The corrosion susceptibility of 13cr and S13cr martensitic steels in a NaCl 5% solution with different surface preparation and aeration conditions

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Abstract

The corrosion susceptibility of 13Cr and S13Cr martensitic stainless steels was evaluated in a NaCl 5% solution by polarization curves and impedance experiments. Different aeration conditions and different surfaces preparation, based on literature reference and ASTM G5-94 standard, were tested. The steels' characterization was carried out by chemical analysis, SEM, OM and hardness testing. All steels presented different corrosion rates only by changing the surface preparation, from one to twenty-four hours of settle down time before the experiments. The 13Cr steels showed the greater difference. When prepared one hour before the experiment, the 13Cr steel's resistance was significantly lower than the S13Cr steels. On the other hand, it presented practically the same corrosion resistance when all specimens were prepared twenty-four hours before, condition that all the steels presented higher corrosion resistance. This condition can be explained by the longer time the specimens had to create and develop the chromium passive layer. Although the passive regime in both surfaces preparation for the S13Cr steels has shown to have practically the same magnitude, the current density was lower for the specimens with a twenty-four hours preparation. The modification of the aeration conditions did not change the steels corrosion behavior.

Keywords: 13Cr and S13Cr martensitic steels, SSC, surface preparation.

Introduction

The world demand for oil and gas is huge and does not show intent to decrease. In the search for less expensive solutions for field developments in the oil production industry, the oil companies are looking for cheaper materials with satisfactory mechanical strength and corrosion resistance. Delivery capacity is also a factor to consider[1].

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Conventionally, the use of CRAs (corrosion resistance alloys) is considered when the corrosivity of the produced fluids makes carbon steels uneconomic. It follows that the primary requirement for CRAs is adequate resistance to corrosion by the water phase of produced fluids. In addition, to have practical use, CRAs must be compatible with the other environments encountered in oil and gas field production facilities. This trend results from a combination of pressures which include: the production of more corrosive fluids, more hostile operating locations, a requirement for improved equipment reliability with associated, escalating, safety and environmental considerations. Simultaneously, there is remorseless pressure on the industry to reduce costs. Thus, increasingly the trend is to seek the lowest overall cost of equipment ownership, rather than just its lowest initial cost. Whilst CRAs may offer the lowest life cycle cost, they carry a heavy initial cost penalty, compared with, traditional 'carbon steel' equipment. Clearly, it is important to ensure that the most economic CRAs are specified whenever they are required[2].

The practices established for qualifying carbon steels are generally not applicable to CRAs. In the absence of an established methodology, manufacturers, designers, test laboratories and operators have had different and conflicting opinions of the test requirements for CRAs. Inappropriate testing has resulted in conflicting data and suboptimal selections[2].

The corrosion resistance of stainless steels increases with increasing content of Cr and other elements involved and stabilize the passivation film (Mo, Ni, N, Cu, Co, Ti, W), giving rise to special alloys called Corrosion Resistance Alloy (CRA) - such as martensitic and supermartensitic stainless steels[3].

This study aims to evaluate the behavior and performance of stainless steel in produced water in oil reservoirs, using electrochemical techniques. Thus, it will search to define the mechanisms of corrosion expected in the face of metallurgical materials, evaluating their performance simultaneously, evaluating the impact of different surface preparation on test results.

Methodology

Materials

This work covers the study of four different types of stainless steel with 13% of Chromium (Cr), one martensitic (MSS) and three supermartensitic (SMSS). The chemical composition of these steels is shown in Table 1.

Mechanical tests

Hardness HRC tests were performed with the samples as received. The results are shown in Table 2.

Micro-structural Analysis

For the analysis of microstructures sanding was done in the following order, 120, 240, 300, 500, 800, 1200, 1500, which was followed by polishing using Alumina 3 μm felt of 3 μm and then etching with Vilella (100 ml ethanol, 5 ml of HCl and 1 g of pickling acid) for 1 minute.

This solutions was chosen in accordance to Oliveira[3]. In accordance to the author it is a good reagent for enlightening the martensitic grains. After preparation of the specimens the analysis by SEM and OM was done. Figures 2 to 5.

Using the Schaeffler diagram (Figure 1) is possible to predict the phases present in the steel through the compositions of Ni equivalent (Ni eq. = %Ni + 30 x %C + 0.5 x %Mn) and Cr equivalent (Cr eq. = %Cr + %Mo + 1.5 x Si + 0.5 x Nb + 5 x % V + 3 x % Al). Table 3 shows the calculation result and on Figure 1 the approximate location in the Schaeffler diagram for each steel studied.

Electrochemical tests

The electrochemical tests performed were polarization and impedance. Both tests followed the ASTM G5-94[5] sample preparation, i.e., the specimens had a sanding preparation with 80, 240, 340 and 1000, then ground 1 h or 24 h before the tests. The objective is to evaluate either if 1 h or 24 h of settling time for the samples will affect the results.

The polarization tests allow the measurement of the current developed on the specimen as a function of the time and the applied potential. The electrochemical cell is a conventional three-electrode cell, involving the metal surface to be analyzed, a platinum counter electrode, and a Saturated Calomel Electrode (SCE) as a reference. The current density is directly related to the nature and the rate of the electrochemical reactions which occur at the interface between the steel surface and the aggressive solution.

The samples were immersed in the 5% NaCl solution one hour before starting the polarization tests, with the scan rate of 1 mV/s. The steels analyzed were 13% Cr and super 13% Cr steels. Two different aeration conditions have been investigated, naturally aerated and de-aerated, condition that pure nitrogen was used to extract the oxygen[6]. A potentiostat was used to create the anodic potentials.

The measurement of open circuit potential versus time relates the electrochemical potential of the sample interacting with the solution used. In this way, it is possible to infer if the system is in an active or passive state. This method is also used for establishing if the corrosion potential achieved the stabilized state necessary to validate the other methods tests[3].

The impedance of an open circuit represents the difficult level throughout an electrical sign (potential or current) sent to this circuit meets to course it. It is a combination of passive elements of an electrical circuit: resistance, capacitance and inductance[4].

