ESRF	**Experiment title:** Stress and Phase Analysis of Proton-Irradiated Zirconium Alloy Oxides using Nano-beam Transmission X-ray Diffraction	**Experiment number**: MA2902
Beamline: ID11	**Date of experiment**: from: 31/8/2016 to: 2/9/2016	**Date of report**: September 2016
Shifts: 6	**Local contact(s)**: Andrea Bernasconi, Vadim Diadkin	*Received at ESRF:*

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Report:

The corrosion of zirconoium alloys is a life-limiting issue for some nuclear fuel assemblies, but the process is not well understood, particularly under irradiation. Initial oxide growth rates are often observed to be periodic (repeating cycles of rapid then slower oxidation), followed by more rapid linear behaviour ('breakaway oxidation'). The periodic behaviour is believed to be related to oxide microstructure and stress distributions. Nanoscale transmission X-ray diffraction (on beamline ID11) was performed to characterise the stress and phase fraction distributions in a series of oxidised Zircaloy samples, which have been subjected to proton irradiation (to simulate in-operando neutron irradiation) following aqueous corrosion in autoclave. The use of a nanoscale beam enables individual 'strata' of the oxide to be probed, allowing for the derivation of spatially resolved results within the oxide. This is only possible, however, with very precise alignment of the beam.

Samples manufactured specifically for this purpose were prepared in advance of the experiment, with the zirconium alloy and oxide bound between two brass half circles, then mounted within an aluminium tube. A diagram showing the construction of a sample is given in Figure 1a, where the purple region shows the portion of the oxide layer that has been irradiated and the beam travels along the x-axis. This configuration provided a cross-section of the oxide that was sufficiently thin so as to transmit the X-ray beam, whilst retaining the oxide structure during preparation. Samples were mounted on a hexapod stage using a simple clamp, as seen in Figure 1b.

