ICAIC International Conference for Academia and Industry Co-operation
20/11/2023 – 24/11/2023
São Luís - Maranhão - Brasil
IMMSEM International Meeting in Materials Science and Engineering of Maranhão

INFLUENCE OF THE MORPHOLOGY OF EUTECTOID STEELS ON CORROSION RESISTANCE IN H_2SO_4 AQUEOUS MEDIUM WITH AND WITHOUT CO_2

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ABSTRACT

The use of tubular oil production pipelines becomes a serious problem when it comes to their corrosion resistance. Since they are applied in a marine environment, they suffer severely from this electrolyte, as well as being subjected to damage due to the extracted oil. Sulfurous elements are the main causes of corrosion, in addition to the use of CO2, a gas used for oil recovery. Thus, this work aimed to investigate the strength of 3 different wires that constitute the tensile reinforcement of flexible pipelines (risers) when subjected to atmospheres similar to those of oil production. These wires have pearlitic microstructures with different cementites, namely spheroidized, lamellar, and brittle. Both were submitted to H2SO4 electrolyte in atmospheres with and without CO2 and at room temperature and at 80 °C in electrochemical tests of Open Circuit Polarization (OCP) and Linear Potentiodynamic Polarization (LPP). The results were able to confirm the higher corrosion resistance of the lamellar wire in the 3 solutions studied and a lower resistance of the spheroidized wire. These results were complemented by the Raman spectroscopy technique, helping to confirm the presence of salts and oxides produced on the lamellar wire, which led to a reduction in its corrosion levels.

Keywords: *risers; eletrochemical tests; corrosion; Raman Spectroscopy.*

INTRODUCTION

Risers are flexible, duct-like structures used in petroleum production applications [1]. This is arranged vertically along the seabed, interconnecting the platform or oil tankers to the flowlines (pipelines arranged on the seabed). Due to the operating environment in which these pipelines are arranged, they suffer severe damage, especially linked to electrochemical corrosion. This fact is especially due to the presence of seawater, composed essentially of NaCl, in addition to the components existing in petroleum, such as those rich in sulfur [2]. Figure 1 demonstrates the layers of a flexible riser.

Figure 1: Flexible duct and its highlighted layers [3].

Flexible ducts are composed of several layers, among which tensile reinforcement stands out. However, once the outermost layer is damaged, the wires that make up the reinforcement will be exposed, thus causing corrosion damage, initially of the uniform type [4]. Associated with this phenomenon, there are several corrosion products between salts and oxides. For example, there is the formation of $FeCO_3$, Fe_3O_4 and Fe_2O_3. These products depend on the medium where the corrosion develops. Al-moubaraki et. al [5], identified the formation of sulfates, such as $FeSO_4$ and $FeSO_3$, when carbon steels were composed in a solution of H_2SO_4, an acid found in the composition of petroleum, which can have contact with wires in case of rupture of riser layers.

Thus, evaluating the electrochemical behavior of steels in different media can benefit the best choice of different types of materials to be used in exploration pipelines. In addition, being able to characterize the oxides and salts formed as corrosion products will help to understand how susceptible to degradation that material is, and may accelerate or reduce its deterioration. This corrosion resistance will also be directly influenced by the microstructure of the material, making it more or less susceptible to corrosion.

MATERIALS AND METHODS

The materials used in this work are part of the tensile reinforcement of risers. They are wires that have distinct manufacturing profiles and morphologies. These were used in the assays as received.

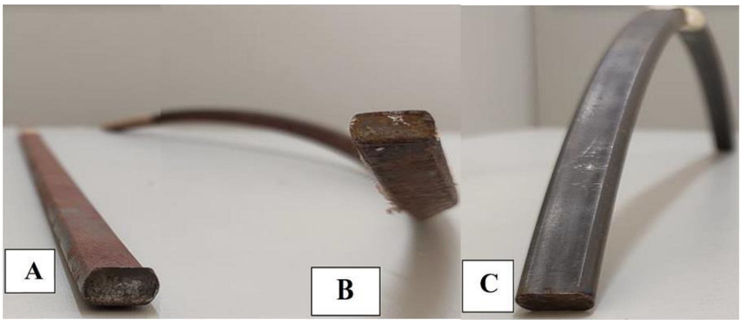

Figure 2: Wires in the as-received state.

