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Investigation of the sintering mechanisms for (U,Am)O_2 pellets obtained by CRMP process

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Abstract

The use of CRMP (Calcined Resin Microsphere Pelletization) process for AmBB (Americium Bearing Blankets) fabrication is today a key research axis in americium transmutation domain, where its very high activity requires minimization of powder dissemination. In this aim, the use of oxide microspheres as compaction precursors is a promising clean alternative to powder metallurgy. Understanding the different steps of densification during CRMP pellet sintering thus appears as fundamental to obtain final materials with the specific features required for AmBB. The densification curve recorded in dynamic conditions shows different sintering steps. A first decrease of shrinkage rate happens at low temperature, around 1100 K. This phenomenon is not normally observed in the sintering of conventional powders. Chemical and microstructural studies were performed on (U,Am)O_2 and also on (Ce,Gd)O_2 surrogate compound to highlight the causes of this low-temperature sintering step. Multiscale reorganization finally appears as the sole explanation, through the sintering of nanometric aggregate present in the green pellet and related to the morphology of the starting microspheres employed as pelletization precursors.

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Keywords: $U_{0.9}Am_{0.1}O_{2\pm\delta}$; CRMP process, sintering, nanoparticles

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1. Introduction

Americium (Am) is generated in nuclear fuels during their irradiation in reactors. Although it only represents a very low amount of spent fuel (<0.05 wt. %), its high activity and heat load render it one of the most problematic actinide for long-term management of spent fuel after Pu recycling [1]. In a closed nuclear fuel cycle scenario, Am transmutation in fast neutron reactors (FNR) could be used to lower Am contribution in ultimate waste [2]. It would consist in the irradiation, in the core periphery, of Am-bearing blankets (AmBB) under the form of $U_{1-x}Am_xO_{2\pm\delta}$ ceramic pellets, as dedicated targets for heterogeneous transmutation. Up to now, AmBB fabrications are based on powder metallurgy processes with ball-milling steps generating large amounts of fine radioactive particles (e.g. UMACS process [3]). However, due to Am presence, dustless processes become mandatory before envisaging an industrial deployment. In this aim, the development of an innovative route using micrometric spherical precursors has been initiated. Through an adaptation of the weak acid resin (WAR) process, the general approach consists in synthetizing micron-sized and brittle spherical $U_{1-x}Am_xO_{2\pm\delta}$ precursors from metal-loaded ion exchange resin microspheres. These soft agglomerates combine the advantages of fine powders, with a good reactivity during sintering, without the major drawback of pulverulent compounds, i.e. high dissemination during handling. The final process is the so-called Calcined Resin Microsphere Pelletization (CRMP) process. It has been tested today at the laboratory-scale, as a feasible $(U,Am)O_2$ dense pellets fabrication route [4,5]. The knowledge of the densification behaviour for green pellets obtained from $U_{1-x}Am_xO_{2\pm\delta}$ microsphere compaction thus appears fundamental to control the microstructure of the sintered pellets and their behaviour under irradiation. In this way, densification study was performed on green pellets obtained through CRMP process. Corresponding shrinkage rate curve shows a two-step densification in dynamic conditions, with the presence of a low temperature extremum, at 1100 K, added to the main densification process which is located between 1500 K and 1700 K. To fully understand this non-common densification behaviour, an iterative study was performed on $Ce_{1-x}Gd_xO_{2-\delta}$ surrogate compounds, looking for chemical or microstructural causes.

2. Experimental

The synthesis route of $U_{0.9}Am_{0.1}O_{2\pm\delta}$ and $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) microspheres (with an average diameter of 300 µm) was the same as described in previous works presented by Remy *et al.*[6,7] and Caisso *et al.*[8], based on the use of exchange resin microspheres as amorphous precursors, loaded with UO_2^{2+} and Am^{3+} or Ce^{3+} and Gd^{3+} cations. Their thermal conversion thus leads to the formation of required mixed oxides microspheres used for compaction.

Room temperature (RT) X-Ray diagrams were recorded on powdered oxide microspheres using a Bruker D8 Advance apparatus equipped with a Cu K_α radiation source and a linear Lynx-Eye detector, in a θ-θ Bragg–Brentano configuration. The step was of 0.02° with a time per step of 0.3 s, for an angular domain from 25 to 120° 2θ. Lattice parameter of the synthesized compound was determined using the Fullprof Suite software [9,10], with a Le Bail method for refinements [11]. Crystallite size was determined using the Halder-Wagner Langford analysis (HWL) [12], via integral breadth method. The instrumental resolution function was calibrated using a LaB_6 NIST standard. Specific surface area of the microspheres was determined by the BET method using a Micromeritics Gemini 2360 Surface Area Analyzer with nitrogen adsorption. Measured specific surface areas can be converted into an equivalent particle diameter, estimated via the following equation:

$$d_B = \frac{6 \times 10^3}{\rho_{th} \times S_{BET}}$$

where: S_{BET} is the specific surface area given in $m^2.g^{-1}$; d_B represents the average spherical particle size in nm; ρ_{th} is the bulk density of the mixed oxide $Ce_{0.8}Gd_{0.2}O_{1.9}$ in $g.cm^{-3}$and equals to 7.232 $g.cm^{-3}$ [13].

Oxide microspheres were uniaxially pressed using 5 mm-diameter three-part die, under different pressures, with a Retsch PP25 press. A constant mass of microspheres equal to 250 mg was weighted to fabricate each green pellet. Dilatometric measurements were performed on as-pressed pellets using a Setaram SETSYS vertical dilatometer. Microstructure and morphology of converted microspheres and pellets before and after sintering were characterized through Scanning Electron Microscopy (SEM) observations, using a Supra 55 ZEISS instrument. Mercury