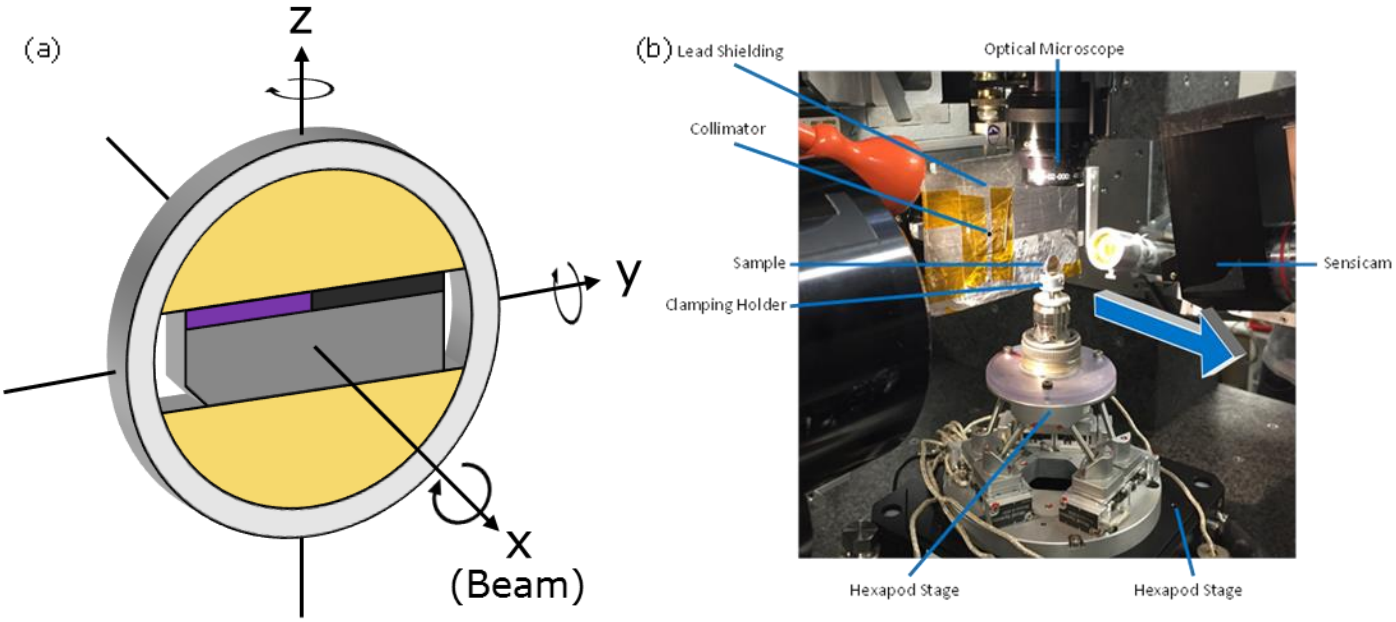

Figure 1. (a) Sample translational and rotational axes, where the beam propagates in the direction of the x-axis, and (b) the effective oxide thickness calculated from the oxide intensity at two different y-axis rotations.

Coarse alignment was performed using the optical microscope above the sample for displacement along the x-axis and rotationally around the z-axis. The Sensicam was used to coarsely position the oxide along the z-axis and rotationally align around the x-axis. Fine rotational alignment around the y-axis was performed using the diffraction signal of the oxide. This was achieved by integrating the signal from a small portion of the detector, known to contain the oxide signal, whilst displacing the sample in the z-axis. The plot of signal versus distance was then used to calculate the apparent oxide thickness, as in Figure 2. The sample alignment was optimum at the rotation that produced the minimum apparent thickness.

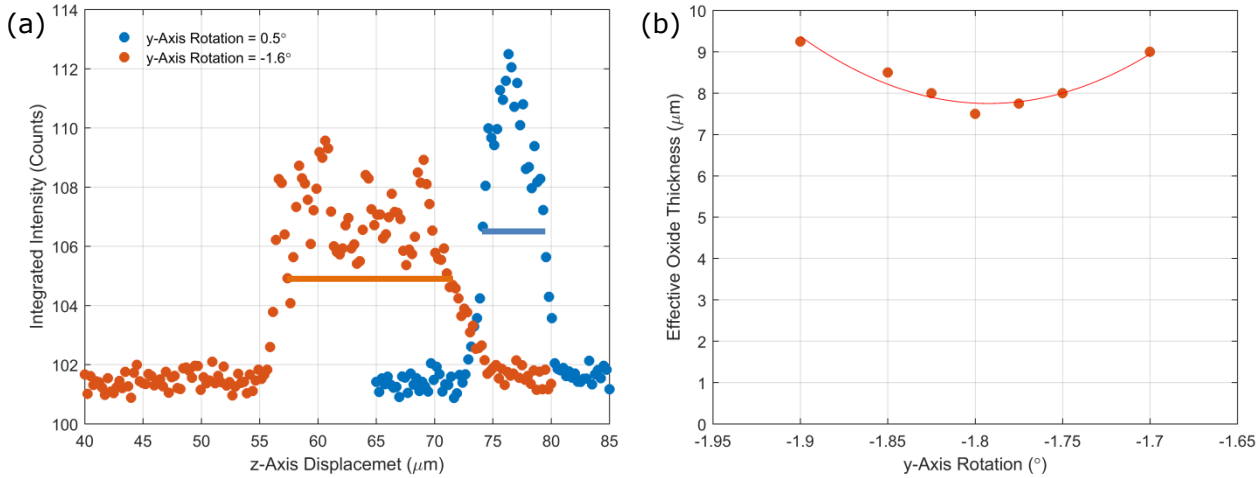

Figure 2. (a) Integrated oxide signal as a function of z-axis displacement and y-axis rotation, and (b) rotational alignment around the y-axis to minimise the effective oxide thickness determined from the diffraction signal. Note that (a) and (b) are the most illustrative examples and are not from the same alignment.

