

Corrosion resistance of rolled and rerolled super martensitic steel in media containing chlorides and hydrogen sulfide

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ABSTRACT

In the oil and gas industry, super martensitic steels have been used primarily in the manufacture of seamless steel pipe for use in drilling oil and gas. The objective of this work is to evaluate the corrosion resistance of rolled and rerolled super martensitic steels in electrolytes of aqueous solution of NaCl 35 g/L, and aqueous solution of NaCl 120 g/L, sodium acetate 0.4 g/L, with pH 4.5 (standard solution), saturated and unsaturated with H₂S, simulating the service conditions of petroleum industry in the pre-salt operation. For this evaluation, the electrochemical tests used are electrochemical impedance spectroscopy (EIS) and cyclic polarization test. The characterization techniques used are optical microscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The effect of H₂S saturation of the solutions studied on the corrosion resistance of steels was detrimental. The super martensitic steel in the rerolled condition showed a higher corrosion resistance than the rolled steel in an aqueous solution of 35 g/L NaCl and in a standard solution saturated with H₂S. In the 35 g/L NaCl aqueous solution saturated with H₂S and in the standard solution, the rolled steel showed a higher corrosion resistance than the rerolled steel. In an aqueous solution of 35 g/L NaCl, the rolled and rerolled steels showed pitting diameter of 140µm and 100µm, respectively.

Keywords: polarization, rolled super martensitic steel, rerolled super martensitic steel.

1. INTRODUCTION

Super martensitic stainless steels have been widely used in the oil and gas industry due to their good mechanical properties, good weldability and corrosion resistance acceptable in environments containing chlorides, CO₂ and H₂S. Thus super martensitic steels have increasingly replaced the duplex stainless steel that has a high cost of production in many onshore and offshore applications. In the oil and gas industry, super martensitic steels have been used primarily in the manufacture of seamless steel pipe for use in drilling oil and gas [1-11].

Compared to conventional martensitic stainless steels, the super martensitic steel contains up to 3wt.% higher in molybdenum (Mo) content and up to 6wt.% over nickel (Ni) content. Molybdenum is added to improve corrosion resistance of steel, while Ni is added to stabilize austenite (γ) at elevated temperatures while avoiding the formation of δ -ferrite. Levels of carbon (C) reduced to 0.01% (w/w) contribute to improve the weldability [9, 10, 12-20].

The objective of the present work is to evaluate the corrosion resistance of rolled and rerolled super martensitic steels in electrolytes of aqueous solution of NaCl 35 g/L, and aqueous solution of NaCl 120 g/L, sodium acetate 0.4 g/L, with pH 4.5 adjusted with acetic acid (standard solution), saturated and unsaturated with H₂S, simulating the service conditions of petroleum industry in the pre-salt operation. The research has technological relevance because it deals with an industry demand interested in distinguishing the behavior against corrosion of two industrial conditions of a super martensitic steel for application in the oil and gas industry. For this reason, the work presents an innovative aspect.

2. MATERIALS AND METHODS

The electrolytes used were: an aqueous solution of NaCl 35 g/L, and of NaCl 120 g/L, sodium acetate 0.4 g/L, with pH 4.5 adjusted with acetic acid (standard solution), saturated and unsaturated with H₂S, simulating the service conditions of petroleum industry in the pre-salt operation.

The steel studied was the super martensitic steel, in industrial rolled and rerolled conditions. The chemical composition of super martensitic steel is shown in Table 1.

Table 1: Chemical composition of super martensitic steel (wt.%).

STEEL	Cr	Ni	Mo	C
VM13CRSS	12.00	6.00	2.00	0.02

The electrochemical impedance spectroscopy (EIS) was performed by varying the frequency of 1MHz to 1mHz using potential amplitude of 10mV. The open circuit potential was measured for one hour before each EIS measurement. Cyclic polarization curves were obtained at the potential rate of 0.167 mV/s and the reversal of potential was made when the current reached $5 \cdot 10^{-3} \text{ A/cm}^2$ after the breakdown potential.

All measurements were performed using a Princeton Applied Research potentiostat (Versa Stat 3). The collection, storage and processing of impedance and cyclic polarization data were performed using the Versa Studio software. Data processing was accomplished by running the program ZView.

