

FUEL/TARGET CONCEPTS FOR TRANSMUTATION OF ACTINIDES

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Abstract

Four different concepts for fuels and targets for transmutation of (minor) actinides are discussed in the present paper. These include thorium-based mixed oxides, inert matrix mixed oxide, and composites based on mixtures oxide powders (CERCER) or mixtures of oxide and metal powders (CERMET). Fabrication methods have been investigated, especially taking account of the specific requirements for handling significant quantities of minor actinides (dust-free processes, remote handling). The processes tested at ITU are based on sol-gel and infiltration (INRAM) techniques or combination thereof. The processes are being validated first using cerium and then plutonium as simulants for the minor actinides, before the actual fabrication of Am- and Cm-containing materials begins in earnest following the completion of the construction of specially designed shielded cells (the MA-lab).

1. Introduction

Various fuel cycle concepts for partitioning and transmutation (P&T) of actinides are under discussion at present. In an evolutionary strategy, fast reactors are introduced in which the minor actinides are mixed with the plutonium in a mixed oxide, either uranium-based or eventually thorium-based. In such a multiple recycle scenario, the possibility to reprocess the fuel is of key importance. In a radial strategy, dedicated “transmuters” such as accelerator driven systems are introduced, with the aim to eliminate plutonium and minor actinide in a separate “second stratum” [1]. Dedicated fuel types are considered for this second stratum, which are characterised by a high minor actinide content and a high extent of transmutation. The latter can be achieved best if uranium is omitted from the fuel, as breeding of transuranium elements is avoided. This is especially important when the second stratum is a once-through process.

For the uranium-free fuels a wide variety of alternative matrix materials are considered, true inert material and “quasi” inert materials based on thorium. The actinide phase and the matrix can be combined in a homogeneous fuel form in which the actinides form a solid solution with the matrix, well known from the uranium-plutonium mixed oxide fuels. However, most inert-matrix mixed oxides of this type are generally characterised by a relatively low thermal conductivity. To overcome this, composite fuel forms are considered in which the matrix (a ceramic or a metal) improves the thermal properties of the fuel.

At the Institute for Transuranium Elements (ITU) some of these fuel and target options for transmutation of actinides are being studied, with emphasis on clean and, thus, dust-free fabrication methods for minor actinides (specifically americium and curium). A process consisting of a combination of SOL-GEL and infiltration techniques [2,3] is being developed and used for the fabrication of the following oxide-based fuel/target forms in a pellet-type fuel packing:

- Thorium-based mixed oxide (THOMOX), with the actinides incorporated as a solid solution in a ThO_2 matrix.
- Inert-matrix mixed oxide (IMMOX), where the actinides are incorporated in an yttria-stabilised zirconia (YSZ) solid solution.
- Ceramic-ceramic composite (CERCER), in which the actinides are in (near) spherical YSZ particles which are dispersed in a MgO matrix.
- Ceramic metal composite (CERMET), again with the actinides in spherical YSZ particles, which are dispersed in Mo, Fe or Zr matrices.

Currently these processes are being tested and validated with cerium and plutonium. The actual fabrication of Am- and Cm-containing materials will be performed in shielded cells, which are under construction at present. These cells, which form a complete fabrication chain (the MA-Lab), are equipped with gamma- and neutron shielding in the form of lead (50 mm) and water (500 mm).

2. Thorium-based mixed oxide

The fabrication of thorium based mixed oxide fuels and targets for transmutation can be achieved directly using the sol-gel method to give the $(\text{Th,MA})\text{O}_2$ product. This process has been validated at the ITU for the Uranium analogues in the SUPERFACT and TRABANT irradiation experiments in Phénix and HFR Petten, respectively [4,5]. The particular advantage of the process lies in the wide range of actinide content, which can be obtained. In the SUPERFACT experiment, for example, $(\text{U}_{0.55}\text{Np}_{0.45})\text{O}_2$ and $(\text{U}_{0.6}\text{Np}_{0.2}\text{Am}_{0.2})\text{O}_2$ targets were prepared, while in the TRABANT1 experiment

