



	Experiment title: Study by XAS of UO ₂ doped with chromium and of the iodine diffusion in this nuclear fuel	Experiment number: MA-240
Beamline: BM30B	Date of experiment: from: 14 October 2006 to: 18 October 2006	Date of report: 01/07/2007
Shifts: 12	Local contact(s): Dr. H. PALANCHER	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Dr. P. MARTIN^a, *Dr. H. PALANCHER^{a,b}, *Dr. G. CARLOT^a, P. GARCIA^a, Dr. C. RIGLET-MARTIAL^a, Dr. C. SABATHIER^a, Dr. C. VALOT^a ^(a) CEA-Cadarache (DEN/DEC) F-13108 Saint Paul lez Durance. ^(b) CRG FAME, ESRF, F-38043 Grenoble Cedex.		

The behaviour of nuclear fuels at high burn-up is mainly limited by the release of fission products. One of the solutions under study to increase the fuel lifetime is to increase the size of the fuel grains in order to extend the diffusion path of the fission products in the direction of the grain boundaries, from where release is possible. However, the presence of foreign elements in the fuel matrix is likely to increase the diffusion kinetics of the fission products too. Indeed, we have shown in a recent study based on SIMS measurements that iodine diffusion is substantially inhibited in chromium-doped samples. Identifying how chromium may influence the transport of iodine was the first aim of these measurements.

Our second objective was to understand how Cr₂O₃ additions might influence grain growth. As pointed out by EPMA (Electron Probe Micro-Analysis) measurements, chromium presents an heterogeneous distribution in Cr doped UO₂ samples. Indeed, small chromium oxide precipitates (3µm) have been identified in the UO₂ fuel. As mentioned in our proposal, the installation of two mirrors in the Kirkpatrick-Baez geometry on BM30B was supposed to enable us to use a 15×15µm² beam and to determine therefore the oxidation states and the local environments of chromium atoms present in oxide precipitates and within the UO₂ grain.

Experimental

The starting material was a series of pellets prepared from a UO₂ powder mixed with Cr₂O₃ (0.1 %wt) and sintered at 1700°C during 4 hours. Scanning electron microscopy analyses of the samples confirm the expected UO₂ grain growth: the average grain size was about 50 µm (compared to 10 µm measured on undoped UO₂ samples). X-ray diffraction patterns collected on each pellet do not reveal the presence of other phase than UO₂. Iodine was introduced in the samples by using implantation of 10¹⁴ iodine.cm⁻² at 800 keV leading to a local iodine concentration close to that of chromium in the depth probed by the X-ray beam. All the UO₂-Cr doped samples (implanted with iodine or not) were annealed at 1400°C or 1700°C for 10 hours under reducing atmosphere.

Results

First of all, at the time of our measurements (Oct. 2006), the experimental set-up used to move the mirrors was not designed to micro-focus at the chromium K edge (5.9 keV). Thus, all the measurements presented here were obtained with a 200×300 µm² beam.

Furthermore, the acquisition of good XAS data on diluted light elements (elements with edge below uranium L₃(17.166 keV)) in UO₂ sintered samples is strongly damaged by diffraction peaks due to the matrix [2]. In order to minimize this phenomenon we used a rotating sample-holder. Compared to the September

2005 experiment, an improvement of the signal quality has been obtained, which allow us to go up to 11 \AA^{-1} in the EXAFS acquisition (in September 2005 we had to stop at 8.5 \AA^{-1}). In addition it was impossible to distinguish structural signal from noise due to the diffraction peaks (the ring was operating at $4 \times 10 \text{ mA}$, which makes even more difficult and longer the obtention of good signal to noise ratio with a light dilute element in a heavy matrix like UO_2). Thus, considering this loss of time and also that the beam line was not working in the expected mode (macro beam instead of micro-focusing) only a part of the accepted experiment could be achieved.

Concerning the first objective on the impact of the chromium on iodine behaviour, the iodine-implanted samples do not show any difference in both EXAFS and XANES spectra compared to the same samples without iodine (*Cf* Fig. 1). At the moment, the assumption on the existence of chemical interaction between iodine and chromium seems to be invalidated.

