



	<b>Experiment title:</b> XAS study of chromium in MOX fuel and PuCrO <sub>3</sub>	<b>Experiment number:</b> ME-1256
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## Report:

High local Pu concentrations and fission gas release in the mixed uranium oxide-plutonium oxide (MOX) fuels irradiated to high burn-ups significantly affect the fuel performances. On the whole, the manufacture of MOX fuel consists in UO<sub>2</sub> and PuO<sub>2</sub> powders co-crushing, milling, pelletizing and sintering. An evolution of the manufacture route giving rise to a microstructure optimization of nuclear fuel pellets could allow us to improve the fuel performance.

Pu should be dispersed as homogeneously as possible in a (U,Pu)O<sub>2</sub> solid solution by an enhanced powder process. In this aim, several doping agents have been studied. Encouraging results were reported for coarse-grained UO<sub>2</sub> by the addition at low concentration of Nb<sub>2</sub>O<sub>5</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> or Cr<sub>2</sub>O<sub>3</sub>. In the case of Cr<sub>2</sub>O<sub>3</sub>, the first results for MOX show an increase on grain size and, above all, an increase of the Pu spreading. Pu distribution and grain size are both key parameters to reach high burn-ups.

Under the temperature and atmosphere conditions used during sintering, Cr<sub>2</sub>O<sub>3</sub> is particularly interesting because of its property to give rise to a liquid phase (eutectic Cr<sub>s</sub>+Cr<sub>3</sub>O<sub>4s</sub> → CrO<sub>l</sub>) which usually helps grain growth. Moreover, the possible presence of Cr<sup>3+</sup> in the fluorine lattice of (U,Pu)O<sub>2</sub> could increase point defect concentration and enhance Pu diffusion. A specificity of the Cr-doping in presence of plutonium is the formation of a line compound the composition of which is PuCrO<sub>3</sub>. It is the main difference between the U-O-Cr system and the Pu-O-Cr one at the temperature and atmosphere used during sintering. A PhD thesis is ongoing to determine the mechanisms allowing the microstructure enhancement of a Cr-doped MOX pellet.

**The aim of this study is therefore to examine Cr<sub>2</sub>O<sub>3</sub> impact on Pu distribution when the dopant is introduced up to 2000 ppm as a powder during the UO<sub>2</sub>-PuO<sub>2</sub> milling and to determine the sintering temperature dependence.** We had to verify the formation of a (U,Pu)O<sub>2</sub> solid solution in the presence of a doping agent (introduced under chromium sesquioxide form) and determine the oxidation states of U and Pu. **Moreover, we want to improve our knowledge of the crystallographic structure of PuCrO<sub>3</sub> and obtain data on oxidation states of Pu and Cr in this compound.** EXAFS turned out to be a key technique to probe Pu and U environments or oxidation states and to evaluate the structural order.

During our experiment, we analyzed three samples with 2000 ppm of Cr<sub>2</sub>O<sub>3</sub>, *Mic55*, *Mic67* and *Mic7540*, obtained by the usual MOX powder process (*MIMAS*, *miconization of a master blend*) for a sintering temperature of respectively 1530°C, 1630°C and 1700°C. The Pu/(U+Pu) ratio of the samples was equal to 11 wt%.

A PuCrO<sub>3</sub> sample was analyzed. PuCrO<sub>3</sub> had been obtained by sintering a PuO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> powder mixture heated at 1700°C under argon. A small amount (less than 3 wt%) of PuO<sub>2</sub> and amorphous chromium oxide still remained after the thermal treatment. Prior to the experiment, PuCrO<sub>3</sub> crystal structure was investigated by XRD. The first results are summarized in this table :

Pbnn	a = 5.439 Å	b = 5.498 Å	c = 7.720 Å
	Cr-O = 1.97 Å	Pu-O = 2.34 - 2.66 Å	Pu-Cr = 3.19 Å

For each sample, fluorescence and transmission signals were collected at the uranium (17.126 keV) L<sub>III</sub> edges, plutonium (18.056 keV) L<sub>III</sub> and (22.266 keV) L<sub>II</sub> edges and chromium (5.989 keV) K edge. Energy calibration of XANES data was achieved using the Cr foil (5.989 keV), Y foil (17.052 keV), Zr foil (17.998 keV) and Rh foil (23.220 keV) references located behind the second ionization chamber. As observed on these XANES spectra, the white line positions are those of the UO<sub>2</sub> at the uranium edge, and those of PuO<sub>2</sub> at the plutonium edge.

