

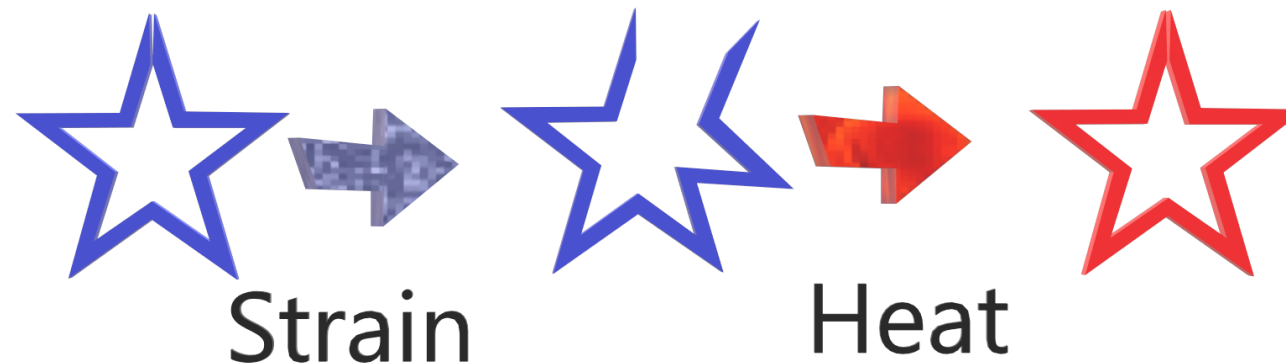
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Electrochemical and Morphological Characterization of Fe-28Mn-6Si-5Cr Shape Memory Steel

CMDWC
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1. Introduction

- Shape Memory Steel (SMS) is a kind of smart material that combines the structural properties of steel with the Memory Shape Effect.
- The Memory Shape Effect (SME) is the property thanks to which the material can be deformed beyond its elastic limit and shaped back to its original state due to a phenomena called Martensitic Transformation, and it is thanks to the unique changes in the microstructure of the SMS.
- The martensitic transformation is created by submitting the material to stress and reversed by a heating process.



1. Introduction

The SMS is being studied to be used in many applications to take advantage of its properties, being some examples:

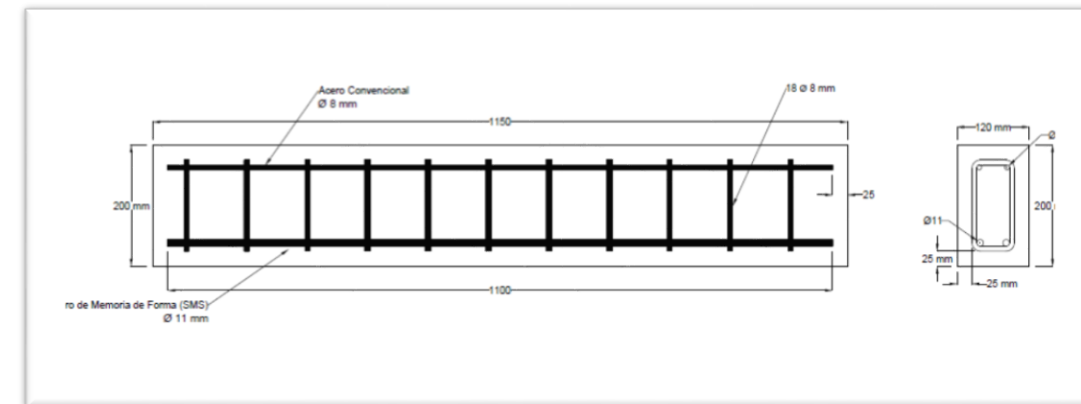
- Pipeline coupling in petrochemical plants, using the SME to ensure tight fittings.
- Earthquake damper, to exploit the energy dissipation property intrinsic of the SME.
- Structural use in reinforced concrete beams, in prestressed applications.



Pipeline coupler



Earthquake damper



SMS prestressed beam

2. Objectives

The aim of this current work is to:

- Characterize the microstructure of the SMS.
- Identify the activation temperature of the alloy.
- Study its electrochemical behavior and compare the results with those of a reference commercial steel.

3. Experimental Setup

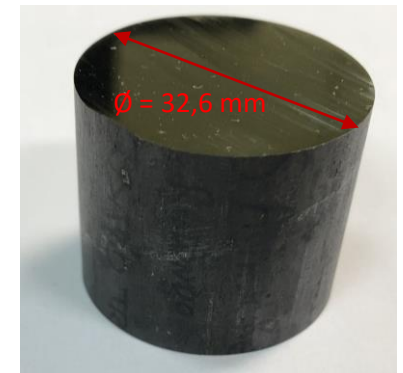
3.1 Materials

The materials used will be:

- Shape Memory Steel (SMS): a Fe based alloy that has the Shape Memory Properties described previously. It is composed of **Fe-28Mn-6Si-5Cr**.
- Carbon Steel: a Fe based alloy with a low percentage of C.



Carbon steel sample



Fe-28Mn-6Si-5Cr sample

3.2 Experimental Techniques

- Microstructure characterization will be performed with Light Optical Microscope (LOM) and Scanning Electron Microscope (SEM).
- Activation temperatures were assessed with DSC techniques were done with a heating rate of $2.5 \text{ }^{\circ}\text{C min}^{-1}$ in a stream of N_2 (50 ml/min), in a 40 μL Al crucible.

3.2 Experimental Techniques

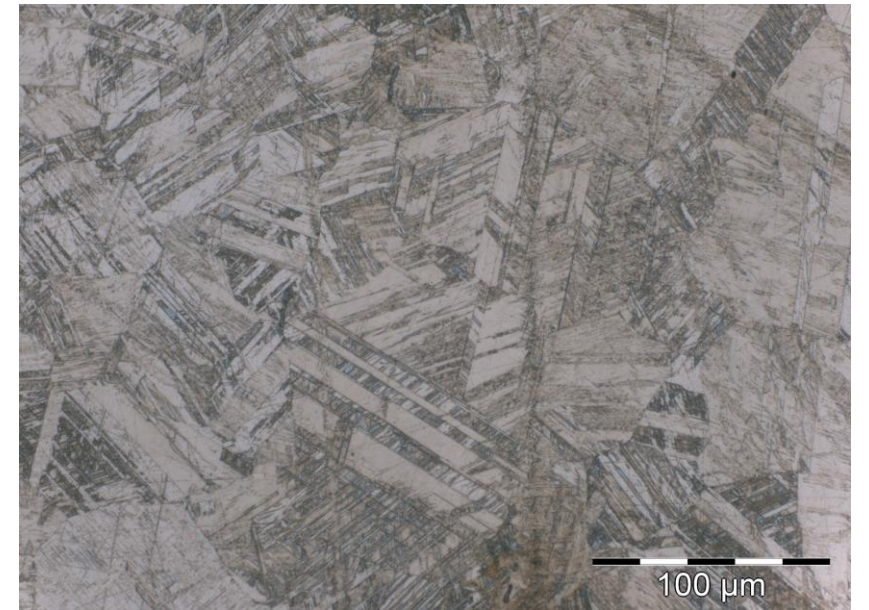
- Electrochemical tests were performed with a three electrode electrochemical cell (RE = Hg/HgO ; CE = Ti-MMOx). The test surface was 0,636 cm² and was tested with an Autolab potentiostat.
- The used electrolyte is a 0.1 M NaOH + 0.1 M KOH solution (pH = 13).
- Passivated samples will be attacked with Cl⁻ until pitting by the addition of incremental amounts of a NaOH 0.1 M + KOH 0.1 M + NaCl 5M solution.
 - OCP measurements were performed to check the passivity process during 7 days.
 - Voltammetry tests were performed from -0.15 V_{OCP} to +1.5 V_{OCP} with a scan rate of 2 mV s⁻¹. Samples were stabilized for an hour before performing the test.
 - EIS test were performed with a frequency range being 10 kHz to 1 mHz, 7 points for each decade, and with an amplitude of 5 mV_{RMS}. The measurements were performed every 12 hours.

