ESRF	**Experiment title:** **Determination of the size distribution of bubbles in ceramics using SAXS: UO_2 and CeO_2 a surrogate ceramic of the nuclear fuel.**	**Experiment number**: MA - 3276
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Report:

In the framework of microstructure evolution of spent fuel UO_2 during irradiation, this experiment aimed at drawing a comprehensive picture of the behaviour of fission gases formed in-pile, in particular Xe and Kr. Such rare gases are known to form nano-bubbles in the grain interior due to their very low solubility in the ceramic matrix UO_2. The investigation of the size distribution of such bubbles (size, density and content) is of prime importance since it may alter the thermo-mechanical properties of the fuel.

The main objectives of this experiment were fourfold:

1. to demonstrate the technical feasibility of SAXS on UO_2, which has never been reported yet to our knowledge,
2. to measure the bubble size distribution as a function of different parameters like the energy of ion implantation, fluence and ex-situ thermal annealing performed on depleted virgin UO_2 implanted with Kr, Xe and He.
3. to obtain the bubble size distribution as a function of temperature by in-situ thermal annealing performed on implanted CeO_2, a surrogate material of UO_2, to determine the bubble coarsening mechanism that is activated in the material.
4. to get access to the internal pressure of Kr-containing bubbles using ASAXS.

<u>Experimental method</u>

The first challenge of this experiment relied in the preparation of relatively thin samples, around 30 µm in thickness to ensure a satisfactory transmission with a surface of ~3x3 mm², using a brittle ceramic like UO_2 and CeO_2. This was achieved successfully through an optimised procedure.

Among UO_2 samples that were planned to be investigated, only Kr and Xe-implanted samples were brought to the experiment because He-implantation was post-poned for year 2017. In total 11 UO_2 samples were prepared successfully, 9 Xe-containing samples (with various implantation and annealing conditions) and 2 Kr-containing samples (identical implantation with two annealing conditions). UO_2 samples were sent to the ESRF safety office by special transport one month before the date of the experiment.

Two energy set-ups were used:

- E = 17,1 keV, slightly below the U L3-edge (17166 eV); this allows to reduce absorption for UO_2 samples and then to prepare samples with reasonable thicknesses.

- 6 energies slightly below the Kr K-edge (14326 eV) were chosen to perform ASAXS experiments, intiallly chosen for Kr-containing CeO_2 samples. E = 14,126 keV was also used to perform in-situ measurements on CeO_2 samples. Isothermal heat treatments at 800°C for 12h were performed using the furnace designed by the SIMAP lab and D2AM beam line staff.

All experiments were conducted in the time of the beamline allocation without any major technical problem. The camera used was the photon counting XPAD3 detector of the beamline. The transmission of the samples was very satisfying (around 30-40%), so that it was also possible to measure UO_2 samples at the lowest energy, in particular ASAXS measurements on Kr-containing UO_2 samples could be performed.

Results

Regarding all the data collected during the experiment, only part of them have been treated yet. However it appears that the scattering signal from nano-bubbles is so low in certain samples that it cannot come out from the background noise. This is in particular the case of CeO_2 samples and part of UO_2 samples. This bad signal on background noise ratio arises from various effects:

1. Most of samples were implanted under such conditions (energy in the range of 140-800 keV, 1.10^{16} at.cm^{-2}) that the implanted region is very narrow (less than 1 µm) and then scattering from nanobubbles contained in this area is very low. However similar conditions used on He-implated Si allows accurate measurements in a previous experiment (see report 02-01-683).
2. Kr or Xe are heavy atoms (contrary to He used in Si), and nanobubbles are not empty but are expected to be pressurized, so that the contrast between matrix and bubbles might be small.
3. UO_2 samples, for safety reasons, were embedded in a tight kapton enveloppe. However kapton has a high scattering peak in a q-range that, unfortunately, is located in the q-range corresponding to the size of nano-bubbles (~1-2nm in diameter). Moreover correction of background noise using the kapton envelope alone are not completely satisfactory (maybe due to a rotation of the kapton background sample as compared to the orientation used for samples).

However, at least two samples have given very promising results: the two Kr-containing UO_2 samples measured in anomalous mode. Figure 1 displays results an example of anomalous response of the Kr-containing UO_2 samples, clearly showing a monotonous change with increasing energy. Modelling of the scattering signal from bublles with size-dependent Kr-content will be carried out to rationalize the current observations.

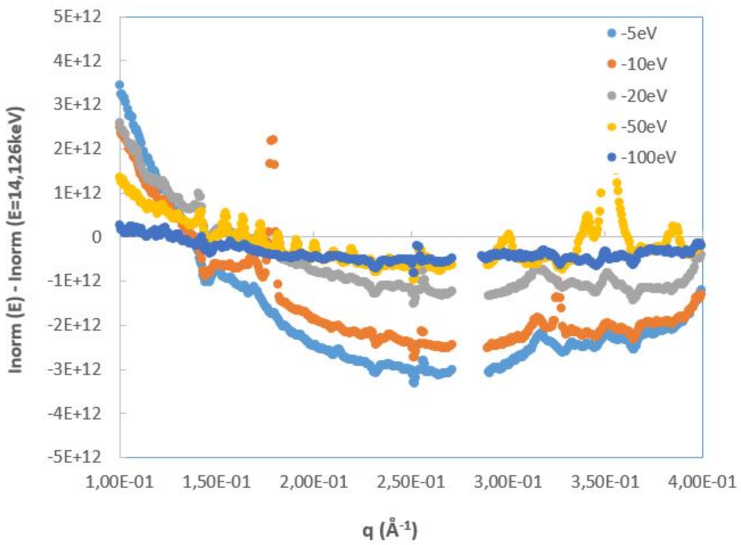

Figure 1 : Anomalous response of Kr-containing UO2 sample

Conclusions and acknowledgments:

In spite of technical challenges, this experiment was a success, in particular regarding the anomalous measurements which are expected to give essential data on the Kr-content of nanobubbles. To get better signal/noise ratio in the future, we plan to:

- replace kapton envelope by another material (mica for example),
- use more concentrated samples,
- study He-implanted samples.

We are grateful to the ESRF staff, especially on the BM02/D2AM beam line for giving us the opportunity to perform this challenging experiment and for their help during the experiment. Special acknowledgement is addressed to Dr. Frédéric De Geuser for his support before, during and after the experiment.