Amerindium based pyrochlore for HELIOS irradiation experiment

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Abstract – Transmutation of highly active long-lived nuclides into shorter life nuclides is a promising option for the reduction of the nuclear waste radiotoxicity. Previous irradiation experiments which were carried out on 241Am bearing spinel targets have shown a significant volume swelling that results from helium production. As a consequence, the helium release and trapping is considered as a key parameter for fuels and targets design. In this way, HELIOS irradiation experiment aims to increase knowledge between microstructure and in pile fuel behaviour for minor actinides transmutations in heterogeneous mode: “once through”. For this program, five pins containing either Am based cercer or cermet (solid solution) were prepared. The CEA was responsible for fabricating the pin containing Am2Zr2O7 pyrochlore in a MgO matrix which was chosen for its satisfying thermal property and irradiation behaviour. R&D and fabrication steps carried out in Cadarache and Atalante facility to achieve the compound preparation are described in this paper. The first results on the obtained pyrochlore show that the materials exhibit the expected properties.

INTRODUCTION

The HELIOS irradiation experiment prepared under a European cooperation program will test the performance of new compounds for the transmutation of minor actinides in heterogeneous mode [1-2]. The HELIOS irradiation in the Petten High Flux Reactor is designed to test new targets comprising pyrochlore or yttriated zirconia with high americium content (18 wt%) that should present a very stable crystalline structure under irradiation [1-2]. The experiment comprises five pins containing cercer, solid solution and cermet [3]. The CEA was responsible for fabricating the pellets for Pin 1, consisting in americium pyrochlore Am2Zr2O7 macrodispersed in a magnesia matrix with open porosity. Magnesia was selected as a matrix material for its good thermal conductivity and neutron resistance. Macrodispersion of pyrochlore in the compound should limit its interactions with the matrix, and the microporosity constitutes a release path to the cladding plenum for helium arising from alpha decay and for volatile fission products. This work describes the preparation of the pellet column for the HELIOS irradiation. Am2Zr2O7 pyrochlore was obtained by blending americium and zirconium oxides. It was then dispersed in a porous magnesia matrix. The resulting ceramic-ceramic (cercer) pellets were visually satisfactory, with 8.5% porosity.

PELLET FABRICATION PROCESS

The pellets were fabricated with a classical powder metallurgy process. The process flow diagram in figure 1 describes the steps detailed in the following paragraphs. After sintering, the
resulting material was a zirconium and americium oxide CERamic-CERamic composite with pyrochlore structure diluted in an MgO matrix.

Fig. 1: Fabrication procedure

**Pyrochlore synthesis**

The pyrochlore synthesis process is based on the results of pre-tests with Ce$_2$Zr$_2$O$_7$ and Pu$_2$Zr$_2$O$_7$ [1], with particular attention to the heat treatment. To control the zirconium concentration in the future pyrochlore, zirconia was oven-dried for 24 h. After oven-drying the powder was conserved under dry conditions. The quantity necessary was then weighed out and immediately blended with americium oxide. The two oxides AmO$_2$ and ZrO$_2$ were blended in an oscillating ball mixer-mill for 45 minutes at 15 Hz to ensure satisfactory homogeneity and particle size distribution. The milling media were made of stainless steel, as experience had shown no appreciable pollution by the steel. The mixture was transferred to an alumina crucible and firstly heat treated in reducing atmosphere at 1173 K, and then in neutral atmosphere at 1873 K. The resulting aggregate (figure 2) was easily removed from the crucible.

![Fig. 2: Pyrochlore after heat treatment](image)

The mixture was granulated in an oscillating mixer-mill. The powder was screened with a stainless steel mesh to select the final grain size. The finer grains were separated, and those with a too high diameter were milled again.

**Americium-zirconium pyrochlore fabrication**

The magnesia and pyrochlore were mixed in a stainless steel container without milling media. The magnesia-pyrochlore mixture was press-compacted in a three-piece die under a low pressure. The resulting pellets were granulated with a steel screen. The aggregate was submitted to uniaxial pressing using three-parts die at 200 MPa. The punches and die were lubricated with stearic acid. The sintering cycle was carried at 1873K during 4h in neutral atmosphere. The pellets were stored under inert argon atmosphere. Pellets transfers were performed in air; the transfer times were optimized to prevent reoxidation.

**CHARACTERIZATION**

After pressing and sintering, pellets were visually inspected to eliminate those with possible pressing defects. The remaining pellets had no visual defects.

**Density**

The total porosity measured by the difference between the theoretical density and the geometric density was 8.5%. The open porosity could not be measured as the hydrostatic
measurement method could not be implemented at the end of the fabrication process.

**Structural analysis**

The pyrochlore structure was demonstrated by X-ray diffraction analysis. The lattice parameter was estimated at 10.648 Å [3]. With eight patterns the theoretical density of pyrochlore is 8545 kg/m$^3$.

The diffraction patterns in Figures 3 and 4 were obtained at a 3-months interval, and show no structural changes. A slight shift in the pyrochlore peaks toward higher values appeared to occur with aging.

**SEM study**

The composite structure (aggregate size and distribution) was characterized by optical and electron microscope observation combined with image analysis techniques for quantitative assessment. For electron microscopic characterization, each sample was metallized by gold sputtering to a thickness of a few nanometers. The following devices were used:

- optical microscopy: Olympus GX100 with image analysis (particles > 2 µm),
- electron microscopy: JEOL T330A in a hot cell with elemental analysis,
- sputter coating: Polaron SC7640,
- cutoff saw and polisher: Buehler.

**Pellet metallographic morphology**

The following figures were reconstituted from optical microscope images.

![Fig. 3: Pyrochlore X-ray diffraction spectrum on May 5, 2006](image)

![Fig. 4: Pyrochlore X-ray diffraction spectrum on August 4, 2006](image)

![Fig. 5: Radial cross section](image)

![Fig. 6: Axial cross section](image)

Figures 5 and 6 show the radial and axial cross section of a Helios pellet obtained with an optical microscope. The pellet appearance was uniform over the entire surface.
CONCLUSION

Fabrication of $\text{Am}_2\text{Zr}_2\text{O}_7$ pyrochlore compound in the Atalante shielded was successful and confirmed by X-ray diffraction spectrum. The compound was used to fabricate $\text{Am}_2\text{Zr}_2\text{O}_7$-$\text{MgO}$ CerCer pellets with a tailored porosity around 8.5% and an americium volume concentration of 0.69 gAm/cm$^3$. In addition to the fabrication step, the physicochemical properties of the pellets meet the specification requirements. Nine pellets from the fabrication batch were packaged and shipped to ITU Karlsruhe for insertion in the cladding for the HELIOS irradiation experiment.

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