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Exploring Environmental Reactions in "Real World" Materials using *In Situ* Analytical TEM

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Environment-sensitive behaviour of materials encompasses a broad range of degradation phenomena in metals and alloys. The interaction of metallic materials with the environment is of fundamental importance in understanding a material's performance in "real world" applications. Of particular significance is the effect of liquid and/or gaseous environments on the material of interest. The ability to visualize the localised changes associated with oxidation in gaseous environments and dissolution reactions in liquids coupled with qualitative STEM-XED spectrum imaging and analysis is now providing unprecedented opportunities for real-time observations that can lead to improved mechanistic understanding of nanoscale oxidation, and localised dissolution/corrosion, including the local electrochemical changes.

We have been applying several Protochips *in situ* platforms to examine both gaseous and liquid environmental interactions in structural alloys such as Ni-base alloys (Alloy 600) and steels. The Protochips Atmosphere system interfaced with an FEI Titan G2 200 kV S/TEM equipped with X-FEG and Super X (4 SDDs) has been successfully used in a variety of gaseous environments. Similarly, the Poseidon series of liquid and electrochemical holders permit the direct evaluation of electron-transparent alloys in a variety of liquids including acids and have been used successfully in a variety of analytical TEMs, including the FEI Talos F200 with the Super X multiple SDD configuration. Critical to any *in situ* experiment is the preparation of representative electron-transparent samples, so as to provide a valid link with bulk behaviour. Electron-transparent specimens were prepared using the hybrid method [2]. These specimens can then be attached to an Atmosphere heating chip with Pt, Figure 1, or to the specially-designed electrochemical chip (Protochips "Manchester" chip) for liquid or electrochemical experiments, Figure 2.

A series of examples will be discussed that are related to the detailed study of bulk material behaviour including localised oxidation reactions pertinent to stress corrosion cracking in Ni-base alloys as well as the detailed study of steels in liquid and gaseous environments. The successful experiments using the gas reaction cell system in a variety of H_2-containing environments at elevated temperatures can be further refined to assess variables such as H_2 and O_2 partial pressures, and can also be used to assess localised reactions in 1 bar gas over a range of temperatures of interest and thus provide insight at the nanoscale about diffusion-induced grain boundary migration, internal oxidation, and the role of carbides in preferential oxidation. Similarly, the detailed *ex situ* and *in situ* electrochemical response of austenitic stainless steel in dilute acidic solutions with respect to both temperature and compositional variations will be discussed with respect to degradation phenomena.

References:

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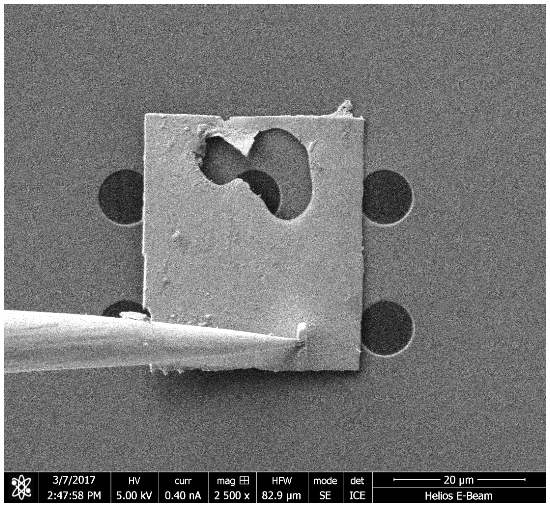

Figure 1. Secondary electron (SE) image of electron-transparent section extracted from an electropolished steel foil and placed on the heating chip for the Atmosphere holder.

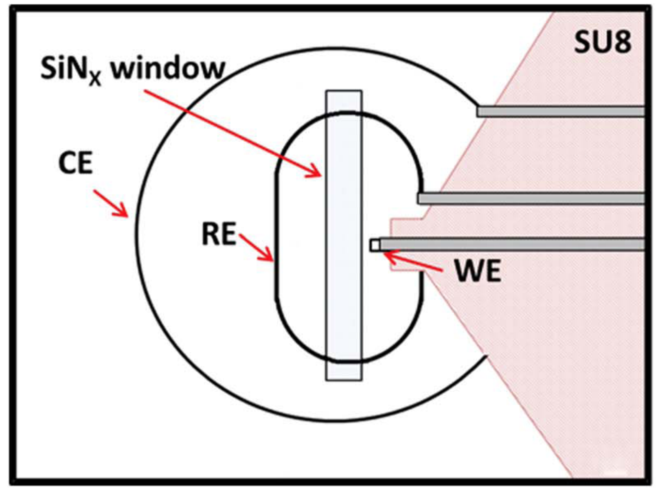

Figure 2. Schematic of modified electrochemical chip ("Manchester" chip). From [3].

