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Fabrication of transmutation fuels and targets: the ECRIX and CAMIX-COCHIX experience

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Abstract

This paper describes the developments and results of the fabrication technology of target materials prepared for the ECRIX and CAMIX–COCHIX experiments concerning the transmutation of americium in uranium-free targets. In these irradiation experiments, planned for the PHENIX reactor, several target concepts will be tested: microdispersed composites of $AmO_{1.6}$ in MgO (ECRIX), micro- as well as macrodispered composites of $(Am,Y,Zr)O_{2-x}$ in MgO and homogeneous $(Am,Y,Zr)O_{2-x}$ (CAMIX–COCHIX) material. Results of the completed fabrication campaign of ECRIX in the Atalante facility of CEA and the pre-qualification tests (with Ce and Pu) for CAMIX–COCHIX at ITU are given.

1. Introduction

Transmutation of long-lived radionuclides is a potential option for reducing the impact of the back-end of the nuclear fuel cycle. Worldwide numerous studies are being undertaken to investigate the feasibility of this option. In France this has been laid down in the law of 1991, and a large programme devoted to transmutation of long-lived radioactive elements is being carried out at the CEA since then [1]. One of the goals of this program is the demonstration of the transmutation of actinides, with emphasis on americium in uranium-free targets.

The choice of the inert matrix for the uranium-free fuels is a key aspect of the research and a significant amount of work has been done in the past decade, particularly by the EFFTRA group [2] and by the CEA through the MATINA experiments [3]. In-pile and out-of-pile studies on a series of ceramics that were initially selected [4] have reduced the number of candidates dramatically. In particular, magnesium aluminum spinel ($MgAl_2O_4$), used in the pioneering EFTTRA-T4 experiment on americium transmutation [5], is no longer considered because of its limited stability under radiation. At present time, the research on ceramic oxides is focussed on two materials: magnesium oxide (MgO) for fast reactor (high power) applications and zirconium oxide for thermal reactor (low power) applications.

In the next series of irradiation experiments that are planned in the PHENIX fast reactor to test the optimized conditions of americium transmutation in a fast or moderated fast flux, several target designs with these materials will be investigated. In the ECRIX experiment two composite targets of americium oxide in MgO (microdispersed) will be irradiated. In the CAMIX–COCHIX experiment [6], in order to minimize helium and fission product damages, new fuel concepts are developed, one homogeneous target (solid solution) of americium oxide in yttria-stabilized $(Am,Y,Zr)O_{2-x}$ and two composite targets of $(Am,Y,Zr)O_{2-x}$ particles in MgO (micro- and macrodispersed) will be irradiated.

The fabrication of these targets has been and still is a real challenge, as it requires the development of new

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technologies that are significantly different from traditional fuel fabrication, in combination with increased difficulties arising from the handling of the highly radioactive americium. At the Atalante laboratories of CEA-Marcoule and the Institute for Transuranium Elements (ITU) in Karlsruhe special facilities have been/are being installed for this purpose. In the Atalante facility of CEA, a classical powder metallurgy process has been used successfully for the ECRIX fabrication [7]. At ITU an infiltration technique (INRAM) has been tested for the fabrication of $(Am,Y,Zr)O_{2-x}$ particles [8]. The mechanical blending of these particles with MgO has been optimized for the CAMIX–COCHIX experiment, with cerium and plutonium as stand-in for americium [9]. The results of these developments and tests will be described in this paper, with emphasis on the efforts to optimize the processes to yield materials within the required specifications.

2. General characteristics of PHENIX transmutation targets

In all fuel materials the americium content is 0.7 $g\,cm^{-3}$. The main characteristics of each target are the following:

- *ECRIX*: CERamic–CERamic type composite in which particles of americium oxide are microdispersed in an inert matrix of MgO. The size of the americium containing particles is between 1 and 50 μm.
- *CAMIX-2*: CERamic–CERamic type composite in which particles of an americium–zirconium–yttrium oxide compound $(Am_{0.20}Zr_{0.66}Y_{0.14})O_{1.83}$ are microdispersed in a MgO matrix. The size of the americium containing particles is between 30 and 50 μm.
- *COCHIX-3*: CERamic–CERamic type composite in which particles of an americium–zirconium–yttrium oxide compound $(Am_{0.20}Zr_{0.66}Y_{0.14})O_{1.83}$ are macrodispersed in MgO. The particle size of the americium particles is between 90 and 130 μm.
- *CAMIX-1*: Homogeneous compound of an americium–zirconium–yttrium, $(Am_{0.06}Zr_{0.78}Y_{0.16})O_{1.89}$, mixed oxide.