4. Results

4.1 Microstructural characterization

Regarding the LOM images, the following observations of the microstructure can be made:

- γ -Austenite phase is found, with clearly defined uniform grains that are randomly oriented.
- Deformation twins are also spotted on the inside of the grain.
- Within the γ -austenite grains, dark parallel lines can be defined as ϵ -martensite.

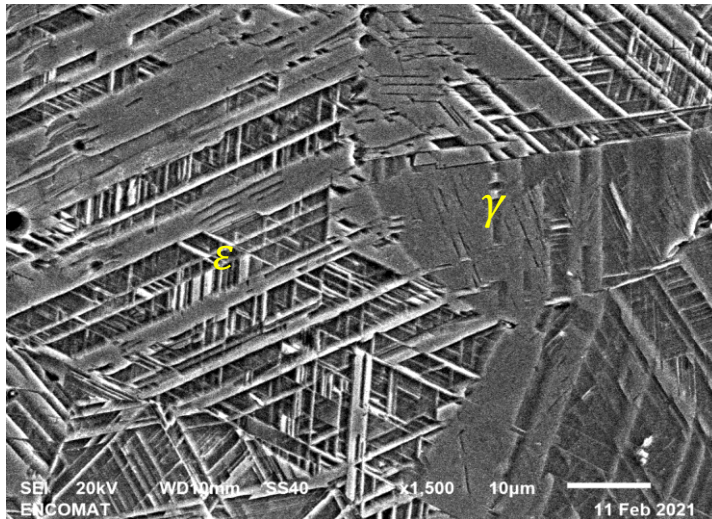


LOM micrograph showing a general view of the SMS alloy

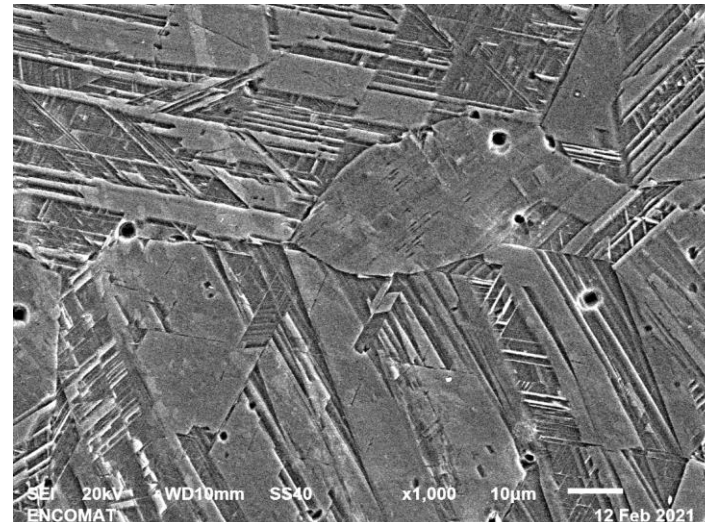
4.1 Microstructural characterization

SEM observations confirm the identification of both **microstructures** previously characterized, while at the same time highlighting the following:

- The ϵ -martensite phase is composed of regularly spaced individual plates with irregular thickness.



SEM micrograph showing a general view of the SMS alloy

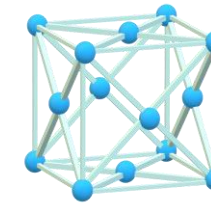


SEM micrograph showing the alloy after heating $T > 160\text{ }^{\circ}\text{C}$

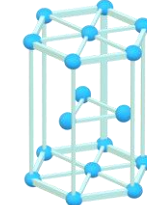
- It is also notable the descent in the ϵ -martensite percentage after being submitted to a heating process with a temperature over $160\text{ }^{\circ}\text{C}$ for 5 minutes.

4.2 Thermal analysis

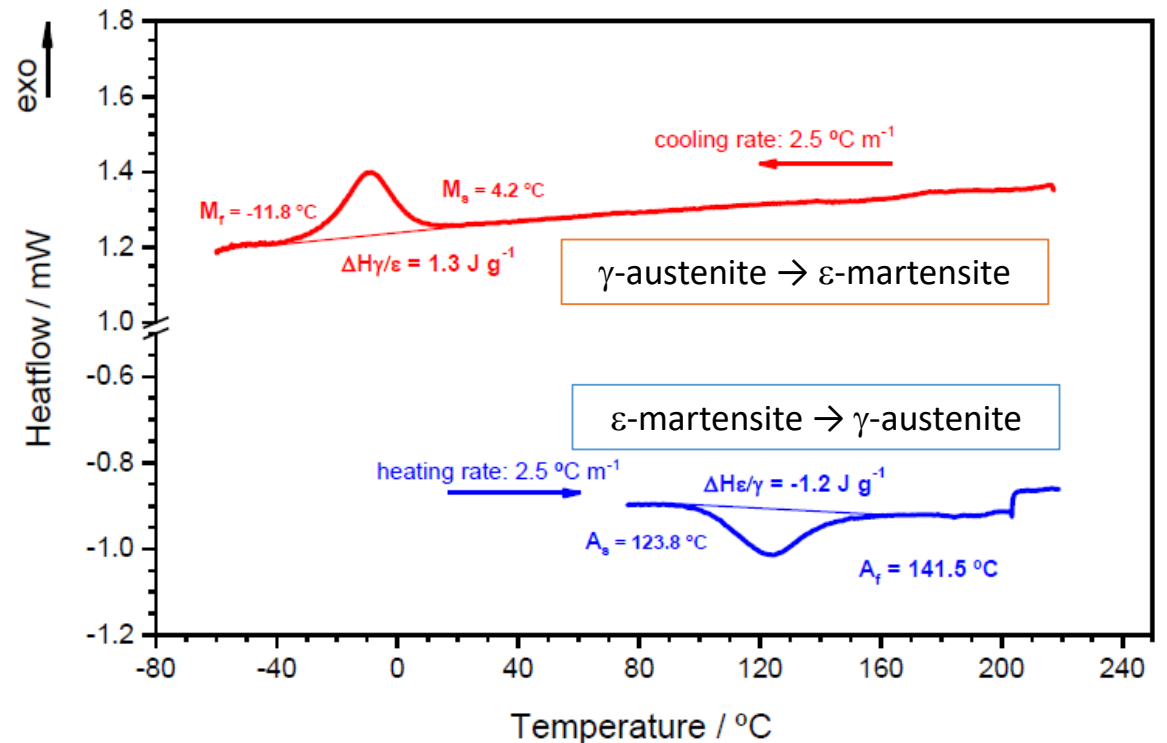
- Characterization of the temperatures in which the SMS experiences thermal-induced transformations from ϵ -martensite (hcp structure) to γ -austenite (fcc structure).
- The transformation from ϵ -martensite to γ -austenite starts at A_s , finishes at A_f , and the same is applied to the reverse transformation, ϵ -martensite to γ -austenite, that starts at M_s and finishes at M_f .



