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ELECTROCHEMICAL BEHAVIOUR OF AUSTENITIC STAINLESS STEEL IN 3.5 WT% NaCl SOLUTION IN THE PRESENCE OF CAFFEINE ENVIRONMENTAL FRIENDLY CORROSION INHIBITOR

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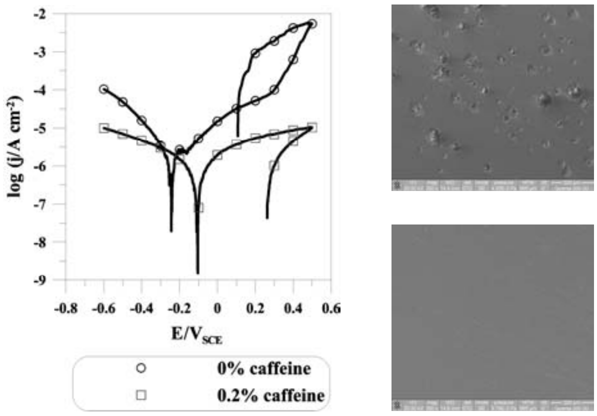
The corrosion inhibition behaviour of caffeine on austenitic stainless steel in 3.5 wt% NaCl solutions at 25 °C was studied by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. The results obtained by potentiodynamic polarization measurements are consistent with the results of the electrochemical impedance spectroscopy measurements. Caffeine significantly reduces the corrosion rates of austenitic stainless steel, and inhibition efficiency (IE) increases with increasing caffeine concentrations. The surface morphology of the corroded austenitic stainless steel samples in 3.5% NaCl solution in the absence and the presence of 0.2% caffeine, after polarization tests, were evaluated by scanning electron microscopy (SEM).



INTRODUCTION

Among metals, austenitic stainless steel is extensively investigated in corrosion studies because of its wide application in different corrosive environment.[1] One of the important and practical methods of protecting steel from corrosion is to use inhibitors.[2] Corrosion inhibitors are compounds that are commonly added in small quantities to an environment for preventing corrosion.

Do to the increase of environmental awareness, research in corrosion prevention is oriented to the development of the so-called green compounds with good inhibition efficiency and with low risk of environmental pollution.[3-5] A number of organic compounds have been widely used as potential corrosion inhibitor.[5-10]

Caffeine is a natural organic substance existing in different parts of a great number of vegetables.[11-13] Caffeine is effective, environmental friendly corrosion inhibitor.[14,15] Also, caffeine is biodegradable and environmentally benign with minimal health and safety concern.

The aim of this paper is to study the corrosion inhibition behaviour of caffeine for austenitic stainless steel in 3.5% NaCl solution by potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS) technique.

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MATERIALS AND METHODS

Materials

The austenitic stainless steel, used in these tests, was mirror-polished (with 400 to 2000 grit emery paper and alumina suspension), washed with bi-distilled water, ultrasonically degreased in ethanol and dried in air. The chemical composition of investigated austenitic stainless steel is reported in previous cited work[1]. Samples were embedded in a polytetrafluoroethylene (PTFE) holder specifically designed to connect to a rotating disc electrode (type EDI 101T; Radiometer Analytical, France). A polymeric resin was used to ensure a tight seal between the specimen and the PTFE holder, to avoid crevice corrosion.[16]

Electrochemical measurements

Corrosion tests were performed electrochemically at room temperature (~ 25 ^oC) in a 3.5 wt% NaCl in distilled water. The concentration of caffeine used for the study ranges from 0.1 wt% to 0.4 wt%.

The test specimens were placed in a glass corrosion cell, which was filled with fresh electrolyte. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum coil as the counter electrode. All potentials referred to in this article are with respect to SCE.

Electrochemical measurements were performed using a potentiostat manufactured by PAR (Model PARSTAT 4000, Princeton Applied Research, USA). The instrument was controlled by a personal computer and specific software (VersaStudio, PAR, USA).

