ESRF	**Experiment title:** Helium solubility study by High Resolution Powder Diffraction in hyper-stoichiometric uranium dioxide (UO_{2+x}), mixed uranium cerium oxide $(U,Ce)O_2$ and CeO_2	**Experiment number**: MA-3450
Beamline: BM25A	**Date of experiment**: from: 05/07/2017 to: 09/07/2017	**Date of report**: 06/11/2017
Shifts: 12	**Local contact(s)**: Aïda Serrano, German Castro	*Received at ESRF:*

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Report:

In pile, nuclear fuels produce gases (in particular Kr, Xe and He) in large amounts as a result of the fission events and alpha-decay of some radioactive actinides. These gases have a significant influence on the properties and integrity of fuel rods since they can cause rod over-pressurization or extensive fuel swelling. In addition, their solubility and their transport are strongly related to the nature and concentration of point defects. Both solubility and transport are significantly modified by their segregation on extended defects and their precipitation as bubbles. In addition, fuel chemistry under irradiation in operating also leads to nongaseous fission products with an oxidation state which differs from that of the fresh fuel (+IV) which leads to a varying oxygen partial pressure. This latter makes the concentration of point defects vary, i.e. the concentration of potential He atoms [1]. It is essential to get further insight into the behaviour of He in nuclear fuels and their interactions with point defects, to develop and validate the models of solubility for helium and then models of fission product release in the scope of transport implementation in nuclear simulation codes. Garrido [2] and Belhabib [3] were the only two experimental works about He insertion in stoichiometric UO_2 and have shown that up to 300°C Helium was trapped in the centre of the UO_2 lattice cell and could move to other places from 600°C on and disappear totally from the crystal structure at 800°C.

This experiment was built up and performed in collaboration with BM25A beamline and the ESRF SAFETY group. It consisted in filling part of capillaries with depleted UO_2. The

aperture of the capillaries were sealed with porous quartz endcaps with a P2 class size in order to let He, Ar, H_2, H_2O and O_2 go through and letting UO_3 or UO_2 vapors condense. The capillary is mounted on the diffraction setup and heated by means of an air blower. The gas circuit made it possible to mix Ar with Ar/H_2 (and He with He/H_2), the incoming oxygen content was modified and then measured by means of a zirconia doped with yttria electrochemical cells (SETNAG Gen'air device) , whereas the outgoing gas oxygen content was monitored by the same kind of electrochemical probe (SETNAG's Jock'air device). The wavelength was $\lambda=0.51673\pm3.10^{-5}$Å and the 2θ range was 5 through 33 degrees.

The X-Ray patterns of UO_2 at 800°C with $pO_2 = 2.65\ 10^{-17}$ atm under $He/5\%H_2$ and $Ar/5\%\ H_2$ (total pressure p=2 bars) show differences in peak widths at small diffraction angles : peaks are larger with a helium atmosphere, as well as a disappearance of peaks at high angles ((422), (511)+(333), (600) and (442)). This may be due to the capability for helium to diffuse into the UO2 lattice at high temperature. Helium can then be located in the center (octahedral site) of UO_2 conventional lattice cell, and its thermal motion may add a contribution to oxygen atom thermal motion, thus enlarging peak width or even make peaks disappear. However UO_2 lattice parameter was in fair agreement with its known Vegard's law [4]. Up to now a simple Pawley adjustment has been made on these results.

As a conclusion, the feasibility of an High Resolution X-Ray Diffraction experiment up to 800°C with depleted UO_2 under an atmosphere with a controlled oxygen partial pressure on BM25A beamline has been demonstrated. Some improvements could be done to enforce deviation from stoichiometry to the desired values between 2.00 and 2.25 by using for instance CO/CO_2 instead of H_2/H_2O as a chemical buffer. Also sample preparation could be enhanced in order to get a higher count number by filling shorter capillaries. It has led to differences in X-Rays patterns between He and Ar carries gases that require further investigation with for instance a study of the peak profiles whose width is mainly due to oxygen thermal motion and may be affected by the presence of He in the lattice cell.

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[1] "European Energy Research Alliance - Joint Research Program on Nuclear Materials, Thermodynamic and Atomic Transport properties of mixed oxide FUeLs - Desciption of work 2016-2020.
http://www.eera-jpnm.eu/filesharer/documents/EERA_JPNM_General_DoW%202016_v1_final.docx

[2] F. Garrido, L. Nowicki, G. Sattonnay, T. Sauvage, L. Thomé, Nucl. Instr. & Meth. B, 219-220 (2004) 196.

[3] T. Belhabib, Comportement thermique des défauts lacunaires induits par hélium et les gaz de fission dans le dioxyde d'uranium, thèse de l'Université d'Orléans, 2012.

[4] J. H. Harding, D. G. Martin, P. E. Potter, R. Commission of the European Communities. Directorate-General for Science, Thermophysical and thermochemical properties of fast reactor materials, Commission of the European Communities, Directorate-General Science, Research and Development, Luxembourg, ISBN 9282608298 9789282608296, 1989.

