ESRF	**Experiment title:** Strain and Phase Analysis in Zirconium Alloy Oxides using Nano-Beam Transmission X-ray Diffraction	**Experiment number**: IN831
Beamline:	**Date of experiment**: from: 27/02/13 to: 28/02/13 from: 13/11/13 to: 15/11/13	**Date of report**: 9/9/15
Shifts:	**Local contact(s)**: February 2013: Dr Andrew King November 2013: Dr Gavin Vaughan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Helen Swan – National Nuclear Laboratory

Alice Laferrere – National Nuclear Laboratory

Philipp Frankel – University of Manchester

Paul Styman- National Nuclear Laboratory

Cassie Staines – National Nuclear Laboratory

Helen Hulme - AMEC

Report:

AIM & BACKGROUND:

Zirconium alloys are used extensively in the fuel clad and structural fuel assembly components of light water reactors, however the degree of burn-up the material can sustain is affected by its level of corrosion. The thickness of the oxide layer, the onset of breakaway oxidation and the pickup of hydrogen appear to be critical life-limiting factors.

The formation of zirconium oxide from zirconium is accompanied by a volume expansion of > 50% which results in large compressive stresses in the oxide layer and tension in the metal. Both high compressive stress in the oxide layer and small grain size can stabilise the unstable tetragonal oxide phase. If the tetragonal phase does not remain stabilised, a stable “monoclinic” phase can form, accompanied by a further 5% volume increase. The resulting stresses can cause in cracking and the developments of undulations at the metal-oxide interface.

The aim of this project was to determine how the stress and phase distributions of multilayered zirconium oxide vary with oxidation time and to consider the impact of the monoclinic/tetragonal phase transformation on corrosion kinetics.

EXPERIMENTAL:

Cross-sectional samples of zirconium oxide were produced by exposing Zircaloy samples to a number of aqueous high-temperature environments characteristic of in-service reactor conditions. A range of these samples were developed to represent key stages in the oxidation process. Determination of the stress and phase distributions present in the oxides was undertaken using nano-scale X-ray diffraction (XRD) available on beamline ID11 at the European Synchrotron Radiation Facility (ESRF) in Grenoble.

The oxides studied were approximately 0.5 to 7µm thick and the fine-grained (~20 nm) nature of the oxide meant that the 200nm, 65keV beam line at ID11 of the ESRF could be used to provide a spatially resolved 1D map of the stress distribution. XRD data was output as a series of diffraction rings for each depth into the oxide, an example of which can be seen in Figure 1. These indicate the presence of the various monoclinic and tetragonal forms as identified in Figure 2 and were analysed to obtain the stress and phase distributions with oxide thickness. Radial integration of the diffraction rings were then used to determine the location and thickness of the oxide and each ring could be broken down into a number of diffraction spectra.

These quantitative stress and peak height ratio distributions through the oxides (averaged over the sample thickness in the beam direction, and over the horizontal beam size) could then be plotted and compared with the evolution of the oxide morphology (in-plane and through-plane stress distributions and the tetragonal:monoclinic peak area ratios).

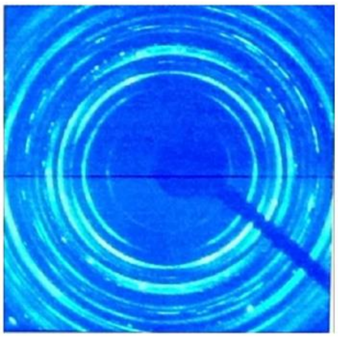

Figure 1: Diffraction patterns (raw data) obtained at a sample-detector distance of ~49.5cm, for Zircaloy oxide

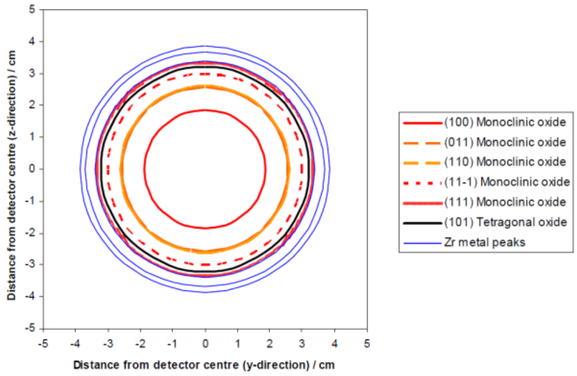

Figure 2: Approximate calculated positions of diffraction rings from monoclinic and tetragonal ZrO_2 and Zr metal for an X-ray energy of 65keV.

RESULTS:

This successful experiment, in two campaigns (February and November 2013) using ID11 has enabled the determination of in-plane and through-plane stresses and the tetragonal phase fraction, fully-resolved with depth into the oxide, for several samples throughout a number of cycles of oxidation. Understanding how strain and phase fraction for multilayered zirconium oxide vary with oxidation time and with depth into the oxide is imperative in determining the potential for cracks to form in the fuel clad, and hence the lifetime of components of light water reactors using these alloys.

It was discovered that the in-plane monoclinic stress relaxes strongly up to each onset of subsequent cycle of accelerated corrosion, known as transition (see Figure 3). These stress-relieved regions correspond to the formation of isolated lateral cracks and their subsequent development into a band of cracking, which, in addition to the observed nano-porosity/through-plane cracking (caused by tetragonal to monoclinic phase transformation and/or tensile in-plane stresses) aids the formation of a percolation path from the oxide surface through to the metal oxide interface, whereupon accelerated corrosion is observed. In addition, the calculated tetragonal phase fractions 'mirrored' the tetragonal phase stresses, demonstrating the stabilisation of the tetragonal phase by high compressive stress.

This work helps demonstrate the importance of the monoclinic/tetragonal phase transformation in Zircaloy oxide in terms of its impact on corrosion kinetics and will be the first step towards developing a physically-based model describing the cyclic corrosion behaviour of zirconium alloys used by the nuclear industry.

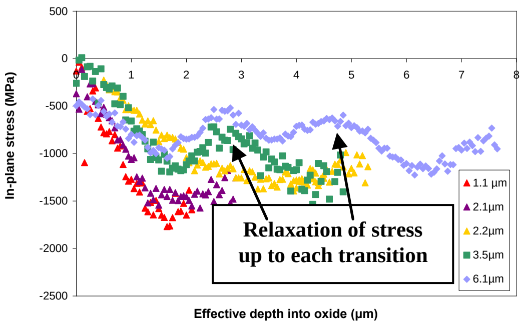

Figure 3: Monoclinic Stress profiles through a Zircaloy-4 oxide in the 1st, 2nd and 3rd cycles of oxidation.[1]

[1] S. Ortner, H. Swan, A. Laferrere, C. English, J. Hyde, P. Styman, K. Jurkschat, H. Hulme, A. Pantelli, M. Gass, V. Allen, P. Frankel, Fontevraud 8 – Contribution of Materials Investigations and Operating Experience to LWRs' Safety, Performance and Reliability, France, Avignon (2014).