All assays were performed in triplicate, for supporting results.

Results and discussion

    1. Chemical Analyses

Comparing the chemical composition of samples with standards (Table 1 and 2) it was found that the MSS is similar to the L80 - 13Cr (ISO 11960, 2004[7]) grade with some variation on Phosphorus (Ph) concentration and presence of Molybdenum (Mo). The standard does not mention about Al, V, Ti, Nb, Co, W and Fe in the steel composition. The ISO 11960 standard also provides information about mechanical properties. The specimen MSS is in accordance with the hardness specified by the ISO 11960 standard (Table 3).

Based on the chemical analyses it is possible to infer that the Supermartensitic Stainless Steels (SMSS) presented less carbon concentration and more concentration of Nickel (Ni) and Molybdenum (Mo) than the Martensitic Stainless Steel (MSS). This results are similar to the work of Hervé MARCHEBOIS et al.[6] that observed the following: super martensitic stainless steels are martensitic stainless steels with less 0,03 wt% Carbon concentration and significant addition of Nickel and Molybdenum.

Analyzing the chemical composition of the SMSS1, SMSS2 and SMSS3 it was observed that they are equivalent to the category 13-5-2 (concentration of Cr, Ni and Mo respectively) and S41426 UNS number (ISO 13680, 2010[8]), although the SMSS3 presented a greater concentration of Chromium (Cr) (Table 1 and 2). The standard does not mention about the Cu, Al, Nb, Co, W and Fe in the chemical composition of the steel. The three SMSS present lower hardness than the hardness specified by the ISO 13680 standard (Table 3).

Table 1 – Specimens Chemical compositions (wt.%)

Steel	C	Cr	Mo	Ni	Si	Mn	P	S	Cu	Al	V	Ti	Nb	Co	W	Fe
MSS	0,22	13,4	0,036	0,06	0,25	0,38	0,03	0,01	0,01	0,02	0,02	-	0,01	0,01	0,03	85,5
SMSS 1	-	12,1	2,045	5,82	0,20	0,42	0,01	-	0,21	0,04	0,04	0,10	0,02	0,07	0,10	78,8
SMSS 2	0,02	12,5	2,000	5,75	0,29	-	0,01	-	0,14	0,02	0,12	0,42	0,03	0,05	0,10	78,1
SMSS 3	0,03	14,6	2,057	6,45	0,25	0,26	-	-	1.112	0,07	0,03	0,01	0,11	0,09	0,09	74,9

Table 2 - Standard Chemical compositions (Max. % wt. fraction or range)

Standard	UNS Number	C	Cr	Mo	Ni	Si	Mn	P	S	Cu	Al	V	Ti	Nb	Co	W	Fe
ISO 13680	S41426	0,03	11,5 - 13,5	1,5 - 3	4,5 - 6,5	0,5	0,5	0,02	0,01	-	-	0,5	0,01 - 0,5	-	-	-	-
ISO 11960	L80 - 13Cr	0,15 - 0,22	12 - 14	-	0,5	1	0,25 - 1	0,02	0,01	0,25	-	-	-	-	-	-	-

Table 3 - Hardness tests

Steel	Average Hardness - HRC (150kg Pre-load)
MSS	24
SMSS 1	23
SMSS 2	25
SMSS 3	24

L80 - 13Cr (ISO 11960,2004)	23
S41426 (ISO 13680, 2010)	27

2. Metallographic Analyses

Based on the Schaeffler diagram (Figure 1) it is possible to forecast the steels' microstructure by calculating the nickel and chromium equivalent (Table 4).
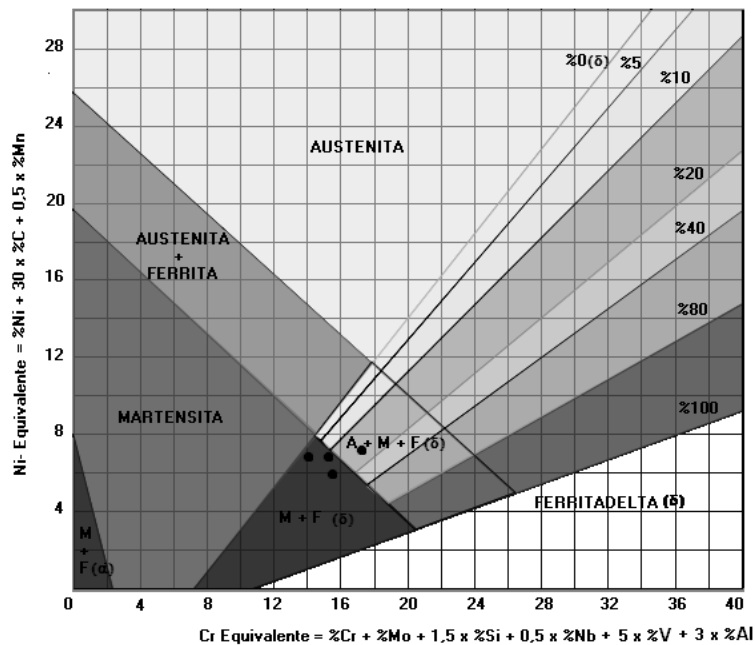

Figure 1 - *Schaeffler Diagram* **(MAGMAWELD, 2010)**

Table 4 - Equivalent Ni and Cr - Schaeffler Calculus

	MSS	SMSS1	SMSS2	SMSS3
Ni Equivalent	6,6985	6,031	6,7135	7,3905
Cr Equivalent	14,029	14,765	15,623	17,421

The MSS, SMSS1 and SMSS2 should present a martensitic combined with delta ferritic phases. The images obtained from the OM (Figures 2, 3 and 4) shows for inference the same result as the Schaeffler calculus. MSS, SMSS1 and SMSS2 present martensitic regions (in black with acicular format) plus delta ferritic regions (in white). The MSS presents a lot more martensitic regions because it has a larger concentration of carbon, element responsible for this phase.

