EUROPEAN SYNCHROTRON RADIATION FACILITY

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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	Chemical and structural characterization of molybdenum in stoichiometric and hyperstoichiometric uranium dioxide	**Experiment number**: CH-5023
Beamline: BM20	**Date of experiment**: from: 21/06/2017 to: 27/06/2017	**Date of report**: 9/09/2017
Shifts: 15	**Local contact(s)**: Andre Rossberg	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Clotilde Gaillard*, Lola Sarrasin*, Yves Pipon*, Nathalie Moncoffre, Institut de Physique Nucléaire de Lyon, France

Report:

The mobility of fission products (FP) is one of the key parameters for the understanding and modelling of the nuclear fuel behaviour during a severe accident in a nuclear reactor such as a PWR. In the frame of a PhD thesis made in collaboration with IRSN, we have focused our attention on the study of molybdenum behaviour in uranium dioxide (either stoichiometric UO_2 or hyperstoichiometric $UO_{2,1}$), under extreme temperature and irradiation conditions. The initial aim of this experiment was to characterize the chemical state and environment of Mo implanted in uranium dioxide pellets after different annealing and irradiation treatments, by XANES and EXAFS measurements at the Mo K edge. However, it was not possible to detect a Mo fluorescene signal at this edge. This is due to the very low Mo concentration in the samples and the high fluorescence signal due to the uranium matrix.

Therefore, we have made measurements at the uranium L_3 edge with the aim to detect structural changes in the UO_2 matrix caused by heavy ions irradiation and oxidation.

25 samples (UO_2 sintered pellets) were analysed by EXAFS. Data treatment is underway, so here are presented the first observations made.

The first kind of samples that were analysed are polycristalline UO_2 pellets irradiated at high temperature (between 600 and 1000°C) with high energy heavy ions. Different irradiation conditions were chosen in order to favour either the formation of electronic defects or balistic defects in the UO_2 bulk. Figure 1 displays the comparision between Fourier Transforms spectra obtained from the EXAFS of a virgin UO_2 with 2 UO_2 irradiated at 800°C, with high enery heavy ions favouring either the production of ballistic defects (Au irradiation) or the simultaneous formation of ballistic and electronic defets (Au+W). The main peaks visible on the TF correspond to the successive shells of oxygen and uranium atoms arising from the known fluorite-type structure of UO_2. It is interesting to note that the sole ballistic defects created at 800°C do not imply any visible change in the UO_2 local structure. It may be related to a temperature activated restructuration of UO_2

microstucture. At the same time, we observe a noticeable change in the TF between UO_2 and Au+W samples on the 5.5 Å peak. It corresponds to an uranium shell located at 5.45 Å.

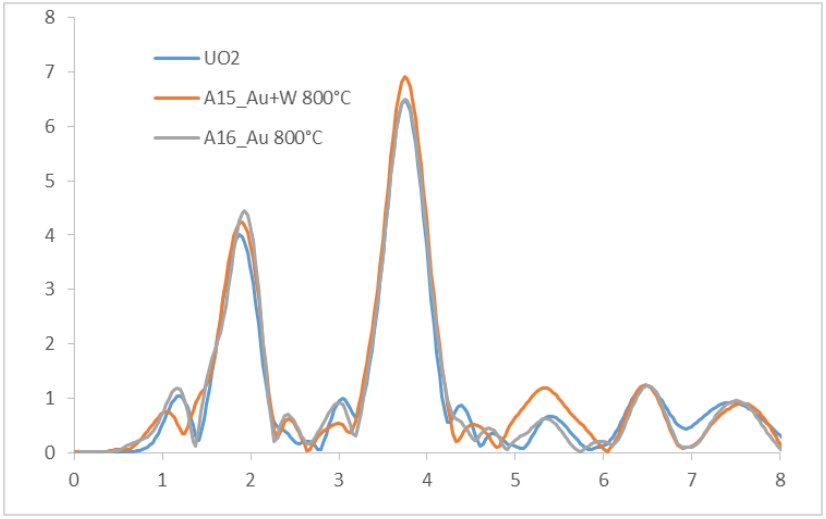

Figure 1: comparision of FT spectra for 3 UO_2 samples, as a function of irradiation conditions

The second example shown in figure 2 concerns the evolution of UO_2 microstructure under oxidation. We show here FT spectra for 3 hyperstoichiometric UO_2 samples, UO_{2+x} with x = 2.03, 2.15 and 2.21. For the latter, XRD characterization has shown the presence of some U_4O_9 phase in the sample.
As compared to stoichiometric UO_2, we observe the apparition of a contribution at short distance (peak below 2 Å) for the higher stoichiometry. This peak was observed by others authors and attributed to the presence of U(VI). Indeed, this species exibits 2 axial oxygens at short interatomic distance that could fit with this contribution. However, this hypothesis is still discussed in the community as it would imply that the U_4O_9 oxide contain not only U(+IV) and U(+V) as commonly admitted, but also U(+VI).

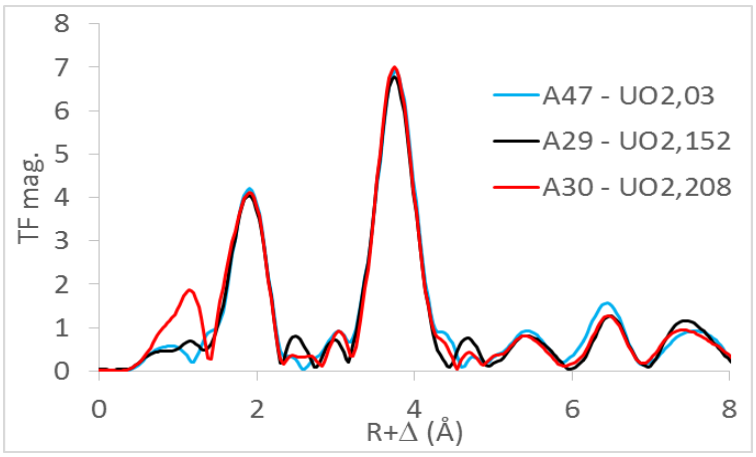

Figure 2: FT spectra of UO_{2+x} samples with x = 2.03, 2.15 and 2.21.