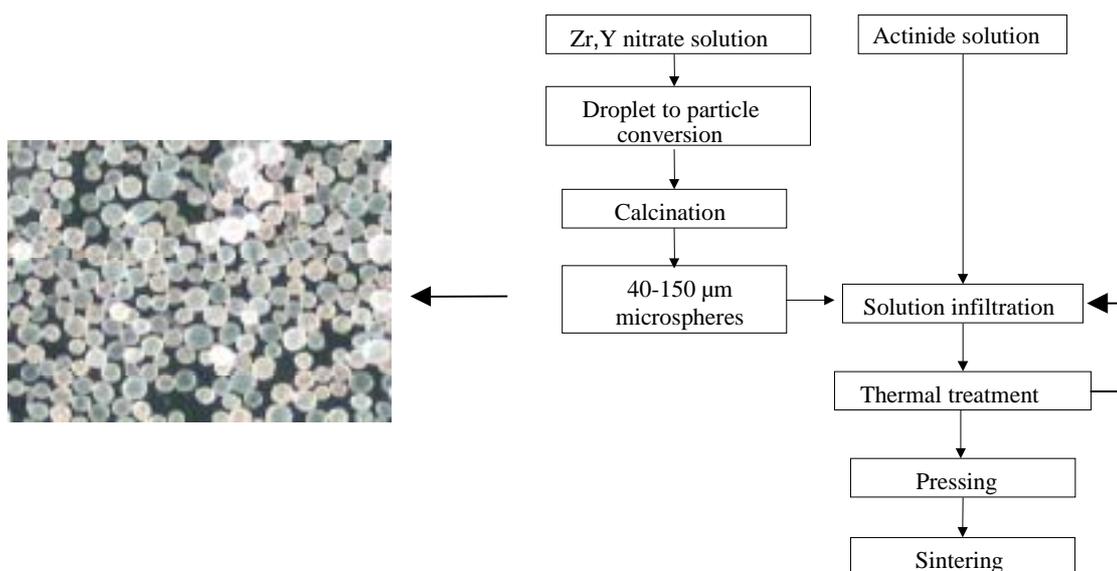
$(U_{0.55}Pu_{0.4}Np_{0.05})O_2$ fuels were prepared. The main disadvantage of the sol-gel method lies in the aqueous liquid wastes produced.

If only relatively small quantities of minor actinide are required (up to 20 mol %), the infiltration (INRAM) procedure, described in detail below for yttria-stabilised zirconia (YSZ) targets, offers an interesting alternative to the sol-gel technique. Due to its partial solubility in weak acid solutions, UO_2 does not readily satisfy one of the basic requirements of the INRAM process. In contrast, ThO_2 is ideally suited, and, given its low activity, microspheres thereof can be produced with limited operator shielding. In a further variation of the process, $(Th,Pu)O_2$ spheres can be manufactured in conventional glove boxes and infiltrated with minor actinide nitrate solutions to give $(Th,Pu,MA)O_2$ products. At the ITU initial investigations have been performed on the production of such $(Th,Pu)O_2$ microspheres. These investigations will be continued and the process tested with the infiltration of uranyl or cerium nitrate solutions, before being validated in the minor actinide laboratory.

3. Inert-matrix mixed oxide

The fabrication process for the inert-matrix mixed oxide fuel/targets is shown schematically in Figure 1. Yttria-stabilised zirconia spheres are produced by a sol-gel process. Feed solutions with a determined Zr/Y ratio are prepared from Zr and Y oxychloride salts. Following addition of a surface active agent and an organic thickener, the solution is dispersed into droplets by a rotating cup atomiser. The droplets are collected in an ammonia bath, where gelation occurs. After ageing, the resulting spheres are washed, dried using azeotropic distillation procedure, and calcined at 1123 K. These spheres have a polydisperse size distribution in the 40 and 150 μm range, and their porosity is about 80%. X-ray diffraction indicates that they have a cubic crystal structure with a measured lattice parameter of 514.0 ± 0.3 pm, which is in agreement with the published value for $(Zr_{0.85}Y_{0.15})O_{1.93}$ (513.9 ± 0.1 pm)[6].

Figure 1. Schematic representation of the fabrication process of the inert-matrix mixed oxide fuels/targets using the infiltration method. A photograph of the polydisperse spheres is shown on the left.

