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Short communication

Bipolar electrochemistry for high-throughput corrosion screening

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ABSTRACT

It is demonstrated that bipolar electrochemistry can be used for high-throughput corrosion testing covering a wide potential range in one single experiment and that this, combined with rapid image analysis, constitutes a simple and convenient way to screen the corrosion behaviour of conducting materials and corrosion protective coatings. Stainless steel samples (SS304), acting as bipolar electrodes, were immersed in sulphuric and hydrochloric acid and exposed to an electric field to establish a potential gradient along the surface. In this way, the same steel sample was exposed to a wide range of cathodic and anodic conditions, ranging from potentials yielding hydrogen evolution to potentials well into the transpassive region. This wireless approach enables rapid simultaneous comparison of numerous samples, and also provides the opportunity to perform experiments on samples that are of a complex shape, or which otherwise are difficult to employ in standard electrochemical corrosion tests.

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1. Introduction

It has recently been shown that bipolar electrochemistry offers a number of interesting advantages when studying surface confined reactions [1]. In such experiments, potential differences are established at the electrode/solution interface along a conducting surface as a result of the presence of an electric field in the electrolyte. This causes the sample to behave as a bipolar electrode with different parts of the surface behaving as the anode and cathode, respectively. Although the bipolar electrode methodology has been used in large scale applications for some time [2,3], its wide electrochemical versatility has only become apparent quite recently [4–9]. In 1986 Fleischmann et al. [4] generated hydrogen and oxygen at different parts of spherical platinum ultramicroelectrodes exposed to an external electric field in a poorly conductive electrolyte. More recently, bipolar experiments have been employed to shape and move nanometre sized objects [5,9], and to improve the detection and separation capabilities of analytical systems [10,11]. Ulrich et al. [8,12] have likewise demonstrated that gradients and surface patterns of self-assembled monolayers can be obtained and studied on gold surfaces by combining bipolar experiments with in situ imaging surface plasmon resonance and imaging ellipsometry. Other groups have also demonstrated gradients of electrodeposited semiconductors [13] and gradients within conducting polymers [14]. Because the bipolar reactions are induced by the electric field in the electrolyte, it is not necessary to connect the object or surface to a potentiostat, which is very advantageous when it comes to very small objects or surfaces that are difficult to contact [15,16]. On the other hand, strict control of the actual potential and current density at every point on the bipolar electrode is not straightforward. Both direct and indirect measures of the current and potential distributions have, however, been demonstrated [8,12], and a theoretical interpretation of the current–voltage characteristics at an aluminium bipolar electrode in a thin layer flow cell has been suggested by Duval et al. [17,18]. It should also be pointed out that unintended and detrimental bipolar reactions also can be found, for example, involving underground installations like pipes and construction elements. These reactions are caused by leakage currents from sources like power lines and public transportation systems, and this phenomenon is therefore normally referred to as stray current corrosion [19].

The aim of this work was to demonstrate that the bipolar concept combined with image analysis can be used to facilitate screenings of the corrosion properties of different materials and surface coatings. At present corrosion tests are usually carried out by recording polarisation curves or by employing chronoamperometric measurements at selected potentials [19]. These experiments are typically carried out on one sample at a time which means that electrochemical corrosion testing involving a large number of samples and different potentials are rather time consuming. In the present work it is demonstrated that the bipolar approach can be used to wirelessly investigate the corrosion behaviour of a sample in a wide potential range. This approach hence offers a facile way to establish a wide range of corrosion conditions for screening of materials and surface coatings without actually contacting the samples.

2. Material and methods

SS304 stainless steel samples were cut into 20 × 10 mm pieces and cast into cylindrical thermoplastic acrylic mounting resins (Struers ClaroFast), 25 mm in diameter and 15 mm high. The samples were grinded and polished using SiC grinding papers and thereafter

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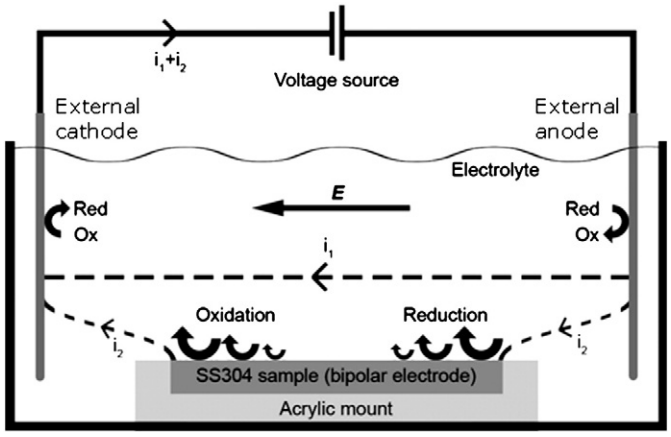

Fig. 1. Schematic fig. of the experimental setup.

employing diamond polishing discs (grain size 6, 3, and 1 μm). Prior to the experiments the samples were allowed to form a native surface oxide film. The steel (from Outokumpu, Sweden) was composed of (in weight-%): 0.015 C, 0.35 Si, 1.74 Mn, 0.031 P, 0.01 S, 18.15 Cr, 8.44 Ni, 0.41 Mo, 0.069 N, 0.25 Cu, 0.001 Ti, and 0.002 Ce, in addition to Fe.