The surfaces of samples of super martensitic steel were analyzed by using a scanning electron microscope coupled to an energy dispersive detector for X-rays. The QUANTA 200 FEG microscope (FEI) and the EDX spectrometer were used. The steel microstructures were analyzed using optical microscopy.

3. RESULTS

The steel microstructures were showed in Figure 1.

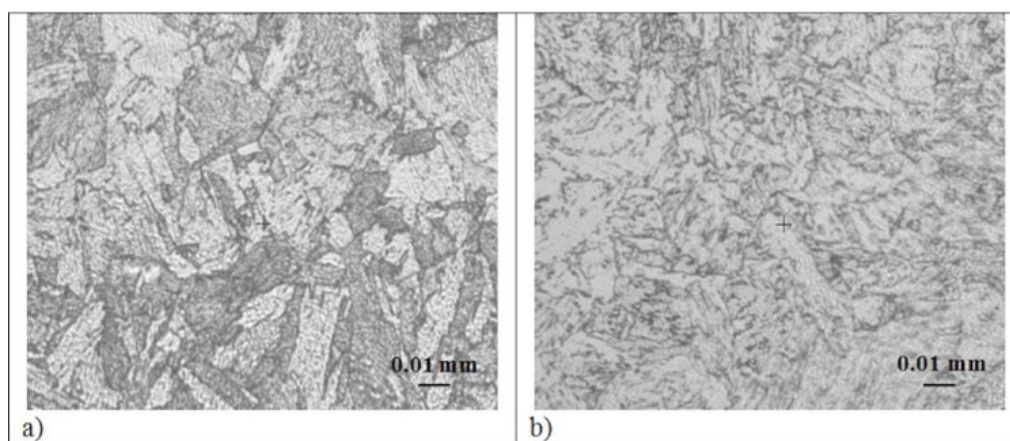


Figure 1: Microstructure of rolled super martensitic steel (a) and rerolled super martensitic steel (b).

The results of electrochemical impedance spectroscopy showed one capacitive arc in Nyquist diagram for both steels in all media (Figure 2).

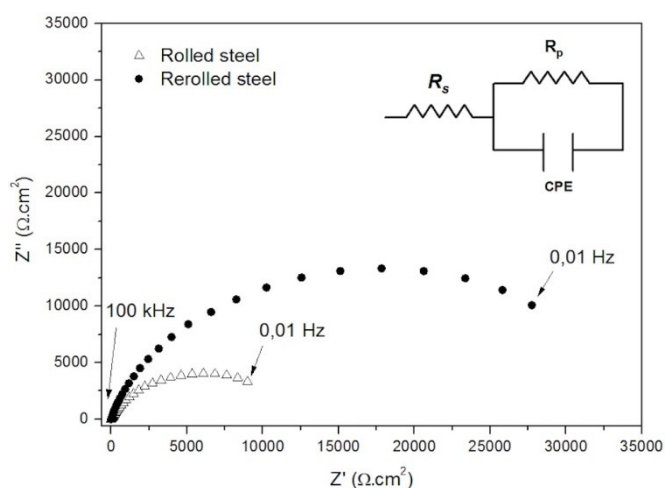


Figure 2: Nyquist diagram of rolled and rerolled supermartensitic steels in NaCl 35 g/L solution and equivalent circuit.

Bode diagram (Figure 3) showed one maximum in phase angle versus frequency curve and one inflection point in impedance modulus versus frequency curve. Analyzing the Nyquist diagram, results of polarization resistance of steels in electrolytes studied were obtained and are shown in Table 2.

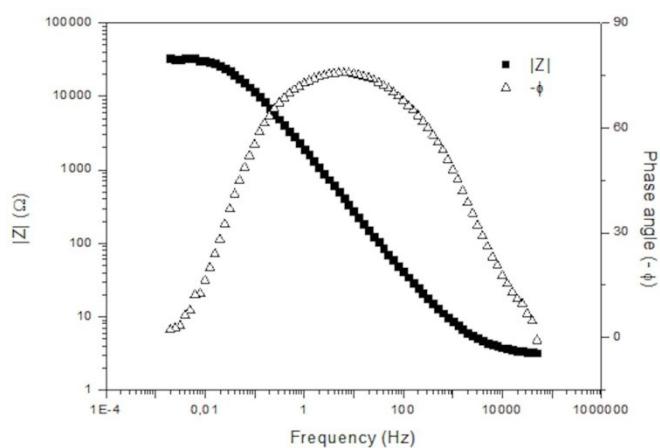


Figure 3: Bode diagram of rerolled super martensitic steel in NaCl 35 g/L solution.

