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EVALUATION OF Ni-Cr-Mo ALLOY APPLIED BY WELD OVERLAY CLADDING ON CARBON STEEL FOR USE IN NaCl 3.5% MASS SOLUTION

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Cladding, UNS 625 Alloy, Localized Corrosion, Weld Overlay, Corrosion Test.

A B S T R A C T

This paper presents an evaluation of specimens prepared by deposition of UNS 625 alloy on carbon steel. The coating was performed using the weld process SMAW (Shielded Metal Arc Welding) to compare with a repair performed on a pressure vessel in a marine facility where severe localized corrosion occurred. The specimens were prepared by qualified welders using E-NiCrMo3 filler. Chemical analyses were performed by X-ray fluorescence to evaluate the degree of welding dilution that increases the iron content and gradually decreases the Ni-Cr-Mo contents in the coating final layer. The application of one layer the iron content was identified as 23.10% and for three layers the iron value was 2.94%. The Standards recommend a value of less than 5% iron. Corrosion and polarization tests were performed, both in NaCl solution at 3.5%, to investigate the corrosion resistance of the deposited metal mainly in relation to crevice corrosion and galvanic corrosion.

1. INTRODUCTION

Severe localized corrosion was found inside a pressure vessel in a marine unit during periodic inspection, where the side thickness losses were greater than 50%. The unit has approximately 3 years of continuous operation.

This equipment consists of a seawater pumping system for cooling various processing systems. It was built with carbon steel (ASTM, 2017) internally coated with epoxy coating (450 mμ) and, in the manhole sealing region, a metallic coating was applied with UNS 625 (Ni-Cr-Mo) alloy (ASTM, 2018), as shown in Figure 1. This vessel has an internal diameter of 1175 mm, side thickness 12.7 mm, a volume of approximately 5.5 m³ and a total mass of over 3.5 tons. The operating pressure and temperature of the vessel range from 550 to 1200 kPa and 25 to 45°C, respectively.

The origin of this corrosion was the failure of the epoxy coating, which covers the carbon steel substrate, leaving it exposed in a region near to a 625 alloy cladding as shown in the schematic in Figure 2.

Whereas the equipment operated continuously for approximately three years, it is valid to assume that the

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failure of the epoxy coating may be, directly or indirectly, associated with the following factors:

- low epoxy resin adhesion to carbon steel or at the interface between epoxy resin and with 625 alloy coating;
- premature aging, fissures, cracks or porosities in the epoxy coating;
- excess chlorine injected into seawater to prevent the growth of marine organisms;
- excessive speed of seawater;
- lack of filter to eliminate sand and particulates in seawater.

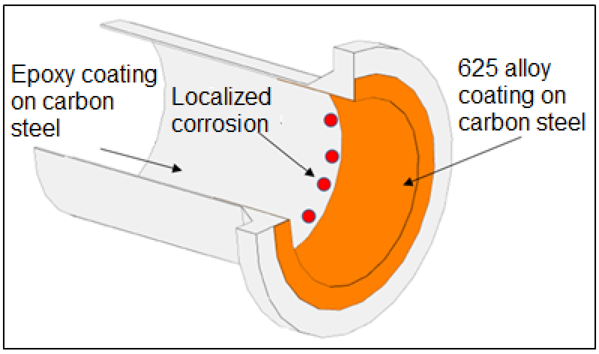

Figure 1. Schematic showing the epoxy coating, the 625 alloy coating on carbon steel and the localized corrosion

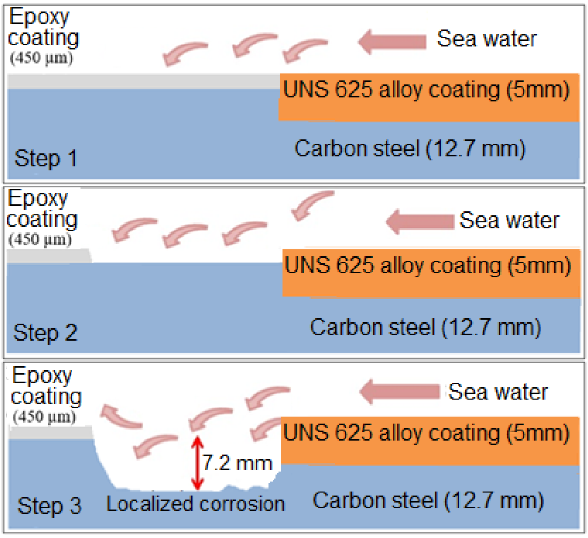

Figure 2. Schematic showing the failure of the epoxy coating and the beginning localized corrosion on carbon steel