At the uranium  $L_{III}$  edge, EXAFS spectra were collected up to  $15 \text{ \AA}^{-1}$  but only up to  $10.5 \text{ \AA}^{-1}$  at the plutonium  $L_{III}$  edge and  $13.5 \text{ \AA}^{-1}$  at the plutonium  $L_{II}$  edge. The plutonium  $L_{III}$  edge limitation is due to the presence of a small amount of americium ( $L_{III}$  edge at 18.514 keV) in the samples (induced by the used plutonium isotopy). At the chromium K edge, EXAFS spectra were collected up to  $12.5 \text{ \AA}^{-1}$  and show a non-linear decrease after the edge. **In MOX, whatever the sintering temperature is, the oxidation state of uranium and plutonium remains equal to +IV, the oxidation state of chromium is +III.**

**In  $\text{PuCrO}_3$ , plutonium and chromium are both at the oxidation state +III.** These results are summarized on in figure 1 for the four samples.  $\text{Cr}_2\text{O}_3$  XANES are added as references for  $\text{Cr}^{3+}$ . No combination of the  $\text{Cr}_2\text{O}_3$  and the  $\text{PuCrO}_3$  XANES allow us to reproduce correctly the XANES of the chromium in the MOX. Considering the absence of the two peaks observed in  $\text{Cr}_2\text{O}_3$  white line and the differences with  $\text{PuCrO}_3$  in each chromium XANES, the main chromium amount in the MOX microstructure is certainly dissolved in the fluorine lattice of  $(\text{U,Pu})\text{O}_2$  (after sintering between  $1530^\circ\text{C}$  and  $1700^\circ\text{C}$ ). **The local environment of this chromium changes gradually with the increase of the sintering temperature.**

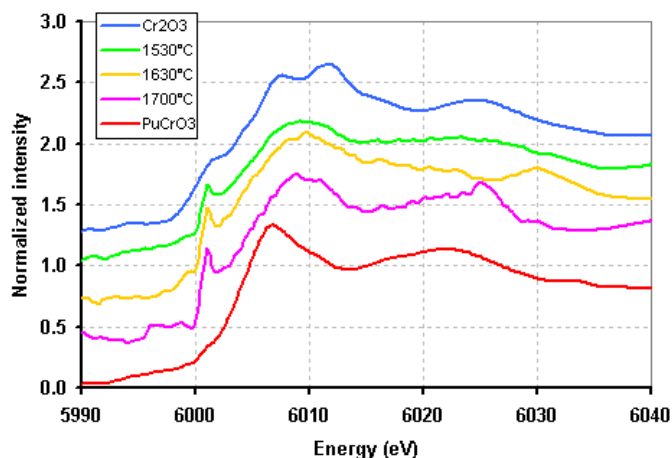


Figure 1 : XANES spectra at the chromium (5.989 keV) K edge.

