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	**Experiment title:** Studying the corrosion of U metal by hydrogen absorption using epitaxial films	**Experiment number**: 28-01-1118
Beamline: BM28	**Date of experiment**: from: 10–Dec–2015 to:16–Dec–2015	**Date of report**: 1–March–2016
Shifts: 18	**Local contact(s)**: D. Wermeille	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The experiments are aimed at studying the earliest stages (induction period) of the uranium hydrogen reaction; a corrosion process that is known to be very aggressive. In this experiment we have examined a number of samples made from thin films (some of them epitaxial) containing U in different orientations to determine whether this method gives complementary information to that obtained by using bulk samples.

In each case we exposed the samples to a commercial supply of 4%H_2/Ar at various partial pressures for various times. The samples were heated to 80 C for most of the exposures, but final heating was to 200 C. We had some difficulties with the apparatus delivering and measuring precise doses of H_2/Ar, and have determined how to improve this with some new parts made at AWE and Bristol.

The samples were mostly epitaxial films of between 30 and 60 nm of uranium deposited on either Nb or W buffer layers of ~ 10 nm grown on sapphire substrates. This procedure is known to produce strongly (110) and (001) textured uranium, respectively [1]. The UO_2 was deposited on top of the uranium either in the sputtering machine in Bristol during growth or was allowed to develop naturally by exposing the uranium to air. The UO_2 films are about 30 nm thick and do not grow epitaxially on U metal, but show strong (111) texture. One sample with uranium grown on glass was examined, but the reflectivity and diffraction measurements were of insufficient quality.

Following the procedure used for bulk samples, the samples were pre-heated to 200 C to activate the samples. In retrospect this heating may have damaged the epitaxy of some of the films, and we need to investigate this further.

Using X-rays of λ = 1.55 Å, reflectivity (from 0.2 to 6^o) and high-angle diffraction (from 23 to 42^o) were measured in each case. The reflectivity is dominated by the thin buffer layers of Nb and W and we need to investigate what happens as a function of heating these more carefully.

A typical diffraction pattern is shown in Fig. 1 below. In this sample the predominant peak is from the U(110), but about 10% of the sample has a (001) orientation. On exposure to H_2/Ar the most dramatic effect is the loss of intensity of the U(110) diffraction peak. This reduces by a factor of 100 over 100 minutes at 140 C. The peak shift also shows that the (110) *d*-space is expanding during hydrogen exposure. On the other

hand, the U(002) diffraction peak reduces only by a factor of 2 under the same conditions. The UO_2 surface film (in this case air grown) is slightly reduced in intensity through hydrogen exposure, and the higher oxides are totally reduced, as expected. Unexpectedly, there are no diffraction signals consistent with UH_3: the expected polymorph, β-UH_3, exhibits its strongest diffraction signal at 30.24° in 2θ.

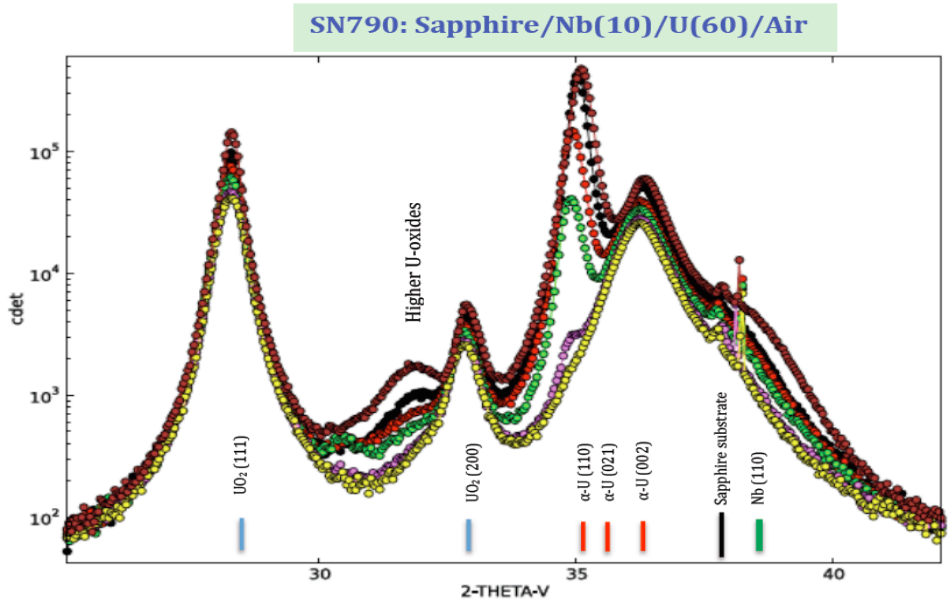

Fig. 1
Diffraction pattern from SN790. (thicknesses in nm.) λ= 1.55 Å.
Brown – pristine
Black – heated 2 hr 80C
Exposed 4%H_2/Ar
at 140C for:
Red – 20 min.
Green – 40 min.
Pink – 80 min
Yellow – 100 min.

The large difference between the (110) and (001) planes with respect to hydrogen diffusion may be understood qualitatively by showing the projections of these planes for the uranium atoms, as below.

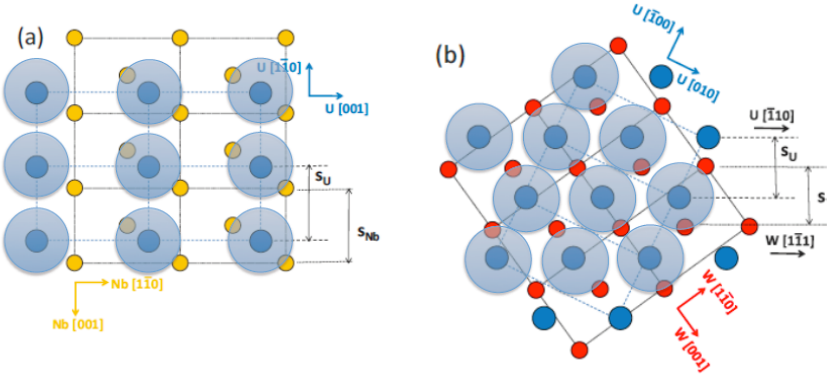

Fig. 2
(a) The uranium (110) plane in projection on a Nb buffer showing large interatomic spacings through which the H_2 can diffuse.
(b) The uranium (001) plane in projection on a W buffer showing a relatively close-packed configuration.

Conclusions

The consumption of uranium can easily be observed using these samples and has shown unexpected variances in the rates at which metal faces are consumed. The lack of detection of UH_3 is puzzling, since uranium is being significantly consumed, and related experiments on bulk samples clearly showed β-UH_3. It may be that the UH_3 is formed as either amorphous and/or nano-crystalline precipitates in this system. We anticipate that further improvements in our ability to model the reflectivity data will shed light on this aspect of the reaction.

The improvements we anticipate are:
a) Improved ability to repeatedly dose H_2/Ar aliquots on to the sample
b) Extensive characterisation of the samples prior to exposure to improve understanding of the reflectivity
c) Improved understanding of how the buffer layers may change with either heat treatments or hydrogen exposures to remove this uncertainty from the reflectivity model.

[1] R. Ward *et al.* J. Phys. CM **20**, 135003 (2008)