



Scanning microelectrochemical characterization of the effect of polarization on the localized corrosion of 304 stainless steel in chloride solution



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ABSTRACT

Corrosion processes occurring on stainless steel 304 surfaces under anodic polarization were characterized using scanning electrochemical microscopy (SECM) and the scanning vibrating electrode technique (SVET), complemented with conventional potentiodynamic polarization curves. Stable pit formation on the samples was monitored by SVET as result of surface modification under electrochemical control. The operation procedure may involve the previous electrochemical reduction of the passive oxide layer if the media is not aggressive enough to induce pitting at small overpotentials. Additionally, the sample generation – tip collection operation mode of the SECM enabled to detect local release of iron (II) ions, as well as their conversion to iron (III), both processes being greatly affected by the potential applied to the substrate.

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1. Introduction

Corrosion problems affecting metals have been recognized for centuries, especially in relation to iron and iron-based materials, and even affect stainless steels as they are susceptible to localized corrosion phenomena, particularly pitting corrosion in halide-containing environments. This kind of attack usually appears distributed in random manner, though it is believed to arise from small chemical asymmetries in the system. Degradation starts within the range of micrometers or below, so that any measurement performed on the specimen must be interpreted in terms of highly localized processes. Due to the electrochemical nature of the corrosion reactions, electrochemical techniques have constituted the main source of information for the analysis of the general behavior of a corroding system, though techniques such as DC potentiometric polarization curves, electrochemical impedance spectroscopy and electrochemical noise analysis, are unable to provide data resolved at the local scale.

Real time electrochemical information in the micrometer scale can be achieved when measurements are performed using capillary microcells [1–3], by selecting small portions of the surface that can be distinguished by some microstructural difference. Yet limitations occur during the characterization of the interactions among distributed heterogeneities present in the surfaces, because the complete surface of the sample is not in contact with the test solution during the measurements. On the other hand, high spatial characterization is achieved using *in situ* atomic force microscopy (AFM). This technique allows monitoring topographical changes occurring on representative areas of the metal when immersed in a liquid phase [4–6], though it lacks chemical selectivity.

These limitations have been the motivation for the development of various microelectrochemical techniques able to locally evaluate the corrosion behavior of the substrate under study by simultaneously recording electrical and chemical information. Among them, scanning electrochemical microscopy (SECM) provides adequate sensitivity to investigate the interactions of surface features with the electrolytic environment in contact with the surface [7,8]. By adequate selection of the operation mode of SECM, the chemical species participating in corrosion processes can be monitored with high spatial resolution. For that purpose, a micro-disk microelectrode, with typical dimensions between 10 and

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25 μm diameter, can be placed in close proximity to the sample, and be used to scan the surface and collect species either produced or consumed by the substrate undergoing corrosion. The possibilities for this chemical analysis include the monitoring of chloride anions [9], and proton activity [9–12], as well as other ions and neutral species either produced or consumed in the anodic [13–21] and the cathodic half-cell reactions [12,13,15,17,19,20,22–24]. Iron (II) can be detected in this way, because it is easily oxidized to iron (III) at the microelectrodes. This reaction has been selected to image metastable pitting, localized corrosion, and protection breakdown on iron-based materials under different environmental conditions [13–21]. On the other hand, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple undergoes a reversible redox reaction in acidic conditions, thus allowing iron (III) species to be imaged over reacting samples as well, from their reduction into ferrous species. Surprisingly, this option has not been exploited in corrosion studies with the SECM until now, probably because iron (II) is regarded to be the main soluble species and it is produced in significant amount to be effectively detected in most investigations concerning iron-based materials, and because of the high tendency of ferric ions to precipitate as iron (III) hydroxide.

Another scanning microelectrochemical technique widely employed in corrosion studies of iron-based materials is the scanning vibrating electrode technique (SVET) [12,25–36]. It images the ionic fluxes of species involved in the electrochemical processes occurring on the corroding surfaces, allowing those related to anodic and cathodic activities on the surface to be distinguished. Despite the rather wide use of SVET among corrosion researchers, polarization of the investigated surface was seldom attempted [25,32,33], and it has been mainly constrained to the coupling of dissimilar metals (i.e., formation of galvanic pairs). The justification for this situation may be found in the loss of sensitivity experienced when non-perfectly symmetrical ionic fluxes from current sources arise from the polarized sample due to the geometry of the auxiliary electrode. This problem remains while scanning heterogeneous specimens such as those undergoing corrosion even if a perfectly symmetrical counter electrode was employed. Despite these limitations, valuable semi-quantitative information on the corrosion processes is obtained using SVET on polarized substrates, as it will be shown in this contribution.

