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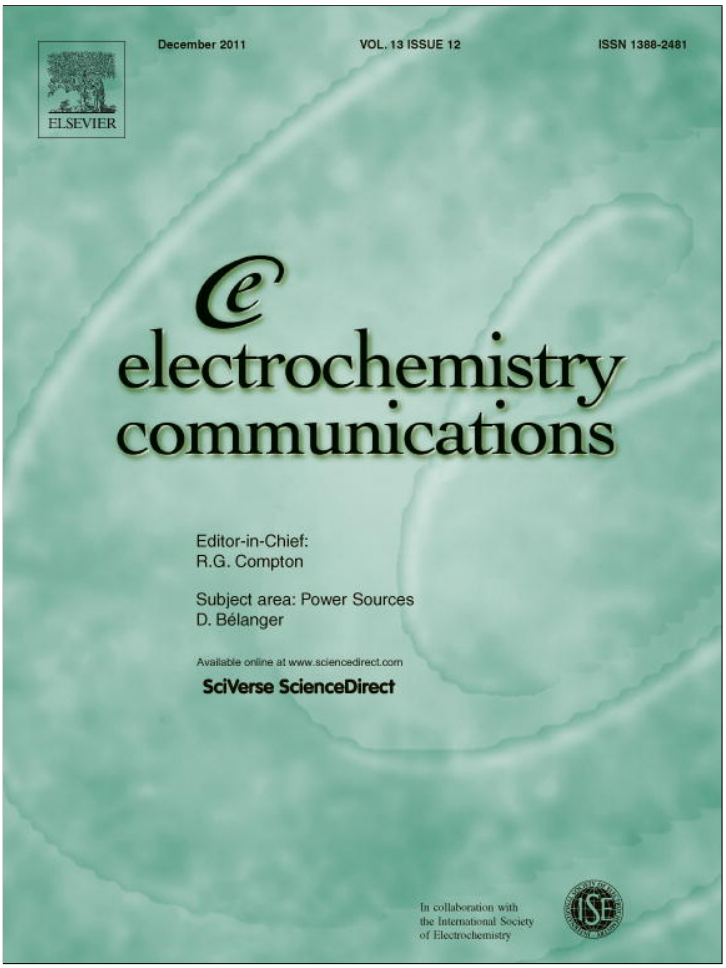

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Temporal series micrographs coupled with polarization curves to study pit formation under anodic polarization

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ABSTRACT

This work presents the coupling of polarization curves and temporal series of in-situ micrographs during pit corrosion, thus allowing the current, the number of pits, and their area as a function of potential to be examined. Upon analyzing the data, it is possible to propose that the current slope changes are associated to the beginning of pit area growth without any change in their number. The pit potential is clearly correlated with the explosion in the number of pits. Finally, using the charge, the number of pits and their area, it was possible to estimate the mean pit depth and its growth law during the experiments.

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1. Introduction

Pitting corrosion is important due to its unique characteristics such as high corrosion rate and localized attack, which lead to a severe increase in system failures [1]. Another important characteristic of this kind of corrosion is its non-linear dynamic behavior. In general, pitting corrosion is investigated using in-situ electrochemical techniques to follow both potential and current. The disadvantage with this approach is the lack of surface coordinate information as both parameters are associated with the addition of individual events occurring on the whole surface. Until now there have been very few investigations using in-situ characterization for this kind of process, which allows surface coordinate information of pit growth to be obtained. Recently, Amin et al. [2,3], using electrochemical techniques and ex-situ scanning electron microscopy, studied pitting corrosion of aluminum and observed a sudden increase in current during the polarization curves (PC) at a critical potential (E_c). In this case, the authors used SEM images, an ex-situ analysis, simply to confirm the existence of pits on the electrode after the electrochemical experiment. To avoid the loss of surface coordinate information, a new approach to investigate these phenomena using digital image processing was proposed by Punckt et al. [4] using in-situ ellipsomicroscopy for surface imaging (EMSI) and electrochemical noise (EN). The authors obtained a direct correlation between in-situ pit images and current noise. It was proposed that the sudden onset of corrosion could be explained by an autocatalytic growth in the number of metastable pits, which results from interaction among them. In a similar study, Organ et al. [5] proposed a spatiotemporal model of interactions among metastable pits and the transition to pitting corrosion, considering different experimental conditions that are important for cluster formation and thus greatly influence these localized attacks.

