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:** The Corrosion of Uranium Dioxide in Aqueous Environments	**Experiment number**: 28-01-1034
Beamline: BM28	**Date of experiment**: from: 25 Sep 2013 to: 01 Oct 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

Miss Elizabeth Cocklin* University of Liverpool

Dr Ross Springell* University of Bristol

Miss Milly Stitt* University of Bristol

Miss Sophie Rennie* University of Bristol

Report:

Given the increasing global interest in nuclear energy, understanding the corrosion of spent nuclear fuel under storage conditions is of great importance. In particular, predictions for the likely mid and long term effects of nuclear waste containment strategies are dependent on experimental data. Building on research conducted during a previous XMaS experiment (see report for 28-01-997), we aimed to probe the long-term corrosion of UO_2 single crystal thin films of [001], [110], and [111] orientations. By conducting such experiments, we are able to measure the dissolution rates in-situ, watching in real time, the surface corrosion of UO_2 that would normally take place over hundreds of years.

Uranium dioxide, single crystal, thin film samples were grown via reactive DC magnetron sputtering at the University of Bristol. Characterisation showed that high quality single crystal UO_2 thin films have been grown in the [001], [110] and [111] orientations. To compare the corrosion rates for each crystal orientation, 80 Å, single crystal UO_2 [001], [110], [111] thin films were grown on YSZ substrates.

As developed in the previous experiment (28-01-997) the dissolution of the sample surface was achieved through utilising the radiolysis effect from an intense beam of 15 keV x-rays, whilst exposing the samples to MilliQ pure water. After exposing the sample to radiolytic products, the droplet was removed to avoid any unwanted radiolysis. After each exposure, crystal truncation rods were measured as these allow us to model the structural changes to the surface and thus obtain a better understanding of the corrosion mechanism.

Oxidative dissolution was investigated for UO_2 thin films grown in the [001], [110] and [111] orientations. Figure 1 shows the data from the dissolution of an 80Å UO_2 [111] thin film, where the intensity of the (111) Bragg peak is shown as a function of radiolytic exposure. Similar results were also found for the [001] and [110] orientations.

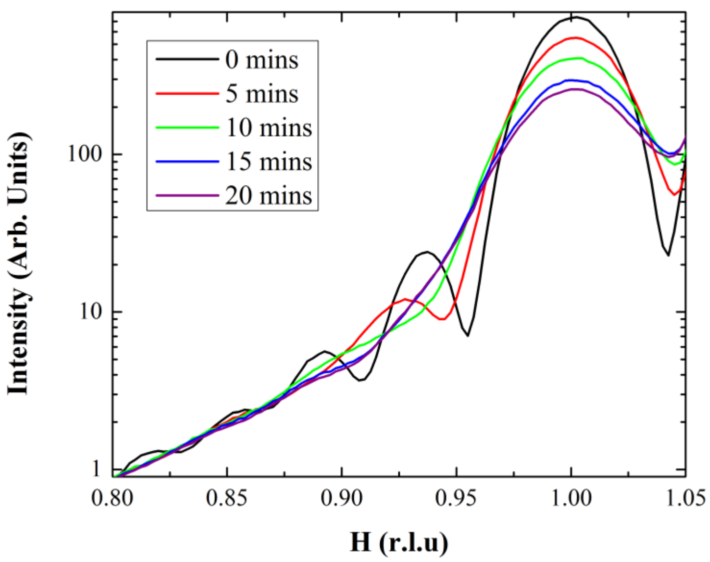

Fig. 1 – Intensity of the (111) Bragg reflection as a function of radiolytic exposure. The roughening of the surface can be seen in the decreased intensity of the Laue fringes and the reduction in material is clear from the reduced (111) intensity and increased fringe separation.

For comparison with the corrosion rates of the single crystal samples, the oxidative dissolution process was also instigated on polycrystalline UO_2 thin films. Initial results show that rates of dissolution varied between samples, suggesting that grain boundaries play a significant role in determining corrosion rates.

The effect of pH was also investigated, where a solution of pH 11 was shown to totally inhibit the dissolution process and a pH 2 solution rapidly increased the rate of corrosion.

Throughought this experiment we have addressed the issue of crystallographic orientation-dependence and pH variation on the corrosion rate, using the radiolysis of aqueous solutions in contact with UO_2 surfaces. More importantly, we have identified that the high flux of x-ray photons (approx. 2×10^{11} photons at 15 keV) mimics the radiolysing effects of the radiation fields at the surface of spent nuclear fuels. This allows us to study the surfaces of nuclear materials in their so-called ‘hot’ state without ever having to handle highly radioactive waste fuel. This opens up the real possibility to study the effects of storing next generation spent fuel without ever processing them through a reactor.