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Application of Weak Acid Resin process to the production of spherical and calibrated oxide precursor bearing uranium and americium: overview of 10 years research at CEA

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Abstract – *This paper is dedicated to the adaptation of the Weak Acid Resin process (WAR) to the elaboration of uranium-americium mixed oxide microspheres as precursors for the fabrication of Americium Bearing Blankets (AmBB). It describes successive developments of WAR process from lanthanide simple oxide synthesis to actinide(s) bearing mixed oxide preparation. Recent studies demonstrated the scientific feasibility of the preparation of a dense uranium-americium mixed oxide pellets with 10 $_{at}$% of Am vs heavy metal and with 95 % of theoretical density (TD) from those innovative microsphere precursors.*

I. INTRODUCTION

Americium is responsible for the main long-term radiotoxicity and heat load of the ultimate nuclear waste after sole Pu recycling in MOX [1]. Therefore, in France, the management of long-lived radionuclides such as Am has become a priority and its transmutation in Sodium Fast Reactor (SFR) is foreseen [2,3]. Am heterogeneous transmutation is considered as the reference mode and consists in irradiating uranium–americium mixed oxide compounds ($U_{1-x}Am_xO_{2\pm\delta}$) located at the core periphery. These compounds correspond to dense ceramic pellets with a U/Am ratio of 90/10 and are currently fabricated by powder metallurgy processes. Nevertheless, this family of processes involves mixing and grinding steps which generate large amounts of fine (sub-micronic) and highly contaminant particles. For a future large-scale deployment, a dust free route involving the handling of agglomerated americium-containing precursors if possible in the form of micronic spheres is therefore mandatory [4]. Consequently, alternative processes were developed on the basis of sol-gel technique combined or not with impregnation or by using beads of weak acid resin (WAR) as organic template. The former sol-gel-infiltration process however did not succeed to provide round shaped particles but rather "fiber-like" particles due to partial dissolution of UO_2 spherical matrix (obtained by sol-gel method) during infiltration step by the Am nitrate solution [5]. For pure sol-gel process, the radiolysis impact of americium on the stability of the sol has not been assessed yet and up to now studies were limited to surrogate materials like Nd [6]. The latter so-called WAR route allows to synthesize regular shaped microspheres of americium containing oxide materials and is based on the production of oxide microspheres from loaded ionic exchange resin and their subsequent thermal conversion into oxide. The original procedure developed at Oak Ridge National Laboratory [7,8] was dedicated to the production of uranium carbide kernels for tristructural isotropic coated particles (TRISO fuels) from intimately mixed carbon and oxide precursors and had been adapted at CEA Marcoule to the production of pure oxide materials [9].

In fact, it can produce single oxide or mixed oxide microspheres in the 100-700 µm range and their synthesis was tested and validated for lanthanide and actinide based materials [10,11].

II. WAR PRECURSOR SYNTHESIS

II.A. Principle

The WAR conversion process is based on the fixation of U(VI) cations [12] and other actinide/lanthanide elements into beads of carboxylic ion exchanger [13].

As-loaded resin microspheres are then heated in air up to 800°C to remove organic materials and supply the metallic oxides in the form of microspheres. At this stage, uranium is present as triuranium octaoxide (U_3O_8) and is intimately combined with actinide or lanthanide.

An ultimate reduction step is then necessary to adjust the oxygen stoichiometry of the uranium oxide to a value close to 2 and is performed through an ultimate heat treatment in Ar/H_2 reductive atmosphere. Those different steps are summarized in Figure 1.
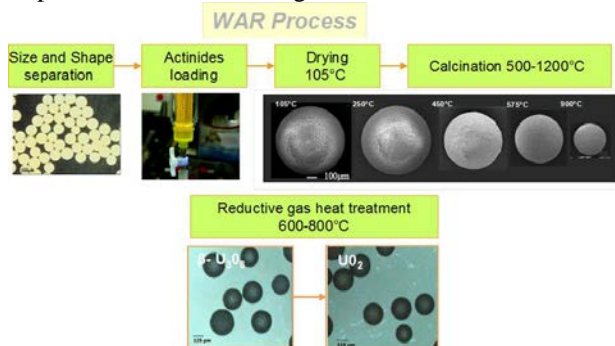

Fig. 1. Principle of the WAR process applied to the synthesis of uranium dioxide based materials.

