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Liquid *In Situ* Analytical Electron Microscopy: Examining SCC Precursor Events for Type 304 Stainless Steel in H_2O

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In situ transmission electron microscopy (TEM) has become an increasingly important research area in materials science with the advent of unique microscope platforms and a range of specialized *in situ* specimen holders. The ability to image and perform x-ray energy dispersive spectroscopy (XEDS) analyses of metals in liquids are particularly important for detailed study of the metal-environment interactions with specific microstructural features. In particular, these capabilities now make it feasible to explore what has been termed "SCC precursor phenomena" – that is, those sub-micron scale reactions between an alloy of interest and the environment. This topic is especially timely for this Swann Memorial Symposium, as Peter Swann's activities in this area, particularly in the 1970's concerning the initiation and early stages of transgranular SCC in austenitic stainless steels, were clearly prescient. In this study, we have used liquid cell TEM with XEDS to explore the "precursor phenomena" that can promote the development of defect initiation in Type 304 austenitic stainless steel. For this work, the FIB lift-out technique was used to extract specimens to be studied in the liquid cell TEM specimen holder. This technique has been applied to examine the localised dissolution of MnS inclusions, which can lead to pit initiation.

FIB sections containing MnS inclusions were prepared from a 0.3 wt.% S Type 304 stainless steel for study in a Protochips Poseidon P210 liquid cell and P510 electrochemical cell *in situ* specimen holders with a 500 nm gap between the amorphous SiN_x windows. Based on initial tests, the electrochemical E-chip configuration was modified to optimize it for electrochemical measurements. The *in situ* experiments were performed in an FEI Tecnai T20 analytical electron microscope operated at 200 kV and equipped with an Oxford Instruments X-Max^N 80TLE Silicon Drift Detector (SDD) for spectrum imaging and analysis. A Zeiss Merlin FEG-SEM equipped with two Oxford Instruments X-Max^N 150 SDDs was used to analyse the bulk samples from the *ex situ* tests. MnS XED spectrum images in 1 bar air and after 24 h in deionised H_2O in the P210 are shown in Fig. 1, and the XED sum spectrum obtained after dissolution is presented in Fig.2. The relevance of the *in situ* observations were confirmed by *ex situ* exposure of a bulk sample containing a Pt line sputtered next to MnS inclusions (to simulate the Pt-coated FIB section) since Pt would support galvanic corrosion, and possibly accelerate the dissolution rate [1]. XED spectrum images obtained from a bulk specimen containing MnS inclusions are shown in Fig. 3a; the same area after 8 days in deionised H_2O is shown in Fig. 3b. Both *ex situ* (Fig. 4) and *in situ* electrochemical polarisation data will be discussed with respect to localised corrosion.

Dissolution of MnS inclusions in low alloy steels is associated with Environmentally-Assisted Cracking [2]. Recent research has also indicated that MnS inclusions may also be associated with SCC as well as low crack growth rates in austenitic stainless steels during certain conditions of corrosion fatigue in primary water environments in light water reactors.

References:

[1] Zhang, X. G. (*2011*). Galvanic corrosion. Uhlig's Corrosion Handbook, 51,123.
[2] H. Hänninen et al. (*1990*) Effects of MnS Inclusion Dissolution on Environmentally-Assisted Cracking in Low-Alloy and Carbon Steels. Corrosion: July 1990, Vol. 46, No. 7, pp. 563-573

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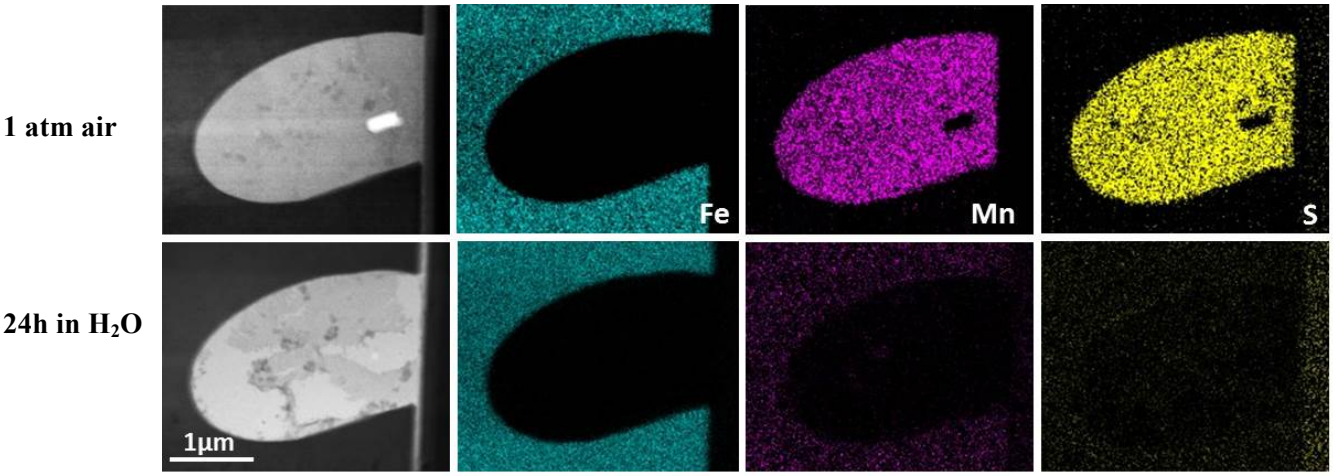

