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A new chemical route of nuclear fuel (U,Pu)O_{2±δ} by advanced thermal denitration in the presence of organic additive.

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INTRODUCTION

Within the U and Pu recycling process from nuclear spent fuels, the conversion of purified U and Pu solution on to oxide powder is a key step at the interface between the separation / purification processes and (re) fabrication stages of uranium-plutonium oxide fuels or MOx ("Mixed Oxides"). In order to simplify the industrial process, conversion must be able to integrate the fluxes with the minimum of possible adjustments while leading to oxides or mixtures of oxides adapted to a direct shaping of fuels. In the framework of generation IV reactor deployment that includes a multi-recycling of Pu, new conversion routes have to be developed to suit the new needs: increase of the quantity of oxides to synthesize, reduction of dust generation, no redox adjustment of feed actinide solutions, simplified effluent management, no proliferation risk. Currently, the production of MOx is based essentially on the mixture of single actinide oxides, UO₂ and PuO₂ powders (MIMAS and COCA) [1]. In the future, to obtain a better homogeneity of Pu repartition in the MOX associated to Pu multi-recycling, the use of a mixed oxide has to be favored explaining the large number of studies conducted to define a co-conversion route leading to the production of mixed oxides containing both uranium and plutonium. Different routes including mixed oxalate U(IV) / Pu(III) precipitation[2]; (NH₄ (U,Pu) CO₃) carbonate route also named ADPuC [3], and; the denitration of actinide salt, MDD (modified direct denitration) process [4], ... However, all these methods do not match all the future needs of the nuclear fuel cycle, already exposed above: oxalate co-precipitation requires a redox adjustment and brings filterability difficulties, ADPuC route produces effluents hardly manageable, as for internal or external gelation routes (ammonium nitrate solutions) and finally all the so far denitration routes need a NOx treatment and produce dust oxides either directly or due to the requirement of a milling step prior to fuel fabrication. Therefore, the development of a new synthesis route tackling all these issues appears essential for generation IV deployment.

In the literature, another synthesis route of mono or poly cationic oxides, referenced as NPG (nitrate polyacrylamide gel) [5], permits to obtain good cation stoichiometry accuracy but has never been applied to actinide oxide synthesis. In this process, a cationic solution is embedded inside a polymeric gel that is then dried to form a xerogel to be calcined to make the oxide form. This

present work explores the so called "advanced thermal denitration in the presence of organic additives" conversion route, based on this method, to make mixed actinide oxides which so far had not been attempted before. It will also describe all the development to suit the requirements linked to the production of nuclear fuel precursors (no Sulphur, no chloride, safe reagents).

Description of this new synthesis route

The various steps that take place during this synthesis process are shown Figure 1: the actinides (uranium and plutonium) are mixed into a nitric solution using the same stoichiometry that the targeted ratio expected in the final oxide.

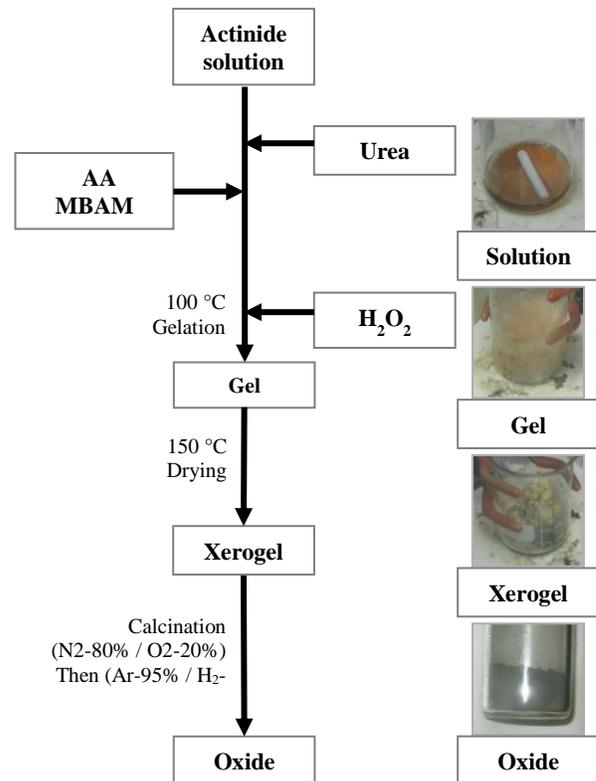


Fig. 1. Flowsheet of "advanced thermal denitration in the presence of organic additives" synthesis route (photos illustrate the case of the (U,Pu)O_{2±δ} synthesis).

