

Interaction between alternating current and cathodic protection over nano sized/structured surface metals

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ABSTRACT

Serious cases of corrosion of metallic structures under both alternating current (ac) and cathodic protection (cp) have been reported. The objective of this research is to propose a mechanism by which ac affects the nano sized/structured surface films formed on metals under cp. A model will be proposed and experimentally validated, in order to relate the metal corrosiveness to its nano sized/structured surface, under the simultaneous effect of ac and cp. This study intends to show how observations made by the ac-Voltammetry can be used to obtain an insight into the nature and mechanism of electrode processes. Once reactions are identified, the intensity and morphology of the surface damage will be related to the amplitude and frequency of the sinusoidal perturbation. Analytical and kinetic studies will be combined with Atomic Force Microscopy (AFM), performed firstly ex-situ and later in the electrolytic cell while the ac-corrosion is simulated, in order to obtain the nano-surface characterization.

Keywords: nano sized oxides film, ac-voltammetry, cathodic protection, ac-corrosion, AFM.

1 INTRODUCTION

It has been reported that metallic structures present corrosion damages while, under cathodic protection, are interfered with alternating currents. Different authors [1-3] have studied the phenomenon mathematically, but the involved mechanism is still not fully understood. It has been suggested that sinusoidal voltages of small amplitudes do not corrode the metal surface; in fact, the application of alternating signals to measure corrosion rates is a common practice today [4]. The analysis of the corrosion of mild steel under cathodic protection and ac-perturbations (e.g., in soil with basic pH at the surface, due to the high cathodic protection levels) calls for the necessity of an improvement of the study from both, the electrochemical and the physical points of view and its evaluation not only at the micro, but also at the nano-scale. The surface oxides film formed on mild steel in a basic NaOH 1M media was analyzed by two groups of researches: one intended to explain the corrosion of the mild steel when it is under ac perturbation, even

being in the range of thermodynamic immunity gained by the cathodic protection level. They suggested the formation of a non protective porous oxide, due to the ac perturbation, that was responsible for the ac-corrosion of the metal [5]. The second group analyzed the oxide film without ac perturbations. Then, based on dc Cyclic Voltammograms and other experiments, a more complete mechanism was proposed, coinciding with the first group, in the presence of that compound responsible of the poor corrosion protection of mild steels under certain conditions [6]. This research, attempts to characterize the surface oxides combining two approaches, i.e. studying the response of the system to dc signals, and analyzing its reversibility to ac perturbations. AFM analysis can complement ac-Voltammetry [7] in the study of the formation and stability of the surface oxides, under ac effects.

2 AC CORROSION. MECHANISM, MODELS AND CHARACTERIZATION

The more important phenomenon to be taken into account in the study of reactions occurring at the metal surface, under the combined effect of ac and dc perturbations, is the presence of the rectifying properties of the electron transfer reactions [7]. These properties are the consequence of changes in reaction rates with differences of potential across the interface. Specifically, when the alternating sinusoidal voltage is applied, periodic concentration changes of the reacting species are produced at that interface, being accompanied by periodical diffusion processes and the flow of a Faradic alternating current, which contains, at least, the harmonic component of the fundamental frequency. Effects of the non-linearity of the redox reactions are evidenced by the partial rectification of the alternating voltage, producing a direct potential and by the appearance of higher harmonics in the alternating current.

2.1 Corrosion mechanism by which ac affects the nano surface film of metals under cp

To propose the ac-corrosion mechanism of the surface metal under cathodic protection and ac-perturbations, this innovative research applies the ac-Voltammetry, used in analytical chemistry with non polarizable working

electrodes, onto a reactive one, to identify and characterize the sequence of reactions occurring at the metal surface, in the presence of ac and dc signals. This characterization is made through the study of the fundamental electrochemistry of the double layer and of the Pourbaix Fe diagram. AC-V, based on Polarography, applies an alternating sinusoidal voltage onto a solid electrode, while it is swept in a direct voltage range and the amplitude of the fundamental faradic current is recorded as a function of the dc potential. Phase angle variations and impedance data are recorded too. The reactions to be tested could behave reversible to dc and to ac polarizations, quasi-reversible with nernstian dc reversibility, or quasi-reversible without it. Applying AC-V, electron-transfer reactions, adsorption/desorption processes can be identified through the ac waves, while changes in the base-current could give information about the double layer. Once reactions are identified, the intensity and morphology of the surface damage will be related to the amplitude and frequency of the sinusoidal perturbation.

