized corrosion, which occurred soon in interface AISI 316-AISI 316 and AISI 316 with polymer support within the corrosion cell goes against the expected value PREN calculated.



Figure 7. Interface AISI 316 - AISI 316 polished.

The corrosion behavior for each surface finish is given to the following conditions turning in Table (5) sanding table (6) and polishing in Table (7).

Table 5. Aspect of corrosion of the alloys pairs of the finish obtained by turning.

Pair of samples	Aspect macroscopic
AISI 420 – AISI 420	Oxide formed at the interface of the pair metallic and oxide formation on the aperture with the polymer
AISI 420 – AISI 316	Large amount of oxide formed by the metal into the gap and on top of the sample AISI 420
AISI 316 – AISI 316	There was no formation of the oxide-metal interface meta, only the crevice with the polymer

Table 6. Appearance of corrosion of the alloys to couple to the finish obtained by sanding.

Pair of samples	Aspect macroscopic
AISI 420 – AISI 420	Oxide formed at the interface with the polymer
AISI 420 – AISI 316	Large amount of oxide formed at the interface of the metallic pair
AISI 316 – AISI 316	There was no formation of metal oxide in the pair, but there forming the interface with the polymer

Table 7. Aspect of corrosion of the alloys to the alloy pairs of the finish obtained by polishing.

Pair of samples	Aspect macroscopic
AISI 420 – AISI 420	Oxide aperture formed in the pair and the interface with the polymer, besides the above surface
AISI 420 – AISI 316	Large amount of oxide formed at the interface of the metallic pair
AISI 316 – AISI 316	There was no formation of metal oxide in the pair, but there forming the interface with the polymer

The macroscopic appearance of corrosion summarized in Tables (5), (6) and (7) associated with the measured values of mass loss by the pair metallic indicated in Table (2). A value obtained and presented outstanding value, was the mass loss presented by the AISI 420 AISI 420 pair, state polished loss did not occur in the metal-metal interface as can be seen in Figure (6), but the interface with the polymer.

The PREN value of AISI 420 already indicates strong susceptibility to localized corrosion, combined with the proviso resulting gap between metal and polymer finishing function of the lower interface of the sample and later have been obtained by turning, so that they stay with the base upper and lower parallel, this causes sizeable gaps between polymer and metal, resulting in intense corrosion process.

Watching what occurred at the interface of AISI 420 samples with the polymer both in Figure (5) as in (6) and considering the appearance of the surface topography via dimensional analysis, noting that the parameter Ra is the arithmetic average of the absolute values of the peaks and valleys of the profile relative to its median plane, and Sq, which is the square root of the arithmetic mean of the squares of the deviations from the median plane relative profile, it turns out that the values of Rq obtained by turning and Sq are the largest, and correlating with Figure (2) indicates that these surfaces will mostly stagnant fluid and provide an ideal environment for the mechanism of crevice corrosion. Performing the calculation of corrosion rate using Equation (4) for the pairs and conditions tested, the values found in Table (8). In this calculation the density was used as an average value between the AISI 420 and AISI 316.

Table 8. Corrosion rate calculated for the pairs and conditions tested.

Finish	AISI 420-AISI 420 (mm/year)	AISI 420-AISI 316 (mm/year)	AISI 316-AISI 316 (mm/year)
Turning	1.596	3.556	0.684
Sanding	1.504	2.006	0.684
Polish	3.556	1.960	0.593

It is possible to verify that the AISI 420, due to lower PREN, have a high rate of pitting and crevice, highlighting the case of the critical interface between the pair AISI 420 AISI 316, where the martensitic stainless steel suffers much greater surface degradation and mass loss. With respect to the pair AISI 420, AISI 420 interface polished, high corrosion rate of 3.556 g/year occurs at the interface with the polymer, no metal-metal interface.

In the case of AISI 420, AISI 316 critical, provided that larger roughness value for the finish turning, it has a higher rate of corrosion due to difference in chemical composition, non-presence of nickel and molybdenum which results in a value of PREN down to the front of the AISI 420 AISI 316, takes a large mass loss in martensitic steel in this way, it proves that care must be taken in selecting materials that will work in media containing chlorides and care at the time to undertake projects related to the presence of cracks and contact dissimilar materials which leads to galvanic pairs.

4. CONCLUSION

The corrosion processes are heterogeneous chemical or electrochemical reactions occurring at the interface between the material and means. In the case of this research, our purpose was to study the mechanism of fractures, which is a serious problem when using stainless steel in environments containing chloride.

In the study, we used as reference ASTM G1, G46 and G31, considering the corrosion test verification in total immersion in the case using seawater from the coast of Paraná state, the test was modified according to the fluid in motion, which allowed the acceleration in the process to obtain significant results 8 days, which otherwise would take 32 days.

Regarding the variables involved, the two alloys with different resistances to localized corrosion and the evaluated PREN by three different surface finishes, it is found that due to the higher resistance presented by the stainless steel AISI316, it has the lowest corrosion rates (mm / year), regardless of the condition of finish. Overall, the most critical case occurs when it forms a galvanic interface due to the difference in chemical composition case AISI316-AISI420, observed when higher rates of corrosion occur.

22nd International Congress of Mechanical Engineering (COBEM 2013)
November 3-7, 2013, Ribeirão Preto, SP, Brazil

Considering the surface finish, the condition of the critical surfaces are machined, which have deep grooves oriented, creating microfractures with the ideal plane, and stagnation region electrolyte, which is confirmed by higher rate of corrosion at the interface obtained by machining.

Thus, it is clear that preventive measures should be taken to avoid fractures in designs where present and to minimize galvanic pairs, with the most similar materials as possible, since it tends to aggravate the process of mass loss through corrosion means in the presence of chloride, in which case many stainless steels and industrial components are subjected.

5. ACKNOWLEDGEMENTS

The PROEPI / IFPR and CNPq for their cooperation and encouragement in research activities, with the support of scholarships for undergraduate research by edict No. 001/2013, INSTITUTIONAL SCHOLARSHIP PROGRAM INITIATION OF SCIENTIFIC JR (PIBIC-Jr) and also for the financial support research by edict No. 007/2013, PROGRAM OF INSTITUTIONAL RESEARCH SUPPORT (PIAP).

The UTFPR - Campus Curitiba the availability of equipment for measuring roughness 3D.

The Laurita Lara Sarneski, Scholar Institutional Program for Scientific Initiation Scholarships Junior (PIBIC-Jr) of IFPR for their cooperation in the preparation of the sample surfaces and 2D roughness measurement.

The People management collaboration in the experiments.

6. REFERENCES

- Azuma S., Kudo T., Miyuki H., Yamashita, M., Uchida H., 2004. "Effect of nickel alloying on crevice corrosion resistance of stainless steels". *Corrosion Science*, 46, p. 2265–2280.
- Brossia Sean, 2005. "Handbook of Environmental Degradation of Materials". p. 47-63.
- Gentil, V. *Corrosão*. 1987. Guanabara, Rio de Janeiro, 2nd edition.
- Lo K.H., Shek C.H., Lai J.K.L., 2009 "Recent developments in stainless steels". *Materials Science and Engineering R*, p. 39-104.
- Silva, A.L.V. da C. e and Mei, P.R., 2010. *Steels and Special Alloys*. Blucher, São Paulo, 3rd edition.

7. RESPONSIBILITY NOTICE

The author(s) is (are) the only responsible for the printed material included in this paper.