Table 2: Electrochemical parameters obtained using polarization and electrochemical impedance spectroscopy.

Electrolytes	Rp	Rp	Epitting.	Epitting.	Ipass.	Ipass.
	($\Omega \cdot \text{cm}^2$) Rolled Steel	($\Omega \cdot \text{cm}^2$) Rerolled Steel	mV(Ag/AgCl) Rolled Steel	mV(Ag/AgCl) Rerolled Steel	A/cm ² Rolled Steel	A/cm ² Rerolled Steel
NaCl 35 g/L Solution	$1.37 \pm 0.08 \times 10^4$	$3.5 \pm 0.28 \times 10^4$	-140±11	-50±3	$9 \cdot 10^{-6}$	$3 \cdot 10^{-6}$
Standard Solution	$1.66 \pm 0.08 \times 10^5$	$7.83 \pm 0.24 \times 10^4$	-200±13	-260±18	$1 \cdot 10^{-6}$	$2 \cdot 10^{-6}$
NaCl 35 g/L Solution saturated with H ₂ S	$9.25 \pm 0.65 \times 10^4$	$3.41 \pm 0.30 \times 10^4$	-370±26	-420±33	$1 \cdot 10^{-6}$	$1 \cdot 10^{-6}$
Standard Solution Saturated with H ₂ S	$1.49 \pm 0.06 \times 10^4$	$1.79 \pm 0.16 \times 10^4$	-390±23	90±8	$3 \cdot 10^{-6}$	$6 \cdot 10^{-6}$

Figures 4, 5, 6 and 7 show cyclic polarization curves obtained for the rolled and rerolled super martensitic steels in media of NaCl 35 g/L solution, standard solution, NaCl 35 g/L solution saturated with H₂S and standard solution saturated with H₂S, respectively.

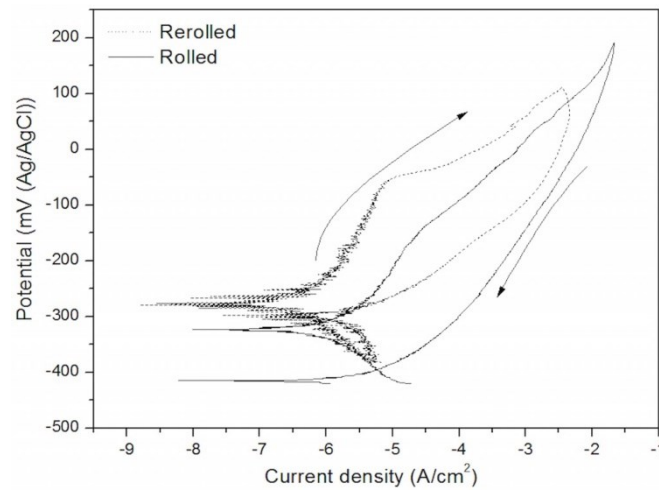


Figure 4: Cyclic polarization curves obtained for the rolled and rerolled super martensitic steels in media of NaCl 35 g/L solution.

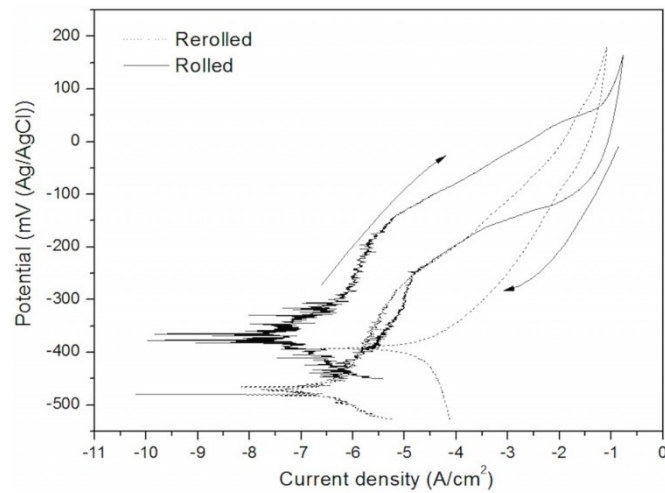


Figure 5: Cyclic polarization curves obtained for the rolled and rerolled super martensitic steels in media of standard solution.