The SMSS3 has greater concentration of Chromium than specified by the ISO 13680 standard. By the Schaeffler calculus SMSS3 should present martensitic plus austenite plus delta ferritic phases. The image obtained from the OM (Figure 5) shows very similar

microstructure as the SMSS1 and SMSS2, that is probably due to the fact that the austenite phase is dissolved in the martensitic phase and can only be found using an EDS.

The SEM images were not able to present the microstructure or any relevant information for this study.
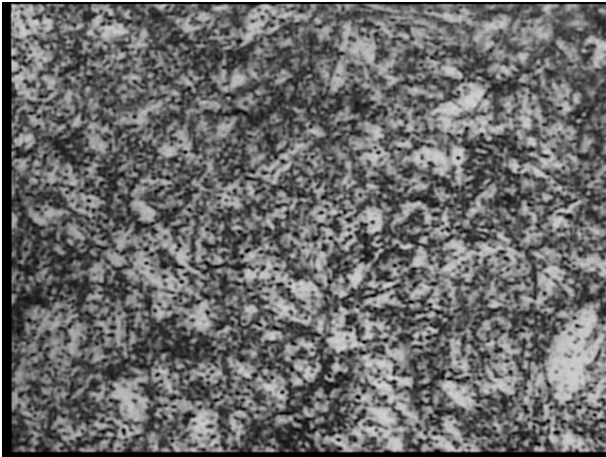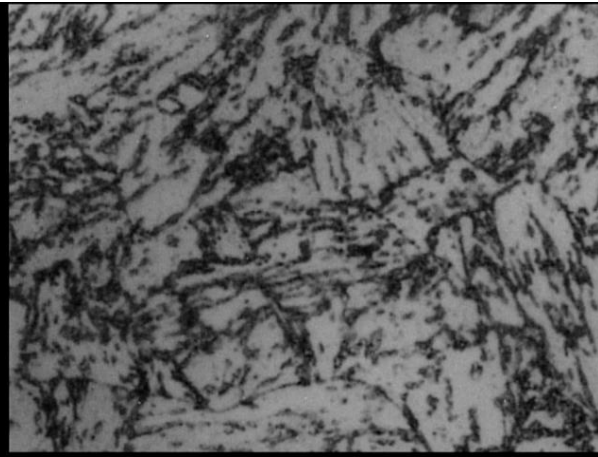

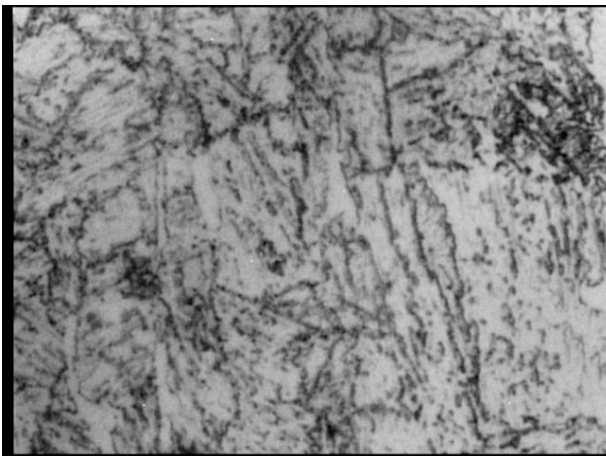**Figure 2 - MSS - MO 1000x – Villela**   **Figure 3 - SMSS1 - MO 1000x - Villela**

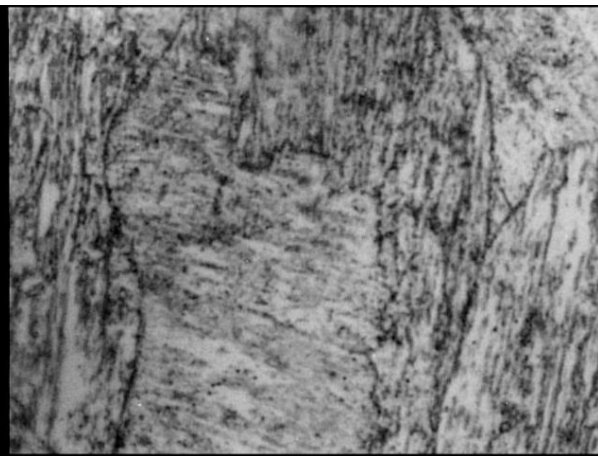**Figure 4 - SMSS2 - MO 1000x – Villela**   **Figure 5 - SMSS3 - MO 1000x - Villela**

3. Electrochemical tests

a. Polarization Tests

The Figures 6 through 9 show the polarization curves for the steels in four different condition, with the surface prepared 1 h or 24 h before the assays and in a naturally aerated condition and de-aerated with nitrogen condition. The tables 5 through 8 show the corrosion and pitting potential, the current density (j) 50 mV and 100 mV above the corrosion potential moreover the domain of passivation.

Note that the aeration condition only changed the corrosion potential, the corrosion behavior stood almost the same. Without oxygen the corrosion potential of all samples was more negative, what is expected since there are more hydrogen ions.

i. MSS - Martensitic Stainless Steel

In the polarization tests, the MSS steel (Figure 6 and Table 5), with the surface preparation done one hour before the test, had the corrosion potential (Ecorr) of - 428 mV (SCE), significantly close to the oxide potential. It can be observed that the steel did not present a passivation process. In other words, the steel presents active dissolution with reduction of hydrogen occurring thermodynamically spontaneous.

When carrying out tests with similar steels and with this surface preparation, it would not be possible to evaluate the passivation domain of this steel. That would not be recommended once that it is an stainless steel, known as a corrosion resistant steel, and this test does not show its regular behavior.

When the specimens were prepared with 24 h before the polarization tests, in the same solution, the MSS steel presented the Ecorr equal to -140 mV (SEC), significantly more anodic than the other surface preparation tested. In that case, it probably demonstrated that a passive film was formed on the metal surface.