γ -austenite (fcc structure)



ϵ -martensite (hcp structure)

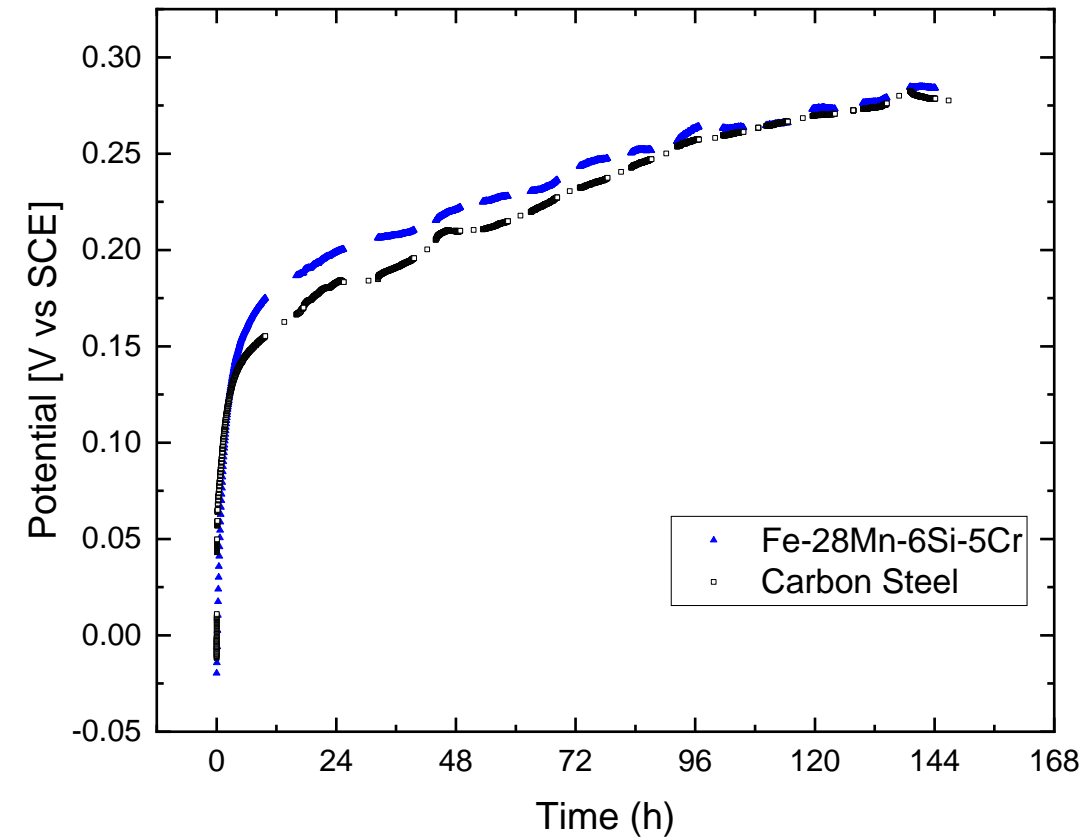


DSC curves of heating and cooling of the Fe-28Mn-6Si-5Cr

4.3 Electrochemical characterization

4.3.1 OCP results

- In the case of the Fe-28Mn-6Si-5Cr, the OCP starts at -20 mV, increasing rapidly and reaching pseudo-stability in the first 25 hours, with values in this stage between 200 mV and 280 mV.
- Similarly, in the case of the carbon steel, the first measurements return a value of -45 mV, with a similar pseudo-stable stage that reaches values between 185 mV and 280 mV after the first 25 hours.

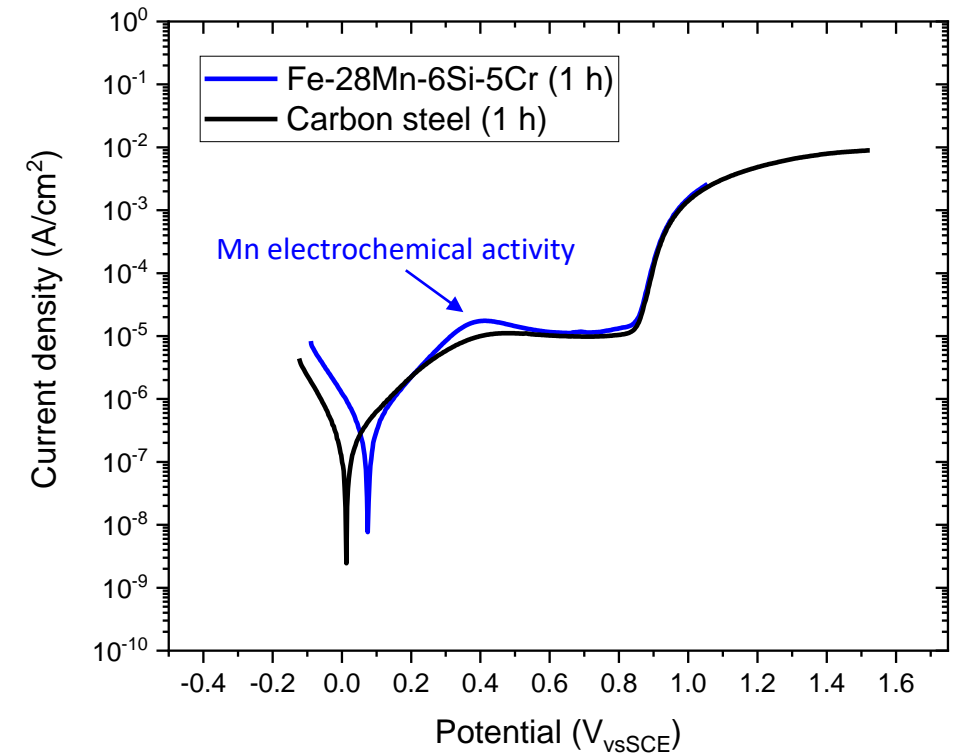


OCP chart of the SMS and Carbon Steel, in pH 13 solution for 7 days

4.3.2 Potentiodynamic (PD) curves

- E_{corr} of the SMS is slightly more anodic than the E_{corr} of the carbon steel.
- The SMS presents a peak associated with the Mn electrochemical activity.

