



Beamline: BM30B	Experiment title: A XAS study of the chemical states of Chromium in UO ₂ fuels doped with Cr	Experiment number: MA-543
	Date of experiment: from: 14 may to: 20 may	Date of report:
	Shifts: 18	Local contact(s): D. Testemale
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Report:

The performance of the UO₂ nuclear fuel at high burn-up is mainly limited by the behaviour of fission products (Xe, Kr, I...). One of the solutions under study to increase the fuel lifetime is to increase the size of the grains in order to extend the diffusion path of the fission products in the direction of the grain boundaries, from where release is possible. Among the various additives under consideration, chromium seems to give the best results as an effective grain growth promoter with a very low initial concentration (0.085 Cr₂O₃ wt%) [1]. Previous XAS experiment performed on BM30B beame-line [2] with samples doped with 0.1 wt% Cr₂O₃ (below the known solubility limit of chromium in UO₂ [3]) have shown that chromium atoms “dissolved” in the UO₂ matrix occupy neither substitutional nor interstitial site of the UO₂ fluorite structure. This result was unexpected and is in contradiction with assumption made in literature[3] and needs to be confirmed by new experiments.

Furthermore, in our group, thermodynamical calculations on the Cr/UO₂ system at high temperature have been performed. To confirm the results of this study, an experimental program has been built to follow both chromium oxidation degree and local environment in function of sintering conditions (temperature, oxygen potential).

Experimental

Two series of pellets have been prepared from a UO₂ powder mixed with Cr₂O₃ (0.2 %wt or 0.1 %wt) and sintered between 1650 and 1760°C for 4 hours under different reducing atmosphere (H₂O/H₂ ratio). Conditions are reported in the Cr-O phase diagram in Figure 1. Moreover, a highly saturated sample where 1% of Cr₂O₃ have been added will be used as a reference sample for chromium localized in precipitate.

Due to the highly crystallized UO₂ matrix and thus in order to eliminate the Bragg peaks in our XAS spectra, samples were placed on a rotating sample holder and a vanadium filter was placed in front of the germanium fluorescence detector. This experimental set-up allows us to collect good quality XANES signal and EXAFS spectra up to 10 Å⁻¹, but no μ-XAS measurements were possible.

XANES spectra collected on samples doped with 1%, 0.2% and 0.1 % and sintered in the CrO(l) stability domain (1760°C) are compared in Figure 2 with Cr₂O₃ reference compound. In any case, spectra are clearly different from Cr₂O₃, which demonstrates that Cr neither dissolved in the UO₂ matrix nor localized precipitate have Cr₂O₃ environment. Anyhow, the white line position clearly indicates that most chromium is trivalent in both cases. Nevertheless, the two low chromium content samples show a strong resonance at ~5997 eV which can not be accounted for trivalent chromium. Such feature has only be reported in the case of Cr²⁺ [4]. Up to now, we have no explanation for this observation since the CrO phase is unstable below 1650°C as observed in Figure 1.

Solubilized and precipitated chromium local environments are very different with strong resonances at ~ 5997 eV and ~ 6000 eV for 0.1% and 0.2 % samples. Moreover, both XANES and EXAFS spectra for these two last samples are almost identical (Cf. Figure 3). This last point was unexpected as chromium contents are different and calculated chromium solubility limit in UO_2 for this sintering conditions is very close to 0.1%. Thus, in 0.2 % sample we expected a huge contribution of second phase chromium as in 1% sample.

From these results, only sintering conditions where reduced (metallic) chrome is stable (conditions B in Figure 1) are of interest as in this case a decrease of chromium solubility is calculated and can induce a modification of solubilized chromium chemistry. And yet, Figure 4 shows a very shallow reduction of chromium between A and B sintering conditions. This evolution can be reproduced by a linear combination of 20% metallic chromium + 80% sample sintered in A conditions.