II.B. Realizations

The WAR process was applied to synthetize simple oxides or mixed oxide microspheres. Up to now, the conversion by the resin process allowed to produce lanthanides and uranium oxides microspheres with a diameter of 300-400 µm but also mixed oxide spherical particles of uranium with neodymium (from 10 to 90 % at/at in Nd), uranium with plutonium (12% at/a in Pu), and uranium with americium (10 and 15% at/at in Am) [10,13]. The morphology of the microspheres was kept intact after thermal treatment and they can be considered as quasi-perfect spheres of metallic oxide(s) as shown in Figure 2.
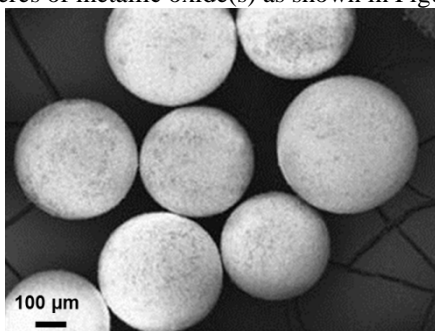

Fig. 2. FEG-SEM micrograph in electron secondary mode of cerium oxide microspheres obtained from the WAR process and calcined at 800°C in air.

III. OXIDE MICROSPHERE CHARACTERIZATIONS

III.A. Microstructural characterization

As can be observed in cross sections of Figure 3, the microstructure of oxide microspheres is very porous and homogeneous with micron scale open porosity which explains the brittleness of such a material and its interest for shaping operations.

As confirmed by mercury porosity measurements, microsphere porosity can be described at three different scales: first, the hundred µm scale which corresponds to the porosity due to the microsphere packing (45 $_{vol}$%, inter-microsphere porosity); second, the µm scale which is linked to the inter-aggregates porosity inside the microspheres (42 $_{vol}$%); third, porosity between the elemental grains in the aggregates (13 $_{vol}$%, intergranular or intra-aggregate porosity).
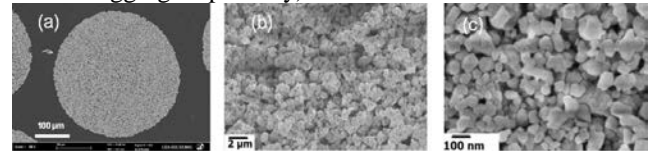

Fig. 3. FEG-SEM micrographs in electron secondary mode of a cross-cut of a cerium oxide microsphere obtained at 800 °C and looked at different scales: (a) view of a cut of a microsphere; (b) view of micronic aggregates; (b) view of nanometric grains.

III.B. Oxide structure

The crystalline structures of the resulting oxides were characterized by powder X-ray diffraction (XRD) on powdered microspheres. The intermediate oxide obtained after calcination under air of a mixed uranium-cerium or americium loaded resin corresponds to an α'-U_3O_8 single phase of hexagonal structure stabilized by the incorporation of Ce or Am. Lattice parameter are distorted as regards c axis which could suggest in the lanthanide case incorporation of Ce in between crystallographic planes normal to c [11,14].

The XRD pattern obtained from the powdered $(U,Am)O_2$ mixed oxide microspheres is characteristic of a single fluorite phase. The single-phased compound obtained for such a mixed system suggests a homogeneous distribution of cations in the oxide material.

III.A. Mechanical behavior

As we mentioned, WAR oxide precursors consist of very porous oxide materials and are considered as non-consolidated microspheres whose mechanical properties are of great relevance for shaping steps such as pelletizing.