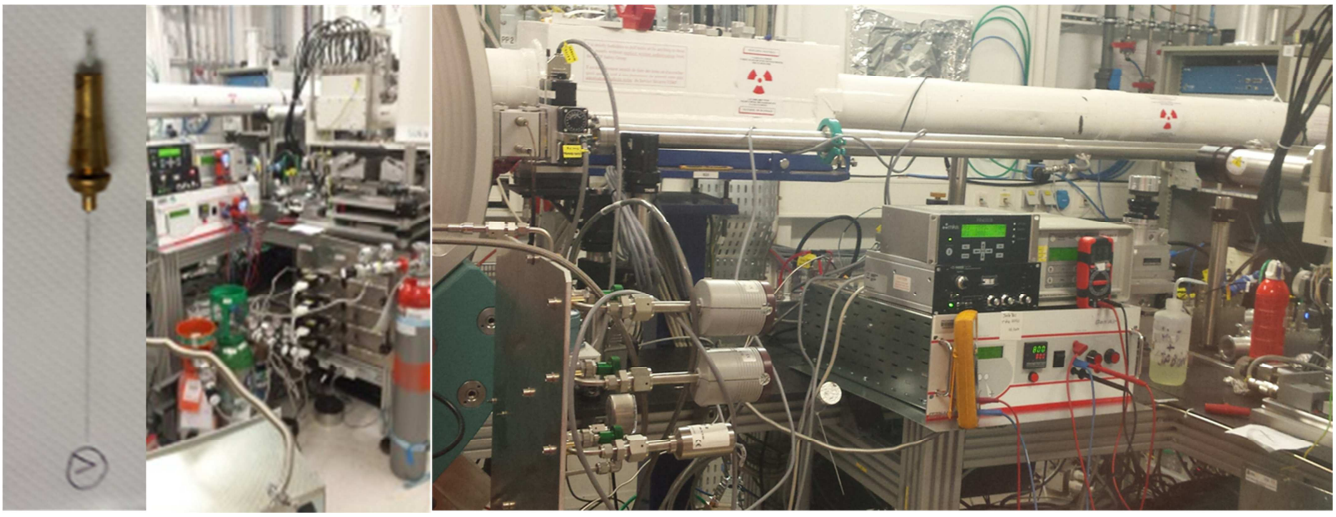

Figure 1: Samples in capillaries and gas control setup

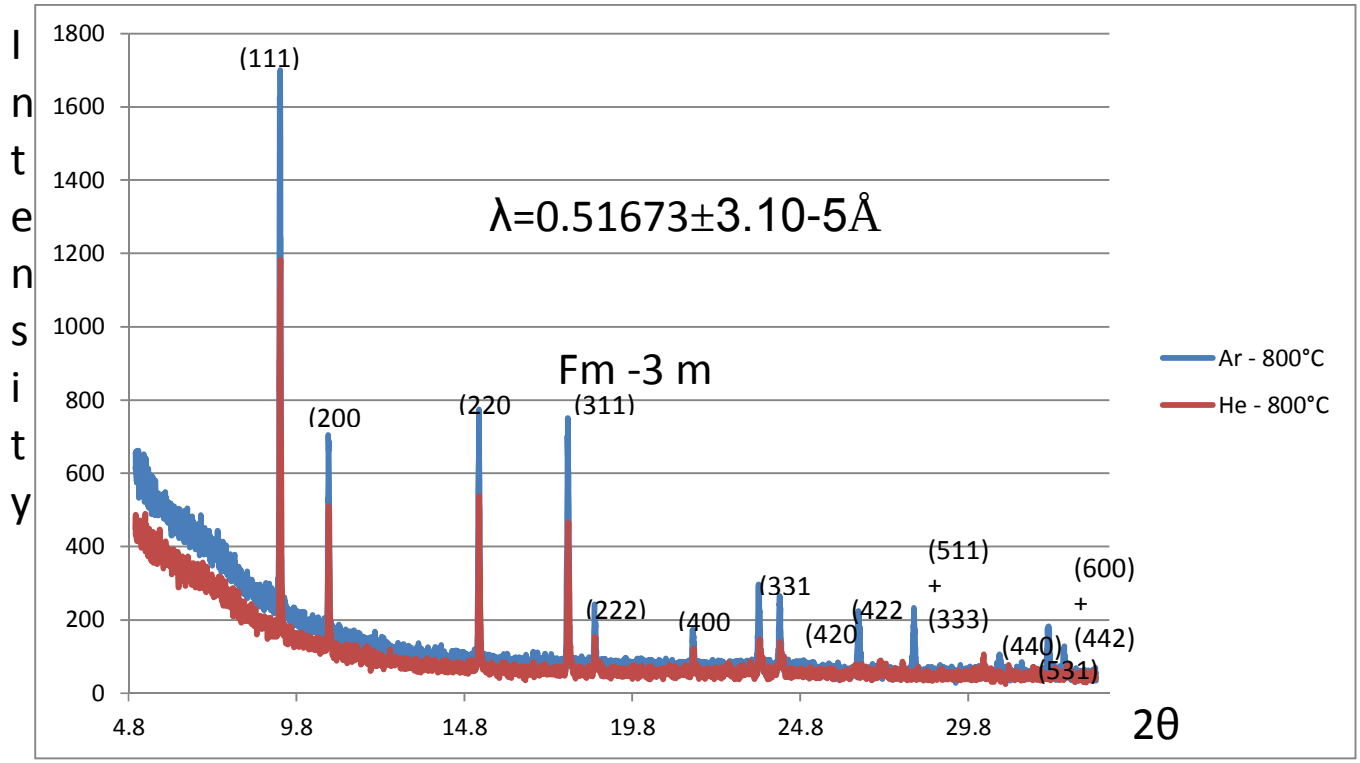

Figure 1: High Resolution X-Ray Diffraction Patterns of UO_2 under Ar/H_2 and He/H_2 atmospheres at 800°C and pO_2=2.65 10^{-17} atm, total pressure p=2 bars