Fourier transforms of EXAFS spectra collected at uranium  $L_{III}$  edges and plutonium  $L_{II}$  edges are given in figure 2 and 3. For both edges, the first peak which corresponds to the Metal-Oxygen shell, is similar for each of the MOX samples and is characteristic of a stoichiometric oxide with an O to M ratio equal to 2. The second peak which corresponds to the Metal-Metal shell, shows differences between uranium and plutonium. Indeed, in the uranium case, all samples give rise to a second peak which is close to that obtained for  $\text{UO}_2$  powder, indicating that the uranium environment in  $\text{UO}_2$  and  $\text{U}_{0.89}\text{Pu}_{0.11}\text{O}_2$  is equivalent due to an  $\text{UO}_2$  matrix effect. In the plutonium case, the large range of plutonium concentration due to the synthesis process (a high plutonium concentrated powder mixture diluted in  $\text{UO}_2$ ), results in a broadening of the peak [1], [2]. The temperature moderates this phenomenon by a more even plutonium spreading in presence of the doping agent. **This accounts for an increase with the temperature of the  $(\text{U,Pu})\text{O}_2$  solid solution homogeneity in presence of a small amount, 2000 ppm, of  $\text{Cr}_2\text{O}_3$ .**

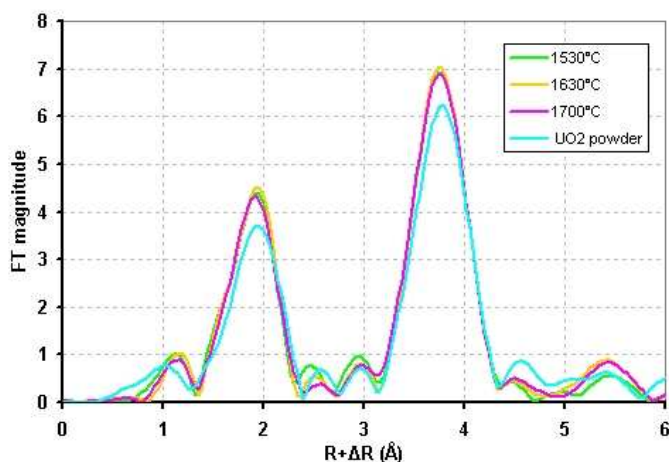


Figure 2 : Fourier transforms of the uranium  $L_{III}$  edge EXAFS ( $k$ -range:  $3 - 12.6 \text{ \AA}^{-1}$ ).

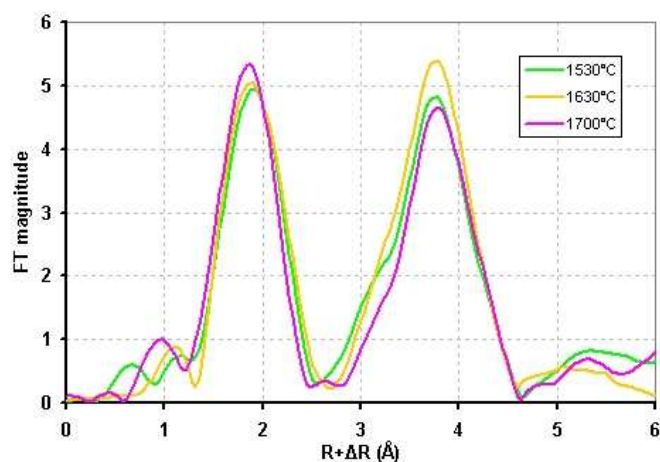


Figure 3 : Fourier transforms of the plutonium  $L_{II}$  edge EXAFS ( $k$ -range:  $3 - 11.9 \text{ \AA}^{-1}$ ).

During this experiment, we have been able to determine plutonium, uranium and chromium oxidation states and local environments in enhanced MOX fuel. The homogeneity of the Cr-doped  $(\text{U,Pu})\text{O}_2$  solid solution with temperature was followed through by EXAFS. Finally, it appears that the environment of chromium added in the MOX powder evolves with the sintering temperature.

[1] : A.Pieragnoli, P.Martin, M.Ripert, H.Palancher, J.Lechelle (2005) *experimental report* ME-939.

[2] : P.Martin, S.Grandjean, C.Valot, G.Carlot, M.Ripert, P.Blanc, C.Hennig (2007) *XAS study of  $(\text{U}_{1-y}\text{Pu}_y)\text{O}_2$  solid solutions* accepted and to be published in *Journal of Alloys and Compounds*.