Imaging concentration profiles of redox-active species in open-circuit corrosion processes with the scanning electrochemical microscope

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Received 20 July 2004; received in revised form 19 August 2004; accepted 17 September 2004

Abstract

Scanning electrochemical microscopy has been used to detect the redox species involved in a corrosion process at the open-circuit potential. During the immersion of pure iron in a neutral aqueous solution, the potential of the ultra microelectrode (tip) was set to either detect the Fe²⁺ ions originating from the electrodissolution of iron at the anodic sites on the metal surface, or the depletion of oxygen in the electrolyte in the proximity of the corresponding cathodic sites.

Keywords: Scanning electrochemical microscopy; Corrosion; Iron dissolution; Oxygen reduction; Localized electrochemical measurements

1. Introduction

The coupling of scanning probe techniques with electrochemistry (scanning electrochemical microscopy, SECM) performed by Bard et al. in 1989 [1] has become a very powerful technique for probing a great variety of electrochemical reactions, due to its high spatial resolution and electrochemical sensitivity. It consists of a mobile ultra microelectrode immersed in an electrolyte solution, which is rastered in close proximity to a solid surface to characterize the topography and redox activity of the solid/liquid interface. Information about reactions that occur in the solution space between the tip and sample can also be obtained, which has facilitated the use of this technique in applications beyond the solid/liquid interface [2]. In summary, the SECM can be employed for chemical microscopic imaging, the measuring of physicochemical constants and coefficients, and use as a micromachining tool [3]. And an ever-increasing number of studies on electrochemical phenomena at solid/liquid, liquid/liquid and liquid/gas interfaces, and materials of biological significance are appearing frequently in the scientific literature [4,5, and references cited therein].

Quite early during the development of the technique, it was considered that SECM would be very promising in elucidating the complex processes occurring in corrosion processes [6]. This technique has already provided very interesting information concerning the initiation of pitting corrosion on various metal samples [7–15], and the growth of passive films on metals [16]. In most cases, the ultra microelectrode was in fact used to initiate the corrosion reaction and to detect the corrosion products, and the substrate under consideration was subsequently polarized. Unfortunately, potentiostatic control does not exactly match the conditions occurring in the majority of the corrosion situations, which typi-
ally result from a distribution of anodic and cathodic sites on the same corroding substrate. In two recent studies from one of our groups, it has been demonstrated that the investigation by SECM of corrosion processes in open-circuit conditions allows to discover early processes both in the pitting corrosion of steels and the swelling of painted metals which could not be observed when experiments were performed under potentiostatic control of the metal substrate under study [17,18].

The corrosion reaction at open-circuit conditions occurs as the result of the local development of anodes and cathodes on the metallic surface, resulting in the formation of local microcells. The metal is oxidized at the anodes, whereas the corrosion process is maintained by the reduction of some species from the environment at the cathodes (for instance, oxygen in neutral and moderately alkaline media, or protons in acidic solutions). Because the corroding metal usually produces $\text{M}^{2+}$ cations transferred under diffusion control at the anodic sites, the system can be studied by SECM. In fact, we have exploited this to image metastable pits on austenitic steel in situ by SECM at the open-circuit potential, by detecting the dissolved ferrous ions that emanated from the pits during the passage of the SECM probe tip [17]. On the other hand, in a neutral aqueous environment, oxygen from the electrolyte is consumed at the cathodic areas, and the reaction may be detected by the scanning tip as local depletion of the oxygen concentration in the electrolyte adjacent to cathodic sites.

In this paper we demonstrate that, in agreement with expectations, mapping of concentration profiles of redox-active species participating in corrosion processes at the open-circuit potential can be performed with great accuracy and resolution using the scanning electrochemical microscope. This originates from the observation that the size of the microelectrode strongly determines the zone at which significant concentration gradients develop, thus expecting that the current detected at a micrometric probe will be indicative of concentrations averaged over micrometric distances, i.e., true local concentration of a species will be monitored [19]. The experimental system selected for this work was the degradation of pure iron in naturally aerated 0.1 M NaCl aqueous solution at ambient temperature. No polarization of the metallic sample was performed, thus allowing the system to evolve spontaneously as it occurs in naturally-driven corrosion processes.

2. Experimental

Experiments were performed on 99.5% purity iron supplied as sheet of thickness 1 mm by Goodfellow Materials Ltd., Cambridge, UK. The sheet was cut into square specimens of about $1 \text{ mm} \times 1 \text{ mm}$, and mounted into an epoxy resin sleeve, such that only the square end surface forms the testing iron substrate. Samples were then polished with silicon carbide paper to 1200 grit and cleaned thoroughly in double-distilled water. The Scanning Electrochemical Microscope was manufactured by CH-Instruments (Austin, TX, USA), and operated with a 10 $\mu$m platinum tip as the probe, an Ag$|$AgCl$|$KCl (saturated) reference electrode and a stainless steel counter electrode. Specimens were mounted horizontally facing upwards. When all the peripherals of the cell were mounted in position and the imposed experimental parameters had been set, the electrolyte was poured into the cell and the probe tip rastered over the surface. The specimen was used unpolarized for all the work, experiencing the corresponding open-circuit potential for the iron electrode in the solution. The SECM was used without a mediator, in the so-called “sample generation – tip collection” mode. Corroding iron releases into the solution the corresponding metal ions ($\text{Fe}^{2+}$ from the iron surface at the anodic sites) which can be imaged directly on the SECM tip by selecting appropriate potential values for them to undergo a re- dox reaction. The potential value was set at $+0.60 \text{ V}$ (Ag$|$AgCl$|$KCl (saturated)) to image $\text{Fe}^{2+}$ ions from their oxidation to Fe(III) species. On the other hand, the cathodic reaction involves the reduction of dissolved oxygen, which can be imaged on the SECM tip in a similar procedure. In this case, oxygen was monitored from its electroreduction at the tip at $-0.70 \text{ V}$ (Ag$|$AgCl$|$KCl (saturated)). The experiments were performed at selected heights of the ultra microelectrode from the surface.