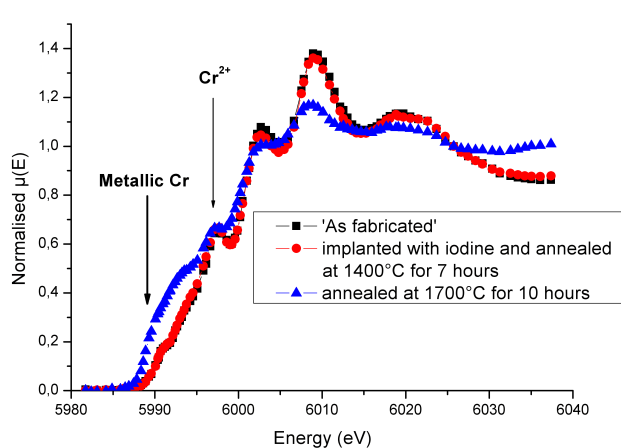


Figure 1: XANES spectra at the chromium K edge collected on three UO_2 samples doped with Cr.

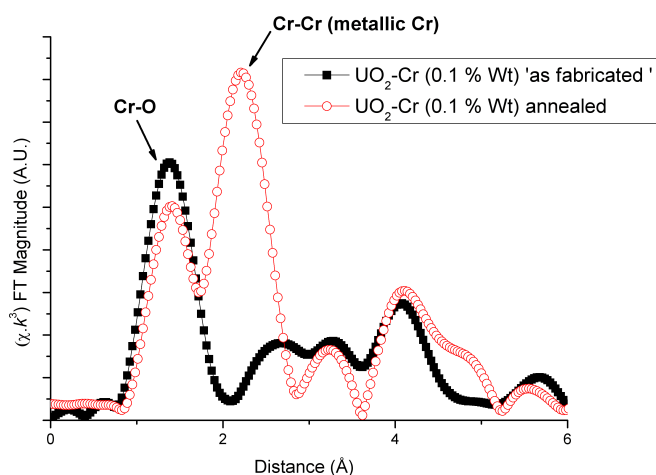


Figure 2: Fourier transforms of EXAFS spectra collected on two UO_2 samples doped with Cr.

Concerning the chromium behaviour in UO_2 , as the Cr concentration in our samples is under its solubility limit in UO_2 [3], no variation of chromium environment was expected after thermal treatment. But, as seen in Figures 1 and 2, a clear modification of both EXAFS and XANES spectra can be observed after a thermal treatment of 10 hours at 1700°C . Furthermore the chromium environment in the 'as fabricated' sample appears to be more complex than an uranium substitution in the fluorite structure. The XANES spectrum shows two different oxidation degrees: Cr^{2+} with an intense pre-peak located at 5995 eV and an intense white line corresponding to Cr^{3+} . The EXAFS fit leads to a first shell with 4 oxygen atoms at 1.93 \AA with $\sigma^2=0.0061 \text{ \AA}^2$. But no Cr-O distance longer than 2 \AA , characteristics of $\text{Cr}^{2+}\text{-O}$, could be introduced in the fitting process. **This indicates a very disordered environment around Cr^{2+} ions and seems to confirm the existence of an amorphous Cr^{2+}O phase in the sample.**

On the thermally treated sample, a significant part of chromium atoms is reduced to metallic state as observed in Figure 1, with a first edge position at 5898 eV which can only be seen in the case of metallic chromium. At the same time, an intensity decrease of the Cr^{2+} peak is observed. This observation is confirmed by the EXAFS fit with a new Cr-Cr shell at 2.6 \AA characteristic of Cr metal bond. At the same time a first shell of 4 oxygen atoms at 1.93 \AA remains. These two shells allow us to reproduce the spectra in the 1 to 3 \AA range. Thus, the chromium atoms located in the CrO amorphous precipitates have been reduced to metallic Cr while the dissolved chromium content in UO_2 remains unchanged.

These results clearly demonstrate that a non negligible part of the chromium introduced during the manufacturing process is not dissolved in the UO_2 structure. The solubility limit of chromium in UO_2 should be re-evaluated before studying the true influence of Cr_2O_3 additions on the fuel grain growth. Moreover, chromium behaviour in UO_2 appears to be more complex than expected since it occupies neither substitutional nor interstitial site of the UO_2 fluorite structure (Cr-O distances equal to 1.93 \AA as compared to 2.36 \AA expected for U-O bond in UO_2).

References

- [1] H. Palancher, P. Martin, G. Carlot, A. Pieragnoli, C. Sabathier, P. Garcia, C. Valot, (2005) experimental report ME-1304.
- [2] S. Pasternak, F. Perrin, G. Ciatto, H. Palancher and R. Steinmann, submitted in Review of Scientific Instruments
- [3] Leeners et al., Journal of Nuclear Materials 317(2003)62.