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Letter

In situ measurement of corrosion on the nanoscale

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ABSTRACT

Measurement of the electrochemical properties phase-by-phase on the nanoscale in real (commercial) alloys is critical to understanding the microstructure-corrosion relationship and subsequently controlling it. This work presents a novel AFM based in situ corrosion probing methodology (for the first time) that is capable of resolving the electrochemical activity (impedance response) into the nanometer range; the method subsequently having major ramifications in the study of aluminium alloy corrosion, the interpretation of corrosion propagation, and the subsequent development of corrosion resistant aluminium alloys.

The correlation of nanoscale surface structure with electrochemical activity is of paramount importance in the investigation of localized corrosion phenomena. The vast majority of engineering metals derive their properties from deliberately heterogeneous microstructures. Such heterogeneous microstructures compromise corrosion resistance by providing local sites (chemical heterogeneities) at which corrosion may initiate [1].

Heterogeneities can exist over a wide size range distribution. In the case of aluminium (Al) alloys, this size range is from about 10 μm for constituent particles, down to a few nm for fine precipitated phases [2]. Indeed, the last two decades have seen extensive investigations into the corrosion behaviour of high strength aluminium alloys [1–7]. These studies have elucidated significant information with combined electrochemical and microscopic investigations down to the microscale [8–11]. Certain aspects regarding electrochemical characterization of such alloys have not yet been resolved – i.e. How small is too small for features to not behave as unique electrochemical entities? What local electrochemical entity is responsible for damage modes such as stress corrosion cracking? etc., with such concerns being an unresolved nano-scale issue.

To date, probing electrochemical activity on submicron length-scales has been explored using a combined Scanning Electrochemical Microscopy–Atomic Force Microscopy (SECM–AFM) method for probing of electrochemical currents over a surface [12]. SECM relies on solution phase ions as the imaging signal; however in this present study, an alternate and complementary method for what is believed to be a higher resolution discrimination of the electrochemical response (i.e. <100 nm) is presented, with the ability to probe individual areas at a time, and in addition, reveal the impedance response on isolated (user selected) features for independent probing. Additionally, the method herein differs from the SECM method more generally [13–14] and the newer offshoot of AC-SECM (employing and alternating current signal) [15] by not requiring a mediated scanning electrode and offering significant improvement in resolution. The approach herein also differs significantly from the Scanning Kelvin Probe Force Microscopy (SKPFM) methods in [16–18], since those tests are conducted in air, and hence are (strictly) insensitive to the effect of an electrolyte.

In this work, the corrosion of the technologically relevant aerospace aluminium alloy AA7075-T651 [19] is investigated. This alloy has been previously assessed in a microstructural sense rather rigorously [20] and, more recently, electrochemically on the micron-plus length scale. On the nanoscale, the microstructure consists of an α-aluminium matrix (with Mg, Zn and Cu in solid solution) and fine η phase ($MgZn_2$) precipitates – which may include a population of the partially coherent η′ precursor phase. Our prior work on characterizing the electrochemical response of η phase alone was focused on the determination of an electrochemical response upon bulk intermetallic analogs on the >50 μm length scale [2]. Such work reveals that bulk η phase is a spontaneously active phase – with a very poor resistance to self-dissolution in 0.01 M NaCl [2]. Whether or not this electrochemical response is preserved when translated to fine nm-lengthscale precipitates embedded in an α-aluminium matrix is unknown – demanding techniques

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capable of probing the electrochemical response on such a fine length scale. The outcome of such knowledge and approaches will be the ability to discriminate on the corrosion susceptibility of real precipitates in real alloys, and serving as a serious alloy design and development tool.

Following significant preliminary work, the ability to reproducibly and carefully resolve the alloy nanostructure for AA7075-T651 (and indeed essentially all Al alloys) via AFM was found to be best when investigating TEM foils – which is a noteworthy contribution to the field in itself. Such foils were produced from 3 mm disks, punched and twin-jet electropolished (using a Tenupol 5) in a Nitric Acid – Methanol electrolyte at −20 °C. A (Scanning) Transmission Electron Micrograph (collected on a Philips TF-20 FEG-TEM operating at 200 kV) is seen along with corresponding AFM images collected on the exact same sample (using an Agilent 5500 SPM with a liquid cell) in Fig. 1. It is seen that the features resolved in the TEM are capable of being resolved via contact-mode AFM with the test specimen being immersed in the test electrolyte of quiescent 0.01 M NaCl (pH ~6.6).

