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Novel Hybrid Sample Preparation Method for *In Situ* Liquid Cell TEM Analysis

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In situ environmental transmission electron microscopy (TEM) research has increased dramatically in recent years [1-3]. However, due to the difficulty in sample preparation, liquid environmental TEM studies have been limited to materials such as nanoparticles or nanowires [3-5]. To date, no work has been reported on conventional metals/alloys in liquid environment. This is due to the significant difficulty in preparation of suitable "bulk" metal specimens that are compatible with the requirements of the liquid cell *in situ* specimen holders. We demonstrate a new sample preparation method for the *in situ* liquid cell TEM study of cold-rolled Type 304 austenitic stainless steel. The proposed new procedure takes advantage of electropolishing and focused ion beam (FIB) sample preparation techniques to extract large electron-transparent site-specific areas with minimum contamination. The liquid cell TEM holder used in these experiments was a Protochips Poseidon 200 liquid cell system, but this novel method can be extended as a general procedure applicable to other types of *in situ* environmental (E)-TEM studies.

The initial specimens were 3 mm diameter discs that had been mechanically thinned to ~150 μm prior to conventional twin-jet electropolishing using Struers TenuPol-5 with an electrolyte of 20% $HClO_4$ - 80% CH_3OH at 20 V and -30±2°C. The thin-foil samples were subsequently examined in an FEI Tecnai F30 field emission gun (FEG) analytical electron microscope (AEM) operated at 300 kV to identify suitable electron-transparent areas. The specimens were then mounted on to a STEM sample holder for imaging in a FEI Quanta 3D dual beam FIB. The thin area-of-interest suitable for *in situ* TEM was located using the STEM image. After confirming the suitable area-of-interest, the sample was tilted to 52 degrees towards ion column and the area was "cut out" using the Ga ion beam at 30 kV and 3-30 nA. The "cut out" area was relatively large (~100 μm x 100 μm) to ensure that the central electron-transparent area was not damaged by the Ga ion beam during cutting.

Two methods of placing the FIB "cut" sample onto the TEM window cell were developed. The first method utilises the electrostatic attraction between the epoxy-coated OmniProbe tip inside the FIB (Fig. 1). Prior to coating, the OmniProbe tip was cleaned using the ion beam (3 nA probe current for 5 min). The epoxy coating was applied externally (outside of the FIB) by dipping the tip into a commercial "superglue". The coated OmniProbe tip had a greater attraction to the sample and provided an effective tool by which the sample could be picked up from the "cut" area and placed on to the liquid E-cell window without the need for attachment using Pt welding/deposition.

The second approach is termed 'cut-and-place'. The thin area of interest was again "cut out" from the electropolished thin-foil specimen in the FIB (3-30 nA 30 kV ion beam) and then welded on to the OmniProbe tip. The "extracted" electron-transparent section was then welded onto the wall of the liquid cell window using a small area of Pt (~1μm x 3μm) and the tip cut free, (Fig. 2). The sample is slightly offset with respect to the window in order to avoid possible redeposition, overcutting, and damage to the cell window.

In situ liquid cell environmental TEM observation of the extracted electropolished specimen immersed in H_2O revealed the formation crystalline deposits and oxides in water with time (Fig. 3). These experimental results demonstrate the successful development of a new hybrid electrochemical-FIB sample preparation method for the environmental TEM dynamic observation of metal in a liquid water environment. The principle of this hybrid TEM sample preparation procedure can be used to prepare samples for other unique *in situ* environmental TEM experiments including *in situ* spectroscopy [6].

References:

