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Imaging Local Surface Reactivity on Stainless Steels 304 and 316 in Acid Chloride Solution using Scanning Electrochemical Microscopy and the Scanning Vibrating Electrode Technique

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ABSTRACT

Passive film breakdown and pit nucleation on 304 and 316 stainless steels in chloride-containing media were investigated using scanning microelectrochemical microscopy (SECM) and the scanning vibrating electrode technique (SVET). Experiments were performed for the alloys either at their corresponding open circuit potential, or under applied polarization, as to image domains of similar topography but different resistance against breakdown of the passive layers formed on these steels. Identification of the iron released species was accomplished, showing that pitting occurs with the formation of iron (II) species only. Detection of iron (III) species occurred when the steel sample was polarized at high positive overpotentials because it served as the reaction site to oxidize the iron (II) ions released from a propagating pit. The obtained results have revealed some difference of the reactivity of both specimens. Moreover the effect of the galvanic coupling has been investigated.

1. Introduction

Local differences in chemical reactivity related to the development of microcells occur in the corrosion reactions, and they can be visualized *in situ* using scanning microelectrochemical techniques [1,2], thus contributing to a better understanding of the behaviour of the system. Among them, scanning electrochemical microscopy (SECM) is a powerful technique for the investigation of the electrochemical processes occurring at the metal/electrolyte interface of corroding systems [3,4]. The scanning probe is usually an amperometric ultramicrodisk (tip) of a noble metal with diameter comprised between 10 and 25 μm, and it is moved in close proximity to the surface of the investigated material to characterize the electrochemically-active species participating in the process. This technique can be operated when the sample is either unbiased in the electrolyte, or under controlled polarization. In particular, the release of iron (II) ions from corroding iron-based materials can be detected at the tip through their oxidation to iron (III). This procedure has been successfully employed to image the metastable

pitting of stainless steel [5], and the breakdown of passive oxide layers and subsequent localized corrosion on iron-based materials [6–11]. On the other hand, the Fe^{2+}/Fe^{3+} couple undergoes a reversible redox reaction in acidic environment, so in principle the release of iron (III) species could also be imaged over reacting samples from their reduction to ferrous species. Yet this possibility has not been exploited for corrosion research using the SECM, mainly because iron (II) ions are produced in significant amount to be adequately detected in most corrosion problems concerning iron-based materials, whereas ferric ions have a strong tendency to precipitate as iron (III) oxy-hydroxides and they may accordingly block the surface of the sensing probe. Alternately, another electrochemically-active species often monitored in SECM studies of corroding systems is the molecular oxygen dissolved in the solution [6,7]. In this case, a redox competition effect between the measuring tip and the sample under investigation occurs when this molecule is consumed in the cathodic sites [12].

Another scanning microelectrochemical method successfully employed to study corrosion processes and systems is the scanning vibrating electrode technique (SVET) [13]. It images the ionic fluxes of species involved in the electrochemical processes occurring on surfaces, especially those participating in the corrosion reactions [14–22]. Thus, the location of any electrochemical reaction that

occurs over an area is detected as long as it originates measurable ionic fluxes over it, allowing the distribution of cathodic and anodic places on the metallic surfaces to be imaged. Such information is relevant to identify the places where the corrosion process can start. A major advantage of SVET is that use of a potentiostat is not required, thus effectively leaving the metallic sample at its corrosion potential in the environment. In fact, external polarization of the substrate has been seldom performed for the characterization of corrosion reactions using SVET [14,18,19]. This is probably due to the loss of sensitivity encountered when the sample is polarized, because the reference signal employed to measure the ionic current fluxes cannot be taken in a position with the adequate symmetry with relation to the auxiliary electrode employed for electrochemical control and polarization of the surface under study. Furthermore, systems experiencing corrosion produce heterogeneous distributions of the corroding microcells that are not symmetrically located in relation to an otherwise perfectly symmetrical auxiliary electrode, thus leading to inhomogeneous current fluxes in the solution. Despite these difficulties, still some valuable information can be collected on polarized substrates, as it will be demonstrated in this work. With this information, passivity breakdown of the passive layer and stable pitting corrosion could be simultaneously studied through the global transient currents and the local ionic current produced as result.

It is well known that 304 and 316 stainless steels are susceptible to pitting corrosion in chloride solution due to localized breakdown of the passive oxide layers. The aim of this work was to visualize local reactivity distributions related to passivity breakdown of 304 and 316 stainless steels promoted by sample polarization while the materials were immersed in aqueous chloride solutions of different composition. The nature and extent of corrosion processes on the two stainless steels were investigated at micro-scale using SECM and SVET. Stable pit growth has been followed by detecting the release of soluble iron ions from the corroding metal, and its dependence with both the applied potential and the composition of the test environment.