Linear potentiodynamic polarization measurement was performed by stepping the potential using a scanning rate of 0.5 mV/s from -0.6 V_{SCE} to +0.5 V_{SCE}. Before starting the measurements, the specimens were left in the solution for 24 hours.

Electrochemical impedance spectroscopy (EIS) was used in this study, based on the fact that it was considered an adequate method to investigate corrosion resistance of metallic materials. The alternating current (AC) impedance spectrum for all samples was obtained with a scan frequency range of 100 kHz to 10 mHz with amplitude of 10 mV. The EIS spectra were obtained at different times after the austenitic stainless steel was immersed in 3.5% NaCl solution in the absence and the presence of caffeine. The polarization resistance (R_p) of the specimens was obtained using ZSimpWin software (PAR USA) to the experimental EIS data.

SEM analysis of corroded surfaces

The surface morphology after linear polarization tests of austenitic stainless steel in 3.5% NaCl solution in the absence and the presence of 0.2% caffeine were analyzed by scanning electron microscopy (SEM), using Quanta 3D scanning electron microscope (model AL99/D8229).

RESULTS AND DISCUSSIONS

The cyclic potentiodynamic polarization curves for the corrosion of austenitic stainless steel in 3.5% NaCl solution in the absence and the presence of 0.2% caffeine at a scan rate of 0.5 mV/s, are shown in Fig. 1. The curves were swept from -0.6 V_{SCE} to +0.5 V_{SCE}. Prior to the potential scan the samples were left under open circuit conditions in the respective solutions for 24 hours.

The values of electrochemical parameters as deduced from these curves, e.g., the zero current potential (ZCP), the corrosion current density (j_{corr}), and the inhibition efficiency (IE%) are shown in Table 1. The IE was calculated using the equation:

$$IE\% = \left(1 - \frac{j_{corr}}{j^o_{corr}}\right) \cdot 100 \quad (1)$$

where j^o_{corr} and j_{corr} are the corrosion current density in the absence and the presence of inhibitor, respectively. The value of ZCP in the presence of caffeine shift to more positive value indicating that the compound act more anodic than cathodic as inhibitor. From Table 1, the corrosion current density of austenitic stainless steel in presence of caffeine is lower than austenitic stainless steel in absence of caffeine. Caffeine (0.2%) provides protection of about 60% in 3.5% NaCl solution.

The austenitic stainless steel in 3.5% NaCl solution in the absence of caffeine show a large positive hysteresis because of being susceptible to pitting corrosion. The area of hysteresis loop is a direct measure of the pits propagation kinetics. The austenitic stainless steel in 3.5% NaCl solution in the presence of 0.2% caffeine showed no positive hysteresis loop in the polarization curve.

Micrographs of austenitic stainless steel in 3.5% NaCl solution in the absence and the presence of 0.2% caffeine are shown in Fig. 2. As stated in the interpretation of the potentiodynamic data, the austenitic stainless steel in 3.5% NaCl solution in the absence of caffeine present susceptibility to localized attack (Fig. 2A).

The localized corrosion on the austenitic stainless steel in 3.5% NaCl solution in the presence of 0.2% caffeine is not evident in Fig. 2B.