With the ability to image the features of interest via AFM and within an electrolyte, we subsequently wish to probe electrochemical phenomena phase by phase. In order to do this, we represent the experimental setup schematically in Fig. 2. From Fig. 2, we observe what we tentatively call the nano-electrochemical cell. Using a Pt-Ti coated silicon AFM tip (MikroMasch), we can image our alloy in the test electrolyte, however we can then use the AFM controller to raise the tip above the surface of a very specific region of interest (i.e. a precipitate). A prior electrical connection beneath the test alloy, the use of a conductive tip, and exploitation of the AFM electronics to allow a direct electrical connection to be made to the conductive AFM tip permits for the establishment of an electrochemical cell. Fig. 2 reveals how we can thus connect the test alloy to an external potentiostat (in this case a BioLogic VMP3 with low-current option). In this instance, the cell is referred to as what is commonly known as a two-electrode arrangement, meaning that there is no unique reference electrode. This is not however considered critical to the test, since we are not seeking in this work to determine the local electrode potential with respect to a reference, but more interested in the highly localized kinetic response of the alloy as result of an applied polarization.

The potentiostat was used to provide a (small) 10 pA current pulse between the AFM tip and the alloy for a duration of 5 s. This square pulse of current was intentionally kept very small to minimize the polarization period and amount, typically leading to a transient potential response with a maximum deviation of ~10 mV achieved on completion of the 5 s applied current signal (data was logged at 100 pts/s). This change in potential of 10 mV was considered appropriate for subsequent analysis in order to determine the localized electrochemical response.

Only the application of a square pulse of current was investigated herein, with the view of using the electrochemical response recorded for determination of a simple 'polarization resistance', and, where required, elaboration of the analysis to yield local electrode impedance.

In regards to the determination of a local polarization resistance, Fig. 3 represents a summary of data collected upon a number of AA7075-T651 specimens, where a distributed value for the resistance to polarization is seen for all tests carried out. R_P was measured herein simply by using the quotient $\Delta V/\Delta I$, where ΔV is determined from the value of potential measured at the completion of the 5 s current signal less the value measured at the commencement of the signal, and $\Delta I = 10$ pA.

Fig. 3 reveals that there is a very reproducible and clear difference in the R_P measured upon the α-matrix and fine η-phase precipitates; revealing that the η phase has a consistently lower R_P value concomitant with higher rates of electrochemical activity.

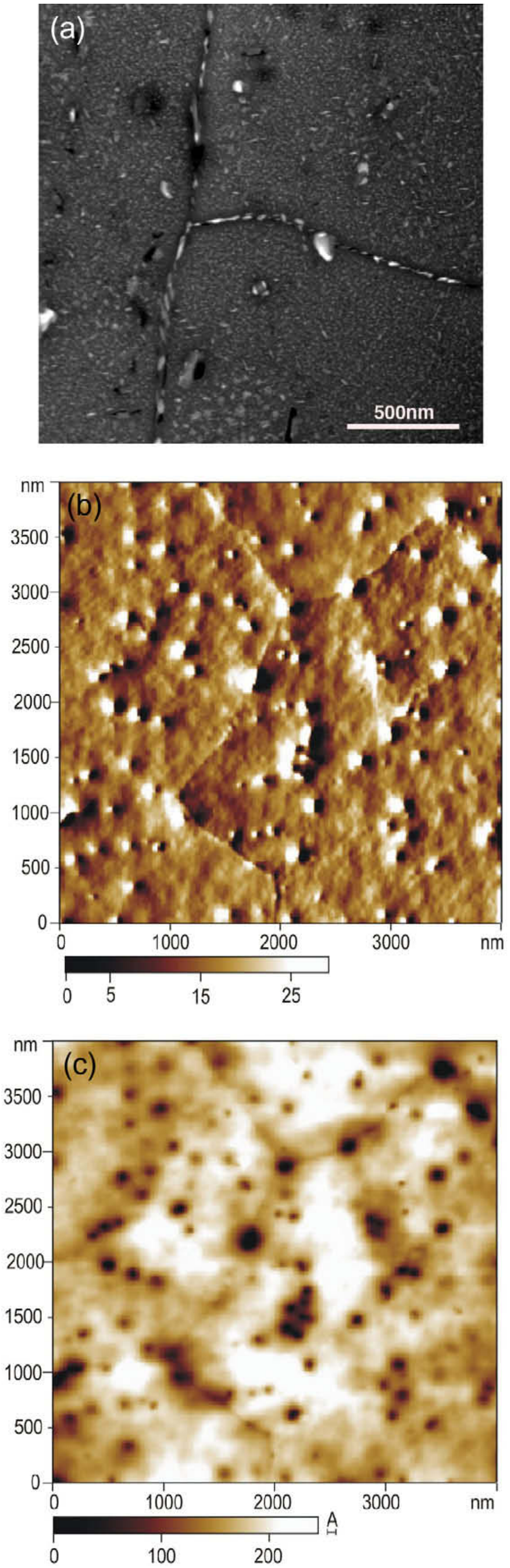

Fig. 1. (a) High angle annular dark field Scanning Transmission Electron Micrograph of AA7075-T651 revealing a random grain boundary triple point. (b) Topography derivative image collected via contact-mode AFM (of the specimen in (a)) showing the ability to reveal the alloy grain and nanostructure. (c) Topography flattened rendering of the image in (b).