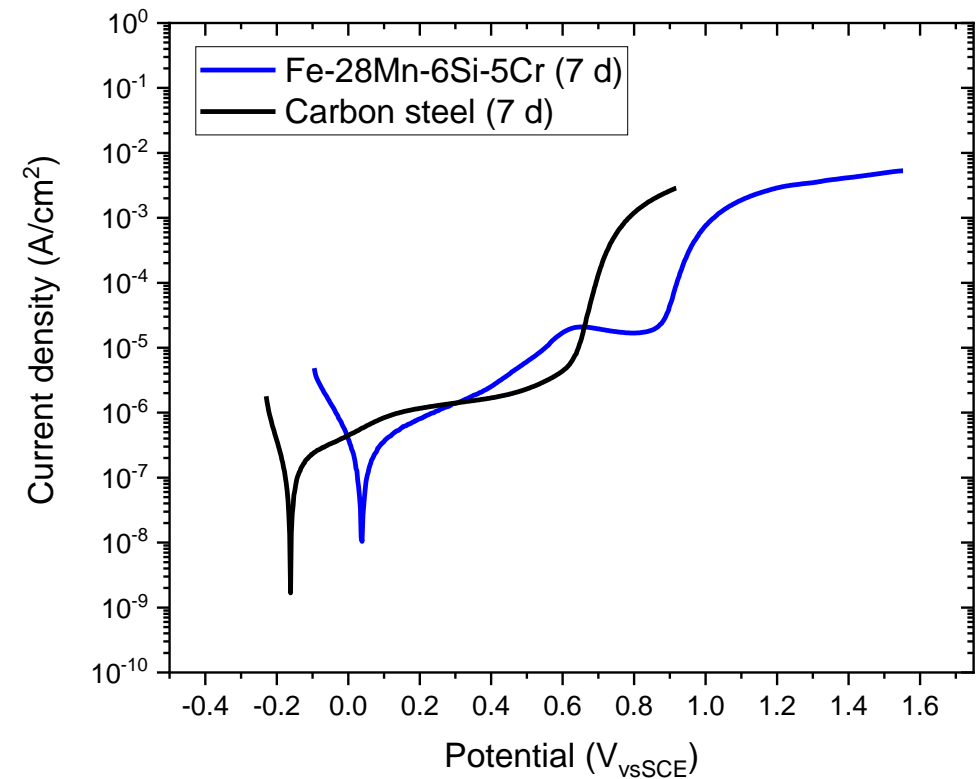
	Fe-28Mn-6Si-5Cr	Carbon steel
E_{corr} (V)	0.072	0.029
j_{corr} ($\mu\text{A}/\text{cm}^2$)	0.302	0.146
R_p ($\text{k}\Omega$)	146	248



4.3.2 Potentiodynamic (PD) curves

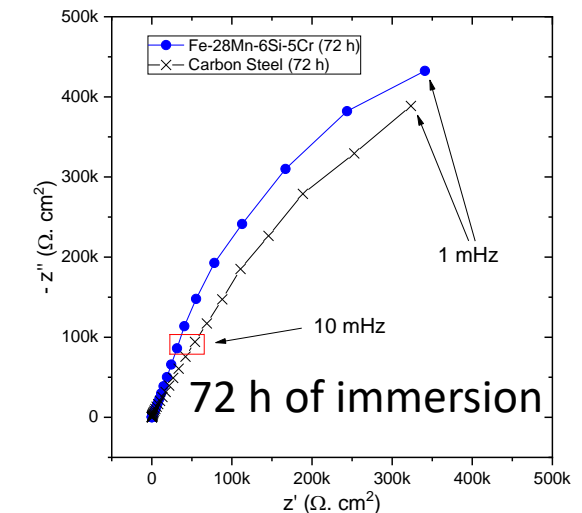
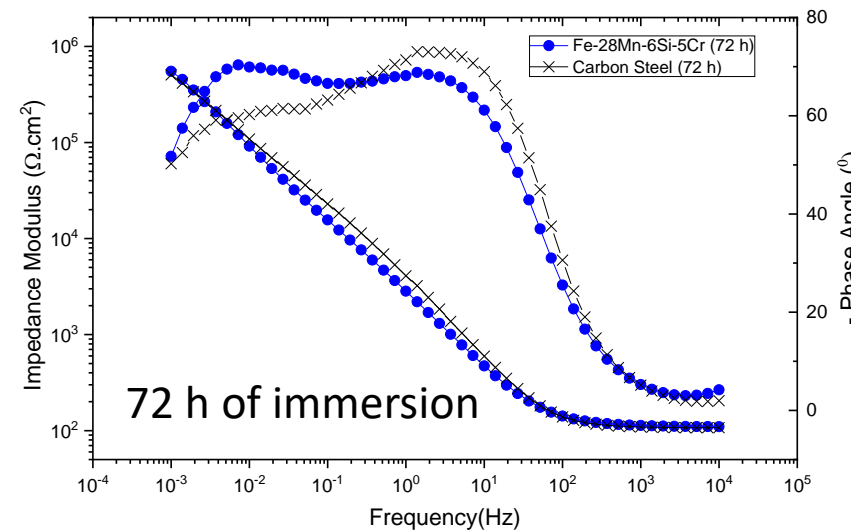
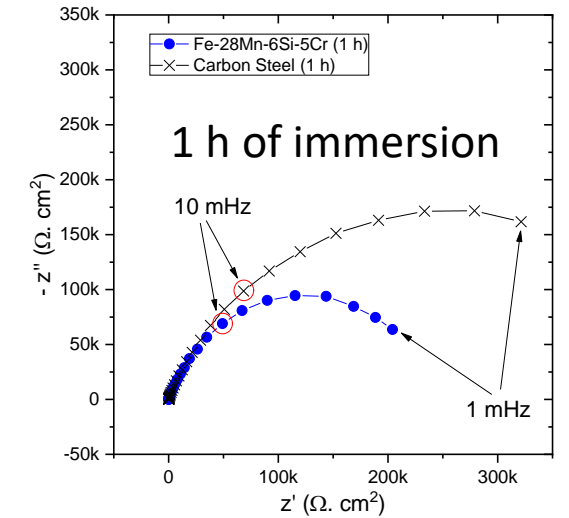
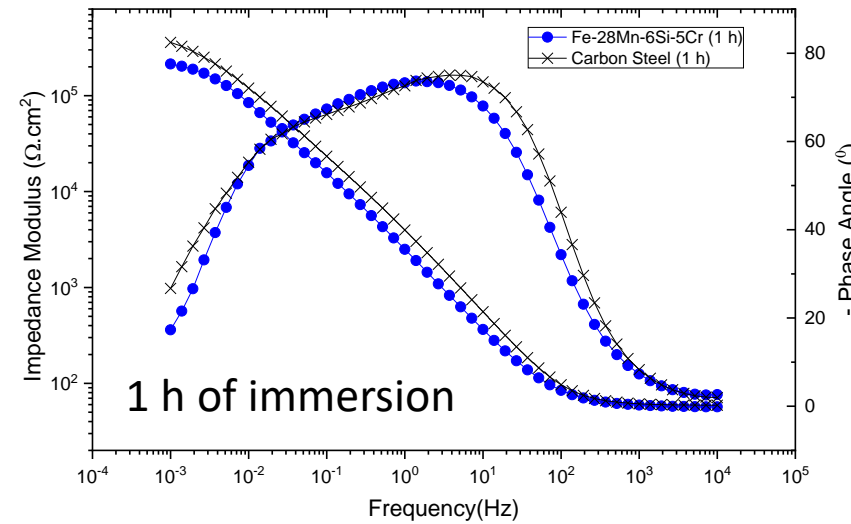
- After 7 days of immersion, there is a decrease in the current density indicative of passivation in both samples.
- The Mn activity peak continues present in the SMS sample.

