ESRF	**Experiment title:** A XAS study of Kr bubble precipitation in UO_2 as a function of annealing conditions and rare gas concentrations	**Experiment number**: MA-241
Beamline: BM30B	**Date of experiment**: from: 11 December 2006 to: 18 December 2006	**Date of report**: 01/09/07
Shifts: 12	Local contact(s): Dr. H. PALANCHER	*Received at ESRF:*

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REPORT:

As described in the our proposal, the experimental result presented here are part of a much wider modelling and experimental program aimed at improving our understanding and modelling of the in-pile behaviour of UO_2[1]. The project is essentially geared towards deriving fundamental properties relative to the behaviour of rare gas atoms (one of the most abundant class of fission products) in UO_2 fuels. The program is based on the study of ion implanted polycrystalline UO_2 samples because it is one way of circumventing the many scientific and technical difficulties inherent to the study of in-pile irradiated UO_2. The use of ion implantation techniques also enables experimentalists to focus on a particular physical or chemical effect, whereas in-pile irradiated materials or fission experiments always involve a myriad of coupled phenomena.

Results obtained with our previous experiment 30 02 658 on beam-line BM30B have given us an insight into the effect of annealing temperature on the pressure inside xenon and krypton inclusions. The experiments also provided information as to the physical state of the gas inside the inclusions and further revealed the far greater sensitivity of XAS to Kr rather than Xe. It has thus been proved that experiments can be performed on Kr implanted samples for which Kr concentrations are closer to those encountered in irradiated fuels. **The aim of the experiment was the study of Kr bubble precipitation as a function of temperature and local Kr concentration very similar to those encountered in-pile. To fully match our objectives, EXAFS data at room temperature and 12 K were needed. But considering the challenge to collect exploitable data, a part of the beam time was dedicated to experimental set-up optimization.**

Experimental

The samples are depleted UO_2 pellets, 8 mm in diameter and approximately 1 mm thick implanted with 400 keV Kr ions. In order to examine the effect of Kr concentrations on bubble precipitation 4 doses were used leading to local Kr concentration of 8, 1.6, 0.8 and 0.4 at%. The temperature effect was studied with two thermal treatments: 600°C for 12 hours and 1200°C for 2 hours.

Results

Concerning the room temperature measurements, EXAFS simulations of krypton inclusion (1-3 GPa pressure range) based on experimental values of DiCicco *et al* [2] give us spectra with amplitude systematically lower than the noise amplitude observed during the experiment. Thus, only XANES data were available for this temperature. Moreover, acquisition of good XAS data at Kr K edge in UO_2 sintered samples is strongly damaged by diffraction peaks due to the matrix. During the experiment we used a newly develop cryogenic rotating sample-holder which allows us to collect spectra at 90K[3]. Good EXAFS spectra up to 8 $Å^{-1}$ was obtained with this set-up. But, as described by Yokoyama *et al* [4], for such temperature anharmonicity of krypton potential is still strong and cumulant expansion is needed to exploit EXAFS data. Clearly, it was impossible to isolate Kr-Kr shell or contribution of matrix atoms at 90K. Unfortunately, no rotating sample holder at lower temperature exists at the moment. In conclusion, as no EXAFS data could be extracted from

our data, we finally decided to focus only on XANES obtained at room temperature using a rotating sample holder.

In Figure 1, XANES spectra obtained for the 4 krypton concentrations are shown. The spectrum obtained for the 8 at. % corresponds to a classical XANES spectra expected for a condensed krypton phase: a strong white line and a resonance located at ~15 eV after the edge. Thus, without thermal treatment an 8 at.% Kr concentration leads to precipitation of krypton aggregates in UO_2. For the three other concentrations, no white line is present but two large resonances noted A and B can be observed. The B resonance intensity appears to be inversely proportional to the Kr concentration whereas the A is the opposite. In Figure 3 and 4, evolutions for 0.8 and 1.6 at.% in function of thermal treatment are displayed. After an annealing of 12 hours at 600°C, an inversion of the ratio between A and B is observed, but no strong white line as observed for the 8 at.% is present.