For U_{0.55}Pu_{0.45}O_{2±δ} syntheses, uranium nitrate (UO₂(NO₃)₂) is dissolved in nitric acid then Pu in a nitric

solution form is added. Total metal concentration was 0.105 mol.L^{-1} , total nitrate concentration was 0.5 mol.L^{-1} . To prevent premature precipitation during synthesis, urea was added to the actinide solution. A mixture of acrylic acid AA ($\text{C}_2\text{H}_3\text{COOH}$) and N, N'-methylene bis (acrylamide) MBAM ($(\text{C}_2\text{H}_3\text{CONH}_2)_2\text{CH}_2$) in a molar ratio of 20: 1 (AA: MBAM) was then added to the previous solution. The resulting fully homogeneous solution was heated up to 100°C and supplemented with $25 \mu\text{l}$ of hydrogen peroxide (30 wt%) to quickly allow complete polymerization into a gel. Hydrogen peroxide is here used in substitution of the common initiators of polymerisation (ammonium per sulphate or AIBN) to suit the specifications for further nuclear fuel fabrication (no Sulphur in the fuel and safe reagents). The xerogel is then formed by dehydration of the polymeric gel using a hot plate heated up at 150°C . Oxidative calcination of xerogel was then performed at 800°C in reconstituted air for 2h leading to the total oxidation of all carbon compounds. A second calcination, performed under Ar-95% / H_2 -5% up to 800°C for 2h, permitted obtaining the targeted mixed actinide oxide.

RESULTS

Thermal decomposition of uranium / plutonium xerogel was studied under reconstituted air (See Figure 2 for TG-DSC curves). Complete degradation of the polymeric network was observed at a temperature of 440°C . The presence of several intense exothermic peaks at about 280°C , 340°C and 380°C in the DTA curve (Figure 2) indicates that polymer decomposition occurs between 280°C and 440°C , the biggest exothermic reaction being at 380°C corresponding to 30wt% loss mass. Thermal decomposition generated a total mass loss of 91%, in agreement with the expected, theoretical value.

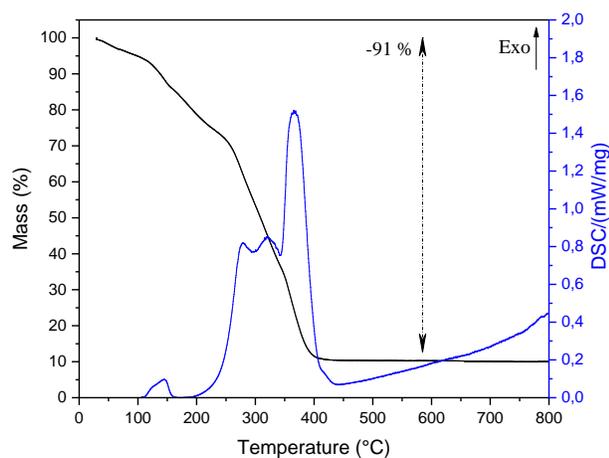


Fig. 2. Flowsheet of “advanced thermal denitration in the presence of organic ddtives” synthesis route (photos illustrate the case of the $(\text{U,Pu})\text{O}_{2\pm\delta}$ synthesis).

At the end of xerogel conversion, after calcination at 800°C in reconstituted air, an intimate mixture of PuO_2 and U_3O_8 oxides was recovered as the XRD analysis attested (Figure 3-a). Similarly, after the calcination in reconstituted air at 800°C during 2h. After calcination in Ar/ H_2 (95%/5%) at 800°C for 2h single-phase oxide was obtained as observed by XRD analyses showing the presence of a fluorite-like structure (Fm-3m) for the sample (Figure 3-b).

