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Real-Time and Correlative Imaging of Localised Corrosion Events by High-Speed Atomic Force Microscopy

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Corrosion is a degradation process that causes failure of metals and alloys across a wide range of applications and industries including nuclear power plants [1]. Key to the prevention of corrosion is understanding why and how it initiates. A large number of failures due to corrosion occur via localised mechanisms, where susceptible points in the material microstructure are preferentially attacked, such as pitting, intergranular attack or stress corrosion cracking. Understanding how localised corrosion first develops is particularly challenging as it occurs at specific locations and over small length (nanometre) and time (sub-second) scales. Many characterisation techniques lack either the spatial or temporal resolution required for in-situ observation, and often struggle to capture the original corrosion event.

Contact mode high-speed atomic force microscopy (HS-AFM) is a technique capable of nanoscale imaging of surface changes in topography. These measurements can be performed in a range of liquid or gaseous environments, and with sub-second temporal resolution, making HS-AFM ideally suited for in-situ localised corrosion studies [2]. The high throughput of the HS-AFM also make it capable of performing large area surface characterisation pre- and post- corrosion. Using this capability, HS-AFM may be implemented alongside other high-resolution techniques that offer complementary information for correlative analysis [2,3].

The experimental set-up used within this work implemented a three-electrode set-up with potentiostatic control alongside HS-AFM measurements, similar to that implemented in other works [3]. A thermally sensitised (70 hrs at 600℃) sample of American Iron and Steel Institute (AISI) Type 304 stainless steel (polished to a mirror finish) acted as the working electrode. The material in its sensitised state allows repeatable study of corrosion phenomena with industrially significant analogues [4]. The electrolyte was a 1% (0.28 M) aqueous sodium chloride (NaCl) solution, known to induce pitting corrosion under the stated conditions [3, 5].

By using parallel potentiostatic control, the reactions occurring on the surface could be measured alongside optical monitoring of the surface using the HS-AFM's optical microscope. Pitting corrosion initiated on the sample surface during a galvanostatic scan (0.05 mA for a sample surface area of 0.13 cm^2). Figures 1a-1c show a series of HS-AFM topographic measurements of intergranular pit progression selected from a continuous observation performed at 2 frames per second. This pit was observed to grow steadily over a duration of 40 s. Line scans collected across the pit shown in each frame are given in Figure 2a, these profiles provide measurements of pit depth and width. Figure 2b demonstrates the variation in pit depth and width with time. It can be seen that the width steadily increases, whilst depth changes at a variable rate. It is likely that this is the result of deposited debris

such as corrosion products.

This study demonstrates the potential of HS-AFM for in-situ corrosion studies. Quantitative analysis of the early stages of pitting corrosion are necessary for accurate computational modelling. Such models are important for greater understanding of the mechanisms occurring and the safe application of susceptible materials in industry. The set-up implemented in this study allowed for electrochemical measurements to be performed in synchronisation with topographic imaging within a liquid environment. The next steps in this study aim to develop the set-up to allow for local measurements of electrochemistry, in order to deconvolute the electrical signals from the numerous corrosion processes taking place on the sample surface [6].

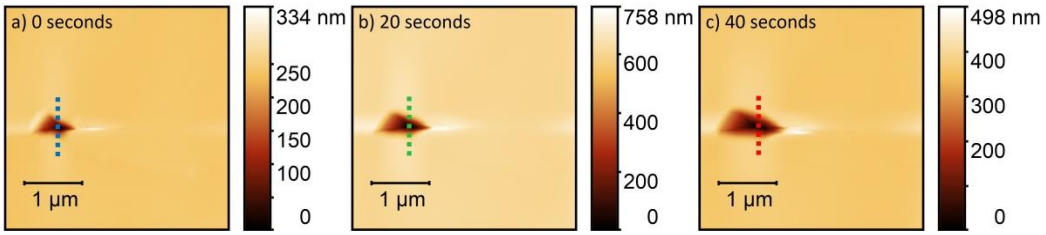

Figure 1. a)-c) Sequential HS-AFM topographic maps showing intergranular pit progression collected at: a) 0 seconds, b) 20 seconds, and c) 40 seconds, with inset colour scales.

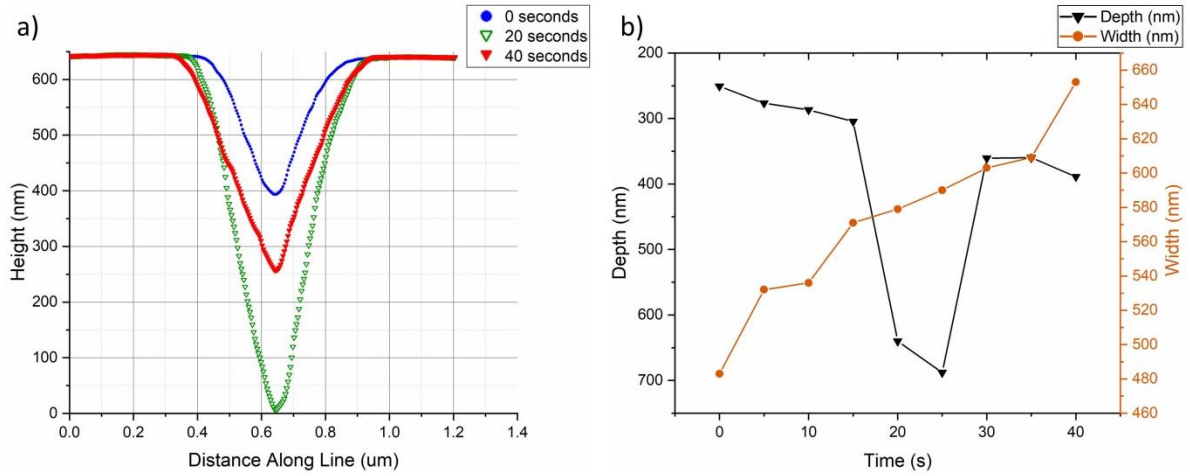

Figure 2. a) Height changes for line scans collected across the dotted line in Figure 1a in blue (solid circles), the dotted line in Figure 1b in green (triangles), and the dotted line in Figure 1c in red (solid triangles). b) The evolution of pit depth (note the inverted scale) in black, and pit width in orange.

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