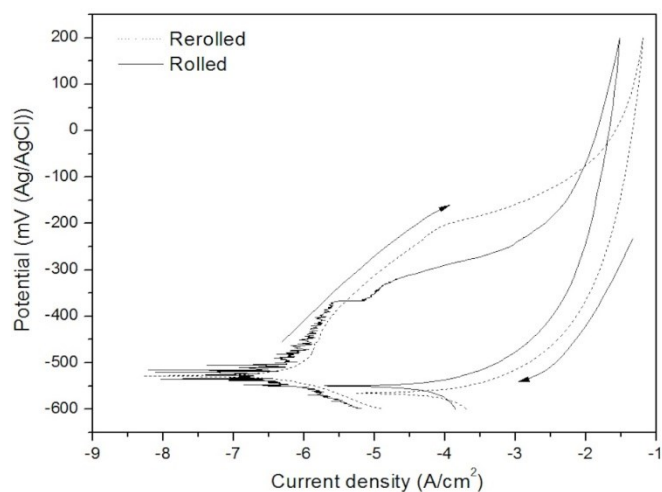


Figure 6: Cyclic polarization curves obtained for the rolled and rerolled super martensitic steels in an aqueous solution of NaCl 35 g/L, saturated with H₂S.

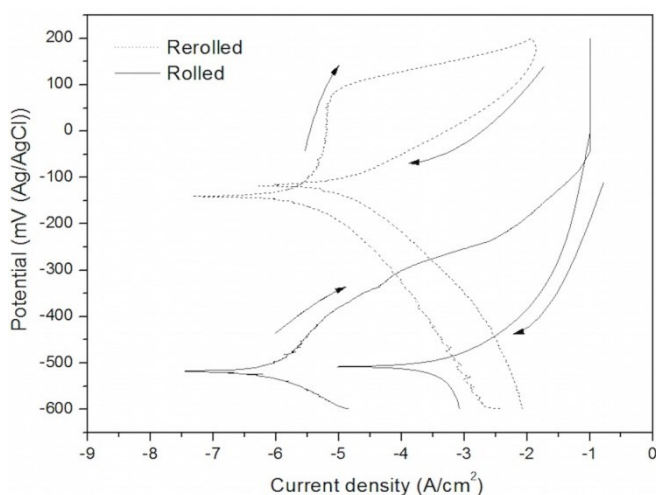


Figure 7: Cyclic polarization curves obtained for the rolled and rerolled super martensitic steels in a standard solution saturated with H₂S.

Figure 8 shows the SEM micrograph of steel surface after polarization in 35 g/L NaCl solution.

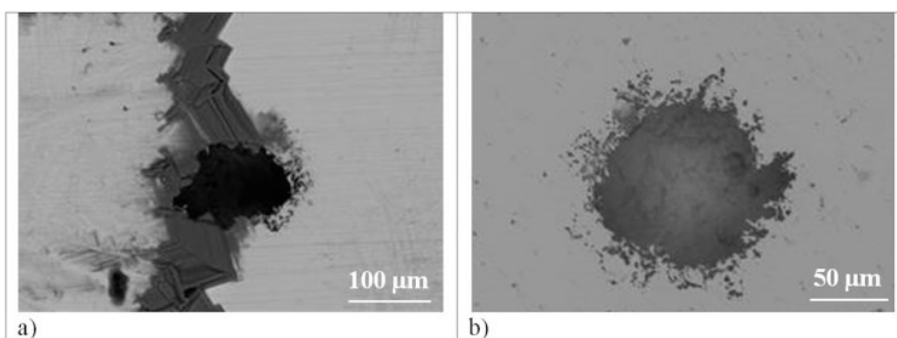


Figure 8: SEM micrograph of rolled steel (a) and rerolled steel (b) surface after polarization test in 35 g/L NaCl solution.

4. DISCUSSION

The steel microstructures (Fig.1) were characteristic of a super martensitic steel and the martensitic phase was observed. It seems that a refinement of microstructure occurred after the rerolled condition. The rolled steels were provided by a steel manufacturer.