	Fe-28Mn-6Si-5Cr	Carbon steel
E_{corr} (V)	0.054	0.094
j_{corr} ($\mu\text{A}/\text{cm}^2$)	0.251	0.120
R_p ($\text{k}\Omega$)	209	246



4.3.3 EIS results

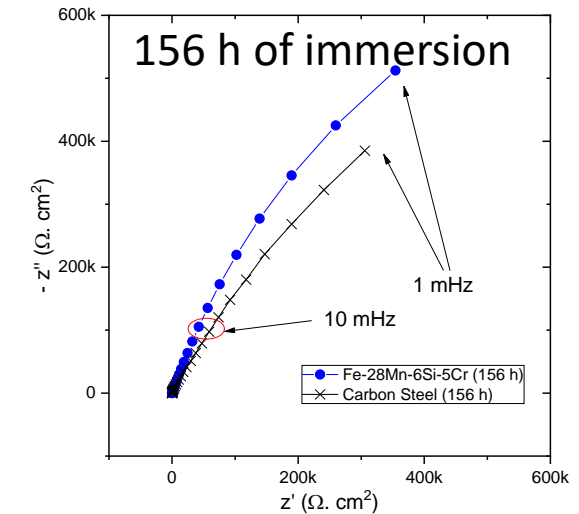
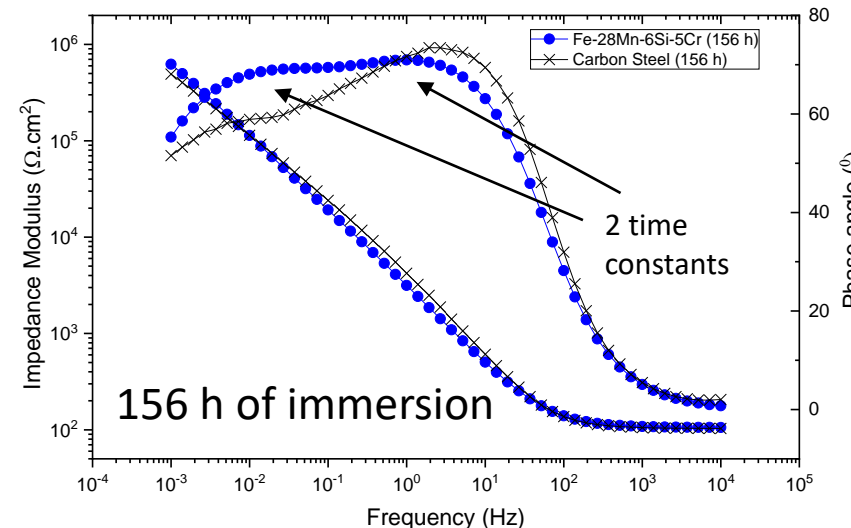
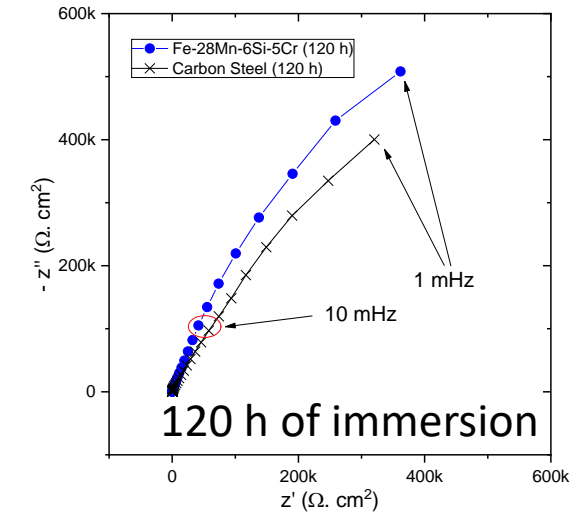
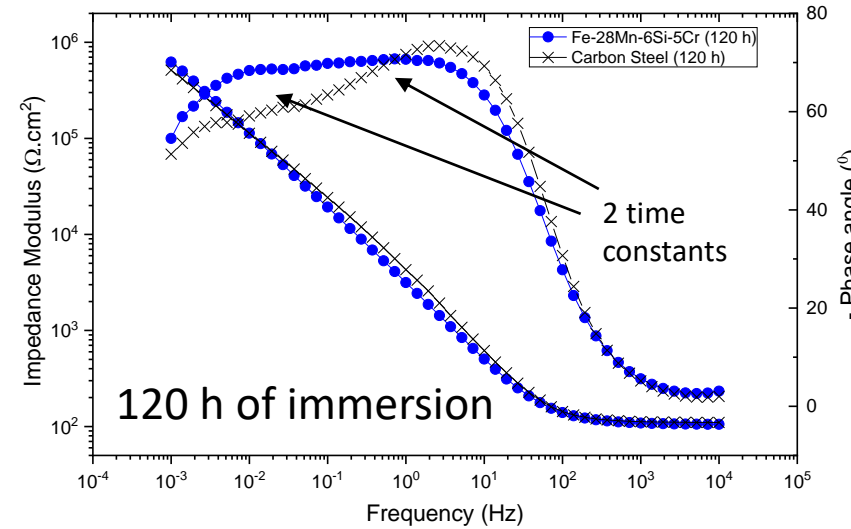
- EIS test results of the Fe-28Mn-6Si-5Cr are compared with those of the carbon steel.
- Impedance increase is observed with immersion time in both samples, indicative of a passivating process, in agreement with the OCP evolution.
- Initially, impedance is higher in the carbon steel sample, although at higher immersion times the value of the SMS has higher values.