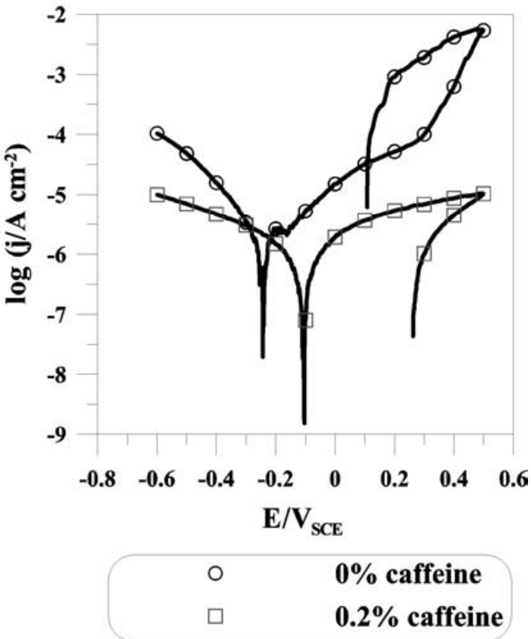
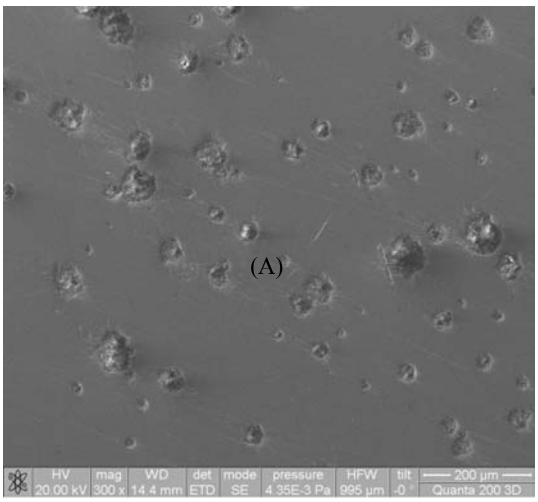


Fig. 1 – Cyclic potentiodynamic polarization curves of austenitic stainless steel in 3.5% NaCl solution in the absence and the presence of 0.2% caffeine, at 25 °C, on semi-logarithmic coordinates.

Table 1

The electrochemical parameters of austenitic stainless steel in 3.5% NaCl solution in the absence and the presence of 0.2% caffeine, obtained from polarization measurements

Caffeine (wt%)	ZCP (mV_{SCE})	j_{corr} ($\mu A/cm^2$)	IE (%)
0	-243	1.2	-
0.2	-104	0.5	58.3



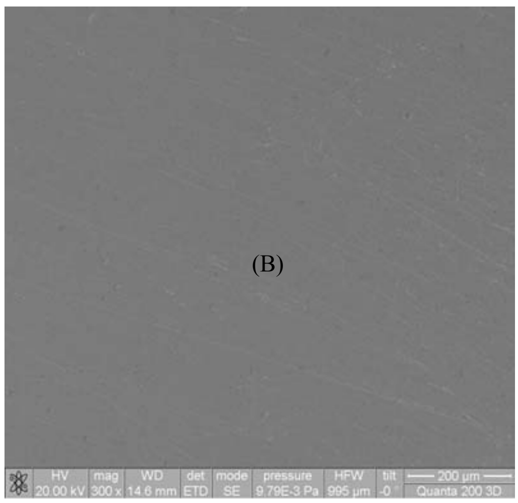


Fig. 2 – SEM photographs of the surface of austenitic stainless steel after polarization measurements in: (A) absence of caffeine, and (B) presence of 0.2% caffeine.

Impedance measurement is widely used to study the corrosion inhibition process. Electrochemical impedance spectroscopy (EIS) results of the austenitic stainless steel recorded in 3.5% NaCl solution in the absence and presence of the caffeine inhibitor, at 25 ^{o}C are shown in Fig. 3.

The Bode-phase plots show two times constant for austenitic stainless steel recorded in 3.5% NaCl solution in the absence of caffeine. The impedance spectra was carried out using an EC (Fig. 4A) with a series combination of the R_{sol} solution resistance, and with two RQ elements in parallel: $R_{sol}(R_1Q_1)(R_2Q_2)$. The high frequency R_1 and Q_1 parameters are the properties of the reactions at the oxide layer/solution interfaces. The R_2 and Q_2 parameters describe the properties for oxide layer formed on the surface. Table 2 shows the results of the fittings.

The polarization resistance (R_p) of the austenitic stainless steel recorded in 3.5% NaCl solution equals the sum R_1 and the passive film resistance R_2. R_p allows a quantitative analysis based on the specific magnitudes of the corrosion rates.