2.1 Modeling the ac-current vs. dc-voltage characteristic of the ac-corrosion process

Several mathematical models have been developed to simulate the current voltage characteristic of the electrode-electrolyte interface, when an alternating voltage is applied, with or without the presence of a direct potential [1-3]. Some of them have assumed a linear current-voltage relationship, when small amplitudes are applied; others have worked with larger amplitudes. It has been established that the total current will have a direct component coming from the faradic rectification effect and a series of harmonic components of the current due to non linear behavior of the electrode [1]. As a first approach, it is intended to model the amplitude of the first harmonic component of the current, $I(\omega t)$, through the equations established by polarographic theories for non polarizable working electrodes [7], but taking into account that, for this specific case of a reactive and stationary solid electrode, without renewal of the diffusion layer, the mean concentrations could be affected by the concentration profiles throughout the diffusion layer.

2.2 Nano Surface Characterization by AFM

It is interesting to relate the ac-perturbation parameters, to the damages occurring at the metal surface and, consequently, to its structure and corrosiveness. The study will be done at the micro and nano scales, because one specific nanostructure could be the responsible of the corrosion susceptibility of mild steel to ac and dc effects, or probably, the presence of alternating voltages could modify the nucleation during the formation of the new faces. AFM will be applied to study the corrosion morphology at the metal surface due to ac and dc polarizations, in this paper ex-situ and latter on, in the electrochemical cell.

3 EXPERIMENTAL

3.1 Reactions occurring on the mild steel surface, under ac and dc polarizations

The AC-V technique, allows identifying the reactions and their reversibility to ac and to dc polarizations. A stationary working mild steel electrode, a Platinum counter of large area and a SCE reference, with Luggin capillary, were used. An ASTM electrochemical cell contained the aerated and non stirred solution of NaOH 1M, pH 13-14 approx. An Autolab potentiostat was used with the following experimental setup: amplitude of the sinusoidal signal of 10 mV vs. SCE, phase angle of zero grades, to better filter the charging currents, sweep range of dc potential for a first set was between -1.5 and 1.5 V vs. SCE at Frequencies: 25, 50, 75, 100, 125 and 250 Hz, and for a second set (the analyzed by AFM) it was between -2.5 and -0.7 V vs. SCE, at 50 Hz.

3.2 Morphology of corrosion on the mild steel surface, under ac and dc polarizations

The Atomic Force Microscope (AFM) has been applied, ex-situ and in tapping mode, to study the corrosion morphology occurring at the electrode surface, due to the effect of dc and ac polarizations. The study of the surface of the polished mild steel sample was performed before and after 10 reversible cycles of AC-V, which applied a sinusoidal voltage of 10 mV vs. SCE of amplitude, at 50 Hz of frequency onto a range of direct scanning potential between -2.5 and -0.7 V vs. SCE.

4 RESULTS AND DISCUSSION

Figure 1 shows the forward ac-Voltammograms of a mild steel working electrode perturbed with an ac-sinusoidal voltage of 10 mV of amplitude, at six different frequencies.

Four peaks can be observed in Figure 1 in the forward direction of the scan. These peaks correspond to the reactions proposed by previous researchers [6] as follows: I and II are associated to the reduction of some adsorbed hydrogen and to the reaction of Fe^0 and Fe^{+2} forming FeO . Peak III, quasi imperceptible to other techniques, could be the reaction of Fe^0 and Fe^{+2} forming $\text{Fe}(\text{OH})_2$. Peak IV corresponds to the formation of magnetite, increasing with cycles and frequencies.

What still remains under verification is the presence of other two peaks (V and VI) that, according to [6] would correspond to the formation of two Fe^{+3} species obtained from the oxidation of magnetite: $3\gamma\text{-Fe}_2\text{O}_3$ and $3\alpha\text{-FeOOH}$, the last one supposed to be responsible for the corrosion of the metal under certain conditions.

The next test, to be presented in another paper, will be the 2nd harmonic Voltammetry, to verify the presence of those peaks, and to calculate the corrosion rate.