[1] J. M. Yuk, *et al*., Science, **335** (6077) (2012) p. 61
[2] H.-G. Liao, *et al*., Science, **336** (6084) (2012) pp. 1011–1014
[3] M. J. Dukes, *et al*., *Chem.* Commun., *49* (2013) p. 3007
[4] N. de Jonge, F. M. Ross, *Nature Nanotechnology*, **6** (2011) p. 695
[5] C Colliex, *Science* **336,** 44 (2012) p. 44
[6] N.J. Zaluzec et al., Microsc. Microanaly. 20 (2014) in press. Doi : 10.1017/S1431927614000154
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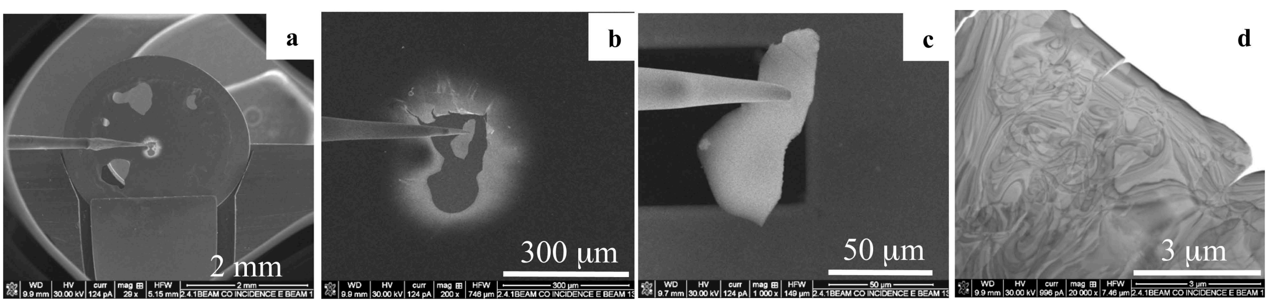

Figure 1. Epoxy-coated manipulator approach: (a) manipulator tip surface prepared for epoxy coating with 3nA ion beam, (b) area of interest is cut free and lifted by electrostatic force (DF-STEM image), (c) sample placed on TEM liquid cell window, (d) BF-STEM image of “cut” area of interest.

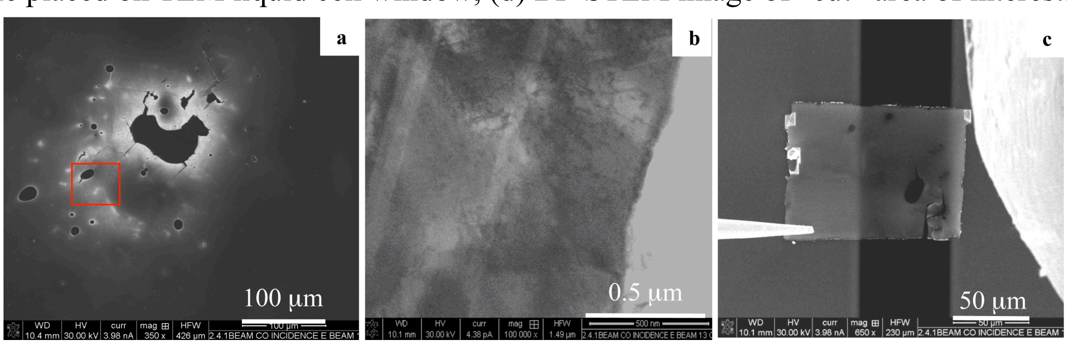

Figure 2. ‘Cut-and-Paste’ approach. FIB images: (a) DF-STEM image of electropolished foil, (b) BF-STEM image of “cut” sample, (c) “cut” sample placed on TEM liquid cell window.

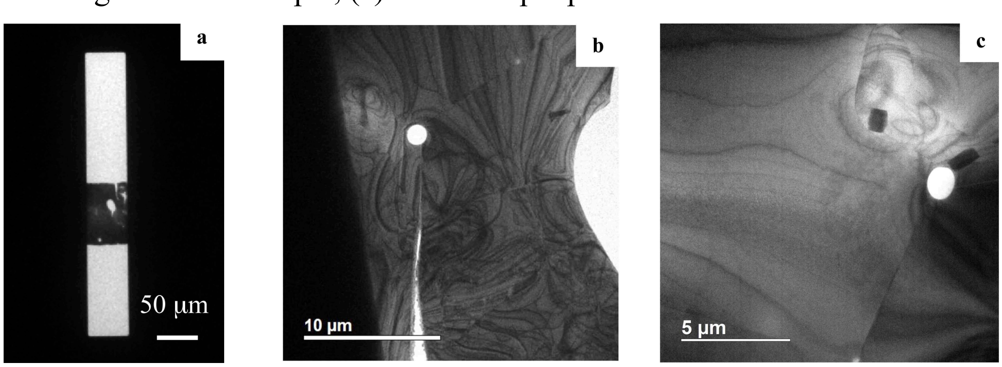

Figure 3. Liquid environment TEM demonstration: (a) low magnification TEM image of hybrid prepared sample on liquid cell window (400 µm x 50 µm), (b) TEM image of sample (no water), (c) sample in liquid H_2O with crystalline deposit formed during exposure under the electron beam.