Therefore, an increase of Ecorr is associated to an increase of the potential at which anodic processes (in particular steel dissolution) becomes significant[5]. The current density (j) which is directly linked to the corrosion rate, is globally lower than the current density (j) developed with one hour preparation, what suggests a slower corrosion rate. Note that with a 24 h preparation the steel presents a small passivation domain with a 176 mV range (Table 5), while with one hour of preparation the steel did not present passivation process.

With the analysis of these tests, it is possible to infer that the preparation time before the tests, 1 h and 24 h, produces very distinct results. A MSS that, following the ASTM G5-94[4] standard, present active dissolution, can show reasonably similar behavior as the SMSS (Figures 6, 7 and 8) only by changing the surface preparation.
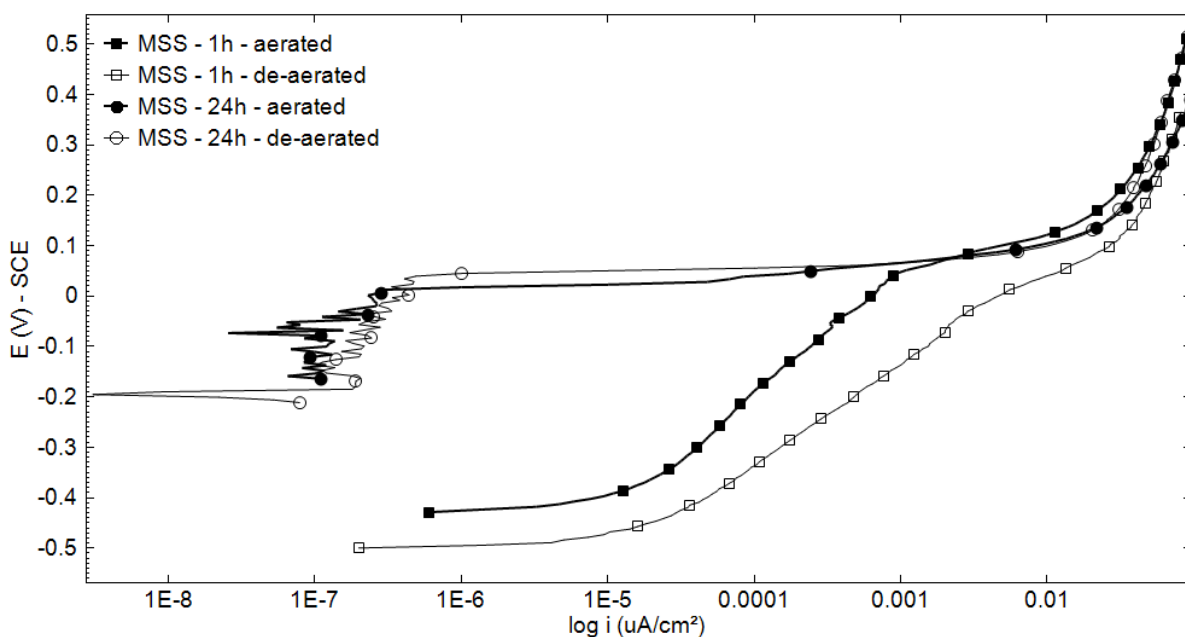
Figure 6 - polarization curves for MSS

Table 5 - Results for MSS polarization

Aeration	Preparation time	Ecorr [V]	Pitting Ecorr [V]	log i (Ecorr + 50mV) [uA/cm²]	log i (Ecorr + 100mV) [uA/cm²]	Passivation Domain [V]
Aerated	1 h	-0,4277	-	1,80E-05	3,70E-05	-
	24 h	-0,13945	0,03676	1,50E-07	1,82E-07	0,1762
De-aerated	1 h	-0,49886	-	1,88E-05	4,81E-05	-
	24 h	-0,21011	0,03555	2,04E-07	1,52E-07	0,2457

ii. SMSS - Supermartensitic Stainless Steel

All the SMSS samples tested presented a passivation process in every condition tested (Figures 7, 8 and 9). A passivation process is determined by the significant increase of the potential with the current density maintained lower than 1 µA/cm². Analyzing the different surface preparation, it is observed that the current density (j) at 50 mV and 100 mV above the Ecorr is substantially lower for the specimens prepared 24 h before the test than the specimens prepared 1 h before the test (Tables 6, 7 and 8). In that case, these behaviors represent higher corrosion resistance with a slower corrosion rate, although the passivation domain does not present greater difference between the two different surface preparation.