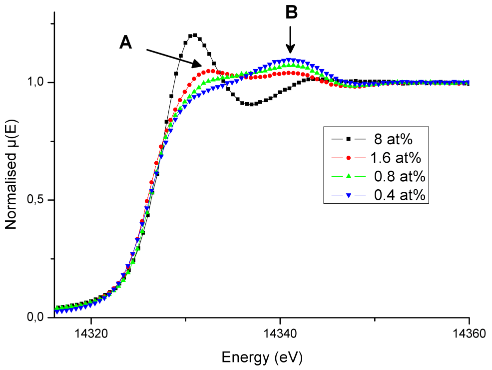

Figure 1: as implanted XANES spectra

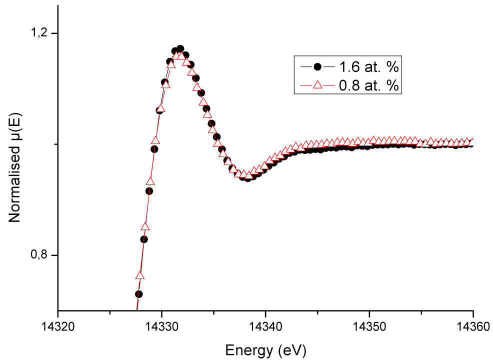

Figure 2: XANES obtained after thermal treatment of 2 hours at 1200°C

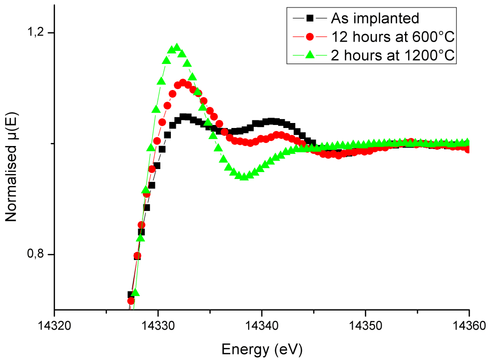

Figure 3: evolution for a Kr initial concentration of 1.6 at. %

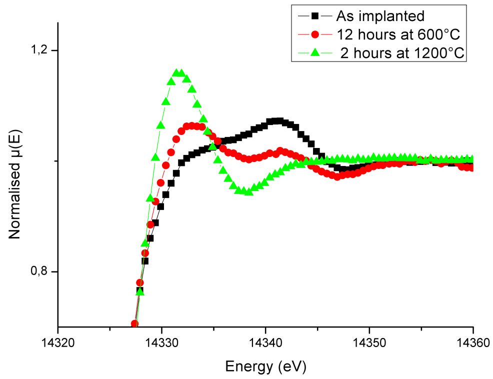

Figure 4: evolution for a Kr initial concentration of 0.8 at. %

As observed in Figure 2, an annealing of 2 hours at 1200°C leads to the same XANES spectrum for 0.4, 0.8 and 1.6 Kr at.% and indicates the precipitation of pressurized krypton bubbles. The pressure into those inclusions seems to be independent of the initial krypton concentration. Based on literature results [2,5], a pressure value of ~1 GPa can be estimated. First XANES calculations performed with FDMNES code show that B resonance can not be attributed to Kr-Kr bond. Furthermore, as the B resonance disappears when krypton atoms form aggregates, this feature can be attributed to Kr-U or Kr-O bonds whereas the A corresponds to Kr-Kr bonds. Clearly, initial krypton concentration has an impact on bubble precipitation kinetic as we can see in Figure 3 and 4.

In order to obtain accurate pressure values, measurements at low temperature (11K) where krypton is solid are necessary. Moreover, at this temperature the anharmonicity of krypton potential is negligible thus allowing an EXAFS analysis without ambiguity. In order to carry out those measurements, we propose to use in our next proposal the new experimental set-up with crystal analyzer available on FAME. With this device, we should be able to separate fluorescence signal from the elastic peak and therefore avoid any Bragg peaks phenomenon.

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