EIS diagrams of the SMS and carbon steel, in NaOH 0.1 M + KOH 0.1 M, at 1 hour and 72 hours of immersion

4.3.3 EIS results

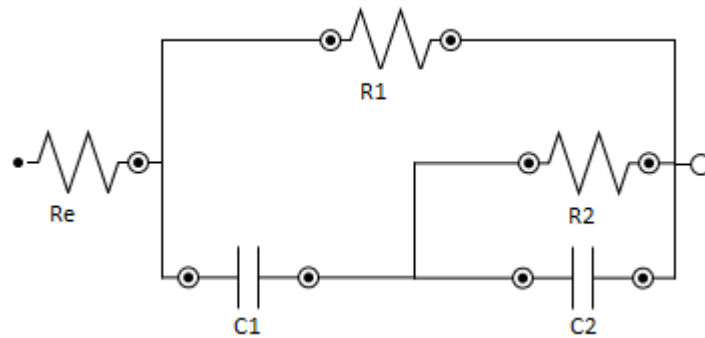
- This tendency is still present until the end of the immersion time.
- No further evolution is observed after 120 hours of immersion time in neither of the samples.
- Two time constants can be appreciated from the Bode plots.



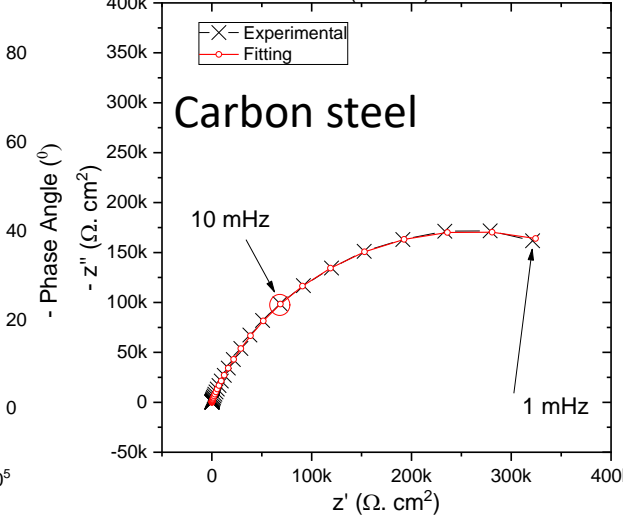
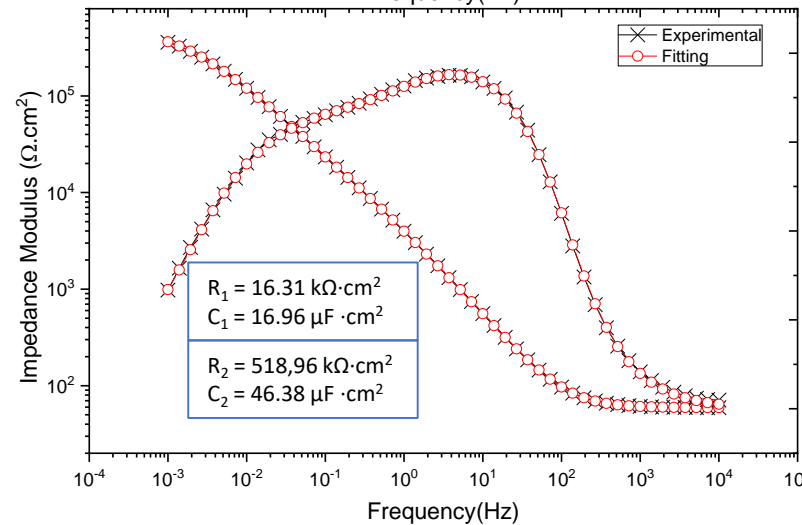
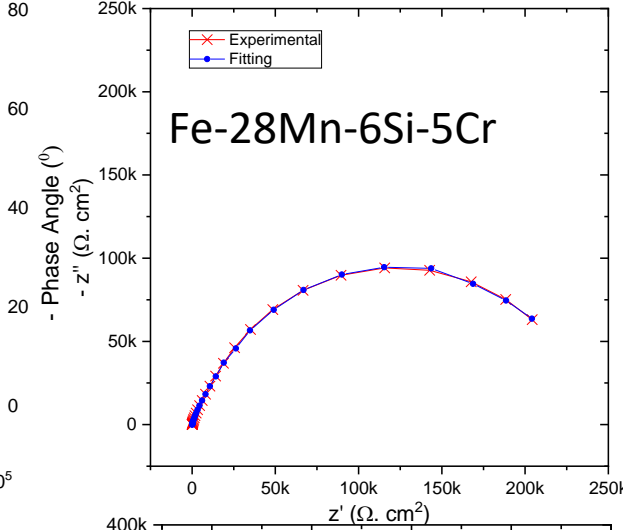
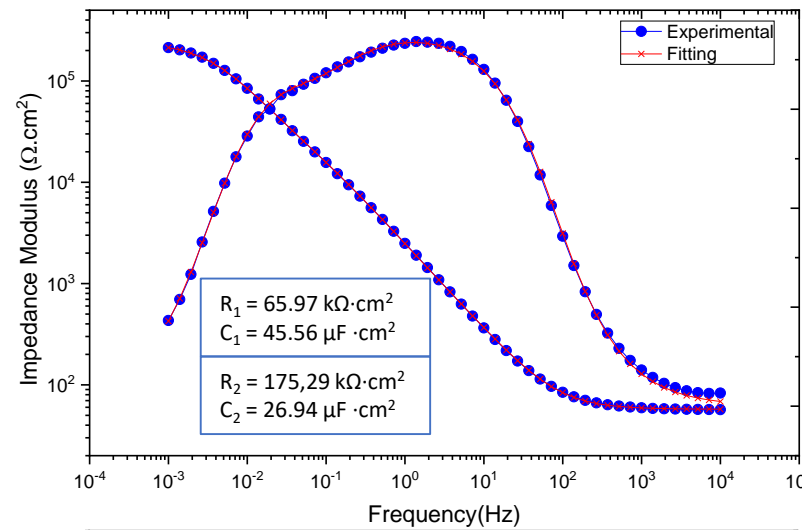
EIS diagrams of the SMS and carbon steel, in NaOH 0.1 M + KOH 0.1 M, at 120 hour and 156 hours of immersion

4.3.3 EIS results

- Electrical equivalent circuit (EEC) used:



- Fitting results are accurate in both materials, as shown in the corresponding Bode and Nyquist diagrams.