The pellet diameter, and thus the gap between pellet and cladding, has been optimised in the design studies. This gap is a function of the thermal diffusivity and will allow the eventual swelling of the pellet material. The mean diameter of the ECRIX pellets was between 5.0 and 5.5 mm and the height between 5.5 and 7.5 mm. The target O/Am atomic ratio is between 1.5 and 1.8. For each target, general characteristics of the pellet materials are described in Table 1.

3. Targets fabrication

3.1. ECRIX pellets

The fabrication of the ECRIX targets has been performed at the Atalante laboratories of the CEA-Marcoule nuclear facility. Magnesia powder was mixed with americium oxide by a classical powder metallurgy route (Fig. 1). Commercial magnesia powder (CERAC M-1017) was calcined at 1073 K to eliminate adsorbed water. Then the powder was compacted into disks at 150 MPa, which were crushed and sieved to obtain granules with 150 μm diameter. Americium oxide was dissolved and purified by chromatographic extraction of Am (VI). Once reduced, Am (III) was precipitated as americium oxalate, then filtered, calcined at 1073 K and sieved to produce pure and fine americium dioxide granules (80 μm). Then, the americium oxide and MgO granules were mixed by an ellipsoidal movement in a simple mechanical mixer. In order to improve the distribution homogeneity of both components, the mixed powder was compacted into pellets at 150 MPa, then pulverized through a particle sieve in a special design granulator with low powder retention to obtain granulates of about 150 μm in diameter. These granules were mixed again and re-pressed in a single acting press at 250 MPa to fabricate the desired pellets. The green pellets were

Table 1
Theoretical characteristics of the materials

	Pellets characteristics			
	ECRIX	CAMIX-2	COCHIX-3	CAMIX-1
Am compound	$AmO_{1.6}$	$(Am_{0.20}Y_{0.14}Zr_{0.66})O_{2-x}$	$(Am_{0.20}Y_{0.14}Zr_{0.66})O_{2-x}$	$(Am_{0.06}Y_{0.16}Zr_{0.78})O_{2-x}$
Am compound (vol.%)	6.7	30	30	100
Am content ($g\,cm^{-3}$)	0.7	0.7	0.7	0.7
Am content (wt%)	17 ± 2	14.3 ± 1	14.2 ± 1	12.0 ± 1
Theoretical density	4.10	4.66	4.66	6.29
Particle size (μm)	<50	30–50	90–130	Homogeneous
Pellet diameter (mm)	5.18		To be settled	

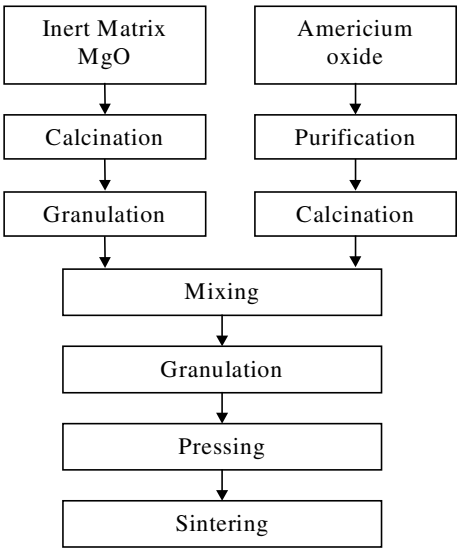

Fig. 1. ECRIX fabrication flowsheet.

