



	Experiment title: Xas study of uranium and plutonium local environment in Cr ₂ O ₃ -doped (U _{1-y} ,Pu _y)O ₂ (y=0,11 et 0,275) mixed oxide	Experiment number: ME-939
Beamline: BM 20	Date of experiment: from: 02 March 2005 to: 04 March 2005	Date of report: 31/08/2005
Shifts: 6	Local contact(s): Dr. HENNIG C., Dr. FUNKE H.	<i>Received at ESRF:</i>
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Report:

The next generations of nuclear power plant (LWR, HTR, GFR) will use, gradually, on mixed uranium and plutonium oxide as the ceramic fuel, namely MOX (Mixed OXide) of generic formula (U_{1-y},Pu_y)O₂. Currently, some nuclear reactors already use this kind of fuel which usually contains 4 to 9 Pu wt%. In UO₂ fuel, the fissile isotope is U²³⁵ which is dispersed homogeneously in the ceramic lattice. In the case of MOX fuel, Pu isotopes are the fissile atoms. To take advantage of the UO₂ fuel acquired experience, Pu should be dispersed as homogeneously as possible in a (U,Pu)O₂ solid solution. Fuel designers and manufacturers are focused on Pu-rich oxide fuel with a fraction of Pu higher than 10 Pu wt% and the improvement of the Pu distribution.

An optimization of the process conditions could allow us to reach this objective. On the whole, the manufacture of MOX fuel consists in UO₂ and PuO₂ powders co-crushing, milling, pelletizing and sintering. With this method, a fluorite-type solid solution (U,Pu)O₂ might be obtained. The formation of the solid solution, with a Pu ratio between 0 and 100%, is thermodynamically allowed but kinetically slow due to the powder process of milling and to the thermal treatment of sintering. Industrially, to keep the compacting ability of a pure UO₂ powder, a powder co-crushing of UO₂-PuO₂ with high PuO₂ content is softly mixed with pure UO₂. Thus, pellets made with this raw materials are constituted of UO₂ and PuO₂ closely mixed aggregates diluted in a majority phase of UO₂. In order to improve compatibility between fuel, clad and coolant, the MOX is usually made with an O/(U+Pu) ratio of 2.00. To get this stoichiometry, it is necessary to maintain a reducing atmosphere in the sintering furnace with a mixture of Ar-H₂-H₂O (ΔG_{O_2} between -350 and -500 kJ/mol at 1700-1750°C). At this oxygen potential, the diffusion coefficients of U and Pu in the (U,Pu)O₂ ceramic are still small. In these conditions, a density close to 95% of the theoretical one can be reached with a grain size slightly smaller than 10 μ m and the phenomenon of homogenisation are limited, two phases with high and low Pu concentration still remaining.

Although encouraging results were reported for coarse-grained and homogeneous MOX in the case of an oxidizing sintering, this approach has been avoided due to an incompatibility with the current technology of the industrial furnaces. Positive results were obtained for coarse-grained UO₂ by the addition of Nb₂O₅, MgO, Al₂O₃, V₂O₅, TiO₂ or Cr₂O₃ and for coarse-grained and homogeneous MOX by the addition of TiO₂, Cr₂O₃ or UOS. **The aim of this study is therefore to examine the impact on the Pu distribution of one of these dopants, i.e. Cr₂O₃ when it is introduced up to 2000 ppm as a powder during the UO₂-PuO₂ milling.** Under the temperature and atmosphere conditions used during sintering, Cr₂O₃ is particularly interesting because of its property to give rise to a liquid phase (eutectic Cr_s+Cr₃O_{4s} → CrO_l) which usually helps grain growth. Moreover, the possible presence of Cr³⁺ in the fluorine lattice of (U,Pu)O₂ could increase the default concentration and enhance the Pu distribution. A PhD thesis is ongoing to determine the mechanisms of the solid solution formation in presence of chromium.

However we had to verify the formation of a (U,Pu)O₂ solid solution in the presence of Cr³⁺ dopant (introduced under chromium sesquioxide, Cr₂O₃, form). EXAFS turned out to be a key technique to probe Pu and U environments and to evaluate the structural order [1].