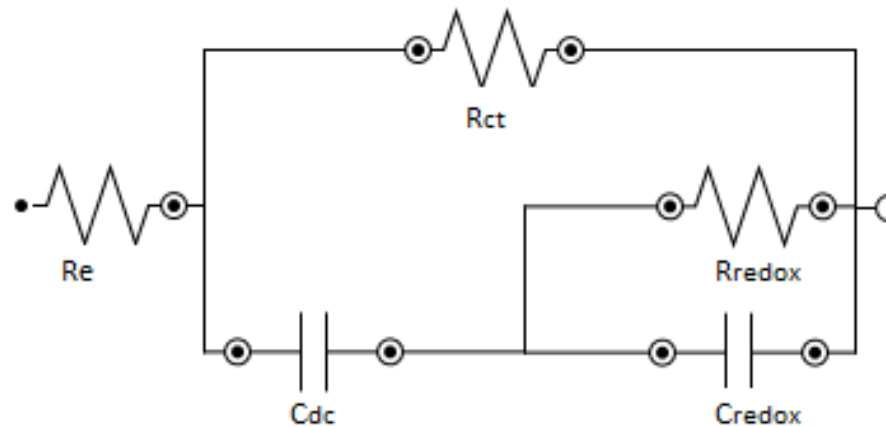


Experimental and fitted data using the proposed EEC of the SMS and carbon steel, in NaOH 0.1 M + KOH 0.1 M, at 1 hour of immersion time. The best fitting parameters are inserted in the Bode plots

4.3.3 EIS results

The 2 constants are interpreted as:

- 1st time constant: it is located in the high frequency range, and is related to the corrosion process. Thus R1 corresponds to the charge transfer resistance (R_{ct}) and C1 is the double layer capacitance.
- 2nd constant: it is located in the low frequency range, and is tied to the redox phenomena for the $Fe^{2+} \leftrightarrow Fe^{3+}$ reaction



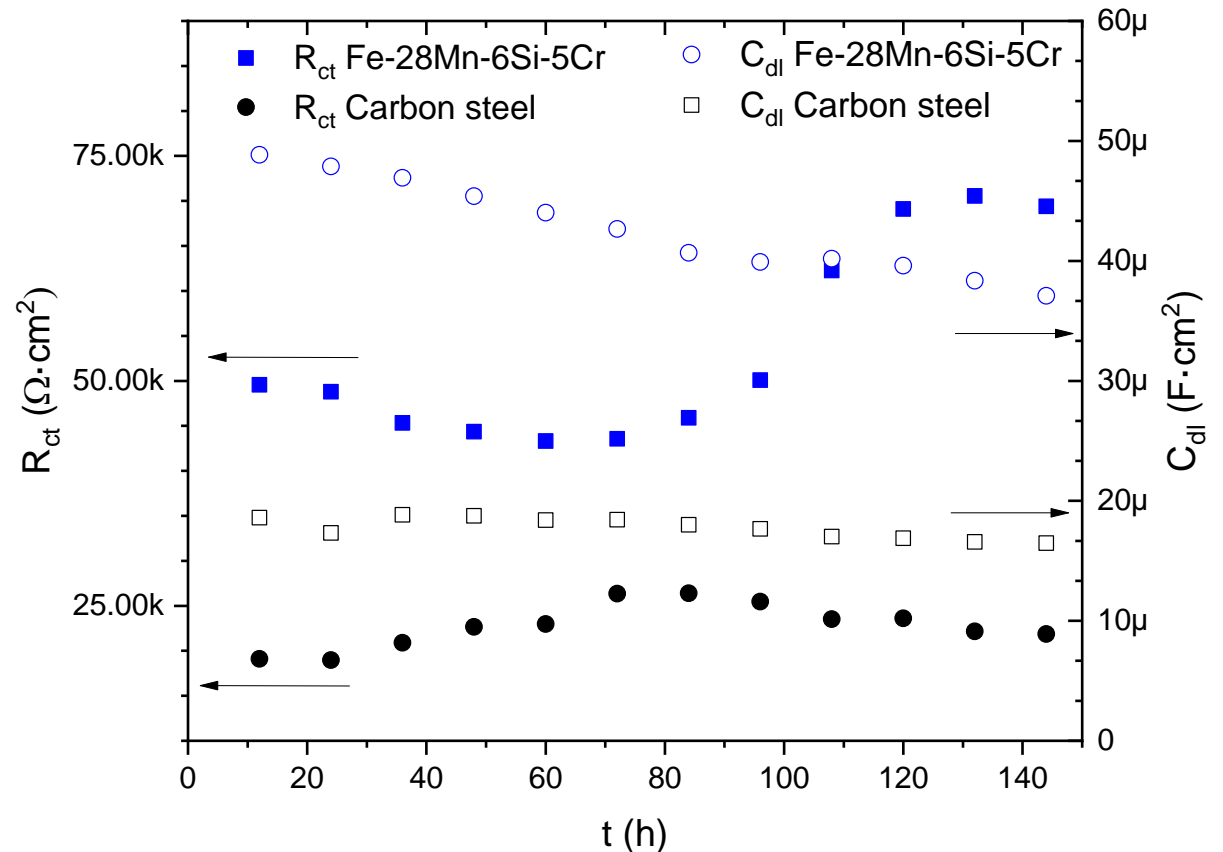
- R_e = Electrolyte Resistance
- R_{ct} = Charge transfer Resistance
- C_{dc} = Double layer Capacitance
- R_{redox} = Redox processes Resistance
- C_{redox} = Redox processes Capacitance

Proposed 2 time constant fitting model with named elements

4.3.3 EIS results

1st constant:

- **R_{ct}** : After a slight descent until the 90th hour, the Fe-28Mn-6Si-5Cr value increases substantially. It shows passivation in long time periods. The carbon steel increases the value until the 80th hour and afterwards remains stable. This evolution suggests a faster passivating kinetics for carbon steel.
- **C_{dl}** : In both materials it is shown a decrease on the value, in agreement with a descent in the active surface.
- Those results are consistent with the generation of the passive layer.