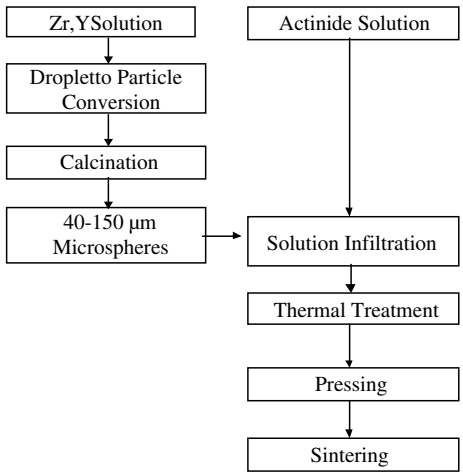

Fig. 2. CAMIX-1 fabrication flow sheet.

sintered in two steps, first at 1273 K during 4 h in Ar/H_2 atmosphere to reduce the americium oxide, then the temperature was increased up to 1773 K in argon atmosphere and remained for 4 h to keep the neutral conditions without damage to the furnace. Four batches of pellets have been fabricated for two target pins and the measurement of material characteristics and properties [10].

3.2. CAMIX–COCHIX pellets

The fabrication of the CAMIX-1, CAMIX-2 and COCHIX-3 targets will be performed in the Minor Actinide Laboratory (MA-lab) in ITU. As the MA-lab will be taken in operation in 2003, the tests have been made with Ce and Pu in non-active laboratories (Ce) or conventional glove boxes (Pu).

The fabrication process for the fuel material of CAMIX-1 is shown schematically in Fig. 2. Yttria-stabilized zirconia (YSZ) spheres were produced by a SOL–GEL process. Feed solutions with a determined Y/(Zr + Y) ratio of 0.17 were prepared from Zr oxychloride and Y chloride in distilled water. Following addition of a surface-active agent and an organic thickener, the solution was dispersed into droplets by a rotating cup atomiser. The droplets were collected in an ammonia bath, where spontaneous gelation occurs. After ageing, the resulting spheres were washed with distilled water, dried using an azeotropic (C_2Cl_4) distillation procedure, and calcined at 1123 K. These spheres have a polydisperse size distribution in the 40 and 150 μm range, a specific surface area of 67.2 $m^2\,g^{-1}$, and their porosity was about 80% of the theoretical density. X-ray diffractometry (XRD) of sintered beads indicated a cubic crystal structure with a lattice parameter of 0.5140 ± 0.0003 nm, which is in agreement with the value for $(Y_{0.15}Zr_{0.85})O_{1.93}$ (0.5139 ± 0.0001 nm).

The calcined spheres were infiltrated with cerium and plutonium nitrate solutions. For cerium, an infiltration solution with various metal concentrations (from 125 up to 200 $g\,l^{-1}$) was used, while for plutonium solutions the metal concentration was 216 ± 1.2 $g\,Pu\,l^{-1}$, which is the maximum obtainable without risk of Pu polymerisation and precipitation.

After each infiltration step they were thermally treated at 1073 K to convert the infiltrated metal nitrates into the corresponding oxides. The metal content was determined by gravimetric analysis of the spheres before infiltration and after the calcination step. The resulting infiltrated beads were free-flowing, and, due to their size and integrity, their physical manipulation does not produce dust in the following fabrication steps. At this stage in the fabrication process, little interdiffusion occurred and XRD measurements show that the materials are comprised of PuO_2 or CeO_2 phases dispersed in YSZ.

The fabrication process for the CAMIX-2 and COCHIX-3 pellets, shown schematically in Fig. 3, partially overlaps with that of CAMIX-1. YSZ spheres were produced as described above. The spheres were then sieved and specific size fractions, and 40–63 and 100–125 μm were selected. The sphere size fractions were then infiltrated in two consecutive steps with either a cerium nitrate solution (300 $g\,Ce\,l^{-1}$) or a plutonium nitrate solution 216 ± 1.2 $g\,Pu\,l^{-1}$. After each infiltration step, they were thermally treated at 1073 K in air for 2 h to convert the infiltrated nitrate phase to the corresponding oxide. The metal content is determined by gravimetric analysis of the spheres before infiltration and after the calcination step. Then the $(Me,Y,Zr)O_{2-x}$ (Me = Ce,