The “in loco” repair of said vessel, was performed by welding (ASM, 1993; Kumar et. al, 2010; O'Brien, 2016; Alvarães et al., 2019; Dai et al., 2019) with compatible fillers and qualified welders. It was decided based on the following points:

- physical characteristics of the equipment and the difficulties of removal it of the marine installation offshore;
- the proximity of pitting and cavities in carbon steel with 625 alloy cladding already applied in the sealing of the manhole;
- the need for the equipment to return to operate as soon as possible.

Weld overlay is a method of application of metal coatings widely used in the chemical, petroleum and gas industry for corrosion protection.

Weld overlay, also known as cladding, is characterized by welding dissimilar alloys, that is, when the process is performed in alloys (substrate and coating), whose chemical compositions and properties are significantly different.

This process aims to improve desirable properties or restore the original dimension of a base metal that has been damaged or corroded. The weld overlay can produce layers, of several metallic alloys, on a substrate in various types of equipment. The metal coating provides protection to the substrate and allows for the integrity of the substrate without degradation of wall strength.

This process offers a high quality product with a low defects rate, adaptable and flexible anticorrosion methods in use (ASM Handbook. 1993; Kumar et. Al, 2010; O’Brien, 2016; Alvarães et al., 2019; Dai et al., 2019).

Considering the properties of weld overlay, the equipment repair was performed in 6 (six) steps, they are:

- initial cleaning with rotary equipment and grinding;
- inspection with penetrating liquids on the cleaned metallic surface aiming at the identification cracks, crevice or porosities;
- filling of the pitting and cavities with welding using SMAW welding process and E NiCrMo3 filler (equivalent to UNS 625 alloy);
- inspection with penetrating liquids on the deposited UNS 625 alloy;
- inspection of the chemical composition of the metal alloy resulting from the welding process, by the PMI (Positive Materials Identification) inspection method and evaluation of the results;
- for end, the application of the epoxy coating with primer and two coats with a final thickness of 450 µm.

This paper aims at a laboratory evaluation of the repair performed on the equipment. Using welders and the same fillers, specimens were prepared under similar conditions, whose results will be presented below.

2. MATERIALS AND METHODS

2.1 Preparation of specimens

The specimens were made with the dimensions of 110 x 85 x 25 mm, from a carbon steel plate ASTM A-516 Gr.70 (ASTM, 2017) The surface for the weld overlay cladding was prepared, according to the procedures performed in the repair of the offshore equipment, i.e.: initial cleaning; penetrating liquids test on the substrate, weld deposition using qualified welders as shown in Figure 3 and SMAW welding process with E NiCrMo3 was used.

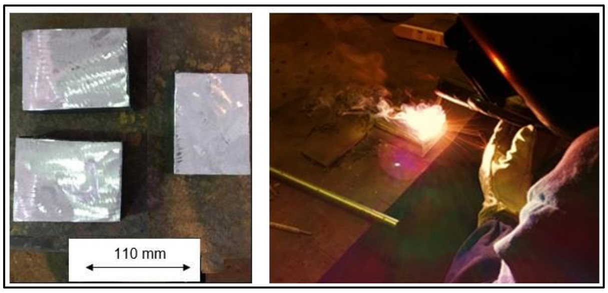

Figure 3. The cleaned carbon steel specimens and the application of the 625 alloy (E NiCrMo3) cladding

In specimen A, B and C, was applied, respectively, one, two and three layers of cladding 625 alloy. Table 1 show the main welding parameters used in the cladding to make the (A, B and C) specimens, such as the heat input, voltage, current, the number and thicknesses of the layers deposited, and the deposition time.

Figure 4, below, shows the specimens already coated and a pattern (model) to discard the edges. The edges may have defects because they have higher cooling rates and are the opening and closing areas of the welding arc. This edge discard is based on the recommendations of the ASME IX standard (ASME, 2017).