These wires had their chemical compositions obtained by means of a Shimadzu PDA 7000 optical emission spectrometer. Below, the results of the chemical composition of these wires are listed.

Table 1. Chemical composition (% wt) of the wires.

Wire	C	Mn	Si	S + P	Cr + Ni +V	Al	Mo +Ti	Fe
A	0.77	0.50	0.20	0.015	0.055	-	0.006	bal
B	0.76	0.56	0.18	0.013	0.042	-	0.007	bal
C	0.73	0.58	0.26	0.007	0.039	0.033	0.004	Bal

The materials were prepared for use in SEM (Scanning Electron Microscopy) in order to have their morphologies characterized. In this way, the wires could be individualized by the profiles of the cementites they presented, since they had perlite as part of their microstructures, as shown in figure 3, in A – spheroidized; B – lamellar; C - discontinous.

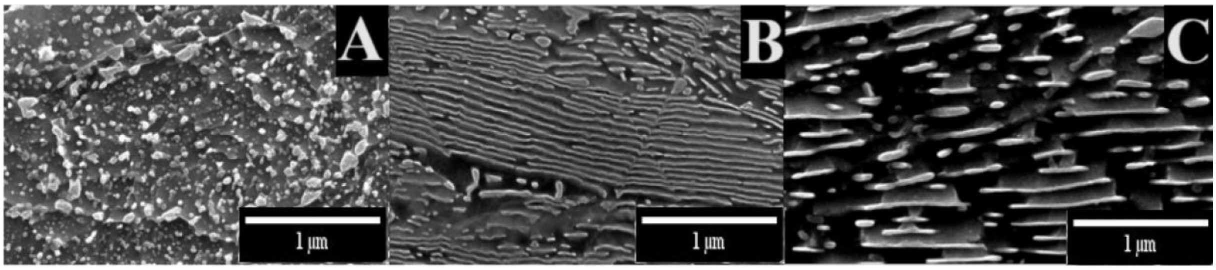

Figure 4: Micrographs of the wires: a) spheroidized; b) lamellar; c) brittle. Results obtained in cross-section.

Eletrochemical tests

For this work, electrochemical tests were used as a way to evaluate the corrosion resistance of the samples used. The Open Circuit Potential (OCP) and Linear Potentiodynamic Polarization (LPP) tests were performed. The samples were extracted from the wires of their frontal surfaces, since this region is the most exposed to degrading solutions when they are being used in oil production activities. The samples were prepared by means of surface treatment with 100, 200, 320, 400 and 600 grit sandpapers, which were later washed with distilled water, alcohol and dried.

The samples were embedded in epoxy resin with a copper conductor wire connection to close the electrical contact. For the tests, an electrochemical cell with 3 electrodes was used, namely the reference electrode Ag(s)/AgCl(s)/Cl-aqKCl saturated, platinum electrode as a counterelectrode, and the samples played the role of working electrode. The tested areas of the samples were approximately 0.25 cm^2. Data were collected using the PGSTAST30 potentiostat (Autolab, Metroh-Eco Chemie) using Nova 2.1 software. The programmed OCP time was 15 minutes, where the sample potential was stabilized under the conditions evaluated. On the other hand, LPP was performed with a sweep speed of 1 mV/s continuously and increasing between -0.1 and 2.0 V of overpotential. The established cut-off current was 1mA. The tests were performed in replication to confirm their reproducibility.

Below are the conditions of the assay with their respective electrolyte solutions.

Table 2: Test conditions.