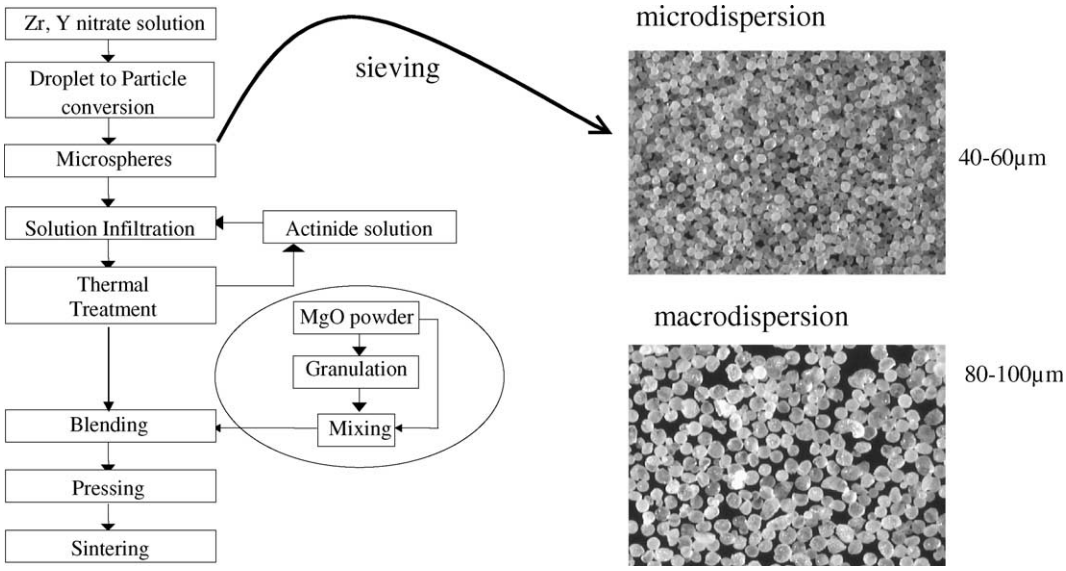

Fig. 3. CAMIX-2 and COCHIX 3 fabrication flowsheet.

Pu) phase was mixed with MgO. A commercial MgO powder was calcined at 1073 K and compacted into discs, which were crushed and sieved to obtain granules. A major difficulty lies in the different densities of the infiltrated spheres and the powder, which can lead to agglomeration and segregation. Systematic investigations were performed to determine the optimum size of the MgO granules. These studies have shown that 50–71 μm MgO granules are required to produce CERCER pellets without cracks and with a random distribution of isolated spheres. Pressing tests on MgO granules without inclusion of YSZ spheres gave densities greater than 95% of the theoretical value (TD) after sintering. For composite fabrication the granules were mixed with the infiltrated YSZ spheres and compacted into pellets following addition of zinc stearate as lubricant. Tests have been performed to identify the maximum number of pellets that can be fabricated from a powder batch without risk of segregation during mixing. Finally, sintering was performed at 1923 K for 8 h in argon.

4. Characterization

4.1. Chemical and physical characteristics

Chemical composition and physical characteristics of the pellets are summarized in Table 2.

4.2. Microstructural characteristics

4.2.1. Homogeneous material CAMIX-1 ($Am_{0.06}Y_{0.16}Zr_{0.78})O_{1.89}$

Visual inspection of the surface of the pellets produced, show that they have a perfect cylindrical geometry and excellent integrity without macro- or microcracks. A pellet was sectioned and polished, and an α-autoradiograph was taken from the polished faces (Fig. 4). The uniform nature of the α-autoradiograph of the pellet indicates that the plutonium is evenly distributed through the pellet. The ceramograph (Fig. 4) indicates it is devoid of cracks or other defects.

