Uranium/minor actinide co-conversion to fuel starting materials for transmutation in Gen-IV sodium fast reactor

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Abstract

Our current R&D aims at elaborating mixed-oxide precursors of uranium and minor actinides for the pellet fabrication of blanket for transmutation. A dustless process which avoids the presence of highly contaminating powder in the fabrication line is highly recommended and motivates our research on the synthesis of minor actinide oxide microspheres with diameter between 100 and 1 000 μm. The resin concept consists in the fixation of actinide cations into beads of ionic exchange resin. The loaded resins are then mineralised to form the oxide microsphere. The spherical morphology is preserved and beads with diameter superior to 100 μm are produced. This work also focuses on the oxide microspheres precursors pelletising step. In optimised conditions, the heat treated particles shows interesting compaction behaviour. As a consequence, a gain in density and a better homogeneity are expected for the green pellet. This latter point results in a lower differential shrinkage during sintering and a possible suppression of the grinding step which is a costly and a very contaminating operation.

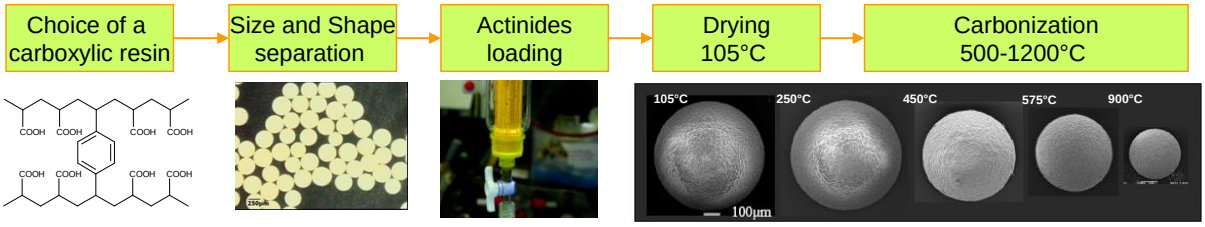
Introduction

This study is devoted to the synthesis of ceramic precursors incorporating minor actinides and to their pelletisation into blanket dedicated to transmutation in sodium fast reactor [1]. More precisely, it concerns the preparation of homogeneous and dense precursor materials of spherical form and millimetric size associating minor actinide(s) with uranium and their compaction and sintering into ceramic pellets. It is based on the resin process called Weak Acid Resin (WAR), which was developed at Oak Ridge National Laboratory in the early 70s [2-4] and CEA-Grenoble [5] to make uranium carbide kernels for the high-temperature gas-cooled reactor. In summary, the spherical carboxylic resins were loaded with uranyle cation, and then mineralised to produce uranium oxide microspheres mixed with carbon and eventually transformed into carbide kernels at higher temperature. Our aim is to develop this process to the management of both uranium and minor actinides and to synthesise microspheres of mixed oxides precursors which are due to be compacted and sintered into fuel pellet.

Oxide microsphere synthesis

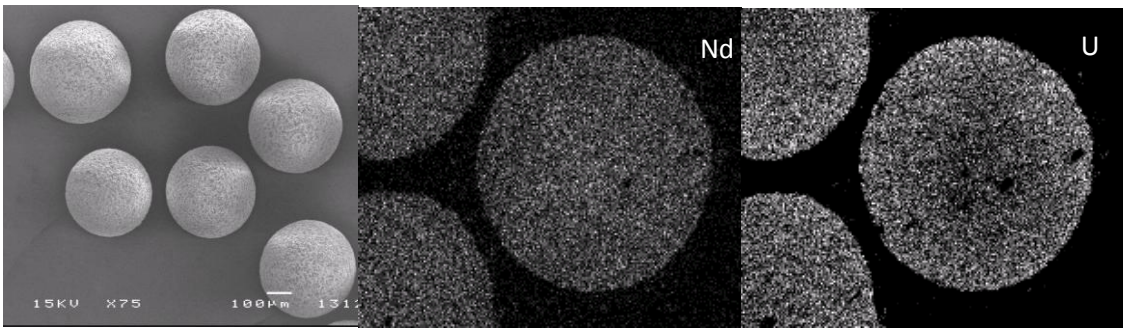
The precursor material synthesis can be divided in two major steps: the loading of resin beads and its thermal conversion driving the fully loaded resin into oxide. The flow sheet of the process is described in Figure 1.

Figure 1: Principle of the oxide microsphere synthesis by the resin process WAR



It applies to the making of simple oxide or mixed-oxide microspheres. Up to now, the conversion by the resin process allowed to produce neodymium, cerium and uranium oxides microspheres with a diameter in the range 300-400 µm but also mixed-oxide spherical particles of uranium with neodymium (from 10 to 90% at/at in Nd) or uranium with americium (10% at/at in Am) [6]. The morphology of the microspheres remains constant after the heat treatment as is shown in Figure 2 for the mineralisation of uranium-americium loaded resin microspheres [7,8]. The microsphere presents a porous structure and a homogeneous distribution of metallic cations as revealed by microprobe analysis of mixed uranium-neodynium oxide kernels (Figure 2) [9].