Comparing the SMSS one to another it is possible to notice that the most resistant is the SMSS 2 (Figure 8 and Table 7), due to the greater passivation domain, lower current density and also lower corrosion potential, i.e. more anodic. All these characteristics point to a greater corrosion resistance. It is interesting to highlight that the SMSS 2 is the sample that presented higher hardness (Table 3). It also has a greater concentration of Titanium (Ti).
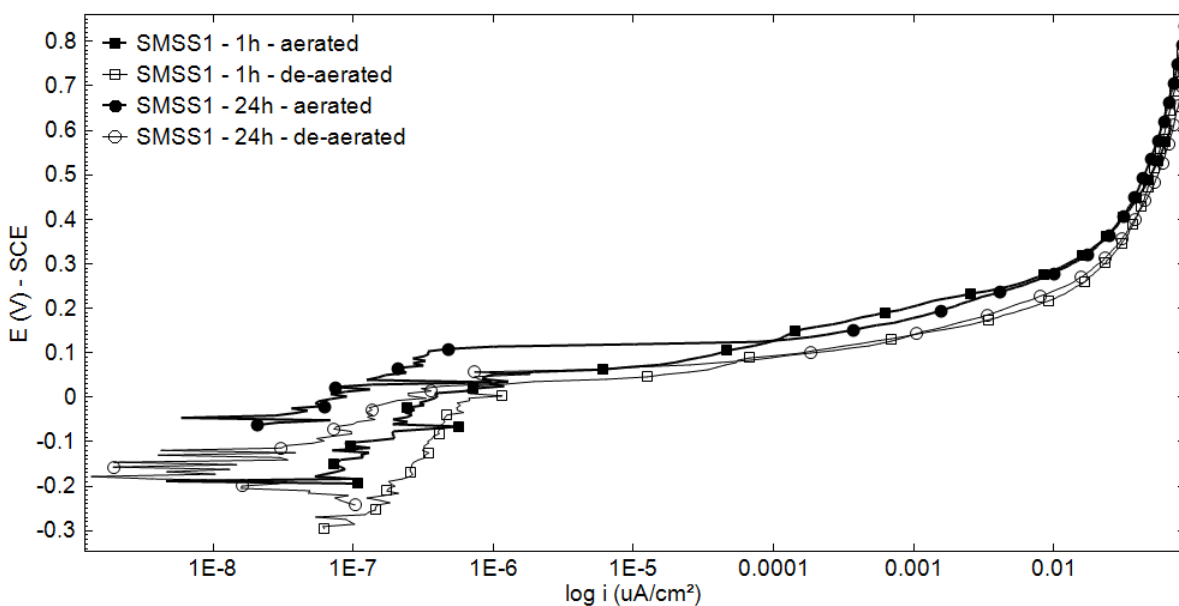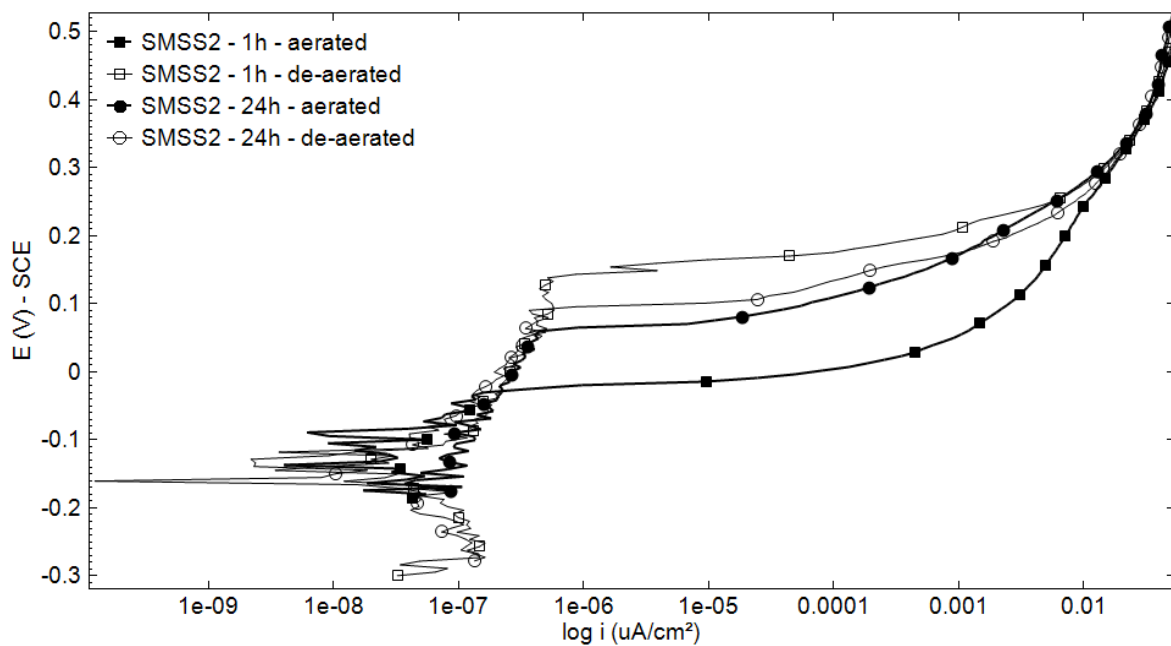

Figure 7 - polarization curves for SMSS1

Table 6 - Results for SMSS1 polarization

Aeration	Preparation time	Ecorr [V]	Pitting Ecorr [V]	log j (Ecorr + 50mV) [uA/cm²]	log j (Ecorr + 100mV) [uA/cm²]	Passivation Domain [V]
Aerated	1 h	-0,1944	0,0326	1,58E-07	3,11E-07	0,2270
	24 h	-0,0721	0,07215	9,75E-08	1,68E-07	0,1443
De-aerated	1 h	-0,29645	0,025787	1,43E-07	1,97E-07	0,3222
	24 h	-0,24094	0,058136	2,88E-08	3,38E-08	0,2991

Figure 8 - polarization curves for SMSS2

Table 7 - Results for SMSS2 polarization

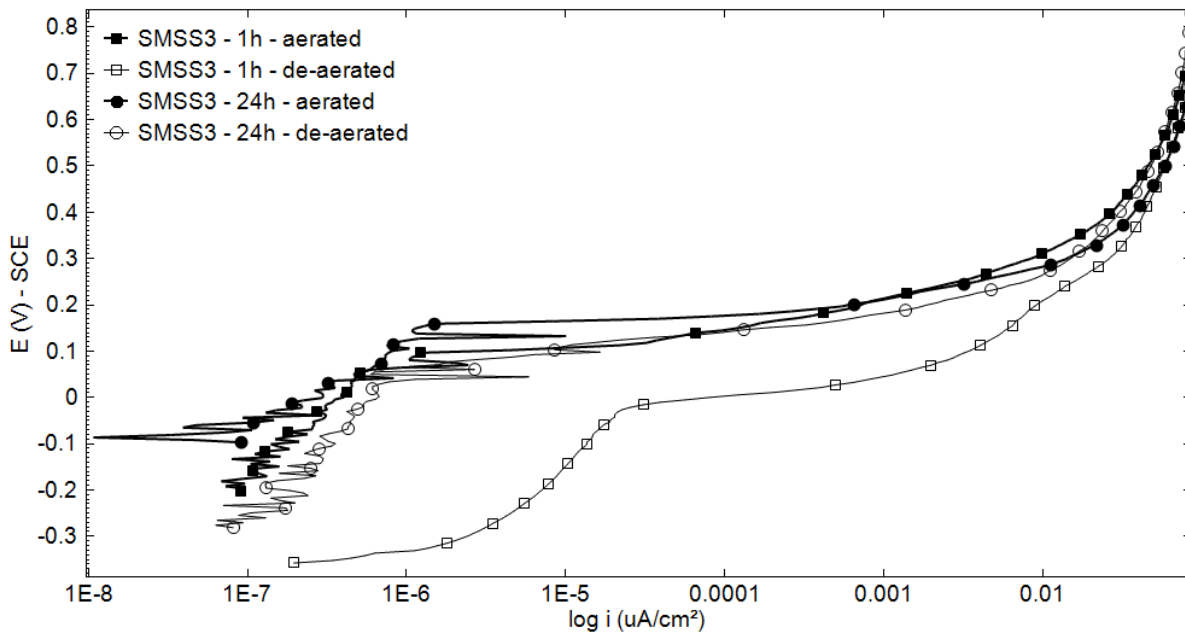| Aeration	Preparation time	Ecorr [V]	Pitting Ecorr [V]	log i (Ecorr + 50mV) [uA/cm²]	log i (Ecorr + 100mV) [uA/cm²]	Passivation Domain [V]
Aerated	1 h	-0,2238	-0,0156	9,47E-08	2,11E-07	0,2082
	24 h	-0,1302	0,0566	9,97E-08	2,16E-07	0,1868
De-aerated	1 h	-0,29877	0,13916	1,61E-07	8,11E-08	0,4379
	24 h	-0,2771	0,0914	8,60E-08	4,86E-08	0,3685