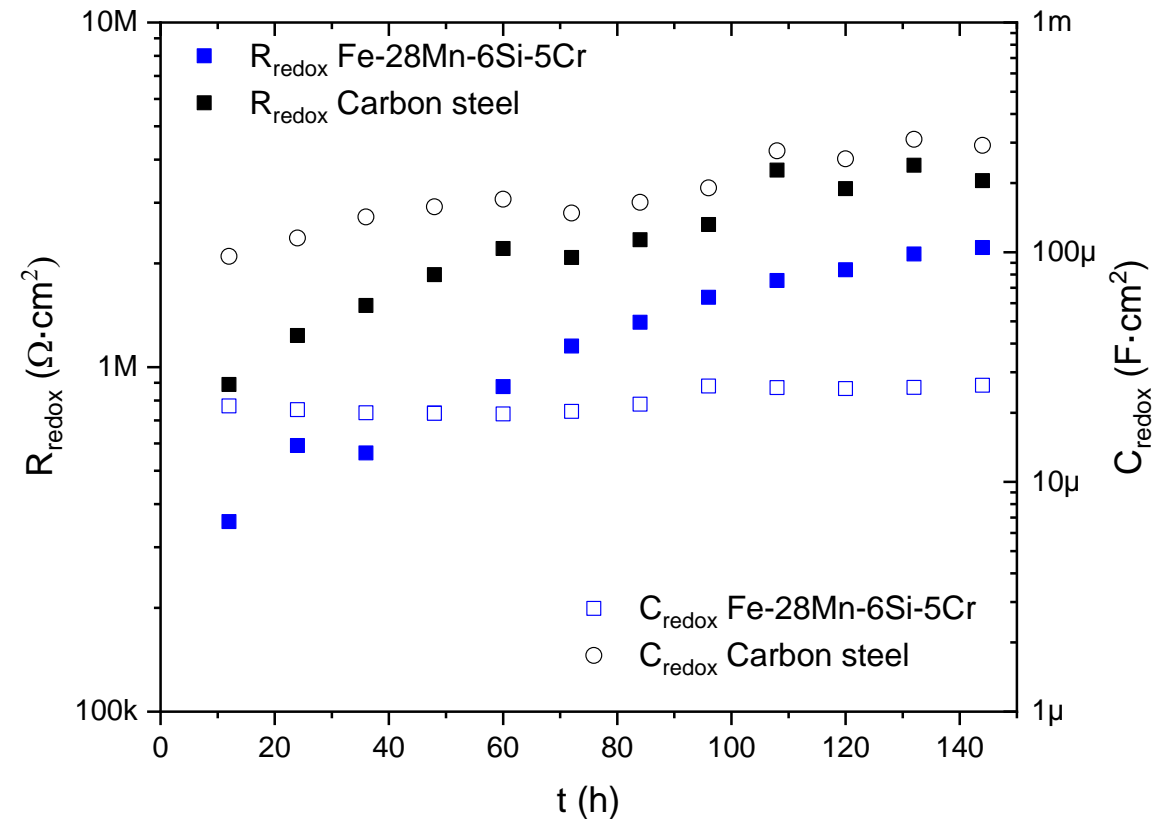


R_{ct} and C_{dl} evolution of the SMS and carbon steel samples in NaOH 0.1 M + KOH 0.1 M for 7 days.

4.3.3 EIS results

2st constant:

- R_{redox} : in both materials the value increases, so the $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ reaction is getting slower.
- C_{redox} : The value stays practically constant.

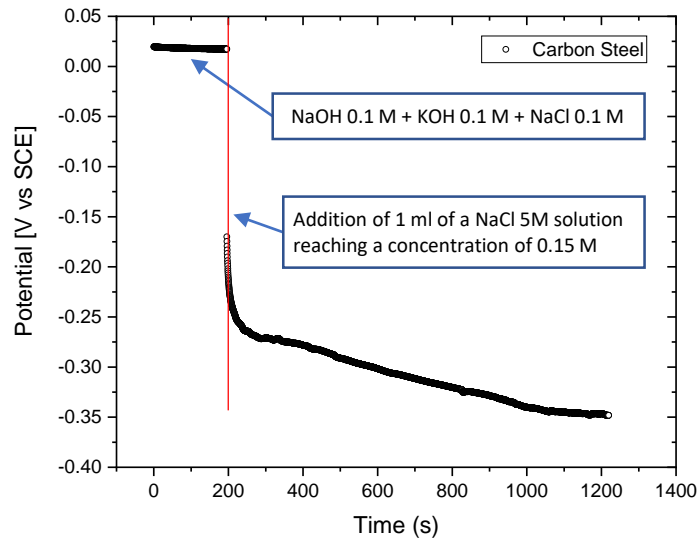


R_{redox} and C_{redox} evolution of the SMS and carbon steel samples in NaOH 0.1 M + KOH 0.1 M for 7 days.

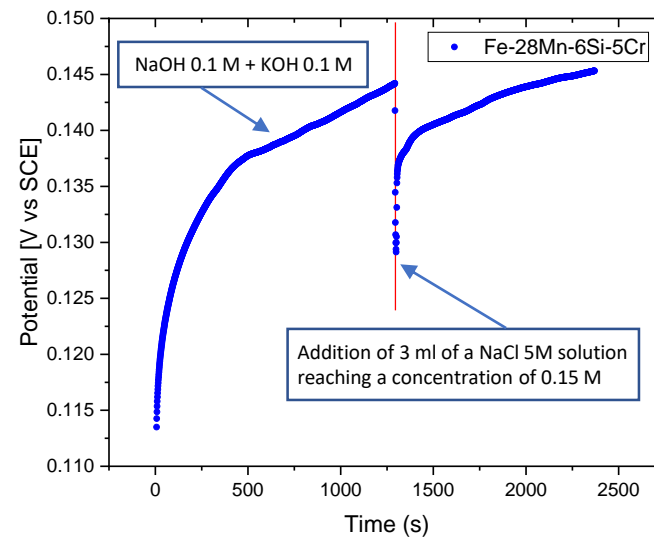
4.3.4 Effect of chloride additions

The carbon steel is more sensitive to the chloride additions. The passive layer is broken with a 0.15 M concentration. In the case of the SMS, concentration for the passive layer breakdown is 5 times higher.

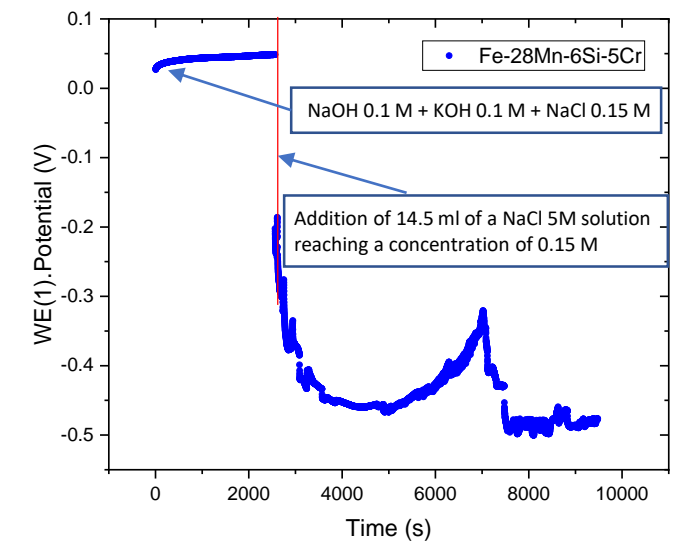
OCP evolution with immersion time and chloride additions



Passivity breakdown of the carbon steel after going from [0.10 M] Cl⁻ to [0.15 M] Cl⁻



Passivity recovery of the SMS after going from [0.00 M] Cl⁻ to [0.15 M] Cl⁻



Passivity breakdown of the SMS after going from [0.15 M] Cl⁻ to [0.75 M] Cl⁻

5. Conclusions

The drawn conclusions in this study are:

- The morphological characterization shows that two phases can be clearly distinguished, γ -austenite and ε -martensite.
- Thermal studies determined the activation temperature, being $A_s = 123.8$ °C, $A_f = 141.5$ °C, $M_s = 4.2$ °C and $M_f = -11.8$ °C.
- The electrochemical study shows that:
 - Passivation occurs in both materials.
 - EIS measurements corroborate the passive state of both materials, with a higher R_{ct} values in the SMS case.
 - Chloride addition studies show that the SMS withholds a 5 times higher concentration of Cl⁻ ion than that of the carbon steel.

6. Acknowledgment

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Thank you for your attention

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