Figure 2: Uranium and americium oxide micro-spheres elaborated by the resin process; uranium and neodymium metal distribution in a mixed-oxide microsphere



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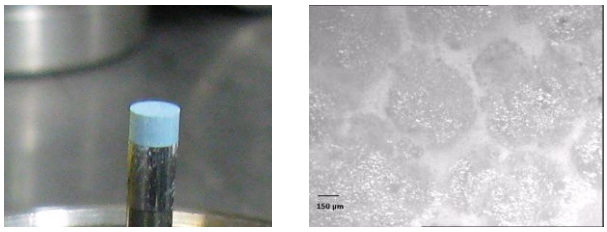
Compaction study

The microspheres were compacted in a specific mould [10],with radial opening minimising fissuring, to give green pellets of cerium or neodymium oxide as shown in Figure 3(a) (surrogates of americium oxide). The length-to-diameter ratio of the green pellets was around 1 and the diameter was 5.2 mm. The compactibility of the microspheres greatly depends on the conditions of calcination, i.e. the final temperature of the heat treatment but also the temperature gradient during the polymer template degradation. In non-optimised conditions the pellets showed a "blackberry" structure [11], meaning that the microspheres boundaries are visible [Figure 3(b)]: the microspheres kept their individual identity and did not disintegrate during pellet pressing. This kind of microstructure leads to high open porosity sintered pellets. In proper conditions, green pellets of cerium oxide CeO_2 with good visual appearance and integrity have been fabricated; the bulk density was around 60%.

Figure 3: (a) Green pellet of neodymium oxide obtained by pelletisation of neodymium oxide kernels; (b) "blackberry" microstructure observed on a cerium oxide green pellet surface

(a) (b)



Sintering behaviour

The densification of cerium oxide pellets was performed in air up to 1 400°C within 10 h. The bulk density and specific gravity reached 95% and 98% of theoretical density (TD) respectively. Sintering started at 800°C and maximum densification rate occurred at 1 100°C. Open porosity and linear shrinkage were closed to 3% and 13% respectively which are typical for this kind of material [12]. Good-looking and dense pellet of cerium oxide could then be obtained in those conditions [Figure 4(a)]. Nevertheless, this study showed that the green pellet microstructure, which depends on the calcination parameters of the microsphere, strongly influences the quality of the sintered pellet. The use of oxide particles of high crushing strength can hinder densification and create a high open porosity in the sintered pellet and lower the bulk density down to 76% of theoretical density [Figure 4(b)].

Figure 4: (a) Dense cerium oxide sintered pellets, 95%TD; (b) fractured cerium oxide pellet showing "blackberry" microstructure, 76%TD

(a) (b)

Conclusion

This study highlights the potentiality of the WAR resin process to convert uranium and minor actinides into microspheres of mixed oxides which are suitable for fabricating dense oxide ceramic pellets. It points out that the synthesis of the spherical precursor must be perfectly mastered in order to succeed in making a homogeneous green pellet leading to a proper densification during sintering. This process, known as Calcined Resin Microsphere Pelletisation (CRMP) allowed to produce cerium oxide pellets of high densities (≥95%TD) at relatively low temperatures (≤1 400°C). Above all, the CRMP process provides an alternative route to "powder-pellet" routes [13]. The main advantages are: *i)* the handling of "free-flowing" particles which facilitates transfer during remote operations; *ii)* the use of dustless microspheres which limits the contamination of hot cells particularly critical with minor actinides; *iii)* the microhomogeneity of the fuel material between uranium and minor actinide(s) which is guaranteed by the mixing in the loaded resin.

References

[1] Grandjean, S., *et al.*, *Proceedings of Global 2009,* Paris, France, 6-11 September (2009).

[2] Weber, G., R. Beatty, V. Tennery, *Nuclear Tecnology,* 35, 217 (1977).

[3] Notz, K., P. Haas, J. Schaffer, *Radiochimica Acta,* 25, 153 (1978).

[4] Haas, P., *United States Patent* 38000223 (1974).

[5] Moreau, C., *et al.*, "Nuclear Power and Its Fuel Cycle", *AIEA Conference*, Salzburg, Austria, 2-13 May 1977, IAEA CN 36/270, p 2 (1977).

[6] Picart, S., H. Mokhtari, I. Jobelin, *French Patent* 2936348 (2008).

[7] Picart S., *Proceedings of Global 2009,* Paris, France, 6-11 September (2009).

[8] Picart, S., H. Mokhtari, I. Jobelin, *Materials Science and Engineering*, 9, 012025 (2010).

[9] Mokhtari, H., Thesis, Paris XI University (2008).

[10] Prieur, D., *et al.*, *Proceedings of Global 2009*, Paris, France, 6-11 September (2009).

[11] Zimmer, E., *et al.*, *J. Nucl. Mat.,* 152, 166 (1988).

[12] Heintz, J.M., J.C. Bernier, *Journal of Materials Science*, 21, 1569 (1986).

[13] Ganguly, C., *Bull. Mater. Sci.*, 16, 509 (1993).