The Bode impedance diagrams for austenitic stainless steel recorded in 3.5% NaCl solution in the presence of the caffeine inhibitor, at 25 ^{o}C are shown in Fig. 5.

Bode plots show that impedance and phase angle is greater for austenitic stainless steel in 3.5% NaCl solution in the presence of various concentrations of caffeine compared to austenitic stainless steel in 3.5% NaCl solution in the absence of caffeine.

According to the impedance diagram, after 1 hour and 24 hours immersion in 3.5% NaCl solution in the presence of various concentrations of caffeine, only one time constant was shown. Using a constant phase element (Q), the simple Randle's equivalent circuit was found to be satisfactory for fitting the impedance data. The model (inserted in Figure 4B) consisted of a solution resistance (R_{sol}) in series with RC parallel combination of (R_2 Q_2) which represents the oxide film resistance and a constant phase element for the oxide film, respectively. In this case, R_2 is the polarization resistance (R_p). The fitted parameters of some experiments are given in Table 2.

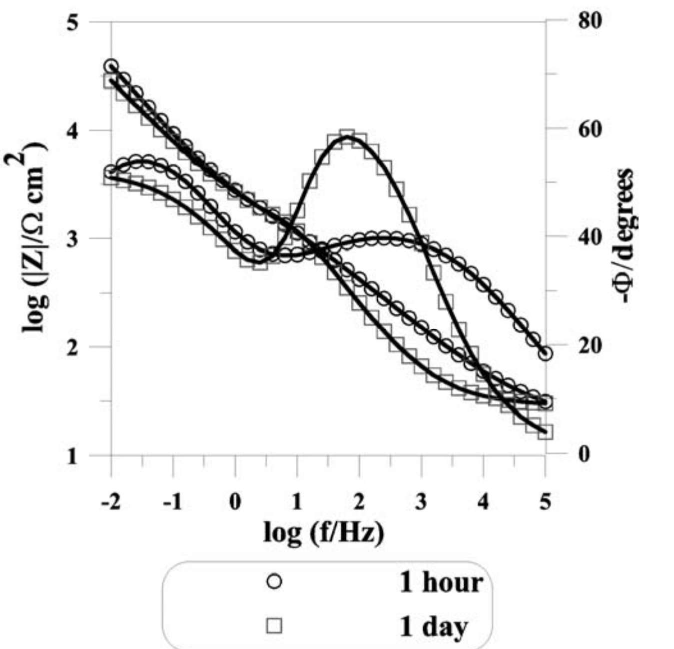
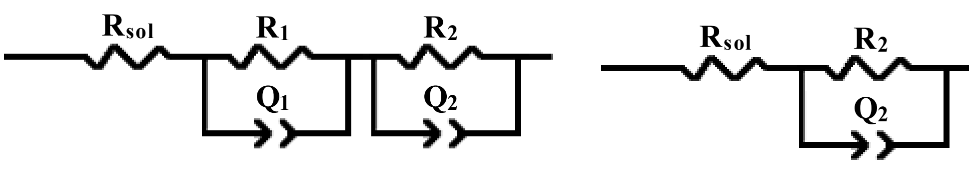


Fig. 3 – Measured (discrete points) and fitted (solid lines) impedance spectra for austenitic stainless steel in 3.5% NaCl solution, at different immersion times.



(A) (B)

Fig. 4 – Equivalent circuits used for fitting the measured impedance spectra.