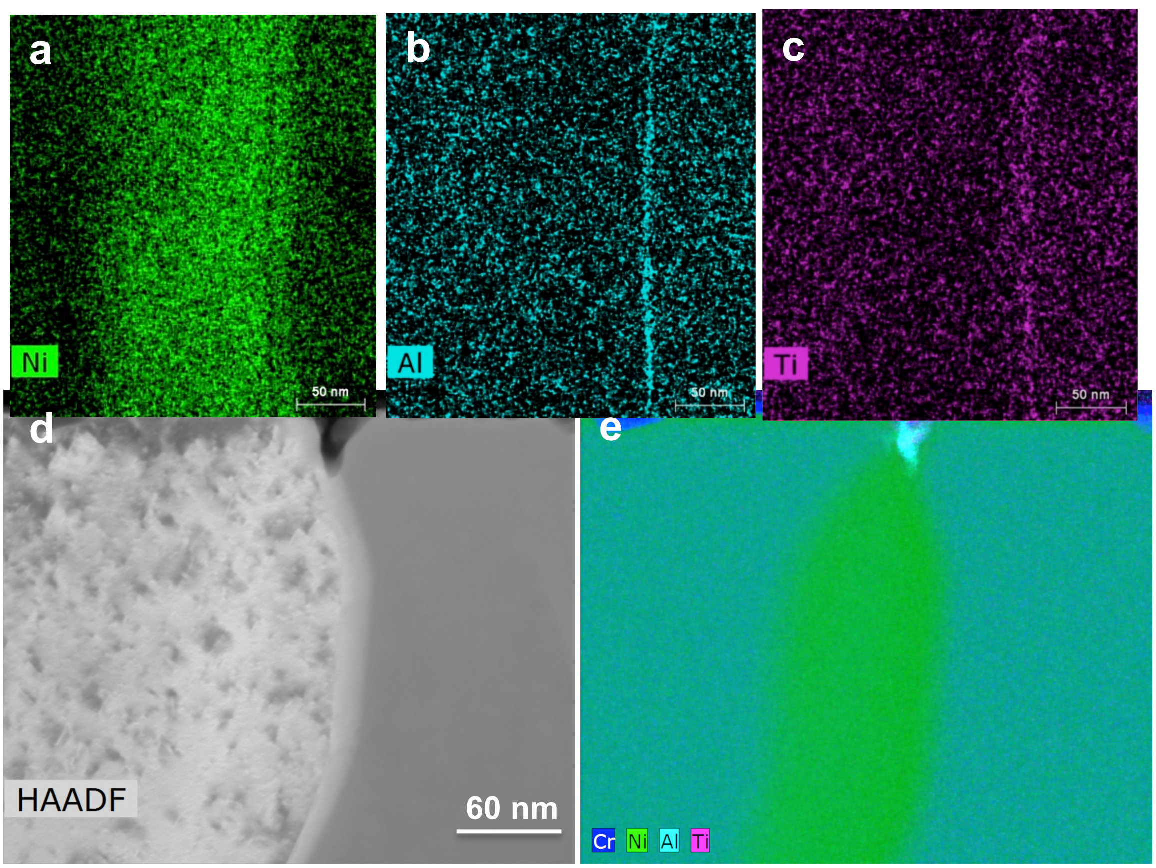

Figure 3. 26h *in situ* oxidation at 400°C of a 300 nm thick Alloy 600 specimen in ~ 1bar H_2-H_2O (v) under reducing conditions. Qualitative STEM-EDX maps for (a) Ni, (b) Al and (c) Ti acquired at 400°C and ~ 1 bar gas (cell gap = 5 µm). FIB-ed cross-section specimen prepared from the thick *in situ* sample: (d) STEM-HAADF image of the migrated boundary, and (e) corresponding composite Ni, Cr, Al, Ti EDX map showing the thin Cr_2O_3 surface oxide and Al/Ti enrichments at the near-surface grain boundary, and the pronounced Cr-depletion/Ni-enrichment in the migrated region.

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