Figure 9 - polarization curves for SMSS 3 Steel

Table 8 - Results for SMSS 3 polarization

Aeration	Preparation time	Ecorr [V]	Pitting Ecorr [V]	log i (Ecorr + 50mV) [uA/cm²]	log i (Ecorr + 100mV) [uA/cm²]	Passivation Domain [V]
Aerated	1 h	-0,1666	0,047	1,20E-07	1,97E-08	0,2136
	24 h	-0,0801	0,17625	1,10E-07	2,22E-07	0,2564
De-aerated	1 h	-0,35629	-0,03585	2,20E-06	4,20E-06	0,3204
	24 h	-0,28	0,06714	7,00E-08	1,53E-07	0,3471

In accordance to the ISO 15156[8] standard the S41426 UNS number (ISO 15156, 2009[8]) has no temperature or chloride concentration limit on service when used as down hole tubular component and for packers and other subsurface equipment for production environments.

However, based on these results, at room temperature and a 5% chloride concentration none of the three different SMSS samples tested, that are similar to the S41426, resisted to corrosion. In other words, all presented pitting corrosion. Therefore it is necessary to review the standard service condition of the S41426 UNS number.

b. Impedance tests

Since it was observed in the polarization tests that the aeration condition did not interfered significantly in the comparison of the two different preparation times the impedance tests were carried out only in the aerated condition.
The impedance tests were carried out with different applied potential, initializing at the OCP (Open circuit potential) and with +50 mV increments, so that the passivation film would be increased until the potential dropped, or the arc size was reduced, comparing with the

previous measured ones. It happens when corrosion started. The aim is to determine what applied potential cause pitting so that it will be possible to identify when the polarization resistance (RP) is reduced.

The figures 10 to 13 present the Nyquist Impedance diagram. These tests were carried out with samples of the MSS and samples of the SMSS 2 that have the best performance between the three kinds of SMSS tested.
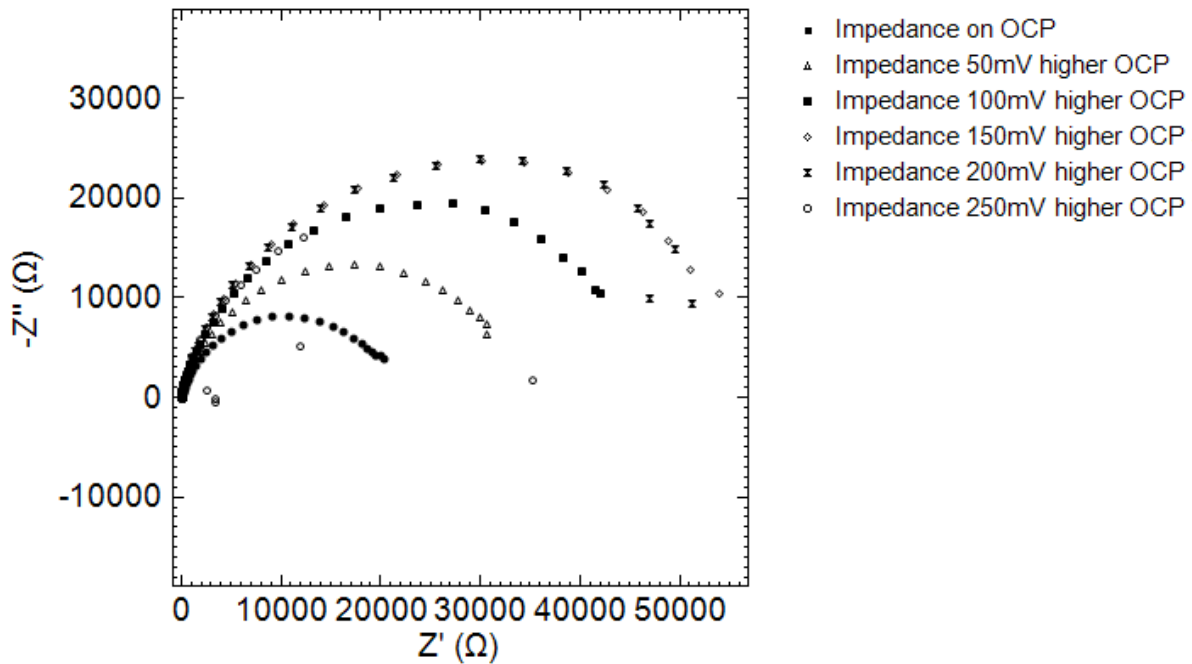