After edge removal, nine samples measuring approximately 10 x 10 mm and 10 x 15 mm, were obtained from the specimens (A, B, and C) by cold cut. These samples will be used in the following tests: determination of the constituent elements (Ni, Cr, Mo) from the 625 alloy cladding and of the total iron by RX fluorescence (PMI test), polarization test and corrosion tests. Figure 5 below shows some cold-cut samples from specimens A, B and C.

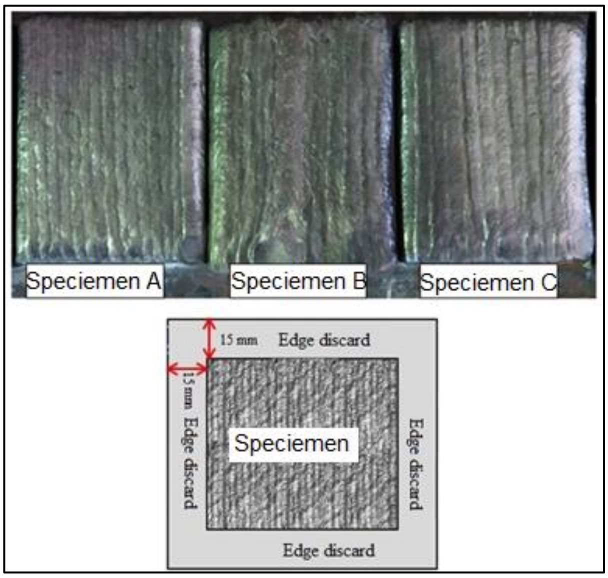

Figure 4. Weld overlay cladding specimens and edge patterning

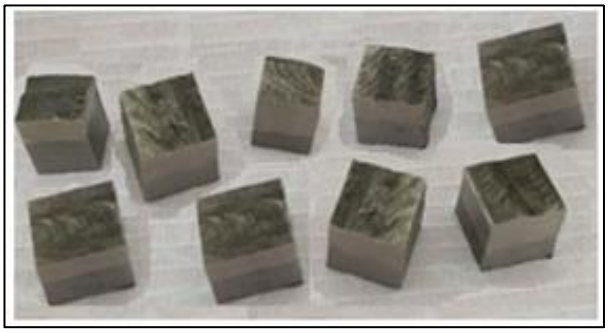

Figure 5. Some cold-cut samples from specimens A, B and C

Table 1. Main parameters used in weld overlay cladding to make the specimens

Parameters	Specimens					
	A	**B**		**C**		
Layers numbers	1	1	2	1	2	3
Thickness, mm	3.72	2.84	1.50	3.24	3.52	1.96
Deposition time, s	38.2	30.0	29.9	24.5	25.6	23.7
Voltage, V	11.6	11.1	11.0	11.4	11.4	11.3
Current, A	80.6	72.5	72.8	98.5	98.5	99.5
Heat Input, J/mm	324	220	217	250	262	243

2.2 Determination of the constituent elements of the 625 alloy cladding and of the total iron (dilution) by RX fluorescence (PMI test)

The main objective of this step is to determine the effect of welding dilution on specimens coated with 625 alloy, which is basically composed of Ni-Cr-Mo-Nb.

In the determination of these elements, X-ray fluorescence (XRF) was used with the portable analyzer NITON XLT 898, positive material identification (PMI) shown in Figure 6. The results show of the residual iron content on the surface of the applied cladding

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# 2764 General Metals
NAV Herramientas
Time 16.2 sec
±Alloy 625  1.7

Ele    %    ±2σ
Mo  8.79 0.14
Nb  3.79 0.08
Zn  0.084 0.040
Ni 64.21 0.33
Fe  2.94 0.15
Mn  0.344 0.147
Cr 19.81 0.30
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Figure 6. X-ray fluorescence (XRF) determination with the portable analyzer NITON XLT 898 on the overlay cladding samples

2.3 Electrochemical polarization tests

For the polarization test measurements, electrodes with an area of 1.0 cm^2 were used on the samples. They were embedded in polyester resin, sanded, and polished with grade 80 to 600 sandpaper grades (Figure 7).