A Delta Elektronika Power Supply ES 075-2 and two platinum electrodes (14 mm wide, separated by 43 mm) were used to establish the electric fields (the stainless steel samples were placed in the centre 11.5 mm from each platinum electrode, Fig. 1). Two digital multimeters (Fluke 77, Fluke, and CM2500, Caltek Instrument) were used to record the total current and the potential difference between the platinum electrodes. The electric fields were established by either controlling the potential difference (5–6 V) or the current (0.1–0.3 A). Experiments with a standard three-electrode cell (using a Ag/AgCl reference electrode and a platinum wire counter electrode) were also performed for comparison. In the latter case, a PGSTAT302N (Metrohm Autolab) potentiostat was used together with 0.20 cm^2 stainless steel samples serving as the working electrodes.

Scanning electron micrographs were obtained by utilizing a Zeiss 1550 SEM/EDS instrument. Generally, an Electron High Tension of 5 kV was used together with a working distance of 5–7 mm. The photo merge feature in Adobe Photoshop CS2 (version 9.0.2) was used to compile pictures to show a large part of the sample surface.

3. Results and discussion

The aim of this work was to demonstrate that bipolar electrochemistry can be used to study the electrochemical behaviour of surfaces in a wide potential window, offering a quick and straightforward method for corrosion screening. As indicated in Fig. 1, the presence of a sufficiently high electric field along the conducting surface results in oxidations and reductions on either side, and the driving force for these bipolar reactions decreases towards the centre. To demonstrate the screening approach, a SS304 sample was immersed in 1.0 M H_2SO_4 and exposed to an electric field (of about 1.3 V/cm) for 120 min. As a result of the bipolar effect a fraction of the total current passed through the steel sample giving rise to corrosion and oxygen evolution at the anodic part and hydrogen evolution and reduction of some of the corrosion products at the cathodic part. As is seen in Fig. 2, the surface of the steel sample was significantly changed as a result of corrosion. It is clearly seen that the degree of the corrosion attack decreased from the anodic edge of the sample towards the centre, and that the corrosion attack mainly was situated at the grain boundaries. In the middle part of the sample, there were, as expected, practically no signs of any reactions. When looking in the more anodic direction (i.e. the left part in Fig. 2), the conditions thus became more and more aggressive. It should be pointed out that it is also possible to analyse the processes on the cathodic part. SEM analyses, for example, indicated that some of the corrosion products from the anodic side, mainly chromium and iron species, were reduced on the cathodic side.

Pitting corrosion is a particularly destructive type of corrosion that metals which form passivating films can be subject to when anions like Cl^- and S^{2-} penetrate the protective oxide film [19]. To demonstrate bipolar pitting corrosion screening, a SS304 sample was placed in the bipolar setup, and a constant current was passed between the two platinum electrodes in 0.10 M HCl. The resulting corrosion images on the anodic part are shown in Fig. 3, and it is clearly seen that the size of the pits formed increases from the onset of pitting near the centre of the surface towards the anodic end. It is also seen that some of the pits eventually merged to form larger pits and that the size of the pits significantly depends on the distance to the anodic edge of the sample (in the lower left part, each data point in the plot corresponds to a pit on the bipolar electrode).

Compared to the conventional use of polarisation curves or chronoamperometric measurements at selected potentials, in which generally only a single sample can be studied, the present bipolar approach offers the possibility to test numerous samples simultaneously

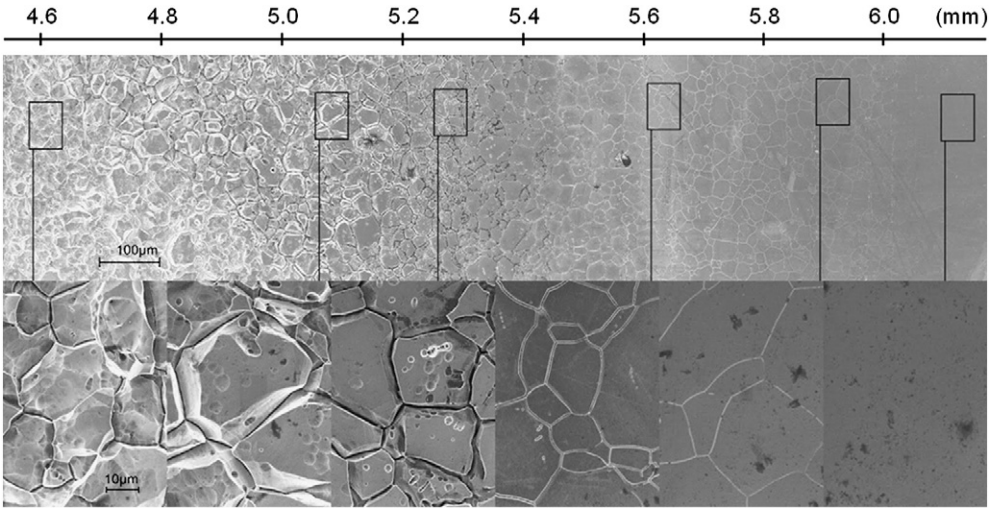

Fig. 2. A large number of individual compiled SEM micrographs showing the entire corrosion gradient on the anodic side of the steel sample (approx. 4.5–6.2 mm from the anodic edge). The lower images depict enlargements of selected regions. The electric field was established by applying 5.4 V between the two platinum electrodes during 120 min (the total current was about 2 A).

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