ESRF	**Experiment title:** EXAFS/XANES investigation of uranium plutonium mixed carbides	**Experiment number**: CH-3083
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Shifts: 12	**Local contact(s)**: Andreas Scheinost	*Received at ESRF:*

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Since the 1960s', uranium plutonium mixed carbides have been studied as potential nuclear fuels for fast breeder reactors [1-2]. To date, only India has successfully used them in liquid-metal-cooled fast breeder reactors (LMFBRs) at large scale. Currently, in the Generation IV framework, mixed carbides (U,Pu)C1+x (a mixture of (U,Pu)C and (U,Pu)2C3) are being considered as promising fuels for both Gas Fast Reactor (GFR) and Sodium Fast Reactor (SFR). Compared to standard Mixed Oxide fuel (U,Pu)O2, mixed carbide should improve reactor performance due to higher thermal conductivity and metal atoms density [3], a better chemical compatibility with stainless steel [4], and a satisfactory in-pile performance at high burnup. Mixed actinide carbides are typically synthesized by carbothermic reduction of a mixture of uranium and plutonium dioxides under vacuum or under argon. A clear understanding of the elementary mechanisms involved into the carbothermic reduction is of main interest to optimize the manufacturing process of industrial fuels. Moreover, the influence of the initial nature of actinides oxides ($(U,Pu)O_2$ obtained by oxalic co-precipitation or mixture of UO_2 and PuO_2 oxides) is also to be studied.

Experimental results

XAFS characterizations at U L_3 and Pu $L_{2,3}$ edges were performed using He cryostat on the following samples

- UC_2, Pu_2C_3
- a biphasic compound PuC + Pu_2C_3,
- a mixed sesquicarbide $U_{1.80}Pu_{0.20}C_3$ obtained from a co-grinded oxides mixture,
- a biphasic compound $U_{0.90}Pu_{0.10}C$ + $U_{1.80}Pu_{0.20}C_3$ obtained from a co-grinded oxides mixture,
- 3 partially reduced PuO_2 + C samples (carbothermic reduction cycle interrupted at 3 different steps).

XANES results obtained at plutonium L_3 edge are summarized in Fig 1 and edge positions are compared in Fig 2. The carbide compounds ($(U,Pu)_2C_3$, (U,Pu)C, and PuO_2 reduced for 2 and 4 hours), the edge positions are ranging between Pu^{+3} and PuN position. These results suggest that plutonium cations have an electronic configuration very closed to Pu^{+3} instead of the expected metallic state.

Furthermore, as demonstrated with EXAFS results given in Fig 3, after 1 hour of thermal treatment the reduction process in the PuO_2+C mixture is very limited. No Pu-C bond is necessary for reproducing experimental data and all parameters (N, σ and R) are similar to those obtained on PuO_2.

After 4 hours of thermal treatment, characterizations performed in our laboratory has demonstrated that even a single Pu_2C_3 is observed by XRD a significant amount of oxygen is remaining in the sample (3 Wt%). EXAFS data obtained allowed us to eliminate the assumption of a solid solution $Pu_2(C,O)_3$. As shown in Fig 4, EXAFS fit demonstrate the presence of an oxygen atom shell around plutonium with a distance (R=2.34(1) Å) equal to the Pu-O distance observed in the PuO_2 structure. The Debye-Waller value measured for this Pu-O distance is equal to 0.008 $Å^2$, twice the value observed for crystalline PuO_2. This 'glassy' PuO_2 is thus in equilibrium with the Pu_2C_3 phase observed using XRD.

