EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** An in-situ electrochemistry study of the surface morphology of UO_2	**Experiment number**: 28-01-997
Beamline: BM28	**Date of experiment**: from: 30 Jan 2013 to: 05 Feb 2013	**Date of report**: 16th October 2013
Shifts: 18	**Local contact(s)**: Didier Wermeille	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. G. Lander*

Prof. Christopher Lucas* University of Liverpool

Dr Ross Springell* University of Bristol

Prof. William Nuttall*

Miss Elizabeth Cocklin* University of Liverpool

Miss Milly Stitt* University of Bristol

Miss Laura Glaubes* University of Bristol

Miss Sophie Rennie* University of Bristol

Report:

Exposing a UO_2 fuel surface to water has the potential to release radioactive material into the environment. Given the global interest in nuclear energy, this process is of great importance, and has thus motivated a wealth of research into understanding the corrosion of spent nuclear fuel. Although there have been many studies into the chemistry and electrochemistry of UO_2 surfaces, they have most commonly concentrated on the spent fuel, which contains a great deal more complexity than pure UO_2, and as a consequence the experimental variables become extremely hard to refine. A simplified approach has been applied by Seibert and co-workers [1] where the corrosion of polycrystalline UO_2 films was investigated, using an electrochemical quartz balance. To build upon the information obtained through this research, we aimed to combine electrochemical techniques with grazing incidence x-ray diffraction, to reveal in-situ information about the oxidation of single crystal UO_2 thin films.

Uranium dioxide, single crystal, thin film samples were grown via reactive DC magnetron sputtering at the University of Bristol. Characterisation carried out at both the ESRF and Diamond Light Source, have shown that high quality single crystal UO_2 thin films have been grown in both the [001] and [111] orientations. Electrochemisty was performed on a range of samples of varying thickness, to mimic the natural exposure of UO_2 to known redox conditions. This was achieved by suspending a droplet of MilliQ water on the surface of the sample whilst remaining at an oxidising potential. However, this effect was unable to be detected through x-ray diffraction measurements as a more dominant effect was observed.

It was found, that holding a droplet of MilliQ water on the surface of the sample whilst exposed to a 15keV x-ray beam, resulted in the corrosion of the UO_2 film. This process mimics the exact reaction which occurs within a storage container, where the residual radiation fields of spent nuclear fuel cause the radiolysis of ground water to produce oxidation products (H_2O_2, $OH^{\bullet}$, O_2). These products then react with the surface of the fuel, causing the dissolution of UO_2 as summarised in the following equation:

$$UO_2 \rightarrow UO_{2+x} \rightarrow UO_2^{2+} \rightarrow UO_3 \cdot yH_2O \cdot$$

Using this technique, a 20 Å single crystal UO_2 [100] thin film was exposed to the radiolised droplet. Crystal truncation rods (CTR) along the [00L] direction were then measured to detect changes in the surface morphology of the film. Figure 2 (upper panel) displays a CTR along the [00L] direction showing the LSAT substrate (001) and UO_2 (002) Bragg peaks. The sample was subjected to two separate exposures after which a significant decrease in Bragg peak intensity was observed, Fig. 1 (lower panel). Further analysis of the exposed sample surface was carried out at the University of Bristol and University of Cardiff using EDX and XPS. This confirmed that the decrease in Bragg peak intensity shown in Fig 1. corresponds to a loss in UO_2 material.

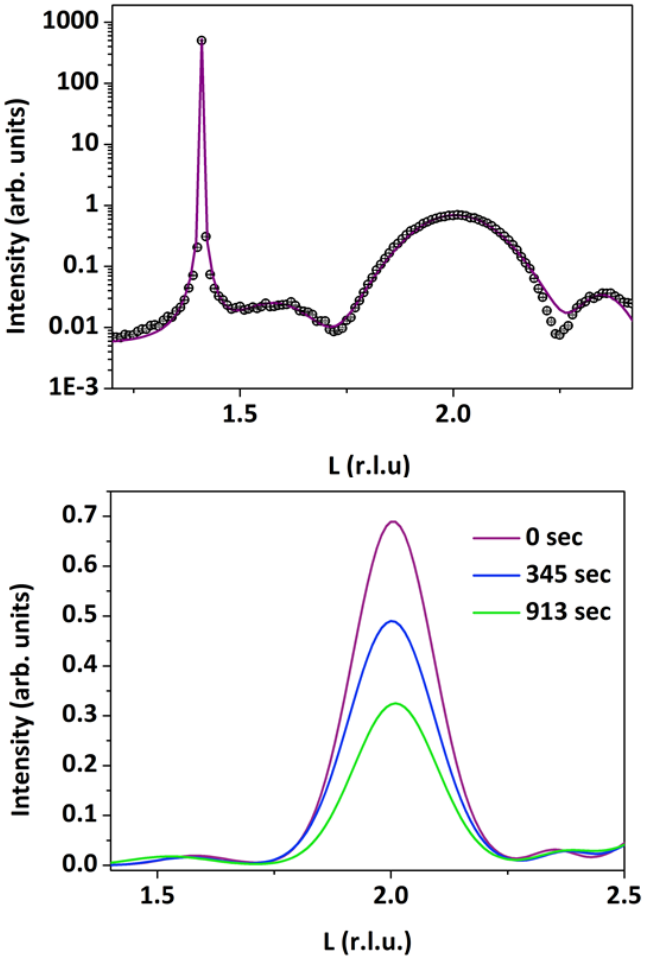

Fig. 1 – Upper panel, truncation rod along the [001] direction showing the LSAT (001) and UO_2 (002) Bragg peaks with Laue thickness fringes. Lower panel shows reduction in UO_2 (002) Bragg peak intensity on radiolysis.

During the course of this experiment we have developed a novel technique through which the corrosion of UO_2 under storage conditions can be reliably replicated. For future work we intend to apply this technique to investigate the rate of corrosion of the UO_2 [110] and [111] orientations along with higher uranium oxide fuels. These investigations will give us further insight into the corrosion of spent nuclear fuel under storage conditions, which is vital in predicting the likely mid and long term effects for nuclear waste containment strategies.

References

[1] A. Seibert *et al.* J. Nucl. Mater. **419** (2011) 112