The equivalent circuit fitted to the data is associated to corrosion on the steel surface. In the 35 g/L NaCl solution and in the standard solution saturated with H₂S, both steels showed a similar value of polariza-

tion resistance of $10^4 \Omega \cdot \text{cm}^2$. In medium of standard solution, the rolled steels showed a polarization resistance one order of magnitude ($10^5 \Omega \cdot \text{cm}^2$) higher than in other media.

The rerolled steel showed a higher corrosion resistance (higher pitting potential and lower passivation current density) in 35 g/L NaCl solution than the steel in rolled condition. In NaCl solution saturated with H_2S , the rolled steel showed a higher polarization resistance and a higher pitting potential than the rerolled steel.

After saturation of 35g/L NaCl solution with H_2S , the polarization resistance did not significantly change but the medium became more aggressive decreasing the pitting potential of steels. All media studied are aggressive to super martensitic steel in relation to other media reported in literature such as natural seawater [21]. Rodrigues et al. [21] studied the effect of phosphorus content on corrosion of super martensitic steels in natural seawater and found higher values of pitting potential (0.290-0.310 V) (Ag/AgCl) than the values obtained in this research (-0.420-0.090 V) (Ag/AgCl).

In acidic standard solution, the rolled steel showed a higher corrosion resistance than the rerolled steel presenting a higher polarization resistance, higher pitting potential and lower passivation current density. However, in this solution, only the rerolled steel presented a repassivation process with a potential protection of -393mV (Ag / AgCl).

After saturation with H_2S of the standard solution, the polarization resistance of steels and the pitting potential of rolled steel decreased. However, the pitting potential of rerolled steel increased after H_2S addition.

Comparing the saline solutions with 35g/L and 120 g/L, the pitting potential decreased as the content of chloride increases as related in literature [22]. However, in this work, the increase in chloride content was associated to the decrease of pH contributing to a more significant increase of electrolyte corrosivity. Wang et al. [23] proposed an equation for solutions containing low chloride concentrations. It has been found that the pit nucleation potential (E_{pitting}) is a logarithmic function of Cl^- concentration. In H_2S saturated solutions, there is the added effect of decreasing the pH, which increases the dissolution rate of steel, rendering the passive film very thin with the possible presence of structural defects [24].

The cathodic reaction of steel corrosion in neutral 35 g/L NaCl solution is:



In NaCl solution saturated with H_2S , the oxygen content decreased, an additional aggressive ion HS^- was added, the solution became acid occurring the predominant cathodic reaction:



The pH of the standard solution is 4.5 and the cathodic reactions of steel corrosion are Eq. (2) and (3).



The cathodic reaction of the saturated standard solution is mainly the hydrogen reduction since the oxygen content decreased. The rerolled steel showed a higher corrosion resistance when the predominant cathodic reaction was the hydrogen reduction and when the cathodic reaction was the oxygen reduction. The rolled steel showed a higher corrosion resistance when the predominant cathodic reaction was the hydrogen reduction in media containing chlorides and hydrogen sulfide. In aqueous solution of 35 g/L NaCl, the rolled and rerolled steels showed pitting diameter of 140 μm and 100 μm , respectively. It seems that the grain refinement of steel restricted the pit growth.

The analysis of scanning electron microscopy revealed the formation of a layer of corrosion product, probably iron sulfide on the surface of steels tested in solutions saturated with H₂S.

5. CONCLUSIONS

The effect of H₂S saturation of a 35g/L NaCl on the corrosion resistance of steels was detrimental, decreasing the pitting potential of steels. After saturation with H₂S of the standard solution, the polarization resistance of steels and the pitting potential of rolled steel decreased. However, the pitting potential of rerolled steel increased after H₂S addition.

The super martensitic steel in the rerolled condition showed a higher corrosion resistance than the rolled steel in an aqueous solution of 35 g/L NaCl and in a standard solution saturated with H₂S. In the 35 g/L NaCl aqueous solution saturated with H₂S and in the standard solution, the rolled steel showed a higher corrosion resistance than the rerolled steel. However, in the standard solution, only the rerolled steel presented a repassivation process with a potential protection of - 393mV (Ag/AgCl).

In aqueous solution of NaCl, the rolled and rerolled steels showed pitting diameter of 140µm and 100µm, respectively.

The analysis of scanning electron microscopy revealed the formation of a layer of corrosion product, probably iron sulfide on the surface of steels tested in NaCl solution and standard solution saturated with H₂S.

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