After this procedure, the electrodes were washed and passed through ultrasonic cleaning equipment for 3 min, to remove residues that may have been aggregated during grinding.

Figure 7. Weld overlay cladding samples for polarization test

The electrode with weld overlay cladding (working electrode) was inserted into a conventional 250 mL polarization cell with a 3.5 % (mass) sodium chloride solution together with a platinum electrode and a Saturated Calomel Electrode (SCE).

The polarization curves were recorded with an Autolab Potentiostat, Type III, varying the voltage at 60 mV/min over a range from -250mV to +250mV, with respect to open circuit voltage. All measurements were performed at a constant temperature of 25 °C and without agitation. All tests were repeated at least three times to ensure good reproducibility. The data obtained were analyzed using Origin Lab Pro software, version 7.1 (Mainier et al., 2018; Barros & Mainier, 2020).

2.4 Corrosion tests

The aim of this test was to observe galvanic and crevice corrosion and check the epoxy resin behavior when misapplied. The samples used were embedded in acrylic resin with the welded surface (625 alloy coating) facing up, as shown in Figure 8.

Figure 8. Samples used in the corrosion tests and immersing into a 100 mL acrylic container containing 3.5% wt. NaCl solution at 40 °C

The qualitative tests consisted of immersing the samples into a 100 mL acrylic container containing 3.5% wt. NaCl solution at 40 °C, without stirring (Figure 8). Two samples size were used, 10 x 10 mm and 10 x 15 mm, for the test times of 7 days (168 h) and 45 days (1080 h), respectively

3. RESULTS AND DISCUSSION

3.1 Determination of the constituent elements of the 625 alloy cladding and of the total iron (dilution) by RX fluorescence (PMI test)

The aiming of this test was to identify and quantify, preferably, the iron content in the layer to explain the dilution process that occurs in the weld overlay and compare the results to the other tests.

The chemical analysis of the filler (E NiCrMo3) used to form the coat layers on the carbon steel substrate of the specimens (A, B and C), are showed on the Table 2.

The chemical analyses performed by PMI test on all samples obtained from the specimens A, B and C, and are represent on the Tables 3, 4 and 5, respectively.

During welding, part of the metal present in the substrate (the base metal, carbon steel) melts and mixes with the metal coming from the filler (E NiCrMo-3), forming a new metal, which chemical composition is a blend of the metals present in this welding. According to AWS Handbook (AWS, 2018), the chemical composition of each of the weld layers can be considered uniform.

The literature (Rowe et al., 2003; Crook, 2005; Wong, 2009; Ebrahimi et. al., 2015) has highlighted the excellent results for nickel alloys, like UNS 625, in various corrosive media. However, not always the coating applied by welding on carbon steel have presented the same results of the "pure" alloys (with low iron content). Therefore, we need to consider the effect of welding dilution during its application.

Knowing that carbon steel has 98% iron in its composition and the filler has 1.2%, this fact increases the iron content and decreases other alloy elements. On nickel alloys, this means that a new alloy is formed with high iron content and consequently a significant reduction in Ni, Cr and Mo content.

Dilution is a welding term used to define the base metal (substrate) amount effectively participates in weld metal. The weld metal, in the other hand, is obtained by mixing the base metal and filler metal. Dilution rate can be calculated from the area of base metal related the total area of weld metal, on a transversal section of the weld (Banovic et al. 2002; Kumar et al., 2010).

Table 6 below shows the calculated weld dilution ratio values for specimens A, B, and C, on a function of deposition areas and the iron amount calculate from the dilution.

Table 2. Chemical analysis of the filler (E NiCrMo-3)

%Ni	%Cr	%Mo	%Nb	%Fe	%Mn	%C	%Si
63.9	22.1	8.8	3.0	1.3	0.04	0.03	0.35

Table 3. Chemical analysis of specimen A with one (1) layer of weld overlay.

Specimen A	Element determined				
	%Ni	%Cr	%Mo	%Nb	%Fe
A1	53.68	17.26	7.28	2.10	**18.80**
A2	52.50	17.05	7.24	2.88	**19.13**
A3	52.21	16.98	7.27	2.83	**19.27**
A4	51.68	17.59	7.41	2.64	**19.57**
A5	52.50	16.60	7.16	2.56	**20.12**
A6	50.64	17.15	7.27	2.90	**20.64**
A7	51.32	16.68	7.27	2.74	**21.46**
A8	51.41	16.32	7.13	2.68	**21.71**
A9	50.50	16.34	6.78	2.48	**23.10**
Average	51.83	16.89	7.20	2.65	**20.42**

Table 4. Chemical analysis of specimen A with two (2) layers of weld overlay.