Considering the above, this study uses a temporal series of in-situ optical micrograph images during an electrochemical experiment to obtain local information about pit area changes and number on a steel surface. The image data have been correlated with the electrochemical information obtained simultaneously. This approach was applied in the investigation of pitting corrosion of AISI 1040 steel in an aqueous solution containing HS^- and Cl^- ions.

2. Experimental procedure

A 31×10^{-3} mol dm^{-3} of HS^-_{aq} solution was prepared by dissociation of $Na_2S \cdot 9H_2O$ (Synth) in a phosphate buffer (pH = 7.9), with 3.5 wt % NaCl (J. T. Baker). This solution was chosen because literature proposes the formation of pits over AISI 1040 samples in it [6,7]. Cylindrical AISI 1040 steel (Sanchelli ($A = 0.709$ cm^2 and 1 cm height) was used as working electrode. Prior to use, the samples were polished with sandpaper up to 1200-grit, then with alumina 25 μm, and degreased in acetone for 3 min in an ultrasonic bath. An Ag/AgCl/KCl (sat.) electrode was used as reference electrode and a Pt wire as an auxiliary electrode.

To perform in-situ image acquisition, the steel electrode was immersed in the corrosive solution in a three-electrode flat-bottom cell. An area corresponding to 0.13% of the electrode surface was observed by an inverted optical microscope (Opton-mod. TNM-07T-PL), and images were collected using the program Scope Photo®

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1.0 with an image acquisition rate of 1 frame every 2 s during acquisition of the polarization curve (PC). It is important to stress that several experiments were performed and a typical behavior were observed in all of them.

To measure the PCs, the electrode was immersed in the sulfide solution for 3600 s until the stabilization of the open-circuit potential, E_{oc}. Following this, a polarization curve was accomplished using $v = 0.1$ mV s^{-1} sweeping the potential from E_{oc} up to a value 200.0 mV more positive.

The images were analyzed with ImageJ software. For the quantitative treatment, images with a resolution of 1280×1024 pixels were scaled to 340.0×272.0 μm. The next step involved image conversion to grayscale (8 b), and then the threshold was set in the first image to detect the area occupied by pits at different potential values. Finally, the images were binarized to separate the background (steel surface) from the object (pits). Therefore, comparing the area of the black regions (bit 0) with the white regions (bit 1) it is possible to determine which part was corroded due to pitting formation and quantify them in number and individual area as a function of the potential.

The pitting potential (E_{pit}) was determined by cyclic voltammetry using the same experimental condition (at $v = 0.1$ mV s^{-1}) as the potential in which the anodic current presents an abrupt increase [8]. All electrochemical measurements were carried out using an Autolab model PGSTAT 30.

3. Results and discussion

After open-circuit potential (E_{oc}) stabilization at −631 mV vs. Ag/AgCl/KCl, the PCs were obtained. Fig. 1 presents the in-situ micrographs collected during the PC and the binarized images at different potential values. A qualitative analysis of Fig. 1 (see arrows) shows that few pits were observed during the PC until the applied potential reached the value of −503 mV vs. Ag/AgCl/KCl. After −466 mV vs. Ag/AgCl/KCl an increase in the number of pits was observed, with an explosion in their number for potentials more positive than −439 mV vs. Ag/AgCl/KCl. Initially, pit nucleation occurs in defects or inclusions that are presents in the surface even at E_{oc}.

Fig. 2 presents both the PC (Fig. 2a) and the pit surface area calculated from the micrographs during the experiment (Fig. 2b). It can be observed that, during electrochemical polarization, the total pit area shows an increase at potentials more positive than −503 mV vs. Ag/AgCl/KCl. At this same potential an important change in the inflection of the current during PC is observed. As there is no change in the number of pits in this potential range (2b), the increase of current is associated with changes in the pit areas. As such, these simultaneous changes could be an indication of a correlation between them.