Table 2
Chemical composition and physical characteristics of the pellets

Compound	Me[a] (wt%)	Me compound[b] O/Me ratio	Density g cm^{-3}	% TD
ECRIX (composite)	16.6 ± 1	1.62 ± 0.04	3.98 ± 0.02	97 ± 0.5
CAMIX-2 (composite)	14.3 ± 1	–	4.23 ± 0.07	91 ± 1
COCHIX-3 (composite)	14.2 ± 1	–	4.21 ± 0.06	90 ± 1
CAMIX-1 (homogeneous)	12.0 ± 1	1.73	5.73 ± 0.06	90 ± 1

[a] Me: Am for ECRIX and Pu for CAMIX–COCHIX.
[b] $AmO_{0.06}$ for ECRIX pellets, $Am_{0.06}Y_{0.16}Zr_{0.78})O_{1.89}$ for CAMIX-1 pellets, $(Am_{0.20}Y_{0.14}Zr_{0.66})O_{1.83}$ for CAMIX-2 and COCHIX-3 pellets.

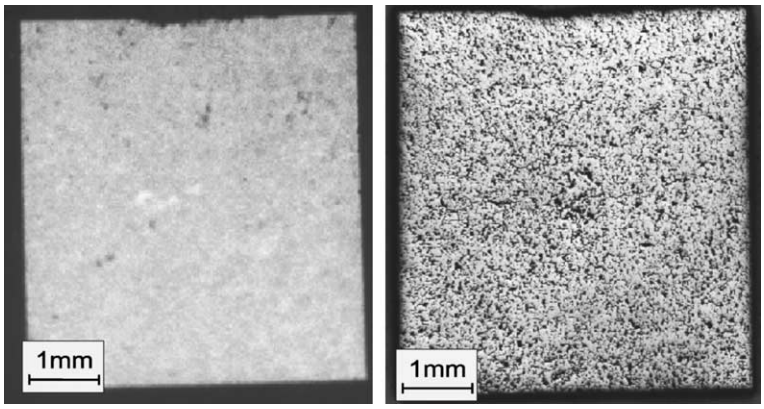

Fig. 4. α-Autoradiograph and optical micrograph of $(Pu_{0.066}Y_{0.157}Zr_{0.777})O_{2-x}$ pellet sectioned in the axial direction.

Table 3
Microstructural characteristics of composite materials

	Max. particles size (μm)	Aspect ratio (D/d)	HR	Actinide phase (vol.%)
ECRIX	>50	–	10–15	–
CAMIX-2	30–50	1.4	12	27 ± 3
COCHIX-3	90–130	1.5	7	27 ± 2

Nevertheless, the contours of original spheres in the pellets can be discriminated, as the porosity is mainly located in the peripheral regions surrounding the original spheres. Almost no pores are observed in the spheres themselves. The same type of porosity distribution was also observed in the YSZ-cerium pellets.

4.2.2. Composite compounds

Ceramographs on axial and radial cross sections have been taken for ECRIX and CAMIX–COCHIX pellets. The microscopy inspection permits observation of the different material and the microstructural characteristics, such as, actinide compound particle size, shape, area and distribution in the matrix and also the gap between the particles and the matrix.

The actinide particle distribution (HR) has been determined by image analysis of the pellet ceramographs, which were divided in more than 10 identical fields. Then, each field was analysed to evaluate the percentage of surface occupied by the actinide particles and the mean value M and the standard deviation σ have been calculated for each pellet. The HR within a pellet has been calculated by using the following formula, where M is the average value and σ the standard deviation of americium particles % (in area) for the whole cross section. Smaller HR values indicate a higher level of microstructural homogeneity (Table 3).

$$\mathrm{HR} = \frac{\sigma}{M} \times 100. \quad (1)$$

Visual inspection of the surface of the composite pellets produced, shows that they have a perfect cylindrical geometry and excellent integrity without macro- or microcracks (see Fig. 5). α-Autoradiograph and ceramograph of each type of pellets confirm CERCER pellets without cracks and with a random distribution of isolated spheres (Fig. 5).