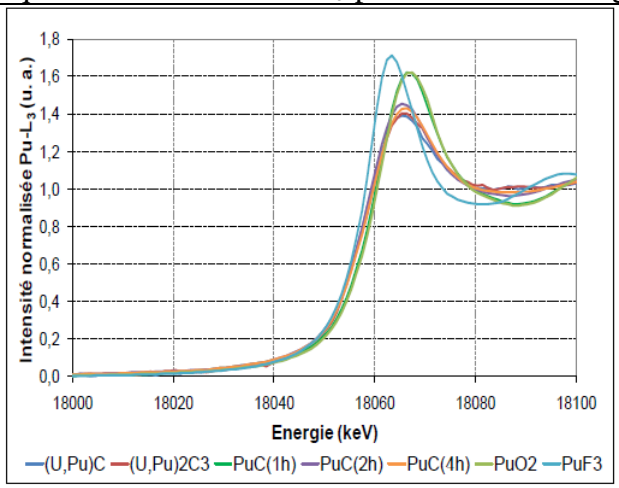


Fig 1: Pu L_3 XANES spectra

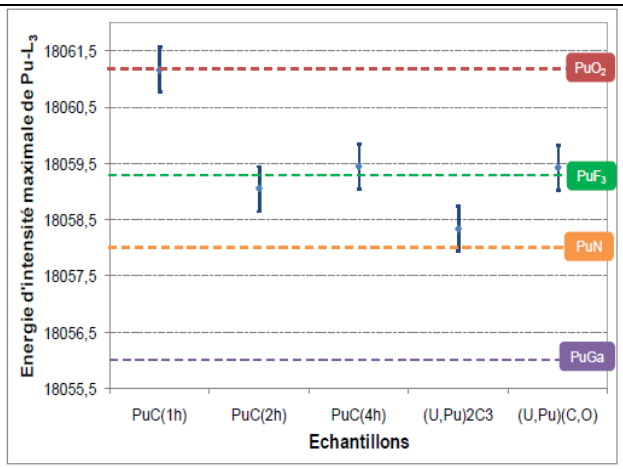
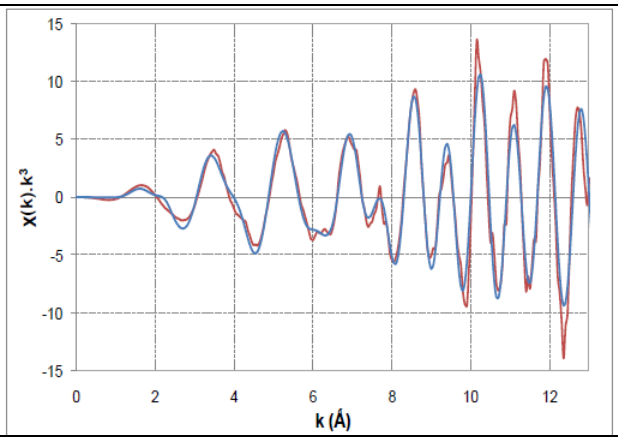


Fig 2: Pu L_3 XANES hite line maxima positions compared to reference compounds



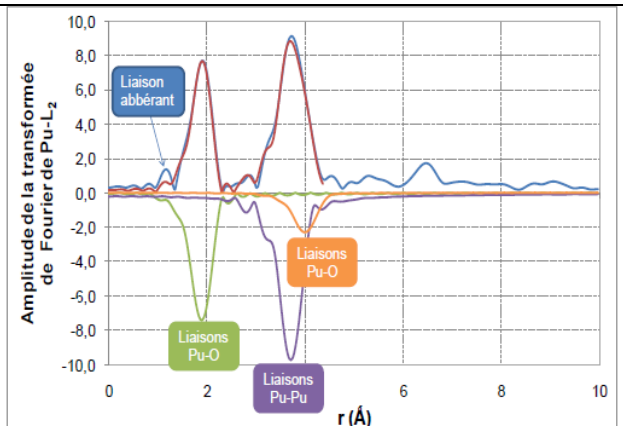
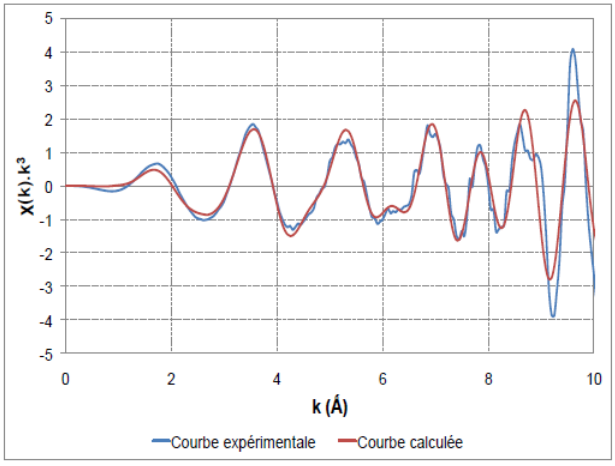


Fig 3: experimental data (-) and fit (-) obtained on PuO2+ C sample reduced during 1 hour



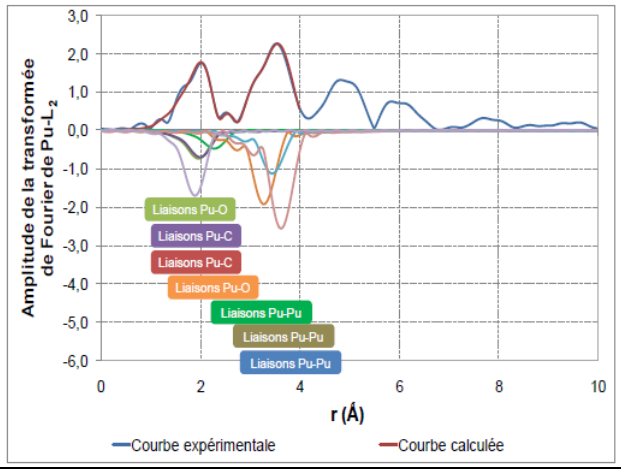


Fig 4: experimental data (-) and fit (-) obtained on PuO2+ C sample reduced during 4 hours

References

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