	<b>Experiment title:</b> <b>XAS study of chromium in advanced nuclear fuel</b>	<b>Experiment number:</b> ME-1304
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## Report

The behaviour of nuclear fuels at high burn-up is mainly limited by the release of fission products. In these measurements, we study one possible solution to improve this behaviour: the low UO<sub>2</sub> doping by chromium. Indeed, it is reasoned that by promoting UO<sub>2</sub> grain growth, the diffusion length for fission products to reach grain boundaries increases, thus presumably reducing fission product release.

However, the presence of foreign elements in the fuel matrix is liable to increase the diffusion kinetics of fission products. To fully understand any influence of the doping agent on the diffusion kinetics of fission products, it is crucial to know in which crystallographic phase chromium atoms are present. The knowledge of how these phases change with temperature is also required.

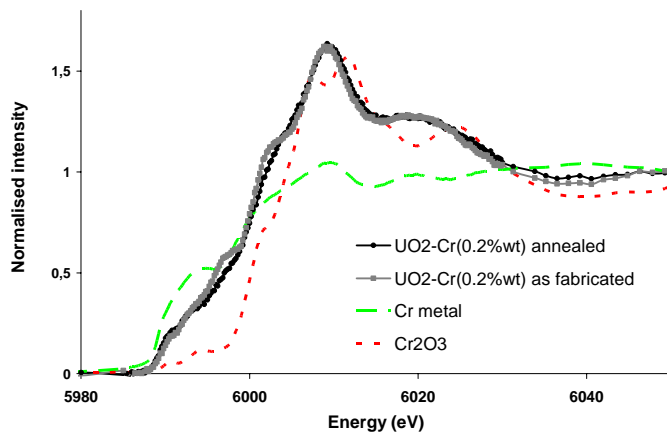
**The aim of these measurements was to investigate by XAS the evolution with temperature of both the local environment and the oxidation state of Cr atoms in doped UO<sub>2</sub>.**

In our study, pellets were prepared from an UO<sub>2</sub> powder mixed with Cr<sub>2</sub>O<sub>3</sub> (0.2 %wt) and sintered at 1700°C during 4 hours. Scanning electron microscopy analyses of the samples confirm the expected UO<sub>2</sub> grain growth: the average grain size was about 50 µm (compared with the 10 µm measured on undoped UO<sub>2</sub>). X-ray diffraction patterns collected on each pellet do not reveal the presence of any other phase than that of UO<sub>2</sub>.

In this report, we focus on the comparative study of two samples. The first is “as fabricated” but the second has undergone an additional thermal treatment: annealing at 1750°C for 4 hours.

To carry out an efficient XANES analysis at the chromium K edge of both UO<sub>2</sub> samples doped with Cr, absorption spectra were also collected on reference compounds Cr<sub>2</sub>O<sub>3</sub> and Cr metal. Figure 1 illustrates the result of this study. A quantitative study is ongoing, but it already appears that the XANES spectra collected on fuels can not simply be interpreted as a linear combination of the spectra representative of metallic chromium and chromium oxide. The hypothesis whereby chromium is soluble in the UO<sub>2</sub> lattice will further be evaluated through XANES spectra simulations.

However it must be noted that the XANES technique failed in differentiating the environment or oxidation state of chromium atoms in the two studied samples



**Figure 1:** XANES spectra at the chromium K edge collected on two UO<sub>2</sub> samples doped with Cr.

(dashed lines indicate XANES signal measured on reference compounds Cr<sub>2</sub>O<sub>3</sub> and Cr metal ).

EXAFS spectra were then collected up to  $10 \text{ \AA}^{-1}$  on the two doped UO<sub>2</sub> samples at the chromium K-absorption edge (cf. figure 2-a). These are significantly different underlining the influence of temperature on Cr local environment in UO<sub>2</sub>. When considering the magnitude of the Fourier Transform of the EXAFS spectra (cf. figure 2-b), it appears that annealing caused an inversion of the magnitude of the first and second shells.