Wires	Condition at 0.1 M H_2SO_4		
A	Saturated with CO2 at 80°C	Saturated with CO2 at 80°C	Aerated at room temperature (23°C).
B			
C			

Raman Spectroscopy

Raman spectroscopy is an important characterization technique for the identification of salts and oxides that form on the surfaces of materials, especially when subjected to corrosion tests [6]. For this study, the wire with perlithic microstructure of lamellar cementite was evaluated using the characterization technique described here, in order to identify salts and oxides predicted in the literature, such as $FeSO_4$ [7] and when corrosion is subjected to CO_2, siderite ($FeCO_3$) [8].

RESULTS AND DISCUSSION

The figures below are illustrated with the electrochemical tests of LPP performed.

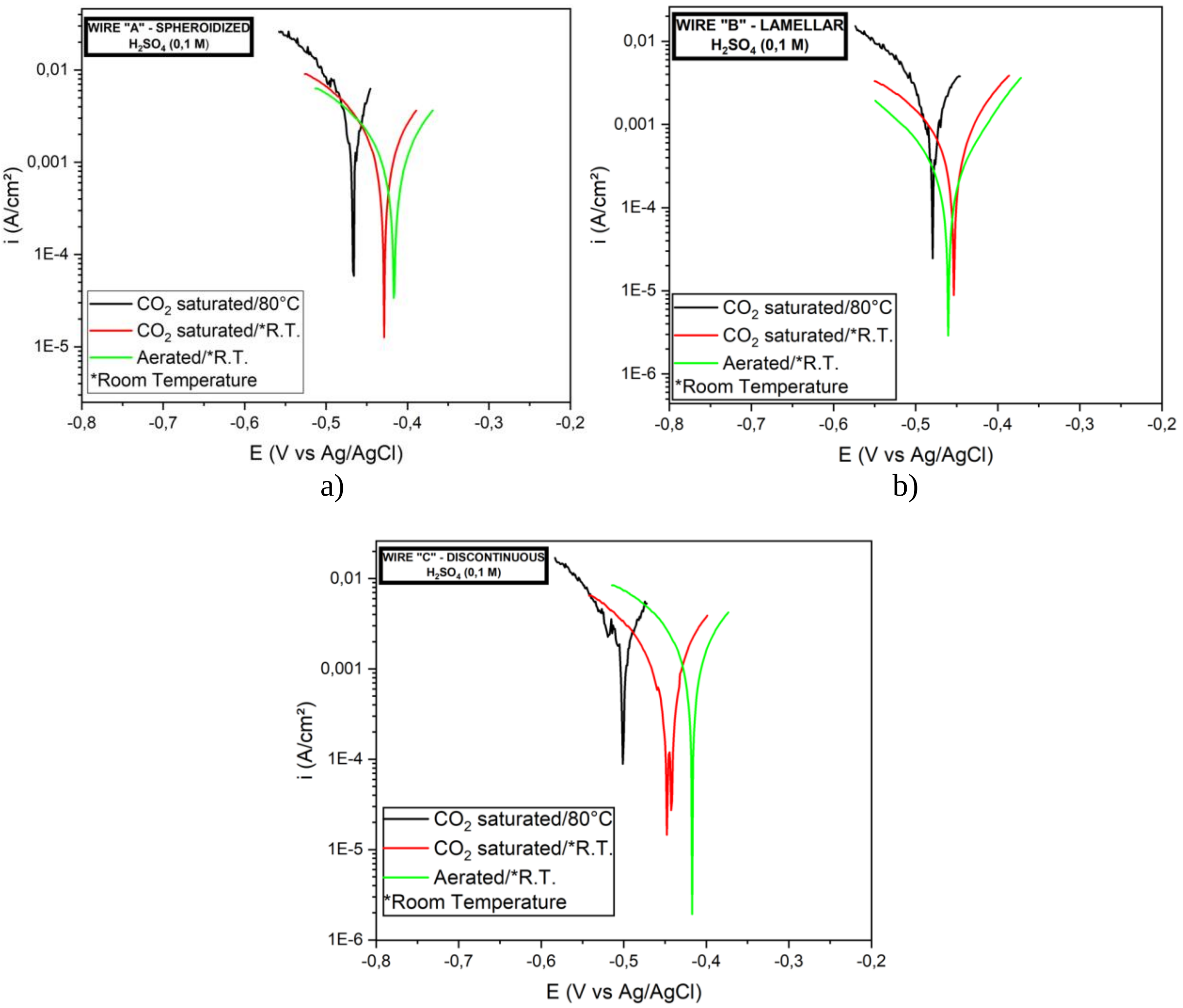

Figure 5: LPP curves using sulfuric acid in 3 different atmospheres. a) wire "A" – spheroidized; b) wire "B" – lamellar; c) wire "C" – discontinuous.

