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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:** **Adding Complexity in the Story of Radiolytic Dissolution of Nuclear Fuel**	**Experiment number**: 28-01 1227
Beamline: BM28	**Date of experiment**: from: 27 Sep 2017 to: 03 Oct 2017	**Date of report**:
Shifts: 18	**Local contact(s)**: Didier Wermeille	*Received at ESRF:*

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Report:

One of the greatest challenges facing our generation is ensuring the safe, long-term storage of spent nuclear fuel, predominantly in the form of UO_2 [1]. Despite the progress that has been made internationally in developing multi-barrier containment strategies, there remains a significant possibility of containment failure and the subsequent release of radionuclides into the environment [2]. This process occurs when the surface of waste fuel is exposed to ground water and the potentially oxidising conditions which lead to the degradation of the fuel matrix. While this has been widely studied, the precise reaction mechanism is still hotly debated and the reaction rate dependence on grain boundary density is yet to be determined.

Through a previous experiment conducted at XMaS (see reports 28-01-997 and 28-01-1034) we have been able to develop a method of simulating the corrosive, oxidative environment which is present under storage conditions [3]. Using a thin film water tension cell, the effect of radiolytic corrosion on UO_2 thin films was investigated, using water and an x-ray beam, as both a source (a radiation field) and a probe, to study corrosion at the fuel/water interface. A combination of x-ray reflectivity (XRR) and high angle x-ray diffraction was used to determine changes in the morphology and crystallinity of the oxide. This study has allowed us to explore the role of grain boundaries on corrosion rates and investigate the reaction mechanism of x-ray driven radiolytic dissolution.

Experimental Results

To improve understading of the mechanism of radilytic dissolytion we investigated effect of the number of corrosion steps (a step being the opening and closing of the beam shutter) for a fixed cumulative corrosion time, i.e. comparing one step of 300 s with 300 steps of 1 s. The results from this investigation are show in Figure 1, where it can be seen that the change in UO_2 [001] sample thickness increases with number of corrosion steps. Complimentary experiments performed using a lab source at the University of Bristol found that this effect was not seen when using H_2O_2 solution to mimick the products of radiolytic dissolution. This fits with our previous comparisons showing that H_2O_2 is not responsible for the majority of the oxidation that occurs during radiolytic dissolution [3]. Considering the reaction mechanism, this result is indicative that corrosion rates are not uniform over the duration of a corrosion step, possibly due to a localised saturation of the solution in the beam path or passivation of the UO_2 surface.

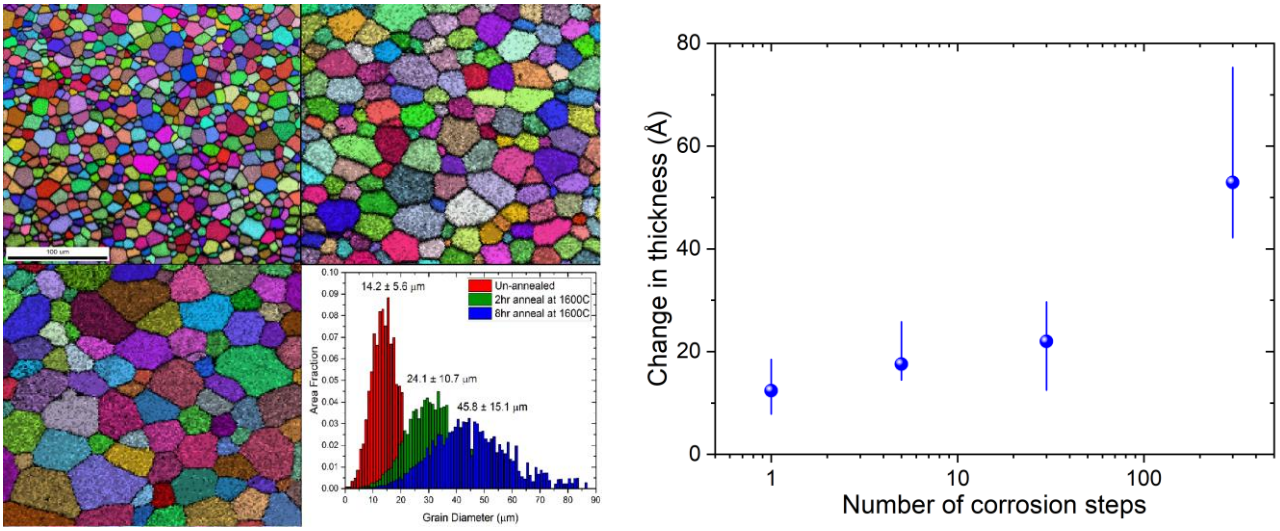

Figure 1: Left panel, grain size distribution in 'polyepitaxial' samples. Right panel, change in UO2 [001] sample thickness as function of number of corrosion steps with a cumulative time of 300 s.

Investigation of the effect of grain size on dissolution rates were performed using novel polyepitaxial thin films of UO_2, where the polycrystalline film grain size is controlled by epitaxial matching to the polycrystalline substrate, allowing film with grain size of 10 – 50 µm to be fabricated. Analysis of the XRR results showed no clear trend in corrosion rate as a function of grain size, however, it was found that roughness of the surface after 300 s corrosion increased with decreasing grain size. From previous investigations it is known that different orientations corrode at different rates [4]. As the distribution of grain surface orientations in each sample is assumed to be the same, it is suggested that the results from this experiment show that there is no strong prefence for intergranular corrosion over intragranular corrosion on UO_2 surfaces.

Conclusions

Adding complexity to our experimental model of a UO_2 surface by using polyepitaxial films has provided new insight into the effect of grain boundary density on radiolytic dissolution. Evidence that the number of corrosion steps for a fixed time period has an effect on corrosion rates shows a need for better awareness of the chemistry of the solution and sample surface. This is problem for which *in-situ* investigations are most likely to provide a solution. In conclusion, the results from this experiment have improved understanding of the radiloytic corrosion mechanism of UO_2 surfaces, helping to understand the degradation of nuclear fuels in long-term storage and guide the next direction of research for this complex problem.

References

[1] World Nuclear Association, Available at: http://www.world-nuclear.org/info/inf103.html.
[2] D. W. Shoesmith, Journal of Nuclear Materials 282, (2000) 1.
[3] R. S. Springell et al., Faraday Discussions 180, (2015) 301.
[4] S. Rennie et al., Corrosion Science 145, (2018) 162.