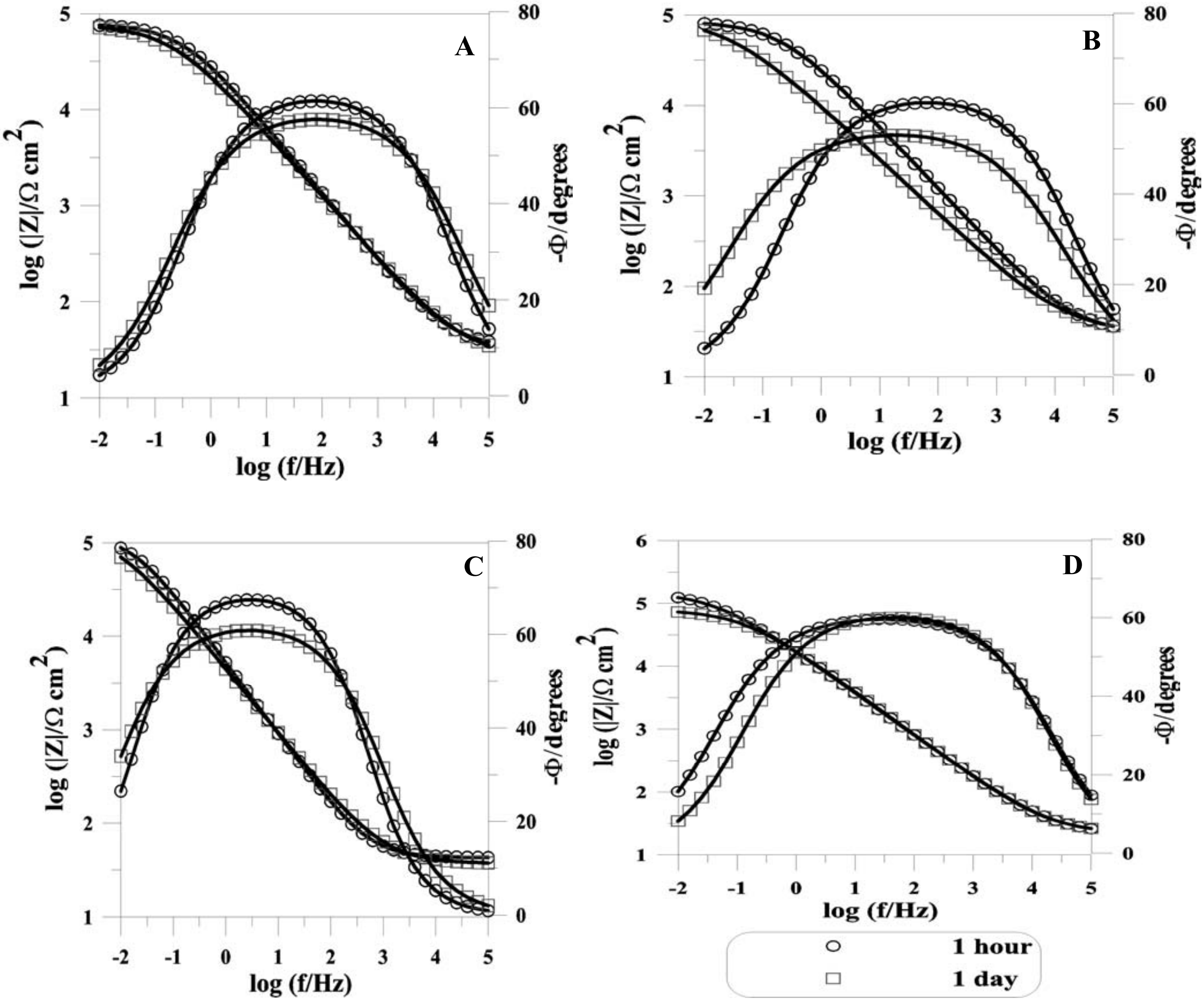


Fig. 5 – Measured (discrete points) and fitted (solid lines) impedance spectra for austenitic stainless steel in 3.5% NaCl solution in the presence of various concentrations of caffeine: (A) 0.1%, (B) 0.2%, (C) 0.3%, and (D) 0.4%, at different immersion times.