2. Experimental

Experiments were performed on 304 and 316 grade austenitic stainless steel supplied as sheet of thickness 1 mm by Goodfellow Materials Ltd, Cambridge, UK. The metals were not analysed, but the nominal compositions provided by the manufacturer were:

- 304 stainless steel: 17–20% Cr, 8–11% Ni, < 2% Mn, < 0.08% C, bal. Fe.
- 316 stainless steel 16.5–20% Cr, < 2% Mn, 8–14% Ni, < 0.12% C, 2.0–3.5% Mo, bal. Fe.

Samples were fabricated from 1 mm thick sheets of the steels. They were cut into ca. 2 mm width and 2 cm length strips, and mounted in an Epofix (Struers, Ballerup, Denmark) resin sleeve of approximate diameter 3 cm, so that only 1 mm x 2 mm metallic areas were exposed to the electrolyte. The resulting mounts contained one strip of each material. These samples were abraded using SiC paper of 1200 and 4000 grit, and subsequently polished using alumina suspension 0.3 μm particle size. The strips of the two steels protruded at the rear of the mount to facilitate electrical connection. In this way, they could be either connected between them to form a galvanic pair, or polarized by an external potentiostat. When only one surface was investigated, the other metallic strip was covered by sellotape in order to prevent any eventual interference resulting from its exposure to the electrolyte.

SECM experiments were carried out in 0.25 M and 0.1 M HCl test solutions, whereas SVET measurements were done in 0.025 M HCl + 0.075 M HClO$_4$. The latter was chosen as to produce a less aggressive attack on the alloys whereas maintaining the same pH in solution as in 0.1 M HCl. All the reagents were of analytical grade and solutions were prepared by using twice distilled water. Experiments were performed at ambient temperature in the naturally aerated solutions.

SECM measurements were performed with equipment purchased to Sensolytics GmbH (Bochum, Germany). The instrument was built around an Autolab (Metrohm, Herisau, Switzerland) bipotentiostat, controlled by personal computer. Platinum microdisks of 10 μm diameter were employed as microelectrode tips. The small electrochemical cell (ca. 3.5 mL volume) contained an Ag/AgCl/KCl (3 M) reference electrode, and a platinum counter electrode. The system was operated in either three-electrode or four-electrode configuration depending on whether the potential of the substrate was left unbiased or under potentiostatic control.

Scanning Electrochemical Microscopy was operated in the Substrate Generation–Tip Collection (SG/TC) mode to detect either iron (II) or iron (III) cations evolving from stainless steel surfaces under different substrate polarization. Tip to substrate distance was established by recording approach curves in the negative feedback mode towards the surrounding insulating sleeve. The tip potential was set at −0.65 V vs. Ag/AgCl/KCl (3 M) in order to register the faradaic current related to the reduction of dissolved oxygen. After the surface was located, the tip was withdrawn 10 μm for scanning parallel to the sample. Both linear scans and 2D maps were recorded at maximum scan rate of 25 μm s^{-1}. Tip potential was alternately set at +0.50 and +0.10 V vs. Ag/AgCl/KCl (3 M) to detect iron species of different oxidation states. The first value was employed to detect iron (II) species through their oxidation at the microdisk. Tip potential was set at +0.10 V for the eventual reduction of iron (III) species evolving from the substrate while polarized more positive than +0.30 V vs. Ag/AgCl/KCl (3 M)

SVET experiments were conducted with an Applicable Electronics Inc. instrument (Forestdale, MA, USA). The sensing probes were 10 μm PtIr wires. They were electrochemically deposited black platinum until they provided adequate capacitance values. Probe vibration in normal direction to the surface was applied, with 75 Hz vibration frequency, with 20 μm amplitude vibration. The substrate to probe distance was fixed at 60 μm. Sample polarization was performed in this case using a potentiostat/galvanostat Model 283 (Princeton Applied Research, Oak Ridge, TN, USA). The current and potential analogic outputs of the potentiostat were connected to analog inputs of the SVET instrumentation, so these two parameters were also monitored in the experiments. A platinum ring covered with black platinum electrodeposit was employed as the counter electrode to minimize asymmetries in current distribution due to the geometry of the system, and an Ag/AgCl/KCl (3 M) was used as reference electrode.

3. Results and discussion

Changes in chemical activity related to corrosion of stainless steel 304 and 316 samples left at their spontaneous open circuit potential during immersion in 0.25 HCl solution were monitored using SECM operated in the SG/TC mode. The tip potential was set at +0.50 V vs. Ag/AgCl/KCl (3 M) in order to monitor the oxidation of dissolved iron (II) into iron (III) species.

Fig. 1 displays the time evolution of iron (II) generation from a 304 stainless steel sample in 0.25 HCl. During the first recorded scan, given in Fig. 1A, high current values in the order of 100 pA were initially registered, evidencing rather high iron dissolution rates leading to the release of bivalent cations. However, current decreased quite abruptly after recording a few scan lines over the metal, and it only increased again towards the end of the scan. This