The aim of this work is to report a combined electrochemical and microelectrochemical characterization of the passivity breakdown of 304 stainless steel in acidic chlorinated solution on polarized samples. Average electrochemical behavior has been explored using conventional techniques, whereas scanning microelectrochemical investigation allowed the spatial resolution of the distributions of the local ionic fluxes related to anodic and cathodic activities, as well as the detection of soluble iron species evolving from the corroding metal substrate. They were monitored using SECM and SVET while the operator controlled the electrical state and conditioning of the investigated surface *in situ*, which is a novel experimental approach to our knowledge. In this way, passivity breakdown of the passive layer, and stable pitting corrosion growth were investigated at the same time by considering the average current transients as well as the local ionic currents related to these processes.

2. Experimental

Experiments were performed on 304 grade austenitic stainless steel supplied as sheet of thickness 1 mm by Goodfellow Materials Ltd (Cambridge, UK). The metal was not analyzed, but had the specified nominal composition of 17–20% Cr, 8–11% Ni, <2% Mn, <0.08% C, Fe in balance. The steel sheet was cut into strips of 2 cm length and 2 mm width, and next mounted vertically in Epofix (Struers, Ballerup, Denmark) resin sleeves of 3 cm

approximate diameter. In this way, only a 2 mm \times 1 mm surface of the material was exposed to the test electrolytes. The mounts were abraded using SiC paper of 1200 and 4000 grit, and subsequently polished using alumina suspension of 0.3 μm particle size. The samples were degreased with ethyl alcohol, cleaned in high purity deionized water, and finally dried under air stream.

The tests were conducted in three chloride containing electrolytes of different compositions, namely 0.1 M NaCl, 0.1 M HCl, and 0.025 M HCl + 0.075 M HClO_4 . The latter was chosen such as to contain a smaller concentration of chloride ions while maintaining the same pH than 0.1 M HCl solution. All the reagents were of analytical grade, and solutions were prepared by using ultra pure water purified with a Milli-Q system from Millipore. Measurements were conducted at room temperature (nominally 20 $^{\circ}\text{C}$) in the naturally aerated solutions.

Electrochemical tests were performed using an Autolab (Metrohm, Herisau, Switzerland) potentiostat controlled by personal computer. A 3-electrode configuration was used, where the steel sample was the working electrode, completed with an Ag/AgCl/KCl (3 M) reference electrode, and a platinum counter electrode. Potentiodynamic polarization measurements were conducted at 1 mV s^{-1} scan rate. The freshly polished surface was left unpolarized for 1 h in the corresponding test solution to allow a stable reading of the open circuit potential (OCP) to be attained. Then, the cathodic Tafel branch was first separately acquired by polarizing the specimen from the spontaneous corrosion potential down to -0.25 V from the OCP. The sample was then retrieved from the solution and subject to surface grinding and polishing steps as before. After stabilization for 1 h in the solution, the sample was now polarized in the anodic direction up to $+1.20\text{ V}$ vs. Ag/AgCl/KCl (3 M), and subsequently potential scan was reversed to monitor the corresponding repassivation behavior. Measurements were repeated by quadruplicate, and average data were obtained for the characteristic electrochemical parameters.

Scanning electrochemical microscopy (SECM) measurements were carried out with an instrument developed by Sensolytics GmbH (Bochum, Germany). The instrument was built around the same Autolab instrument used for conventional electrochemical measurements, though this time operating also as bipotentiostat in some selected experiments. The electrochemical activity of the metallic substrate was monitored by SECM employing a 10 μm diameter platinum microdisk as the sensing tip. The tip to substrate distance was determined from the measurement of *z*-approach curves above the surrounding resin using the reduction of the molecular oxygen dissolved in the electrolyte. In this case, the SECM was operated in the negative feedback mode, with the tip potential set at -0.65 V vs. Ag/AgCl/KCl (3 M). Once the surface was located, the tip was withdrawn to a distance of 10 μm from the sample surface, and scanned parallel to the surface at a scan rate of 25 $\mu\text{m s}^{-1}$ to record SECM images. The SECM was operated in the Substrate Generation – Tip Collection mode for the detection of either iron (II) or iron (III) ions evolving from the corroding 304 stainless steel surfaces. These species could be selectively monitored by adequately setting the potential of the Pt microelectrode. The potential of the tip was alternately set at $+0.50$ and at $+0.10\text{ V}$ vs. Ag/AgCl/KCl (3 M) to detect the generation of Fe(II) and Fe(III) soluble species, respectively. The Fe(II) species were identified through their oxidation to Fe(III), whereas the reverse reaction was employed for the detection of Fe(III).

SVET experiments were performed using an instrument manufactured by Applicable Electronics Inc. (Forestdale, MA, USA). The sensing probe was a 10 μm Pt–Ir tip with a black platinum deposit electrochemically grown to attain an adequate interfacial capacitance. Probe vibrations of 20 μm amplitude in both the normal and the parallel directions to the surface were applied, with 75 and 170 Hz respective vibration frequencies, maintaining a

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