Specimen B	Element determined				
	%Ni	%Cr	%Mo	%Nb	%Fe
B1	61.17	19.35	8.75	3.14	**6.41**
B2	60.34	19.56	8.48	2.95	**8.08**
B3	59.72	18.96	8.14	3.03	**9.40**
B4	60.83	16.89	8.31	2.76	**10.30**
B5	59.59	18.22	7.76	2.71	**10.98**
B6	56.03	16.93	7.77	2.44	**16.02**
B7	54.91	17.44	7.72	2.29	**16.88**
B8	54.91	17.44	7.72	2.29	**16.88**
B9	53.07	17.16	7.68	2.24	**18.80**
Average	57.84	17.99	8.04	2.65	**12.64**

Table 5. Chemical analysis of specimen C with three (3) layers of weld overlay.

Specimen A	Element determined				
	%Ni	%Cr	%Mo	%Nb	%Fe
C1	64.21	19.81	8.79	3.79	**2.94**
C2	64.00	19.99	8.78	3.45	**3.50**
C3	63.75	19.64	8.93	3.53	**3.75**
C4	64.30	18.95	8;89	3.37	**3.93**
C5	63.57	19.76	8.76	3.43	**3.99**
C6	63.50	19.52	8.74	3.73	**4.01**
C7	62.49	19.71	8.61	3.34	**4.40**
C8	63.33	19.72	8.68	3.31	**4.42**
C9	63.27	19.75	8.64	3.33	**4.44**
Average	63.60	19.65	8.75	3.47	**3.93**

Table 6. Calculated dilution ratio values for specimens A, B, and C and iron content

Specimen	Thickness, mm	Dilution ratio, %	Fe %
A	3.72	20.0	23.4
B	5.72	14.0	8.8
C	8.72	9.6	3.4

Based on the results of the chemical analyses presented in Tables 2, 3, 4, 5 and 6 it is observed that:

- the iron content in the filler (E NiCrMo-3) used in weld overlay is in the order of 1.3%;
- the lower the iron content in 625 alloy, the higher the corrosion resistance (Farina, 2014).
- by welding dilution, the iron from the substrate (carbon steel) takes up the space occupied by the other metallic elements (Ni, Cr, Mo, Nb) on the alloy, consequently reducing the concentration of each of them in the weld metal (coating);
- weld overlay applied with higher numbers of layers have lower iron concentrations due to the reduced welding dilution, layer by layer.
- the highest iron content (23.1%) was found in specimen A, while the lowest iron concentration (2.94%) was found in specimen C;
- the dilution ratio calculated from the weld deposition areas on specimens A, B and C were 20%, 14%, 9.6% respectively, and the iron amount calculate based on this rate were 23.40%, 8.80%, 3,40%.
- API 6A standard (API, 2018), ASME IX (ASME, 2017) standards state that the iron content in the coating surface should be less than 5%;
- Ferreira Junior (2020) in his research also found that the overlap of each weld pass also has great influence on dilution. The higher the overlap, the lower the dilution;
- the study conducted by Moradi & Ketabchi (2016) on the weld overlay application of alloy 625 on carbon steel show similar results in terms of the values of the elements Fe, Ni, Cr, Mo and Nb.

3.4 Electrochemical polarization tests

The polarization curves of samples B1, A2 and A9, corresponding respectively to 6.41%, 19.13 %, 23.10 % Fe, in 3.5 % NaCl solution are illustrated in Figure 10. In this graph it is possible to verify the verticalization of the anodic curve showing the active-passive transition.

This same trend of anodic curve shapes with active-passive transition is observed in the works of Lu et al. (2016 a; 2016 b) and Sedriks (1982) with 625 alloy (Ni-Cr-Mo) with iron concentrations ranging from 4.6 to 16% and immersed in 10% sodium chloride solution.