Considering the applied scan rate and the pit area increase, it is possible to calculate the corrosion rate during the PC using the following hypotheses: i) the current only flows through pits with a faradaic current efficiency of 100%, and ii) the current that flows through each pit is proportional to the area of that pit. It is important to stress that two slopes can be observed in the pit area behavior. In the PC, only a very small shoulder can be observed associated to this change. Therefore, it is possible to propose that in-situ micrographs are sensitive even to small changes during pit corrosion under polarization. It was possible to calculate the pit area growth rates, which are 5.48 and 1450 μm^2 mV^{-1}, between −503 and −466 mV vs. Ag/AgCl/KCl, and for potentials higher than −466 mV, respectively. These two corrosion rates are the slopes of total pit area plot in these two potential regions, as indicated in Fig. 2b. The first one was chosen after the pits start to increase in area and the second one after the pit number increases, and therefore, these values characterize two distinct regions during pit corrosion under anodic polarization.

One of the most important parameters during pitting corrosion is the pit potential, E_{pit}. The most accepted method to determine it is an abrupt change in the slope of the current potential curve [3]. Using this procedure, the pit potential is expected to be close to −439 mV vs. Ag/AgCl/KCl as can be observed in the inset of Fig. 2c. Analyzing the number of pits in the potential curve, it can be observed that this potential value occurs just after the number of pits exhibits an important increase. Here, using only the micrographs, we calculated

