ESRF	**Experiment title:** Study of Cr solubility in UO_2 using high resolution XAS	**Experiment number**: MA-661
Beamline: ID26	**Date of experiment**: from: 18 September 2008 to: 23 September 2008	**Date of report**:
Shifts: 15	**Local contact(s)**: Marcin SIKORA	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

M. Fraczkiewicz, P. Garcia, Dr. P. Martin*, Dr. H. Palancher*, Dr. C. Riglet-Martial, Dr. C. Sabathier

CEA, DEN, DEC, CEN Cadarache F-13108 Saint-Paul-Lez-Durance, cedex, France.

Report:

The performance of the UO_2 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 Cr_2O_3 wt%) [1]. Previous XAS experiment performed on BM30B beame-line [2] with samples doped with 0.1 wt% Cr_2O_3 (below the known solubility limit of chromium in UO_2 [3]) have shown that chromium atoms "dissolved" in the UO_2 matrix occupy neither substitutional nor interstitial site of the UO_2 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/UO_2 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). But, collecting high quality EXAFS on light element diluted in a highly crystallized heavy matrix like UO_2 is quite challenging as spectra are systematically polluted with Bragg Peaks [2]. This phenomenon is due to the lack of resolution of Ge solid state detector (~250 eV) leading to an overlap of elastic peak and Chromium K_α fluorescence line. One of the main goal of this new experiment was to check if the use emission spectrometer available on ID26 allow us to solve this problem.

Experimental

Two series of pellets have been prepared from a UO_2 powder mixed with Cr_2O_3 (0.2 %wt or 0.1 %wt) and sintered between 1650 and 1760°C for 4 hours under different reducing atmosphere (H_2O/H ratio). Conditions are reported in the Cr-O phase diagram in Figure 1. In this experimental report, only results obtained for conditions A will be discussed. Moreover, to isolate signal from chromium localized in precipitates, a sample doped with 1%wt Cr (corresponding to 10 times the solubility limit) and sintered at 1700°C during 4 hours in the CrO(l) region was also characterized.

XANES/EXAFS spectra were collected using chromium $K\alpha_1$ (5415 eV) line isolated from raw fluorescence signal using the emission spectrometer equipped with one Ge(422) crystal. The resolution obtained with this experimental set-up was equal to 1 eV. Thus, Bragg peaks due to matrix are now fully removed and good quality EXAFS spectra up to 14 $Å^{-1}$ were obtained. Fourier transforms are compared in Figure 2.

Concerning the 1%wt. Doped sample, EXAFS fit and XANES interpretation lead to the following chromium local environment: ~80% of Cr^{3+} with the Cr_2O_3 structure and the ~20% of metallic chromium. This result confirms that XAS signal is only due to chromium atoms located in precipitates, but either CrO structure nor

significant amount of Cr^{+II} are not detected. Therefore, precipitates composition is due to dismutation of CrO into Cr_2O_3 and Cr during the cooling stage at the end of sintering.
concerning the spectra collected on diluted sample (0.2 and 0.1% wt. condition A) are very similar as observed in Figure 2 and show (in agreement with thermodynamical calculations) that most of the chromium atoms are "dissolved in UO_2 structure". Thank to the XANES, differences can be explained as a perfect 0.2% spectrum is perfectly reproduced with a linear combination of 22% of 0.1% and 78% of 1% wt. Spectra(Cf. Figure 3). Thus, for the 0.2% doped sample, 22% of the chromium atoms are localized into precipitates.
EXAFS refinement performed on the 0.1% and 0.2 wt sample confirmed the the fact that chromium atoms "dissolved" in UO2 structure are surrounded by 6 oxygen atoms at 2 A. Moreover, next coordination shells given in Figure 4, allow us to confirm that chromium atoms occupy neither substitutional nor interstitial site of the UO_2 fluorite structure.

