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$U_{1-x}Pu_xO_{2+\delta}$ fuel precursor synthesis through advanced thermal denitration in presence of organic additive

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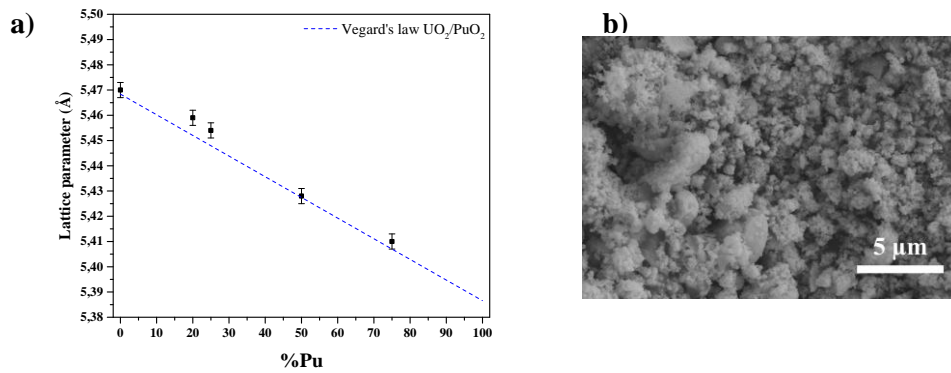
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Within the U and Pu recycling process from nuclear spent fuels, the conversion of purified U and Pu solution onto oxide powder is a key step at the interface between the separation / purification processes and the fabrication of uranium-plutonium oxide fuels called MOx ("Mixed Oxides"). In order to simplify the industrial process, conversion must be able to integrate fluxes with the minimum of adjustments while leading to oxides or mixtures of oxides adapted to a direct shaping of fuel pellets. In the framework of Pu multi-recycling, new conversion routes have to be developed to suit new needs: increase of the quantity of synthesized oxides, reduction of dust generation, no redox adjustments of feed actinide solutions, simplified effluent management, no proliferation risks. To meet these future requirements, CEA is developing a "direct" conversion route based on advanced thermal denitration to obtain mixed actinide oxide $U_{1-x}Pu_xO_{2+\delta}$.

This synthesis method is based on the NPG (nitrate polyacrylamide gel) route developed for non-radioactive materials [1]. Several adjustments of this synthesis were performed prior its application to the production of $U_{1-x}Pu_xO_{2+\delta}$ ($x = 0, 0.20, 0.25, 0.50$ and 0.75) batches. For each sample uranium nitrate ($UO_2(NO_3)_2$) was dissolved in a solution of nitric acid containing Pu at the stoichiometry of the targeted oxide. Total U+Pu concentration was equal to 40 g.L^{-1} , total nitrate concentration was equal to 3.0 mol.L^{-1} . In parallel, a mixture of mainly acrylic acid AA and N, N'-methylene bis (acrylamide) MBAM in a molar ratio of 20:1 (AA: MBAM) was prepared and then added to the actinide nitrate solution and stirred. Once homogeneous, the resulting solution was heated up to 100°C and supplemented with $25 \mu\text{L}$ of radical initiator to quickly allow complete polymerization into a gel. A xerogel was then formed by dehydration of the polymeric gel at 150°C . Xerogel conversion at 800°C in reconstituted air produced intimate mixtures of U_3O_8 and PuO_2 . After the second calcination, performed under Ar/H_2 -5% at 800°C , single-phase oxides were obtained as confirmed by XRD analyses showing the presence of a single fluorite structure (Fm-3m) for the samples $U_{1-x}Pu_xO_{2+\delta}$ ($x = 0$ to 0.75) (Figure 1a), exhibiting a 3D morphology (Figure 1b). For $U_{0.80}Pu_{0.20}O_{2+\delta}$, the amount synthesized allowed the fabrication of a pellet. In this objective, the powder was pressed under 500 MPa in a three part die, no grinding step was used prior to the pelletization. The green density reached was 70% of the theoretical density (TD). The green pellet was then sintered in a dilatometer under Ar/H_2 -4% with 1200 ppm of H_2O and the axial shrinkage was recorded as function of temperature (Figure 2a). The maximum shrinkage rate is observed at 1455°C . The pellet was then maintained at 1700°C for 2h. At the end of this process, the density of the pellet reached $94\pm 2\%$ of TD and exhibited oxygen to metal ratio of 2.00. Visually the pellet did not show any cracks (Figure 2b).

The main objective of this work was to explore the possibility to synthesize and sinter mixed U/Pu oxides by "advanced thermal denitration in the presence of organic additives". Feasibility is demonstrated here by the successful synthesis of $U_{1-x}Pu_xO_{2+\delta}$, whatever Pu content. The direct sintering of the obtained powder without milling step before shaping is possible. Therefore a significant breakthrough in the methods currently used for MOx fabrication is demonstrated. Indeed, this new process allows the synthesis of mixed oxides from solutions resulting from reprocessing without any redox adjustment (*i.e.* using

U(VI)/Pu(IV) nitrate solution) and does not require any filtration and grinding steps, limiting highly



contaminant dust generation.

Figure

Figure 1: a) Evolution of the lattice parameter a with Pu content in $U_{1-x}Pu_xO_{2\pm\delta}$ solid solution, measured by XRD and compared with Vegard's law. b) Microstructure of the $U_{1-x}Pu_xO_{2\pm\delta}$ powder ($x=0.50$)

Figure 2 : a) Dilatometric curve and evolution of the shrinkage rate of the co-converted $U_{0.80}Pu_{0.20}O_{2\pm\delta}$ compound at 2 K min⁻¹ under Ar/H₂-4%. b) Photograph of the pellet after sintering.

Reference

[1] Goupil, G., et al. "Selection and study of basic layered cobaltites as mixed ionic–electronic conductors for proton conducting fuel cells." *Solid State Ionics* 263 (2014): 15-22.