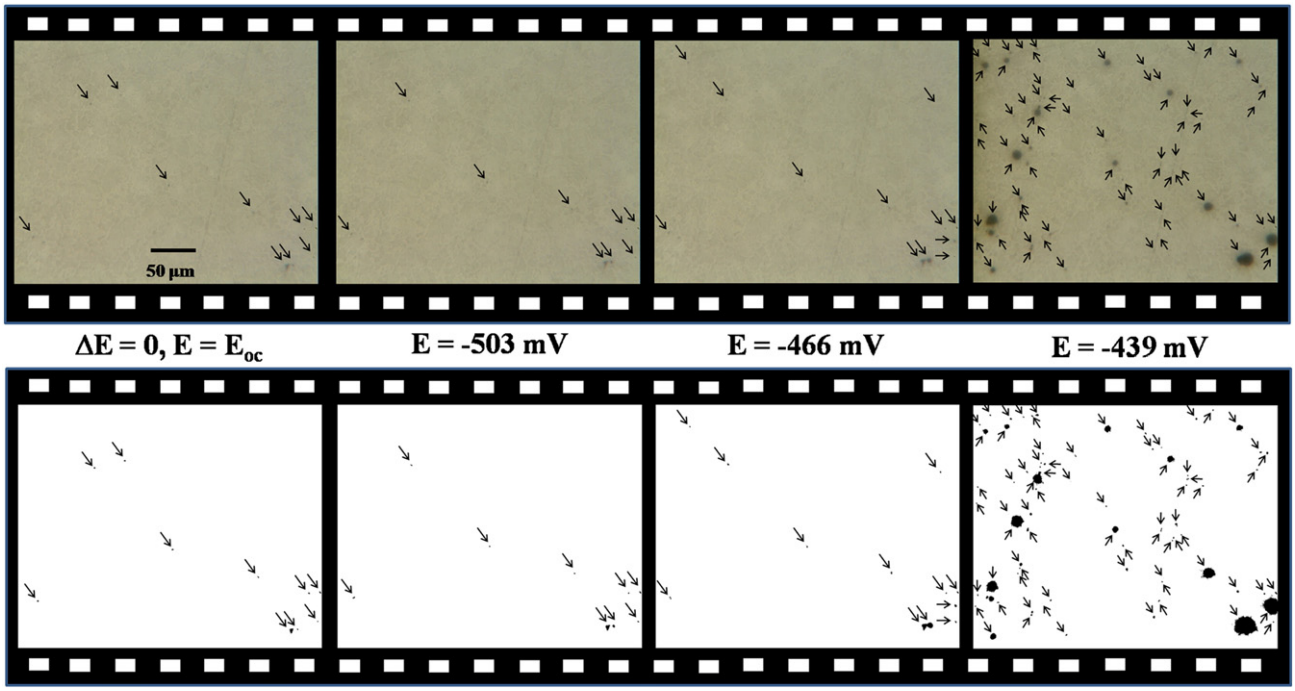

Fig. 1. In-situ microscopy micrograph observations of AISI 1040 steel at potentials of: $E = -631$ (E_{oc}), −503, −466, and −439 mV vs. Ag/AgCl/KCl, obtained during PC in HS^- solution at concentration of 31×10^{-3} mol dm^{-3}, pH 7.9, with chloride ions.

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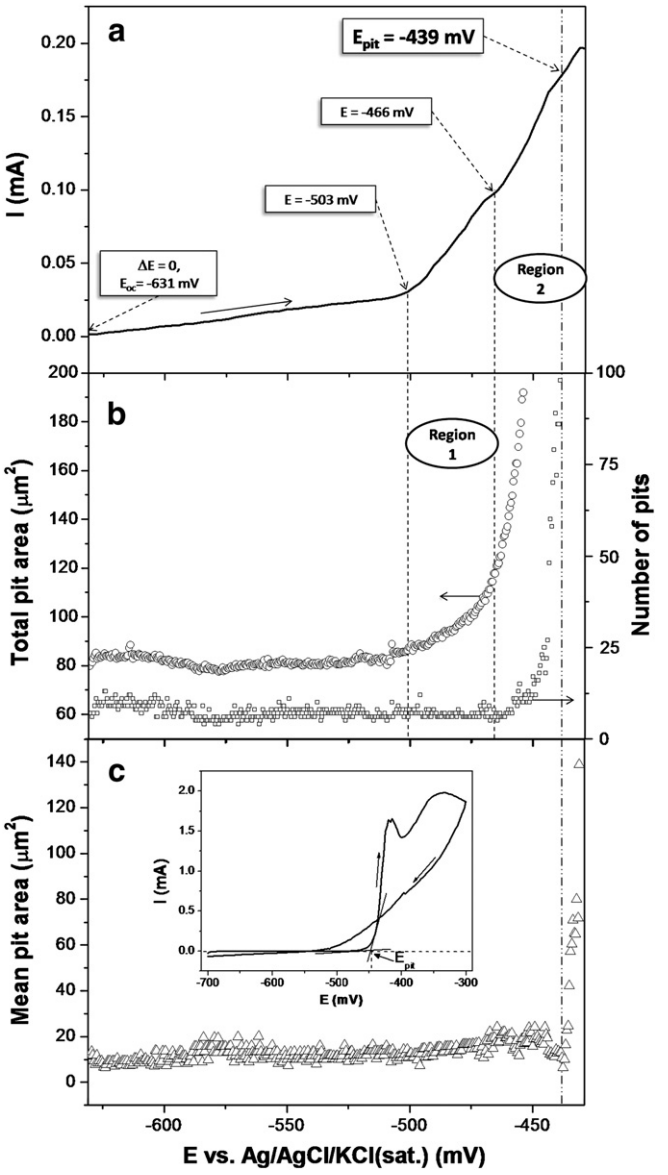

Fig. 2. (a) Current, (b) total pit area and number of pits, and (c) mean pit area as function of the applied potential for AISI 1040 steel in HS^- solution at concentration of 31×10^{-3} mol dm^{-3}, pH 7.9, with chloride ions. (Inset) cyclic voltammetry showing the pit potential.