From the results obtained, it was possible to identify information such as OCP on the X axis and the value of the current density on a logarithmic scale in the ordinates. The higher the current densities, the greater the tendency for the material to corrode. This was a reality observed in the 3 wires under conditions in which there was saturated CO_2 at a temperature of 80°C. One way to obtain more assertive data about the strength of the material is through the calculation of RP (resistance to polarization) given by the ratio between the OCP of the material and its current density [9]. This parameter is used as a comparison between materials submitted in the same condition. Table 3 computes this information for each of the tests performed.

Table 3: Statistical data from the electrochemical tests on H_2SO_4 for the three samples in the three tested solutions (MD = mean and SD = Standard Deviation).

WIRES	STATISTICS	Solutions (0,1 M H_2S0_4)								
		(1) Saturated CO_2/80°C			(2) Saturated CO_2/R.T.			(3) Aerated/R.T.		
		Eletrochemical parameters								
		OCP (V vs Ag/AgCl)	I (A/cm²)	Rp (Ω.cm²)	OCP (V vs Ag/AgCl)	I (A/cm²)	Rp (Ω.cm²)	OCP (V vs Ag/AgCl)	I (A/cm²)	Rp (Ω.cm²)
A	MD	-0,50	9,89E-04	502,40	-0,42	4,21E-04	1.038,99	-0,41	4,72E-04	902,95
	SD	0,04	3,15E-05		0,00	8,40E-05		0,00	9,20E-05	
B	MD	-0,47	6,33E-04	769,23	-0,45	1,79E-04	2.544,78	-0,44	9,19E-05	4.790,87
	SD	0,00	1,18E-04		0,01	2,45E-05		0,01	0,00	
C	MD	-0,51	8,00E-04	686,67	-0,43	1,88E-04	2.309,14	-0,41	6,37E-04	685,84
	SD	0,02	2,00E-04		0,01	1,35E-05		0,00	1,58E-04	

The data in Table 3 allow a vertical and horizontal comparison of the morphology of the material and its resistance to corrosion in the midst of H_2SO_4. The lamellar microstructure "B" wire obtained higher strengths in the 3 solutions evaluated. Lopez et. al (2003) stated that lamellar structures corrode at a relatively low rate because of the massive form of cementite, compared to smaller, but denser morphologies of cementite, such as globular. The same author also states that cementite forms preferential sites with less overpotential, favoring the evolution of hydrogen. Thus, microgalvanic cells are formed between the ferrite and cementite phases, resulting in selective dissolution of ferrite and an influence on galvanic kinetics. The wires with spheroidized and brittle microstructures had lower polarization resistances than lamellar ones, however, the spheroidized wire showed lower RP's in the 3 solutions.

Raman Spectroscopy

Based on the results found, this work focused on the investigation of possible passivating films or protective layers that could reduce the corrosion of the material. Thus, the characterization technique by Raman spectroscopy was used. The sample chosen was "B" with lamellar microstructure, since it presented better results of resistance to polarization. Below are the results of oxides and salts found on the surface of the material, classified in to 3 distinct points of the sample (generalized corrosion (O), no apparent corrosion (□) and localized corrosion (Δ).