5. Conclusion and outlook

The application of innovative and adapted manufacturing techniques, such as powder granulation or porous material infiltration are feasible for the production of ceramic materials with different concepts. Irradiation of the described ceramic materials is envisaged on the restart of the PHENIX reactor (planned for beginning of 2003). The two ECRIX experimental devices have been already manufactured in Atalante and Phénix hot cells and are ready to be irradiated. For the CAMIX-COCHIX experiments, the R&D performed up to now on cerium and plutonium materials is almost complete. The next step will be the start of the MA-lab operation to allow americium target fabrication. The experimental device with the CAMIX–COCHIX pins should be loaded in the PHENIX reactor at the beginning of year 2004.

These experiments, dealing with americium compounds are of major importance for the entire

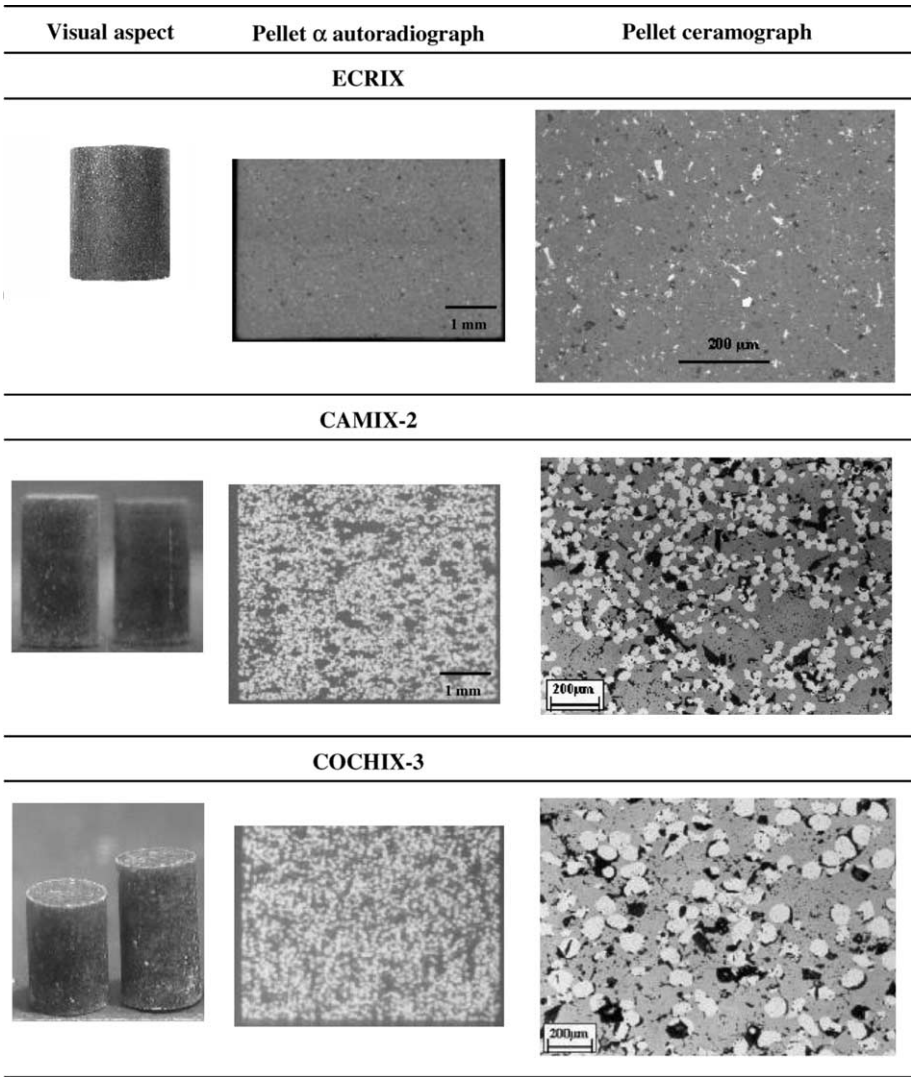

Fig. 5. Aspect, α-autoradiograph and microstructure of the different ceramic composite: ECRIX, CAMIX-2 and COCHIX-3.

CEA transmutation program for the future heterogeneous recycling of plutonium and/or minor actinides targets. This program provides physical and chemical data for model development about materials, pins and device concept. Along with fabrication process testing, these data are necessary to enable a decision on the technical feasibility of transmutation concept for the reduction of long term radioactive waste.

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