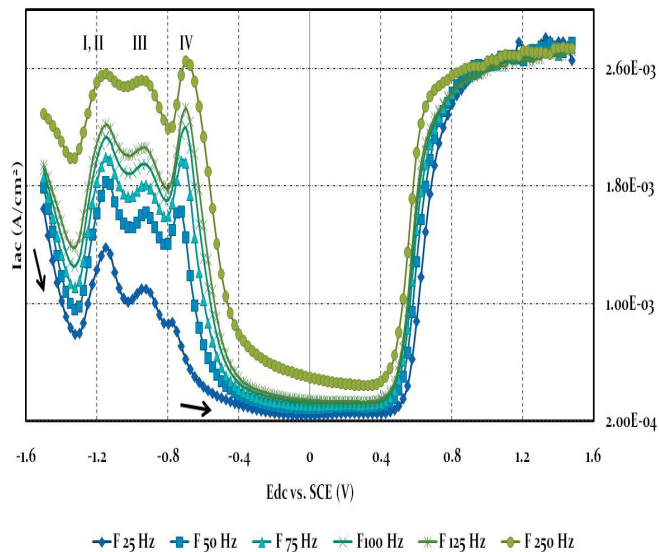


Figure 1: AC-V Dependence of I_{ac} on E_{dc} and Frequency

Figure 2 shows the zoom of experimental forward and backward ac-Voltammograms, for 10mV of sinusoidal amplitude, at six frequencies. The hysteresis observed indicate that dc reversibility does not hold; because the currents tend to depend on the sense of the direct sweep potential. Four peaks can be identified in the forward sense while only two in the backward. There are the crossover potentials where both forward and backward scans yield the same response, being those points the better to calculate transfer coefficients, rate constants and other kinetic parameters needed for the simulation of the ac-waves. The system is not reversible to dc neither to ac polarizations.

The Figure 3 shows the simulation of I and II peaks of the 25 Hz ac-Voltammogram, showed in figure 1.

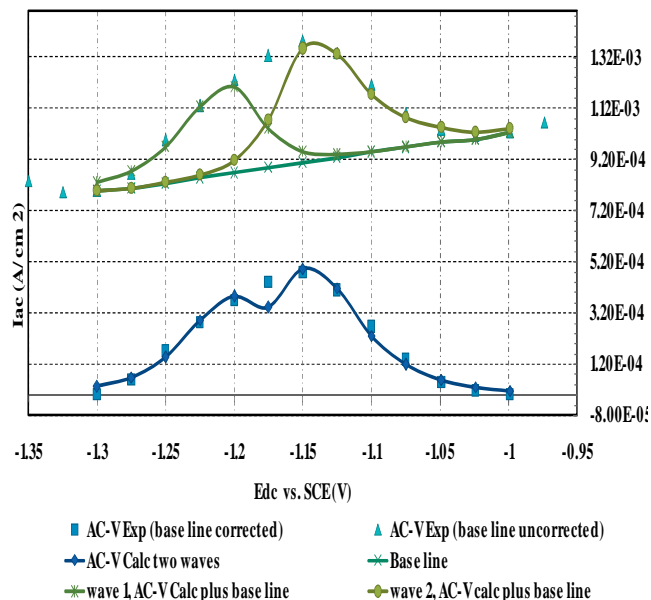


Figure 3: Simulation of peaks I and II of the AC-V at 25 Hz

The upper part of Figure 3 shows one experimental peak composed by two simulated small ones. Those peaks correspond to reactions of the cathodic protection system. At the bottom, the sum of the two simulated peaks is shown.