Figure 10 – Nyquist Impedance Curve for martensitic stainless steel (MSS) in 5% NaCl Solution and with 1 h of prepation.
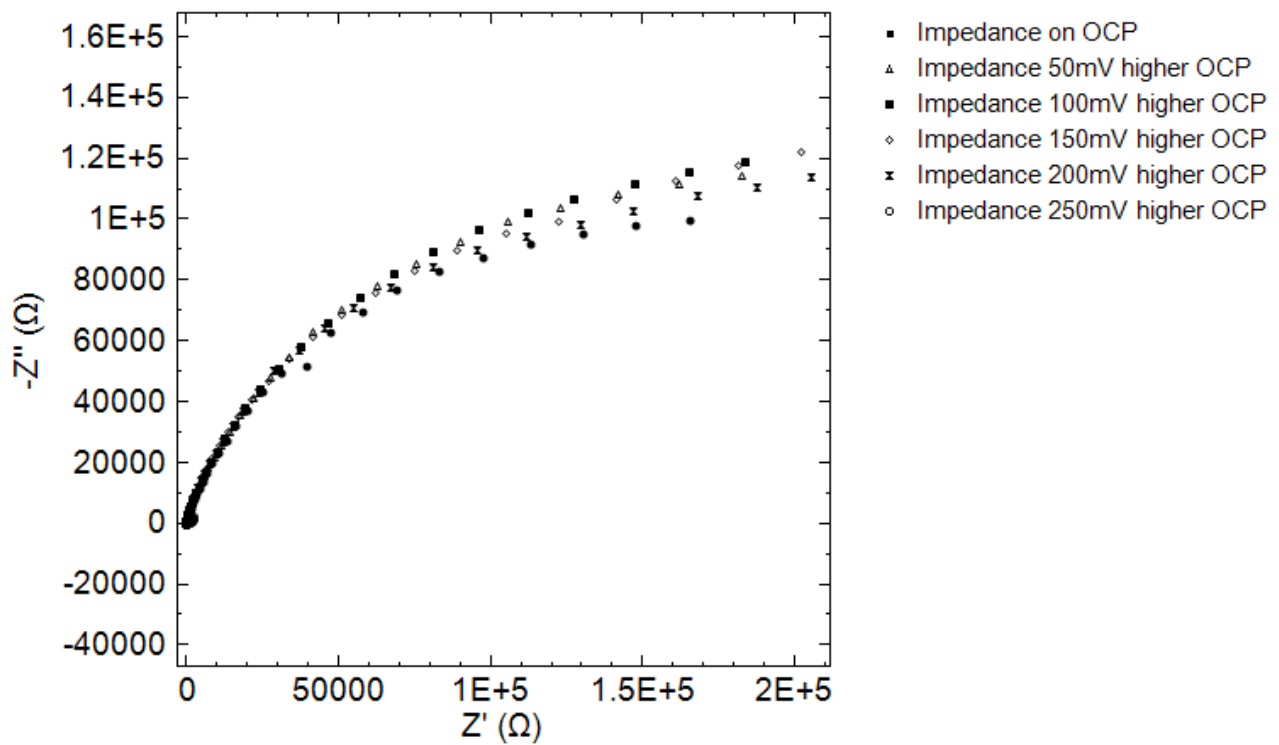
Figure 11 – Nyquist Impedance Curve for martensitic stainless steel (MSS) in 5% NaCl Solution and with 24 h of prepation.
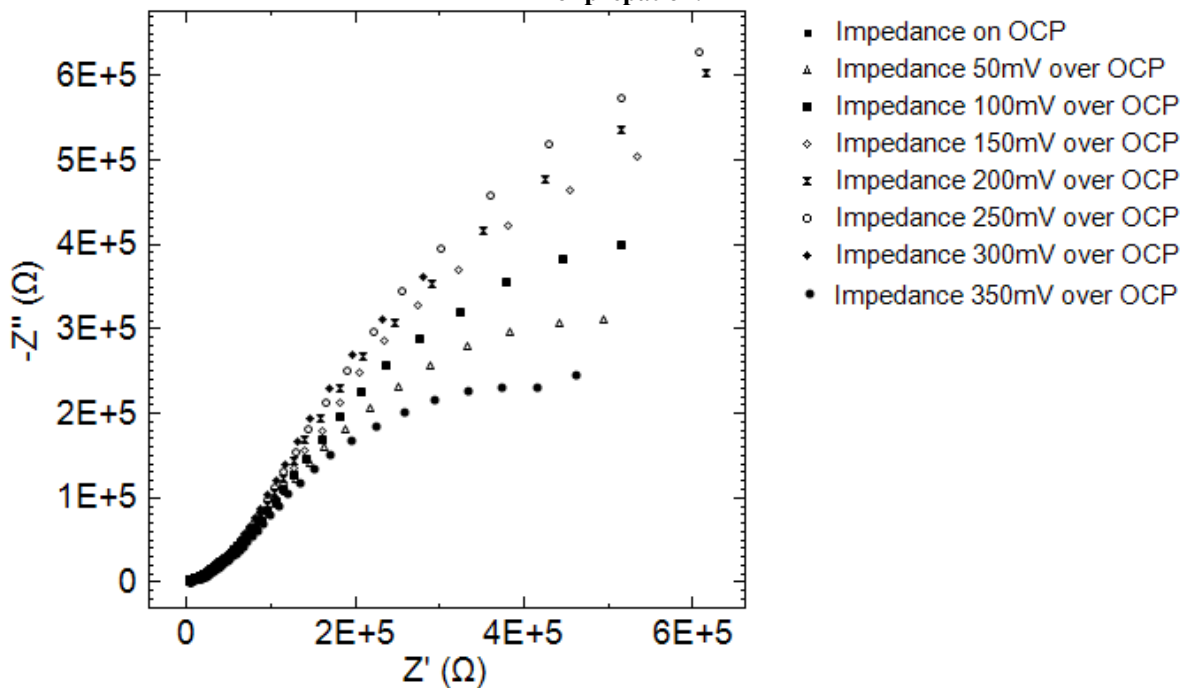