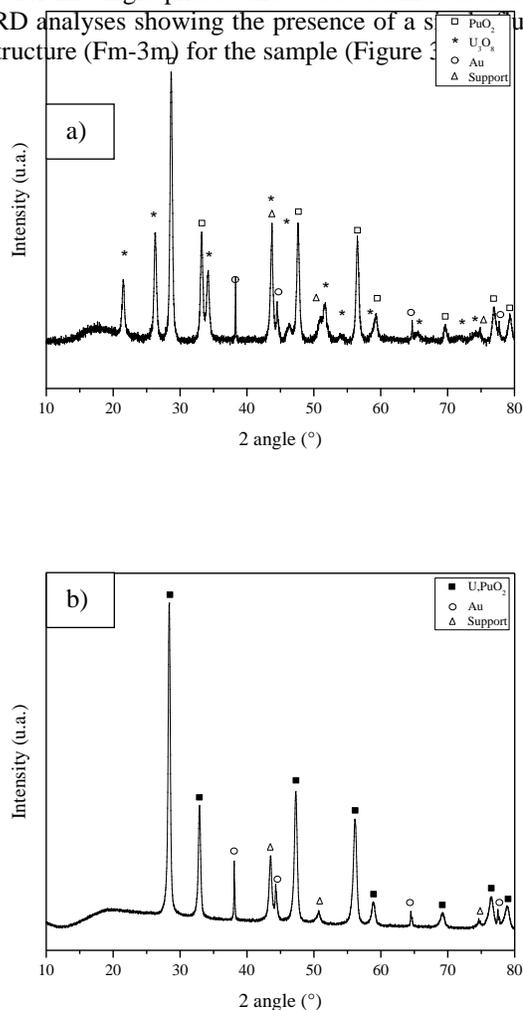


Fig. 3. XRD diagram for a) $\text{U}_3\text{O}_8 / \text{PuO}_2$ converted for 2h at 800°C in reconstituted air and b) $(\text{U,Pu})\text{O}_2$ converted for 2h in Ar-95%/H₂-5%. Peak matches with white squares match the plutonium oxide phase, black stars match the uranium phase, black squares uranium-plutonium phase, white circles match the golden phase and white triangles match the support phase.

The obtained oxide powder was also characterized using a nucleated Zeiss SUPRA 55 / 55VP FEG-SEM (field emission scanning electron microscope). The SEM images (Figure 4) show a typical morphology of samples obtained using a thermal denitration synthesis route. The powder is composed of large agglomerates of several tens of

micrometers length and a hundred nanometers thick constituted of nanoparticles.

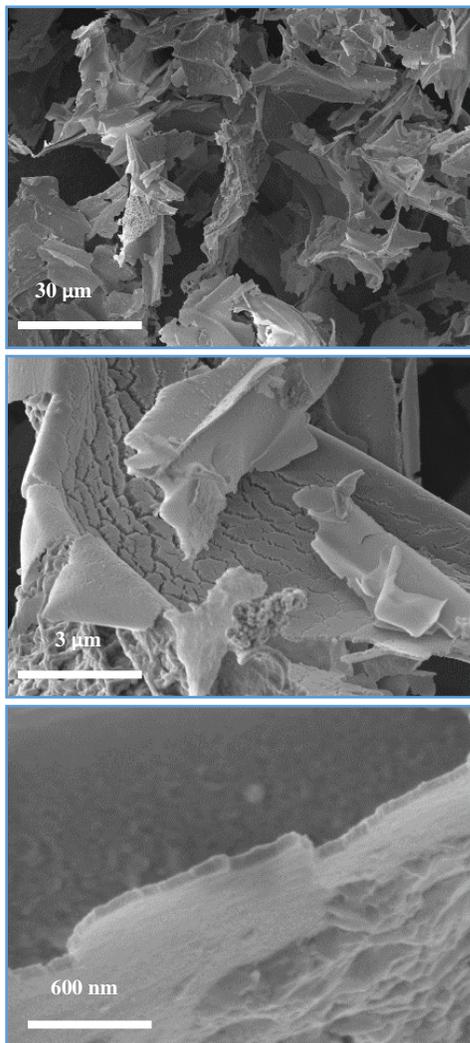


Fig. 4. Scanning electron images $U_{0.55}Pu_{0.45}O_{2\pm\delta}$ converted for 2h at 800 °C in reconstituted air and then under hydrogenated argon (Ar-95% / H_2 -5%) for 2h at 800 °C

Conclusion

The main objective of this work was to explore the possibility to synthesize a mixed U, Pu oxide using the “advanced thermal denitration in the presence of organic additives” synthesis route, a derivative synthesis route from one commonly used in other fields to obtain poly-cationic oxides. Feasibility is demonstrated here by the successful synthesis of $U_{0.55}Pu_{0.45}O_{2\pm\delta}$ batch. This route represents a significant breakthrough in the methods currently used for MOx synthesis. Indeed, it allows the synthesis of mixed

oxides from solutions resulting from reprocessing without redox adjustment using U(VI)Pu(IV) nitrate solution and doesn't require any filtration step. However, the morphology of the produced mixed-oxide powder would probably require new way of MOx fuel fabrication.

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