3. Results and discussion

Fig. 1 shows the steady-state currents monitored at the ultra microelectrode polarized at $+0.60 \text{ V}$ at various heights during a line scan that crosses over the iron specimen. Under these conditions, the concentration of $\text{Fe}^{2+}$ ions emanating from the dissolving electrode could be determined at different heights above the metal surface. That is, curves show the concentration profile of $\text{Fe}^{2+}$ ions as a function of the distance from the iron sample. In all cases, anodic currents were measured at the tip when it scanned over the metal surface, and current values distinctly decreased as the tip moved towards the epoxy sleeve. The absolute value of the current maxima is practically identical in the various line scans, irrespective of the tip distance to the surface. But the ratio between the intensity of the peak and the corresponding background current is greatly increased as the tip height becomes smaller. This effect was expected because the microelectrode consequently approached the source of...
metal ions. This effect is better demonstrated in Fig. 2, which depicts the approach curve for the tip polarized at +0.60 V. That is, once the tip was fixed at a point approximately over the centre of the iron specimen, it was allowed to approach the surface at a constant rate from a height of 1600–10\,\mu\text{m}. The concentration of Fe$^{2+}$ ions steadily increased as the tip approached the substrate, the effect being more noticeable at the smaller heights considered. Since this experiment was performed in the solution resulting from the experiments shown in Fig. 1, a plateau is observed in the current curve at distances higher than 300\,\mu\text{m} as a result of the concentration of Fe$^{2+}$ ions dissolved in the solution from the system.

It is also interesting to note in Fig. 1 the existence of background currents over the resin sleeve. These currents were anodic in nature, and varied significantly with the tip distance. Furthermore, they were always found to be higher at the end that at the beginning of each line scan. The reason for the measurement of background currents in the vicinity of the iron sample results from the diffusion of soluble Fe$^{2+}$ ions, which results in higher values at the end of the line scan due to the movement of electrolyte that results from the rastering tip. Another feature connected to the background currents is the observation that they were higher at large distances from the electrode,

![Fig. 1](image1.png)

![Fig. 2](image2.png)

Fig. 1. Line scans obtained with the SECM (tip potential = +0.60 V vs. Ag$|$AgCl$|$KCl saturated) of iron surface under immersion in 0.1 M NaCl at the open-circuit corrosion potential. The plots were obtained at different heights over the sample as indicated. The curves have been corrected for systematic mechanical drifts of the tip between scans. The current transients are proportional to the concentration profiles of soluble Fe$^{2+}$ ions over the sample. Arrow indicates the direction of tip movement.

![Fig. 4](image4.png)

Fig. 4. Approach curve measured with the SECM (tip potential = −0.70 V vs. Ag$|$AgCl$|$KCl saturated) of iron surface under immersion in 0.1 M NaCl at the open-circuit corrosion potential. The curve shows the concentration profiles of dissolved oxygen as a function of the distance from the iron sample. Arrow indicates the direction of tip movement.
which is the opposite trend to what is observed over the iron sample. This effect is due to the epoxy resin acting as an insulator towards the diffusion-limited oxidation of Fe$^{2+}$ ions at the tip. That is, in this case the UME operates rather in the tip-generation sample-collection mode (TG/SC). As the tip is located closer to the resin, diffusion of the redox species from the solution is increasingly blocked by the insulating portion of the sample. Therefore, this observation is in good agreement with typical SECM operation.

Analogously, the concentration of dissolved oxygen could be monitored by setting the tip potential at $-0.70$ V. In this case, electroreduction (cathodic) currents were measured instead. The line scans measured at various tip heights are plotted in Fig. 3. A decrease in the faradaic currents was observed when the tip was scanned over the metal surface, and the extent of the effect was highly dependent on the height. Finally, the approach curve for the tip polarized at $-0.70$ V is plotted in Fig. 4, allowing for the concentration profile of oxygen in the electrolyte to be monitored as a function of the distance to the metal substrate. Thus quantitative determination of oxygen concentration profiles could also be attempted with the SECM.

4. Conclusion

Direct monitoring of corrosion processes can be made with the SECM when the metal under investigation is not polarized, that is, the substrate is at its open-circuit potential in the environment. The SECM operates in the sample generation – tip collection mode. Concentration profiles of the redox species participating in the anodic and cathodic microcells developed on the metal surface can be measured from the adequate selection of the tip potential. The validity of this system was shown by monitoring the release of ferrous ions at the anodic sites and the consumption of dissolved oxygen at the cathodic sites, during the immersion of pure iron in aerated 0.1 M NaCl aqueous solution. Further work is in progress and will be reported in due course.

Acknowledgments

Funding from the Gobierno de Canarias (Spain) in the framework of Project PI2003/179 is gratefully acknowledged. The exchange of scientists between Spain and Portugal was supported by a Collaborative Research Programme between Spain (Project No. HP2002-055) and Portugal (Project No. E-53-03). Y.G.-G. gratefully acknowledges a research fellowship under the financial scheme of Cajacanarias and the University of La Laguna.

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