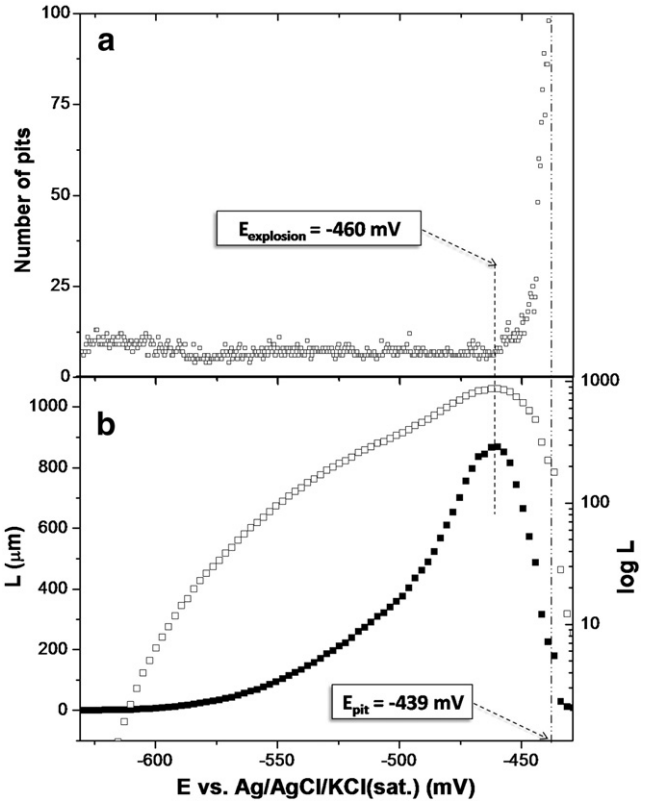

Fig. 3. (a) Number of pits, (b) estimation of mean pit depth (L) as function of the applied potential for AISI 1040 steel in HS^- solution at concentration of 31×10^{-3} mol dm^{-3}, pH 7.9, with chloride ions.

the ratio between the number of pits and the total pit area (Fig. 2c). It can now be clearly observed that there is an important change in the ratio between this ratio and that this change occurs exactly at the E_{pit} value calculated from cyclic voltammetry ($E_{pit} = -439$ mV vs. Ag/AgCl/KCl).

In addition to the described information that can be extracted from the in-situ micrographs, it is also possible to estimate the mean pit depth. Besides those hypotheses described above, i.e., i) the current only flows through pits with a faradaic current efficiency of 100%, and ii) the current that flows through each pit is proportional to the area of that pit, an additional assumption must be made in this case, which is iii) all pits have the same shape, and, in the present case, it is assumed that they have a cylindrical form. Such information can be calculated using the charge (from PC curve), the total pit area and the number of pits (from image analysis). While the number of pits is almost constant, it is easy to calculate their total volume, as the current is associated with the amount of dissolved iron by Faraday's law. Taking into account the iron oxidation, its molar mass (55.874 g mol^{-1}), and the carbon steel density (7.8 g cm^{-3}), the volume of pits (in cm^3) can be estimated. As the pit surface area was measured using image analysis, a mean pit depth value as a function of the potential can be estimated. These data are presented in Fig. 3. It is easy to observe that the validity of the calculations is confined to that region where the number of pits is constant (marked in Fig. 3). After this, as new pits start to grow, the mean value has no physical significance. The mean pit depth extends to 900 μm at −462 mV vs. Ag/AgCl/KCl. Moreover, there is a clear change in the concavity at −503 mV vs. Ag/AgCl/KCl, which is clearly seen from the logarithm mean pit depth representation and it is possible to correlate this with a change in current in the PC. Therefore, a possible meaning of this point in the PC is that it is related to a point where pit area and, as a consequence, the pit depth start to grow with a positive exponent rate law. Of course, these ideas must be investigated further, but it is very important to stress that in-situ micrographs measured during the PC can lead to a new set of data that have not been described previously, as the current does not carry any surface coordinate information about the process.

4. Conclusions

This work presents a method to investigate pitting corrosion under anodic polarization by coupling polarization curves with temporal series in-situ micrographs. It was possible to observe characteristic points on the surface and to measure the number of pits and the changes in their area during the experiments, and thus to use this information together with the charge (from the polarization curves) to estimate the instant mean pore depth. A correlation between the changes in the current and the increase in the pore area was also observed. Finally, it was possible to correlate the pit potential with the explosion in the number of pits that occurs at −439 mV vs. Ag/AgCl/KCl.

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