Fig. 1: BF-STEM and XED spectrum images of MnS Inclusion in E-cell: a) 1 bar air; b) after 24 h in H_2O showing dissolution of MnS during *in situ* exposure in H_2O.

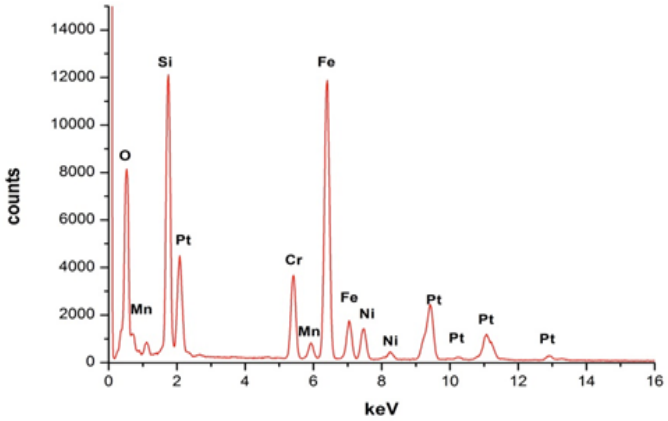

Fig. 2: XED Sum Spectrum from region containing the dissolved MnS inclusion after exposure in H_2O.

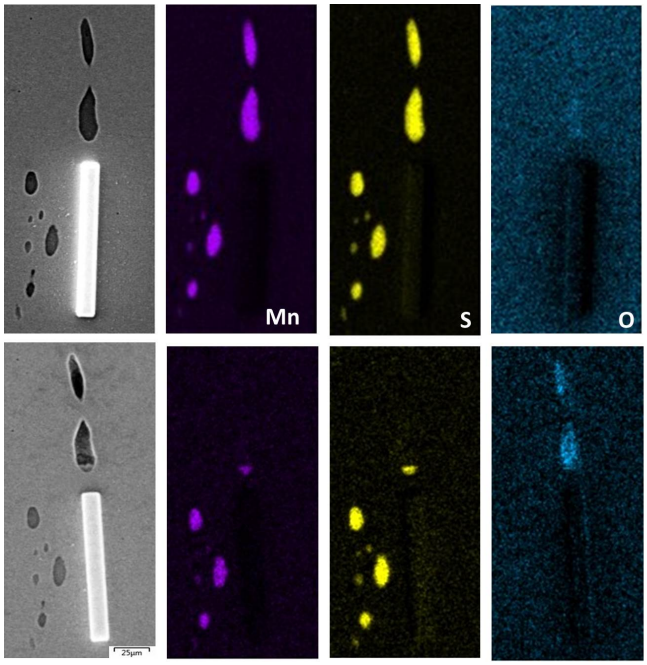

Fig. 3: *Ex situ* observations: SE and XEDS spectrum images of MnS inclusions: a) 0 days; b) 8 days in H_2O. Note the dissolution of the large MnS inclusions above the Pt strip whereas the inclusions covered by sputtered Pt remain intact.

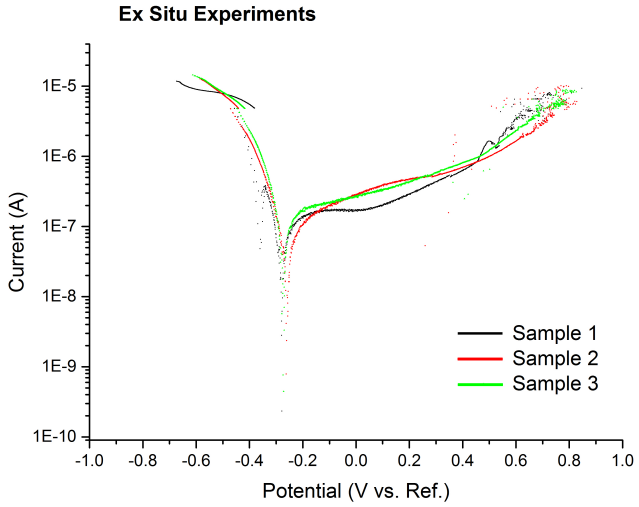

Fig. 4: Polarisation data for Type 304 stainless steel in H_2O using conventional bulk samples.