MS-14-P-2433 The Nanoscale Mechanisms of Zircaloy Corrosion in Simulated Nuclear Reactor Conditions

Annand K. 1, MacLaren I. 1, Gass M. 2

1University of Glasgow, Glasgow, Scotland, 2AMEC Clean Energy Europe, Warrington, England

Email of the presenting author: k.annand.1@research.gla.ac.uk

The nanoscale details of the corrosion of Zircaloy-4 under simulated nuclear reactor conditions in contact with pressurised water or steam have been studied using scanning transmission electron microscopy (STEM). Specifically, we have used dual-range electron energy loss spectroscopy (DualEELS) on a GIF Quantum mounted on our JEOL ARM200F scanning transmission electron microscope to simultaneously study changes in chemical composition and dielectric function of the material at the oxide scale – metal interface with nanometre resolution. This has allowed the correlation of the appearance of different distinct phases with the zirconium-oxygen ratio.

Under all conditions studied, oxygen diffused into the surface of the α-zirconium to levels up to or exceeding 30 atomic %, resulting in measureable plasmon shifts, but a low-loss that still looks similar to that of α-zirconium. This is strong evidence that this layer is therefore metallic α-zirconium containing some interstitial oxygen. Under some conditions, this oxygen-diffused Zirconium is in direct contact with the expected ZrO₂ scale. Under other conditions where oxygen supply through the scale to the metal was limited by diffusion kinetics, an intermediate phase is found between the oxygen-diffused zirconium and the ZrO₂ scale. This phase was found consistently to contain about 30-50 atomic % oxygen and is clearly a suboxide. Two examples of this are shown in Figures 1 and 2 for samples corroded in pressurised steam and water, respectively; in both cases a well defined layer (green in the false colour scale employed here) exists at the interface of order 100 nm wide. Such suboxide areas are also characterised by a well-defined low-loss spectrum which is not a linear combination of those for ZrO₂ and oxygen diffused zirconium, suggesting that this is a distinct crystal phase; this is shown as the green phase in the multicolour phase maps in Figures 1 and 2.

One important difference was observed between corrosion in pressurised water (the normal intended working environment) and corrosion in steam (which should not happen in normal service but can occur in extreme situations). In corrosion in steam the morphology of the metal:oxide interface was observed towards a rougher, saw-tooth form, although the intermediate phases formed were spectroscopically identical to those formed in corrosion in pressurised water. This work shows that nanoresolved electron energy loss spectroscopy can reveal unique nanoscale insights into the precise growth mechanism of oxide scales on zircaloy under different simulated nuclear reactor conditions. This is essential to the understanding of the corrosion mechanisms and thus to the correct prediction of safe operating conditions and lifespan for fuel cladding elements.

Acknowledgement: We are grateful to AMEC Clean Energy Europe and the EPSRC for supporting this work, especially through the provision of a PhD studentship to KA. We are indebted to the University of Glasgow of SUPA for the provision of the JEOL ARM200F scanning transmission electron microscope. The support of Gatan Inc. and especially Paul Thomas in providing tools for the processing of the data was invaluable.
Fig. 1: EELS analysis of the metal:oxide interface post corrosion in steam. Top left: map of oxygen percentage with position showing an interlayer with around 30% oxygen, as also seen in a line plot across the interface. Lower right: composite of four MLLS fit maps for low loss spectra of distinct phases: red—ZrO$_2$, green—Zr suboxide, blue—Zr, yellow—ZrH$_x$.

Fig. 2: EELS analysis of the metal:oxide interface post corrosion in water. Top left: map of oxygen percentage with position showing an interlayer with around 30% oxygen, as also seen in a line plot across the interface. Lower right: composite of four MLLS fit maps for low loss spectra of distinct phases: red—ZrO$_2$, green—Zr suboxide, blue—Zr, yellow—ZrH$_x$. 