Measurements of the crushing force of a single microsphere (Figure 4) and of the microsphere's diameter enabled also the calculation of mechanical strength [15] and its plot versus precursor's calcination temperature. In the case of cerium oxide, results show that the strength is very low but is increasing with calcination temperature

indicating that the material cohesion is reinforced with temperature as aggregates would become denser and their contact between them stronger.
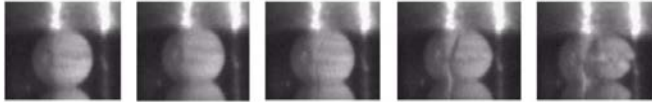

Fig. 4. Crushing test of a single cerium oxide microsphere of 350 µm calcined at 800°C and visualization of fracture mode.

This interpretation was confirmed by modelling studies using the Discrete Element Method (DEM) by describing the microsphere as an assembly of particles at the scale of an aggregate (~µm size) and taking into account their mechanical interactions with adhesion and friction models [16]. Simulations reveal that contact size as well as aggregate densities increase sharply between 800 and 1400°C and helps at describing the microstructure after the pressing step, prior to sintering.

IV. APPLICATION TO PELLET FABRICATION

The Calcined Resin Microsphere Pelletizing process, is inspired from the Sphere-Cal [17] and Sol Gel Microsphere Pelletizing (SGMP) processes [18,19] and is based on the compaction of WAR oxide microspheres into green pellets and their sintering into dense ceramics (Figure 5).

The applied pressure of 500 MPa is sufficient to provide a homogeneous nanostructured green pellet which gives a dense and homogeneous microstructure after sintering.

For mixed compounds of uranium and americium, CRMP process provided uranium-americium mixed oxide pellet of density of 94.9 ± 0.5% TD with dense and homogeneous microstructure composed of grains of 5-15 µm [20]. No traces of microspheres are evidenced which would prove that the microspheres were finely crushed and mixed during compaction, thus avoiding the penalizing "blackberry" effect [21].
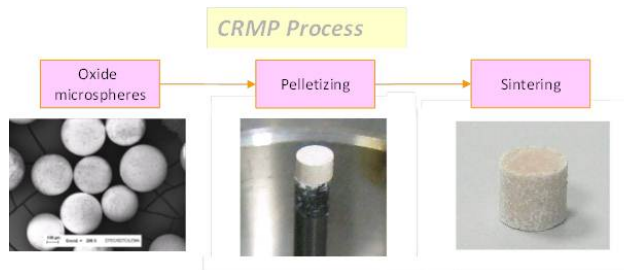

Fig. 5. Principle of CRMP process.

V. CONCLUSIONS

This paper describes the modified version of the Weak Acid Resin process which has been adapted to the synthesis of oxide materials in the form of microspheres.

It recalls the principle of this process and the different syntheses which have been carried out during last decade at CEA Marcoule, from lanthanide single oxide to mixed actinide oxide compounds.

It provides also information about the peculiar characteristics of those microspheres which exhibit a strong open porosity and a multi-scale organization based on assembly of nano-particle aggregates and which are brittle in nature.

The CRMP process, presented at the end, illustrates the potentiality of such precursors for fabricating dense and homogeneous mixed oxide pellets bearing uranium and americium through a dust-free process.

Perspectives of this work are to master the porosity of oxide microspheres in order to synthesize dense mixed-oxide precursors which could be used directly as starting materials for particle fuel, known as Sphere-Pac fuel [22,23].

NOMENCLATURE

WAR: Weak Acid Resin.
AmBB: Americium Bearing Blanket
TD: Theoretical Density
MOX: Mixed Oxide
SFR: Sodium Fast Reactor
TRISO: TRistructural ISOtropic coated particles
FEG-SEM: Field Emission Gun -Scanning Electron Microscopy
XRD: X-Ray Diffraction
DEM: Discrete Element Method
CRMP: Calcined Resin Microspheres Pelletizing
PELGRIMM: PELlets versus GRanulates: Irradiation, Manufacturing and Modelling
PACFA: Procédés Avancés de Conversion et Fabrication de combustibles

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