During our experiment, we analysed samples obtained by the usual powder process the plutonium content of which was equal to 11 wt% (two samples, *a* and *b1*) and 27.5 wt% (one sample, *b2*). For the 11 wt% sample, two ways of synthesis, co-crushing (*b1*) and micronization of a master blend (*a*), have been investigated to determine, during sintering, the impact of mixing on the (U,Pu)O₂ microstructure. As it has been shown for the face centred cubic structure (U,Pu)O₂, the cell parameter of the solid solution obeys a Vegard's law: $a_{(U_{1-y},Pu_y)O_{2-x}} = 5,470 - 0,074y + 0,32x$ (Å)

% Pu	a (Vegard's law) (Å)	First shell Metal-O (Å)	Second shell Metal-Metal (Å)	Third shell Metal-O (Å)
0	5,4700	2.369	3.868	4.535
11	5.4619	2.365	3.862	4.529
27.5	5.4497	2.360	3.854	4.519
100	5.3960	2.337	3.817	4.475

For each sample, fluorescence and transmission signals were collected at the uranium (17.126 keV) and plutonium (18.056 keV) L_{III} edges. Energy calibration of XANES data was achieved using the Y foil (17.052 keV) and Zr foil (17.998 keV) references positioned behind the second ionisation chamber. As observed on these XANES spectra, the positions of the white lines are those of the UO₂ at the uranium edge, and those of PuO₂ at the plutonium edge. Thus, whatever the plutonium content is, the oxidation state of uranium and plutonium remains equal to +IV. At the uranium L_{III} edge, EXAFS spectra were collected up to 15 Å⁻¹ but only up to 10.5 Å⁻¹ at the plutonium L_{III} edge. This limitation is due to the presence in the samples of small amount of americium induced by the used plutonium isotopy (americium L_{III} edge: 18.514 keV).

The evolution of the Fourier transforms are summarised on the figures 1 and 2.

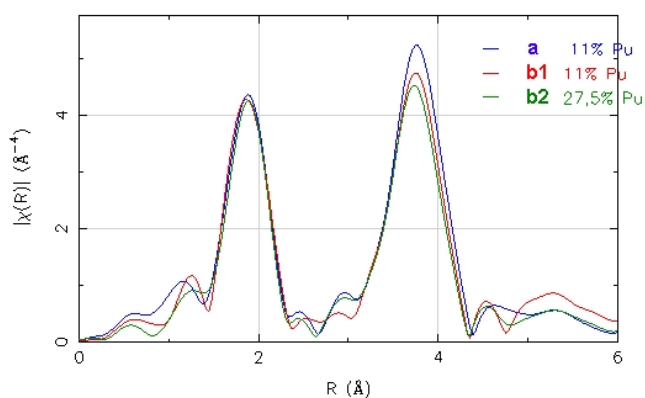


Figure 1 : Fourier transforms of the uranium L_{III} edge EXAFS (k-range: 3 – 12.6 Å⁻¹).

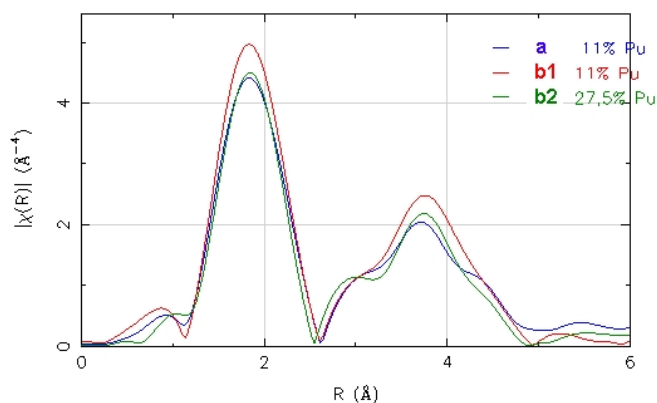


Figure 2 : Fourier transforms of the plutonium L_{III} edge EXAFS (k-range: 2 – 10.5 Å⁻¹).

At uranium and plutonium L_{III} edges, best fits were obtained, in each case, after the introduction of an additional asymmetry term (third cumulant) to describe the first Metal-O shell. For the first three shells, refined distances are in good agreement with those derived from Vegard's law (see table above). This is the signature of the presence of an (U,Pu)O₂ solid solution. Whatever the process and the plutonium content (11% or 27.5%) are, the addition of Cr³⁺ dopant during the synthesis is favourable. In comparison with the spectra obtained on wet route solid solution (co-precipitated, without any dopant and at low temperature) [1], the addition of Cr³⁺ and the different ways of synthesis show that the structure is better ordered. For the first shell (Metal-O) Debye-Waller factors remain low (0.007 Å²) and far below those measured on wet (U,Pu)O₂ prepared without additive [1].

At the end of the allocated beam time, a test at chromium (5.989 keV) K edge was performed. However, a fluorescence signal of too low intensity was collected. Together with the beamline staff, we are already working on instrumental optimization in order to perform successful measurements at low energies. Indeed, a better knowledge of Cr behaviour (quantity of residual Cr and its chemical environment) in the fuel would allow us to understand the responsible mechanism for the solid solution development. Beamtime has already been allocated for this project [2].

[1] : P.Martin, M.Ripert, G.Carlot, S.Grandjean, T.Petit, P.Blanc (2002) *experimental report* ME-312.

[2] : A.Pieragnoli, J.Lechelle, P.Martin, H.Palancher, M.Ripert, C.Valot (2005) *proposal* ME-1256.