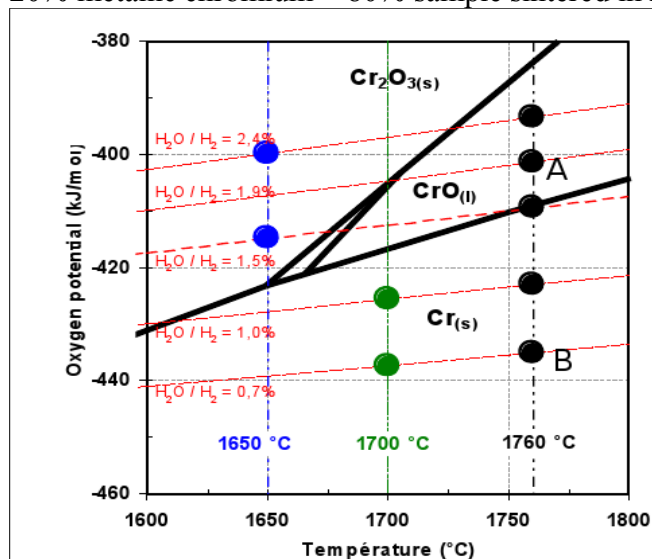


Figure 1 : Sintering conditions

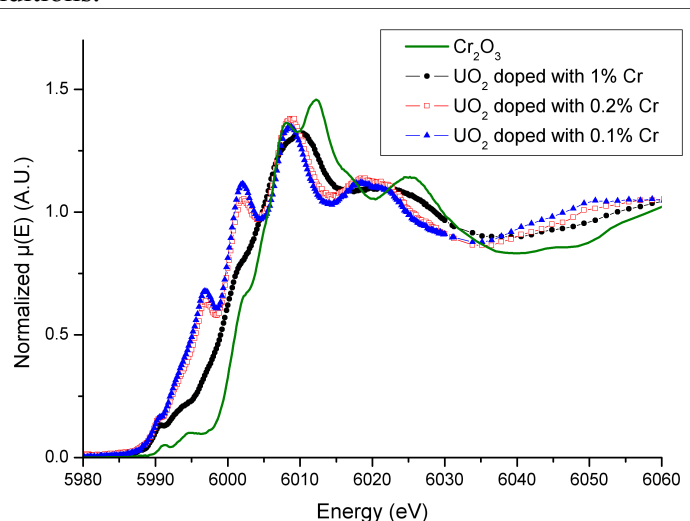


Figure 2: XANES spectra of samples sintered in CrO(l) domain (A conditions).

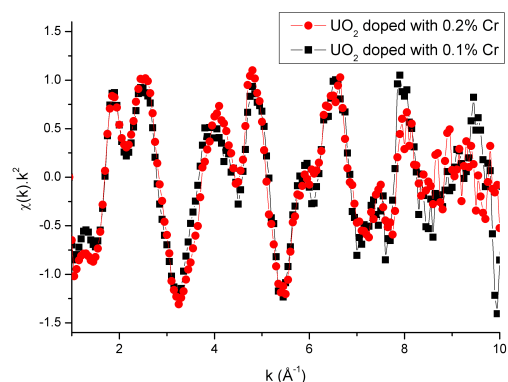


Figure 3: EXAFS spectra of UO_2 doped samples.

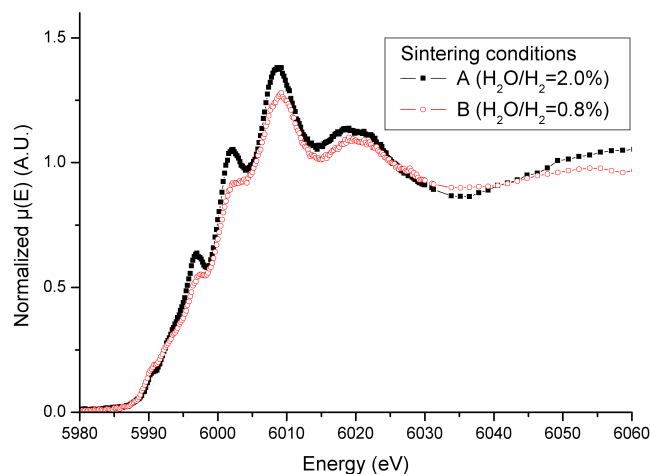


Figure 4: Influence of sintering conditions.

First of all, it seems pretty clear that our model underestimates the chromium solubility in the metallic domain. Therefore, new optimized samples have been manufactured using a higher Cr concentration (~ 3000 ppm). These samples should allow us to understand the origin of Cr^{2+} observed in every XANES spectrum collected. As this oxidation state is rather rare both in minerals and glasses a quantification of $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratio needs a dedicated experiment, since there are almost no experimental data available for crystalline materials. This will be the aim of our next proposal.

- [1] L. Bourgeois *et al*, Journal of Nuclear Materials 297 (2001) 313-326.
- [2] P. Martin *et al*, MA-240 ESRF experimental report (2007)
- [3] A. Leenaers *et al*, Journal of Nuclear Materials 317 (2003) 62-68.
- [4] A. Berry *et al*, American Mineralogist 89 (2004) 790-798.