Once aligned, the specimen was stepped through the beam so that data were acquired along a line beginning in the brass and incrementally progressing through the oxide and then the metallic substrate. The step size during this displacement was 50 nm per diffraction pattern acquisition. The beam size was 50 µm wide (improving counting statistics) by 131 nm tall (sampling only very fine layers of the oxide). The energy of

the beam was ~65 keV, with a wavelength determined from a CeO_2 calibrant as 0.18977 Å. The approximate sample detector distance was 37 cm for each sample, once positioned correctly along the x-axis. All measurements were performed at room temperature. The diffraction signal was generally good, although some samples produced unexpectedly spotty metal patterns, which made it difficult to image the much weaker oxide pattern without saturating the FReLoN detector. This difficulty in imaging significantly extended the time to align the first sample, before a workaround could be devised that would allow faster alignment.

Data collection from four samples was possible in the 6 allotted shifts for the experiment, although three of these samples contained distinct irradiated and non-irradiated regions. Collecting series of data from both irradiated and unirradiated portions of oxide required sample realignment between acquired series, due to the large displacements necessary to move from region to region. Where possible, duplicate series were collected consecutively from closely neighbouring regions in each portion of oxide, to improve the robustness of observations. Table 1 provides details of the ten series that were collected during the experiment, whilst Figure 3 shows where these were located on each sample. Across the four samples studied in this experiment, data have been collected from a total of four material conditions.

Table 1. Details of data series acquired during the experimental beam time.

Series	Sample	Material	Region	Oxide Thickness (μm)	Oxide Damage (dpa)	Further Oxidation
1	S1	Zircaloy-2	Non-Irradiated	1.96	2.0	No
2	S1	Zircaloy-2	Irradiated	1.96	2.0	No
3	S1	Zircaloy-2	Irradiated	1.96	2.0	No
4	S2	Zircaloy-2	Non-Irradiated	1.96	2.0	Yes
5	S2	Zircaloy-2	Irradiated	1.96	2.0	Yes
6	S3	Zircaloy-4	Non-Irradiated	5.19	0.3	No
7	S3	Zircaloy-4	Irradiated	5.19	0.3	No
8	S3	Zircaloy-4	Irradiated	5.19	0.3	No
9	S4	Zircaloy-4	Non-Irradiated	6.17	0.0	No
10	S4	Zircaloy-4	Non-Irradiated	6.17	0.0	No