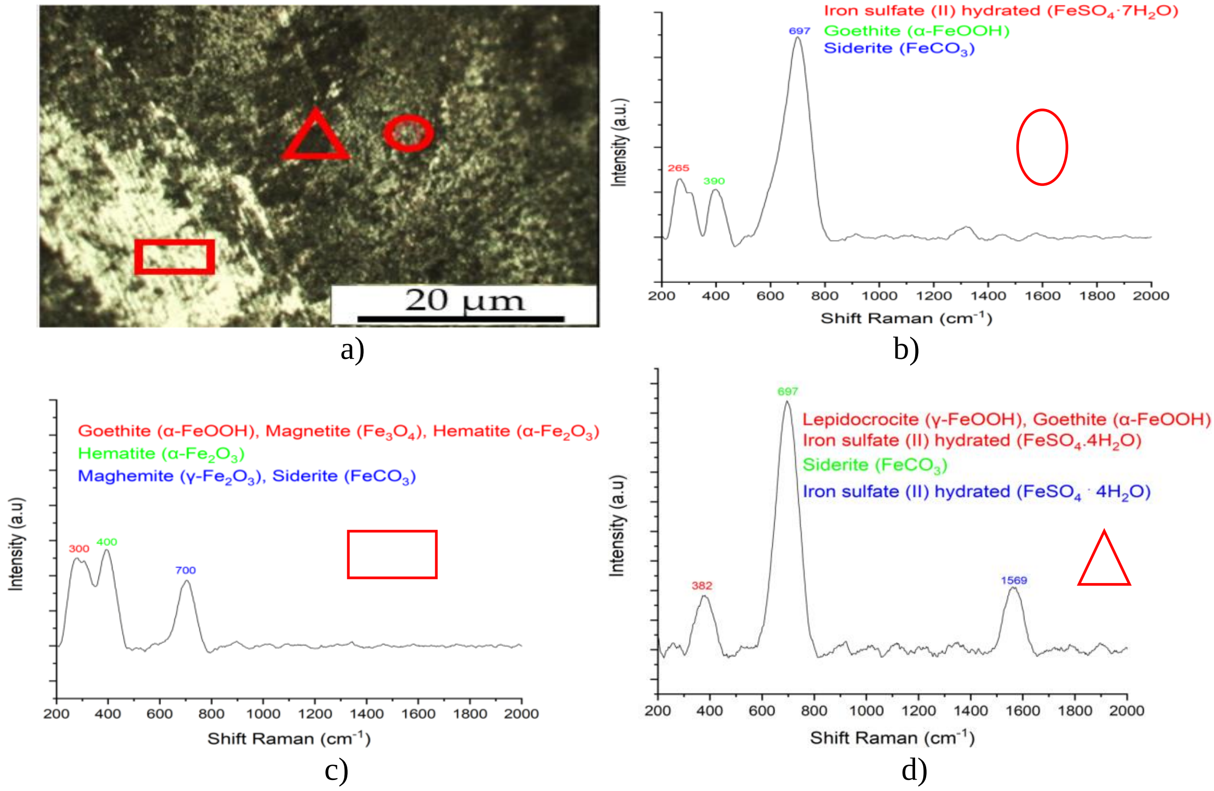

Figure 6: a) Micrograph of the sample highlighting the evaluated points and their respective symbologies - generalized corrosion (O), no apparent corrosion (□) and localized corrosion (Δ); Characteristic peaks for b) generalized corrosion [8,10,11]; c) no apparent corrosion [12-14]; d) Localized corrosion [8, 15].

The highlighted peaks were based on literature and helped to prove films predicted by some authors, which leads us to believe in the minimization of the corrosive effects of sulfuric acid in carbon steels with lamellar microstructure.

CONCLUSIONS

From the present work, the following conclusions could be reached:

- The wire with lamellar microstructure obtained higher Rp results when in CO_2 atmosphere and high temperatures, which helps to confirm what the authors claim about the reduction of lamellar microstructures corrosion in this electrolyte;

- The Raman peaks identified saline compounds such as $FeSO_4$, which was predicted by the literature, as well as siderite and some other important oxides;

- The spheroidized microstructure obtained low corrosion resistance when considered to the other wires, which allows us to conclude that its use should be limited in a sulfurous environment.

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