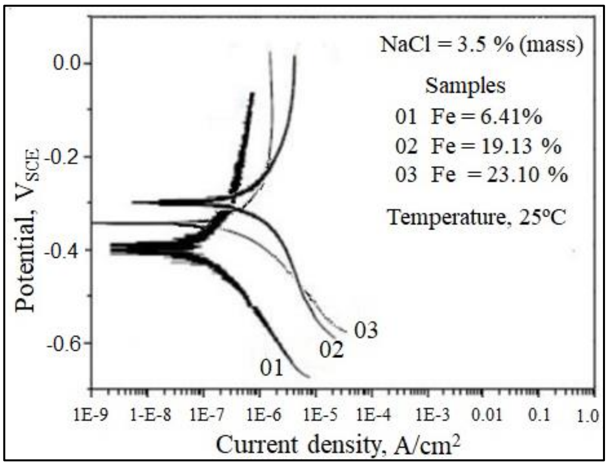


Figure 10. Polarization curves of samples 6.41% Fe, 19.13% Fe and 23.10% Fe at 25ºC in 3.5% (mass) of NaCl

Based on these potentiodynamic polarization curves, the Tafel method was used to determine the values of the corrosion current density (I_{corr}), the corrosion potential (E_{corr}) and the polarization resistance (Rp), the results of which are presented in Table 7.

The sample with the 6.41 % iron content is the dilution that can provide the highest corrosion resistance with a value of Rp = 2.5 x 10^5 higher than the other two samples.

Table 7. Results of current density (I_{corr}), corrosion potential (E_{corr}) and the polarization resistance (Rp)

Samples	I_{corr}, A/cm^2	E_{corr},V	Rp, Ω.cm^2
6.41 % Fe	1.5x10^{-6}	-0.39	2.50x10^5
19.13 % Fe	4.8x10^{-6}	-0.30	0.62x10^5
23.10 % Fe	8.5x10^{-6}	-0.35	0.41x10^5

3.5 Corrosion tests

Figure 11, below, represents the samples 10.3% Fe, 16.88% Fe and 21.41% Fe the carbon steel fully coated by epoxy resin with the weld overlay facing up. The crevices between the epoxy resin and the carbon steel coating by 625 alloy (as shown Figure 8) were carefully sealed to avoid the formation of galvanic piles or crevice corrosion.

The corrosion teste was performed by immersing the specimens into a 100 mL acrylic container containing 3.5% (mass) NaCl solution at 40 °C by and 45 days (1080 h). The samples do not show any localized corrosion points.

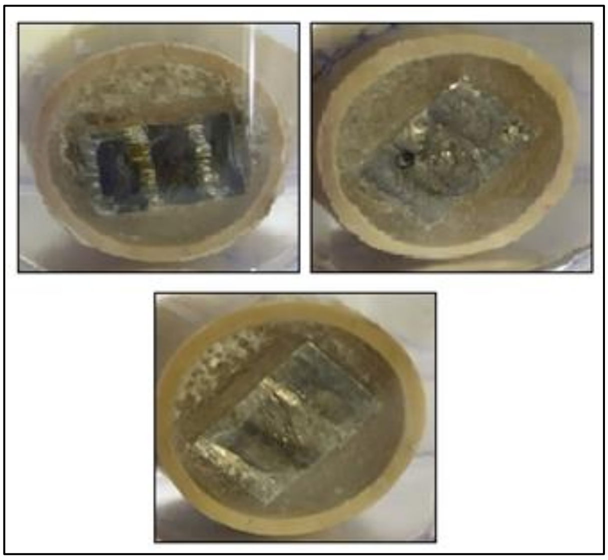


Figure 11. Weld overlay samples immersing 3.5% wt. sodium chloride solution at 40 °C by and 45 days (1080 h) not show any localized corrosion points.

The following Figure 12 represents the samples 8.08% Fe, 16.88% Fe and 20.12% Fe the carbon steel fully coated by epoxy resin with the weld overlay facing up. The crevices between the epoxy resin and the carbon steel coating by 625 alloy (as shown Figure 8) were not sealed to simulate a misapplied epoxy resin.

The corrosion teste was performed by immersing the specimens into a 100 mL acrylic container containing 3.5% (mass) NaCl solution at 40 °C by and 7 days (168 h).