Figure 12 – Nyquist Impedance Curve for supermartensitic stainless steel (SMSS 2) in 5% NaCl Solution and with 1 h of preparation.
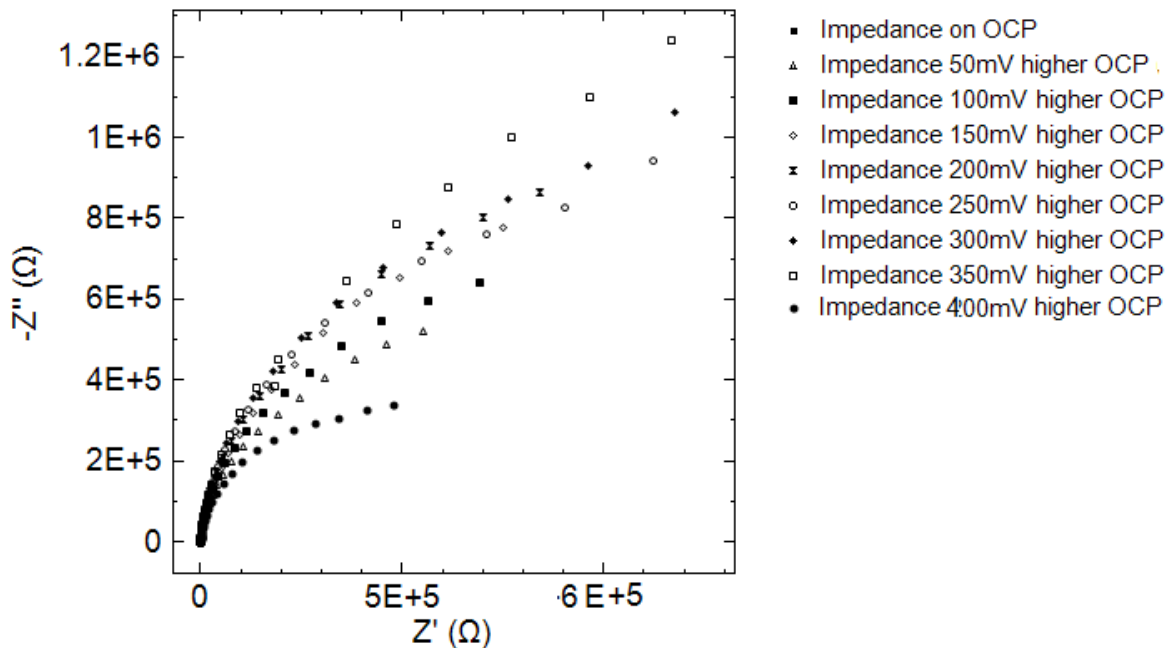
Figure 13 – Nyquist Impedance Curve for supermartensitic stainless steel (SMSS 2) in 5% NaCl Solution and with 24 h of prepation.

Table 9 –Impedance Values from the highest arc of each test

Steel and preparation time	Frequency [Hz]	Z' Real [ohm]	Z" Real [ohm]	Impedance [ohm]
MSS – 1 h	0,009999	51200	9279,7	52034
MSS – 24 h	0,009999	2,0586E+05	1,1357E+05	2,3511E+05
SMSS2 – 1 h	0,009999	6,0874E+05	6,2864E+05	8,7508E+05
SMSS2 – 24 h	0,009999	1,17E+06	1,2382E+06	1,7036E+06

Referring to the MSS, when the tests started after 1 h and 24 h of surface preparation (Figure 10 and 11) the reduction of RP occurred with the applied potential of 250 mV above OCP, where probably occurred the formation of pitting corrosion. However, when the tests were carried out 24 h after the surface preparation (Figure 11) the impedance was greater, which indicates a greater corrosion resistance. In that case, it probably occurred because with 24 h of surface preparation the passivation film has already been formed on the metal surface, increasing its corrosion resistance.

These results with the specimens of MSS are in accordance with the results obtained with the polarization tests, where the specimens that had 24 h of surface preparation presented passivation process, while with 1 h of surface preparation the metal did not present passivation process.

A different behavior was observed with the SMSS2. The RP increased on the specimens that have been tested after 24 h of surface preparation (Figures 12 and 13). The specimens with 1 h of surface preparation presented pitting with the applied potential of 350 mV above OCP, while with 24 h of surface preparation the applied potential was 400 mV above OCP. Besides

the greater RP the sample prepared with 24 h presented greater impedance values, which also confirms the increasing of the corrosion resistance in this situation.

These results also implies the greater resistance showed by the SMSS over the MSS, which presented both RP and impedance values significantly greater.

The impedance values can be checked on Table 9 that show values of the greatest Nyquist arc for each situation, i.e. MSS and SMSS2 with 1 h and 24 h preparation time. The values were acquired from the least frequency measured (0,00099999 Hz).

Conclusion

- The de-aeration condition induced a reduction of the OCP for every steel and condition.
- The aeration condition did not interfered in the comparison of the 1 h and 24 h results because they presented similar behavior.
- The preparation time influenced more on the corrosion resistance results than the aeration condition.
- All the SMSS presented passivation process in every condition tested, that can be an evidence that these steels are corrosion resistant in 5%NaCl aerated or de-aerated condition.
- The three different SMSS samples tested, that are similar to the S41426, did not resist to corrosion when potential was applied, and in the ISO 15156[9] standard the steel has no temperature or chloride concentration limit on service when used as down hole tubular component and for packers and other subsurface equipment for production environments. Therefore it is necessary to review the standard service condition of the S41426 UNS number.
- The MSS presented active dissolution when prepared one hour before the tests, so tests with this preparation will not be able to evaluate the steel's passivation domain.
- The MSS presented though a passivation process similar to the SMSS when prepared 24 h before the tests.
- The MSS presented higher current density when compared to the SMSS in all conditions studied, that implies less corrosion resistance, which might be explained by its chemical composition with less Molybdenum (Mo) and Nickel (Ni) percentage content.
- The SMSS 2 presented the best corrosion resistance among the samples studied, it can be verified by the polarization results, with greater passivation domain and more anodic corrosion potential and also by the impedance results, showing significantly greater impedance values when comparing to the MSS.

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