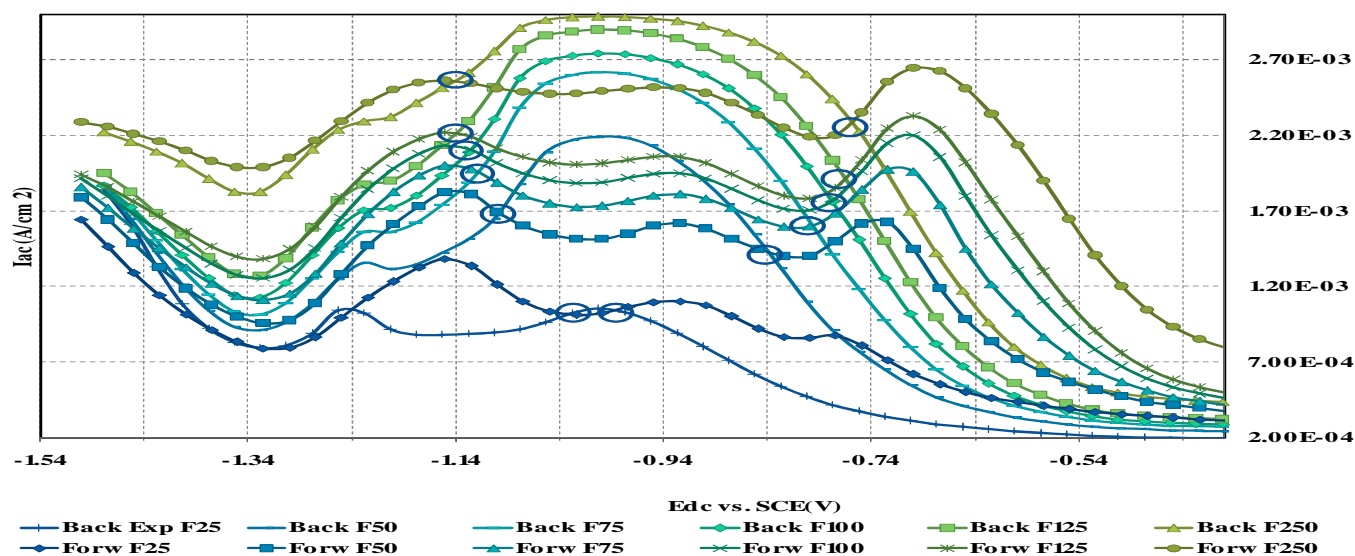


Figure 2: AC-V Dependence of I_{ac} on E_{dc} and Frequency

The analysis by AFM, ex-situ and in tapping mode, of the surface oxides film of the mild steel, after ten cycles of AC-V in the NaOH 1M solution, are shown in Figures 4 and 5. The consecutive cycles of dc plus ac polarization are responsible for the corrosion of the sample in one environment where, in the absence of ac perturbation, it would not occur. Pictures shown are 20 microns wide. The darker color represents a cavity with a maximum depth of 2 microns.

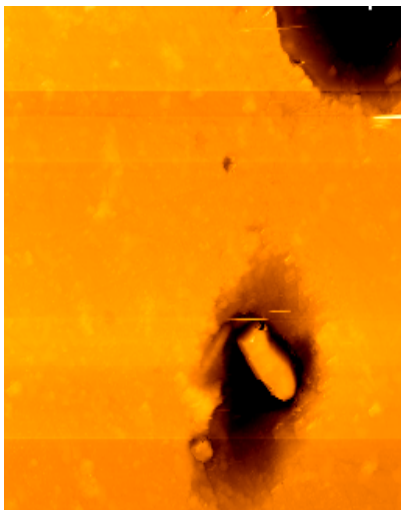


Figure 4: AFM after ten cycles of ACV with 10 mV of amplitude and 50 Hz.

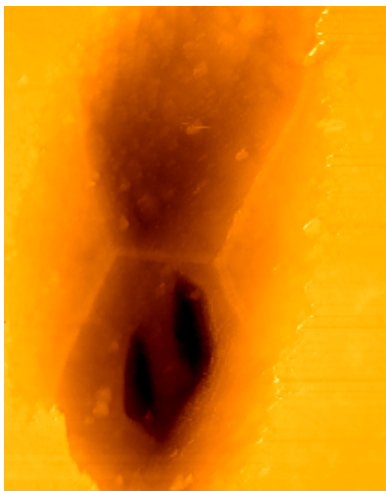


Figure 5: AFM after ten cycles of ACV with 10 mV of amplitude and 50 Hz.

In Figures 4 and 5, the morphology of corrosion can be described as coalescence of pits, some deeper and larger than the others but all like cavities with the corrosion

products inside. All found pits were between 5 and 25 microns of surface area and not deeper than 2 microns.

5 CONCLUSION

The AC-V can be useful for the study of redox processes occurring at the surface of a reactive working electrode under small amplitude signals, and for the study of the ac corrosion produced at the surface when bigger amplitudes are potentiostatically applied. The electrochemistry of the double layer has demonstrated that in the NaOH 1M media, and in the range of cathodic protection of mild steel, there are 3 main reactions that are not reversible to dc nor to ac perturbations and it explains the formation of unstable and porous oxides responsible for the ac-corrosion. The dc processes are not nernstian, and potentials reached depend on the sweep sense. An increase in the charge transfer resistance, due to ac perturbations, is observed, that modifies the faradic impedance and capacitive properties of the system. The ac corrosion has been found in form of pits up to 2 microns deep and from 5 to 25 microns long, produced by the application of cycles of a sinusoidal voltage on the direct potential in the basic environment where normally, the mild steel should be cathodically protected in the absence of ac signals. In the future, this work will be complemented with the AFM in the electrolytic cell and with other techniques to identify the components of the oxides film and to characterize the crystalline structure of the metal in the studied conditions.

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