In order to compare capacitance values for austenitic stainless steel in 3.5% NaCl solution in the presence of various concentrations of caffeine, Q_2 (Table 2), were recalculated, using equation:[17]

$$C = \left(R^{1-n}Q\right)^{\frac{1}{n}} \quad (2)$$

In 3.5% NaCl solution in the presence of various concentrations of caffeine the capacitance (C_2) contains the contribution of both the capacitance of the oxide film on the austenitic stainless steel (C_{ox}) and the double layer capacitance (C_{dl}). These capacitances are in series giving the equivalent capacitance as follows:[18]

$$C_2 = \left[\left(C_{ox}\right)^{-1} + \left(C_{dl}\right)^{-1}\right]^{-1} \quad (3)$$

In 3.5% NaCl solution with caffeine, when caffeine molecules adsorb onto the electrode surface, a new capacitor (C_{ad}) needs to be considered in the equivalent circuit. If the surface is not homogeneously and compactly covered, the current will flow through two parallel paths: the first constituted by series combination of C_{ox} and C_{dl}, the second through the series combination of C_{ox} and C_{ad}.[18] As a result, the C_2 should be given by:

$$C_2 = \left[(C_{ox})^{-1} + (C_{dl})^{-1}\right]^{-1} + \left[(C_{ox})^{-1} + (C_{ad})^{-1}\right]^{-1} \quad (4)$$

Table 2

Impedance parameters of austenitic stainless steel after different time immersion in 3.5% NaCl solution in the absence and presence of various concentrations of caffeine

Caffeine (wt%)	10^{-3} R_1 (Ω cm^2)	10^5 Q_1 (S/cm^2 s^n)	n_1	10^{-4} R_2 (Ω cm^2)	10^5 Q_2 (S/cm^2 s^n)	n_2	C_2 (μF/cm^2)	10^{-4} R_p (Ω cm^2)	IE (%)
After 1 hour time immersion									
0	2.1	8.6	0.74	3.3	5.4	0.78	-	3.5	-
0.1	-	-	-	8.1	2.2	0.79	2.54	8.1	56.8
0.2	-	-	-	8.5	2.2	0.79	2.26	8.5	58.8
0.3	-	-	-	9.1	2.1	0.80	2.17	9.1	61.5
0.4	-	-	-	9.8	1.8	0.80	2.07	9.8	64.3
After 24 hours' time immersion									
0	1.2	9.1	0.65	2.7	5.6	0.77	-	2.8	-
0.1	-	-	-	7.1	2.3	0.80	2.60	7.1	60.6
0.2	-	-	-	7.3	2.2	0.80	2.47	7.3	61.6
0.3	-	-	-	7.6	2.1	0.80	2.36	7.6	63.2
0.4	-	-	-	7.8	1.9	0.80	2.10	7.8	64.1

However, if the coverage is homogenous and compact, all three capacitors are in series and the C_2 will be given as:

$$C_2 = \left[(C_{ox})^{-1} + (C_{dl})^{-1} + (C_{ad})^{-1}\right]^{-1} \quad (5)$$

Since the caffeine decreased the C_2, it is possible that the adsorbed caffeine formed a compact film.

A decrease in R_p is observed with increase immersion time. This suggests, probably, desorption of inhibitor film in time.

The inhibition efficiency IE% of caffeine at each concentration was calculated using the equation:

$$IE\% = \left(1 - \frac{R_p^o}{R_p}\right) \cdot 100 \quad (6)$$

where R_p^o and R_p are the polarization resistance in the absence and the presence of inhibitor, respectively.

The IE increases with increasing caffeine concentrations. The increased IE with increasing inhibitor concentration indicates that more caffeine molecules are adsorbed on the austenitic stainless steel surface restricting metal dissolution.

CONCLUSIONS

Caffeine is effective corrosion inhibitors in 3.5% NaCl solution. Additionally, the caffeine is environmentally benign, biodegradable, and nontoxic. Inhibition effect was studied by potentiodynamic polarization, and electrochemical impedance spectroscopy. Generally all results using both electrochemical techniques confirm each other. Good inhibition efficiency (IE) has been found in 3.5% NaCl solution reaches to 60%. Caffeine acts more anodic than cathodic as inhibitor. SEM studies confirm the inhibitive character of caffeine.

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