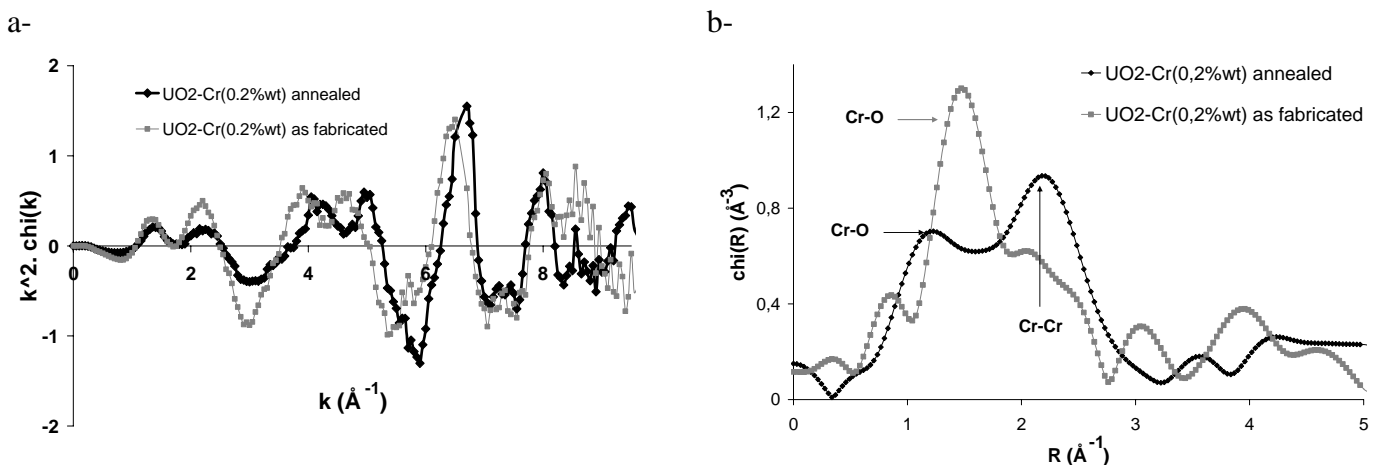
In both samples, the first shell seems to consist of oxygen atoms. A preliminary analysis leads to Cr-O distances of about  $2.0 \text{ \AA}$  in the “as fabricated” sample; this value corresponds to the shortest distance between Cr and O atoms in Cr<sub>2</sub>O<sub>3</sub> ( $1.96 \text{ \AA}$ ). Even if further analysis is required, the Cr-O bond length appears shorter in the annealed sample (about  $1.7 \text{ \AA}$ ).

In the annealed sample, the second shell is very probably due to chromium atoms: the refined distance ( $2.65 \text{ \AA}$ ) is consistent the Cr-Cr bond length in chromium metal (in this material the two shortest Cr-Cr distances are  $2.50 \text{ \AA}$  and  $2.88 \text{ \AA}$ ).

## Conclusion:

EXAFS appears to be a key technique in the characterization of the local Cr environment in Cr doped UO<sub>2</sub>. Leenears et al. (*Journal of Nuclear Materials* 317, 62 (2003)) have reported the presence of large chromium precipitates ( $3 \mu\text{m}$ ) in the fuel. The use of a micro-focused X-ray beam (with a typical size of  $15 \times 15 \mu\text{m}^2$ ) should enable us to probe areas where these precipitates are not present: the collected EXAFS spectra would then be only representative of chromium in the UO<sub>2</sub> matrix. This additional study should:

- give us an additional insight into the homogeneity of the local environnement of chromium atoms in the UO<sub>2</sub> matrix,
- confirm the interpretation of the results of this analysis carried out with a  $200 \times 300 \mu\text{m}^2$  X-ray beam.



**Figure 2:** Comparison of the environnement Cr elements in two UO<sub>2</sub> samples. Figure 2-a shows the EXAFS spectra collected on both samples at the chromium K edge (a-) and their Fourier transforms (b-). Note that in this last figure, no phase correction has been applied.