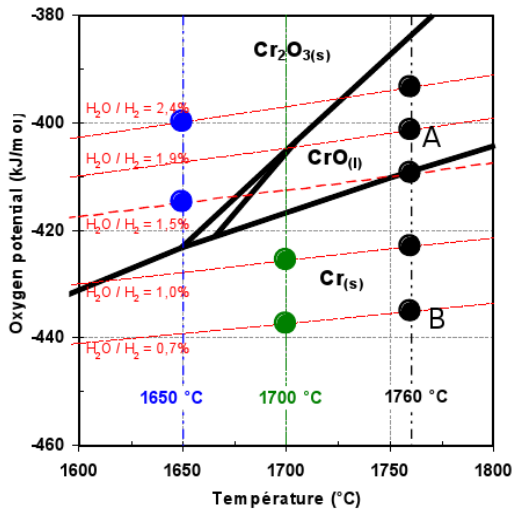

Figure 1 : Sintering conditions

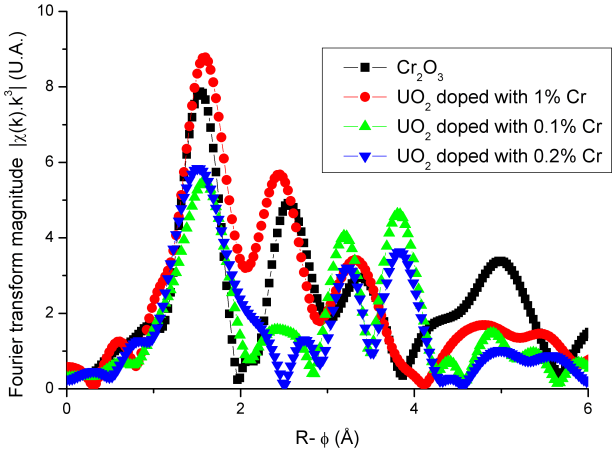

Figure 2 : Fourier transforms

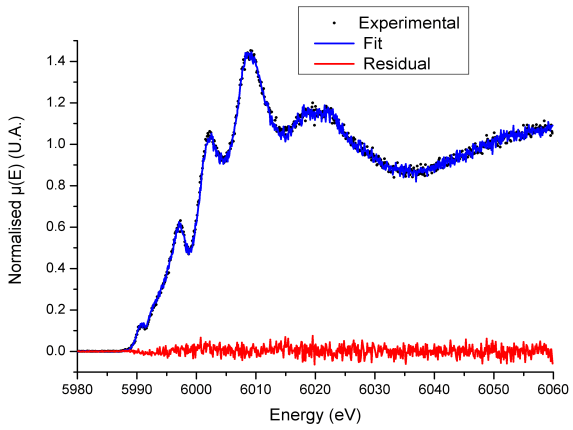

Figure 3 : Fit of XANES spectra collected on 0.2% UO2 doped sample.

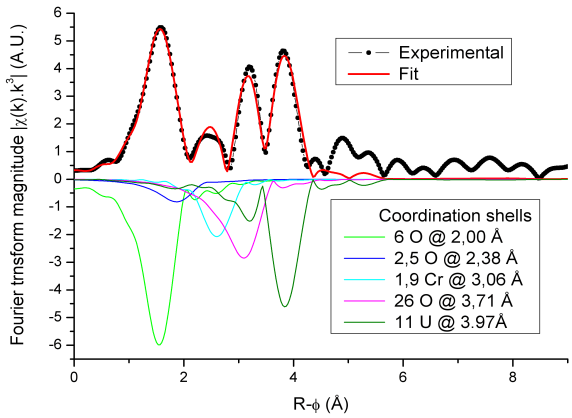

Figure 4: EXAFS fit of 0.1% doped UO2 sample

Thanks to spectrometer available on ID26, Bragg peak free XANES/EXAFS spectra were collected on diluted samples for various sintering conditions and we are now confident with data analysis. The phase composition of chromium precipitates observed for 0.2% sample are now known and is due to the dismutation of the CrO phase. Precise local environment of chromium atoms "dissolved" in UO2 is determined. Data interpretation for other sintering conditions summarized in Figure 1 is in progress.

Reference

[1] L. Bourgeois, P. Dehaudt, C. Lemaignan, A. Hammou, Journal of Nuclear Materials 297 (2001) 313-326.
[2] P. Martin, H. Palancher, G. Carlot, P. Garcia, C. Sabathier, C. Riglet-Martial, C. Valot, ESRF Experimental Report MA-240 (2007).
[3] A. Leenaers, L.D. Tollenaere, C. Delafoy, S.V.D. Berghe, Journal of Nuclear Materials 317 (2003) 62-68.