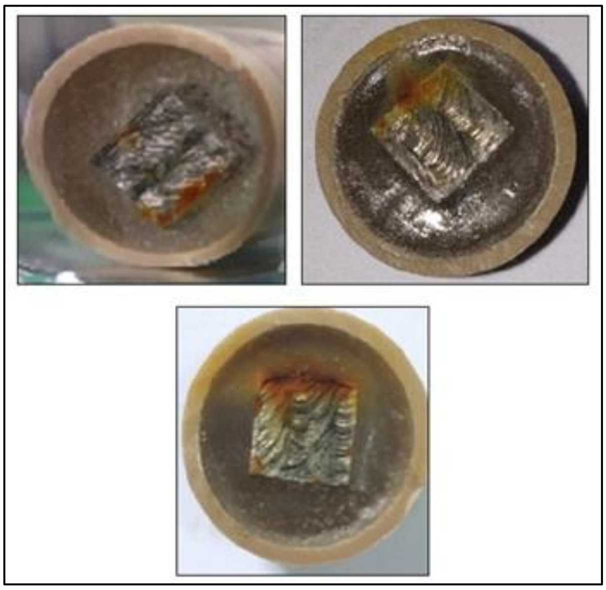
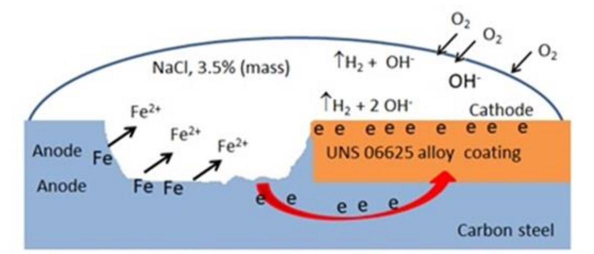


Figure 12. Weld overlay cladding specimens immersing 3.5% wt. sodium chloride solution at 40 °C by and 7 days (168 h) with localized galvanic corrosion or crevice corrosion

The samples show intense localized galvanic corrosion or crevice corrosion, considering that the weld overlay surface has not been properly isolated from the carbon steel substrate with epoxy resin.

The galvanic corrosion observed on the samples can be explained by the mechanism proposed, below, in Figure 13, where the corrosion product, reddish brown, it is identified as ferric hydroxide - $Fe(OH)_3$ or FeO.OH.



$$\text{Anode: } Fe - 2e \rightarrow Fe^{2+} \quad \text{Cathode: } 2H_2O + 2e \rightarrow H_2 + 2\ OH$$

$$Fe^{2+} + 2\ OH^- \rightarrow Fe(OH)_2$$

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2} O_2 \rightarrow 2\ Fe(OH)_3$$

Figure 13. Mechanism of galvanic corrosion

The literature (Jakupi et al. 2007; Shan & Payer, 2010; Jakupi et al., 2012; Ebrahimi et a., 2015) consulted has presented several examples of crevice corrosion in UNS 625 alloy used in sodium chloride solutions.

4. CONCLUSION

Based on the study performed, it is concluded that:

- knowing that in the weld overlay process the filler (E NiCrMo3) which has 1.3 % iron, the substrate (carbon steel) has about 98% iron and the welding dilution, it can be considered that the iron found on the cladding comes from the carbon steel substrate. Something that corroborates the need to perform a good control of dilution of the welding process;

- to achieve the chemical composition of the weld metal required by the reference standards (API 6A - minimum of 5% iron on coating surface), an 8.72 mm thick cladding was required with three weld layers, where the average iron content was 3.40%. For one layer with 4.12 mm and two layers with 4.34 mm, the iron contents were 21.70% and 12.40%, respectively;
- considering that the application of weld overlay was done by welders (humans), it is valid to credit them with the regularities and/or irregularities practiced during field conditions;
- the potentiodynamic polarization tests performed showed that the 6.41% iron surface content obtained the highest polarization resistance (Rp), which refers to the highest corrosion resistance under the test conditions, i.e. 3.5% NaCl at room temperature;
- it should be cautioned that crevice corrosion and/or galvanic corrosion may occur when the carbon steel is not properly isolated from the 625 alloy by well adherent resins resistant to seawater.

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