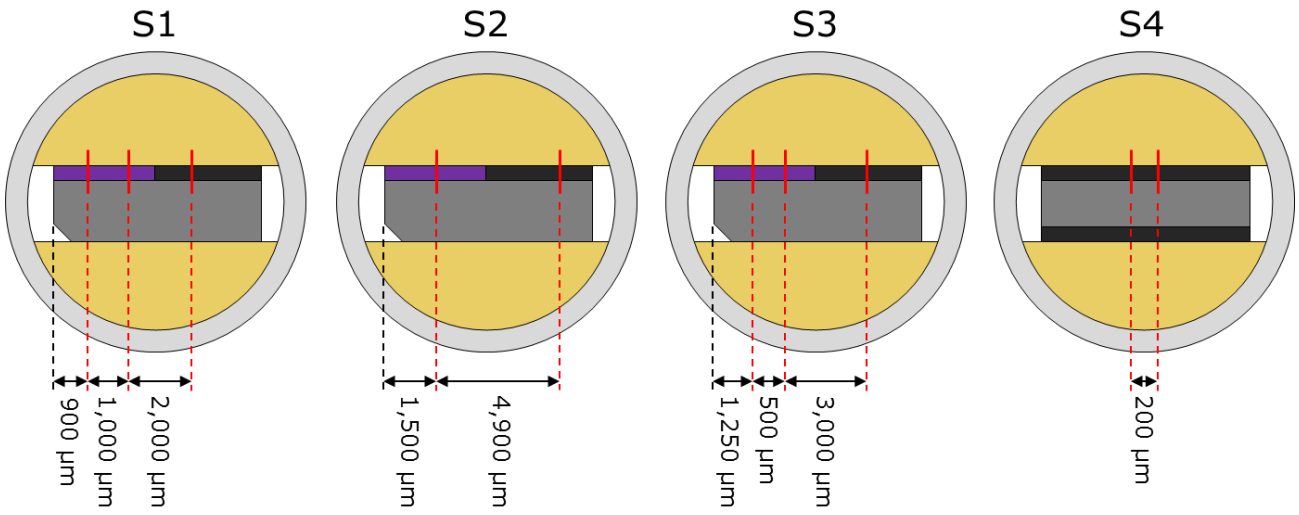

Figure 3. Location and separation of the ten data series collected from the four samples studied during the experiment.

Six individuals attended the ESRF to undertake this experiment, representing a university, a national laboratory and two commercial organisations. Allotted shifts were of 8 hours in duration, staggered by four hours, such that two individuals were always on shift. This shift length was deemed to be the maximum safe working time, mitigating the risk of mistakes or oversights being made from over-tiredness, particularly for those staffing the beam line outside of regular working hours. Shift staggering provided a second set of fresher eyes and hands at any given time. In addition, it also meant that a new individual beginning their shift had four hours to learn from their first overlap, before spending the second four hours teaching the next individual to come on shift. In this way, changes to the terminal macros/commands, sample ordering, machine condition, setup or working instructions were passed on by practical exposure, rather than verbal or written instruction. One of the three individuals with previous experience of experimentation at the ESRF was on shift at any given time.

During the alloted six shifts, more than 50% of the time was spent aligning samples and 25% collecting the ten data series, with the balance split between setup, sample changes and calibrant acquisitions; this is shown graphically in Figure 4. It is suggested that future experiments could improve upon the time required for alignment by developing a sample holder specific to this experiment. This would remain in-place, maintaining the alignment as best as possible, whilst samples were swapped, reducing the time taken for alignment to be completed.

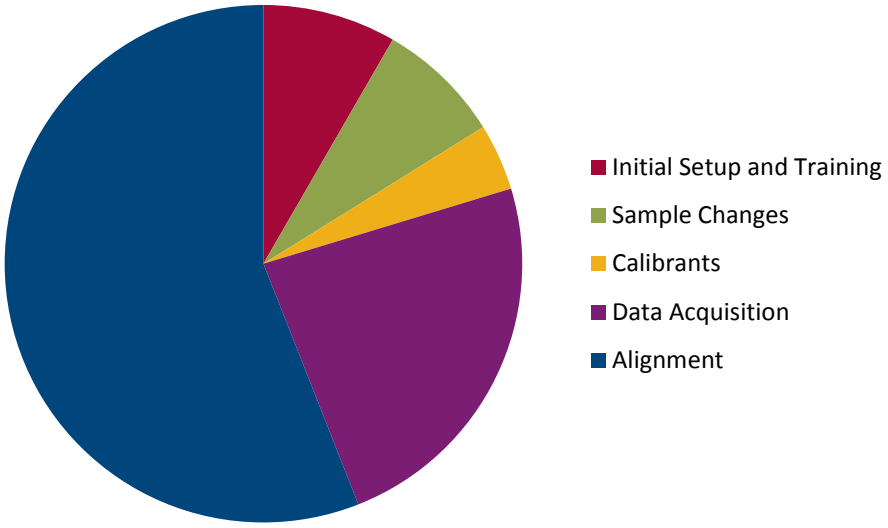

Figure 4. Approximate breakdown of time spent during the experiment.

In conclusion, despite the difficulty involved in performing such a necessarily precise experiment, the session was successful, as data were collected from four samples and seven material conditions. Analysis is in progress as part of a collaboration between The National Nuclear Laboratory and The University of Manchester. The data derived from this experiment, combined with extensive existing microstructural data from other techniques, will improve the understanding of the structure and nature of the oxide subjected to irradiation, and the mechanism of oxidation.