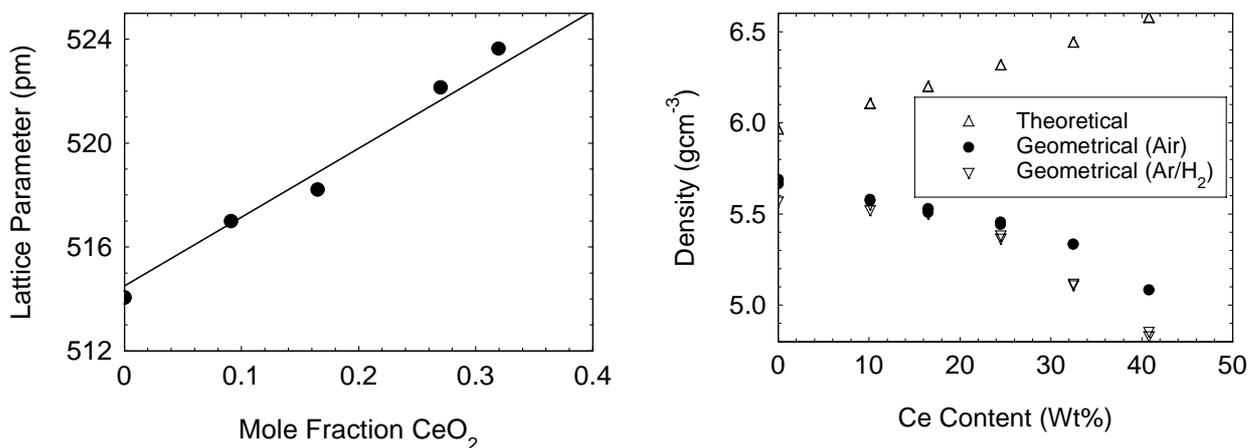


Once calcined the spheres are then infiltrated with a lanthanide (as simulant) or actinide solution. They are thermally treated to convert the infiltrated phase to the corresponding oxide. If higher

quantities of lanthanide/actinide are required this sequence of infiltration – calcination steps can be repeated. The metal content can be determined simply by gravimetric analysis of the beads before infiltration and after the calcination step. The resulting beads are free-flowing (at least for metal contents up to 40 wt%), and can be pressed directly into pellets, following addition of zinc stearate as lubricant. First tests have been made with Ce-nitrate solutions with concentrations of 200 and 400 g·l⁻¹, and second tests with Pu-nitrate solutions with a concentration of 200 g·l⁻¹, which for Pu is the maximum obtainable without risk of polymerisation and precipitation. In the case of Am, however, concentrations of up to 400 g·l⁻¹ can be obtained also.

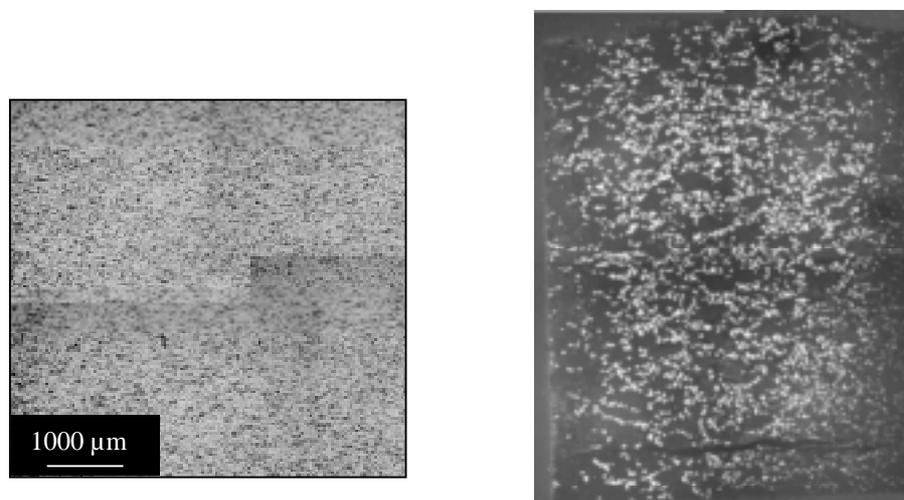
The results of the studies with cerium nitrate (200 g·l⁻¹) indicate that about 40 wt% cerium can be infiltrated into the beads if 5 consecutive infiltration steps are used. X-ray diffraction measurements of the materials after sintering at 1923K for 6 hours in air showed that they have a cubic crystal structure, with the lattice parameter increasing with increasing CeO₂ content as described by Vegard's law (Figure 2).

Figure 2. **Left: lattice parameter of the (Zr,Y,Ce)O_{2-x} spheres as a function of the Ce content; the solid line represent the Vegard's law for the (Zr,Y)O_{2-x}-CeO₂ solid solution.**
Right: geometric density of the pellets as a function of the infiltrated metal concentration.



The density of the pellets manufactured in this way decreases with increasing CeO₂ content (for constant compaction pressure), whereas the theoretical density increases (Figure 2). A ceramograph of a (Zr,Y,Ce)O_{2-x} pellet with 10wt% Ce (Figure 3) indicates it is devoid of cracks or other defects. The experiments with Pu, which are presently in progress, show comparable results. The density decrease may be related to the known change in mechanical properties of stabilised zirconia with increasing extent of stabilisation. It might be overcome by modifying the compaction pressure and the sintering atmosphere; such studies have been initiated.

Figure 3. **Left: Ceramograph of a $(\text{Zr,Y,Ce})\text{O}_2$ pellet with 10% Ce.**
Right: Ceramograph of a $(\text{Zr,Y,Ce})\text{O}_{2-x}$ -MgO composite;
the volume fraction of $(\text{Zr,Y,Ce})\text{O}_{2-x}$ is 20%.

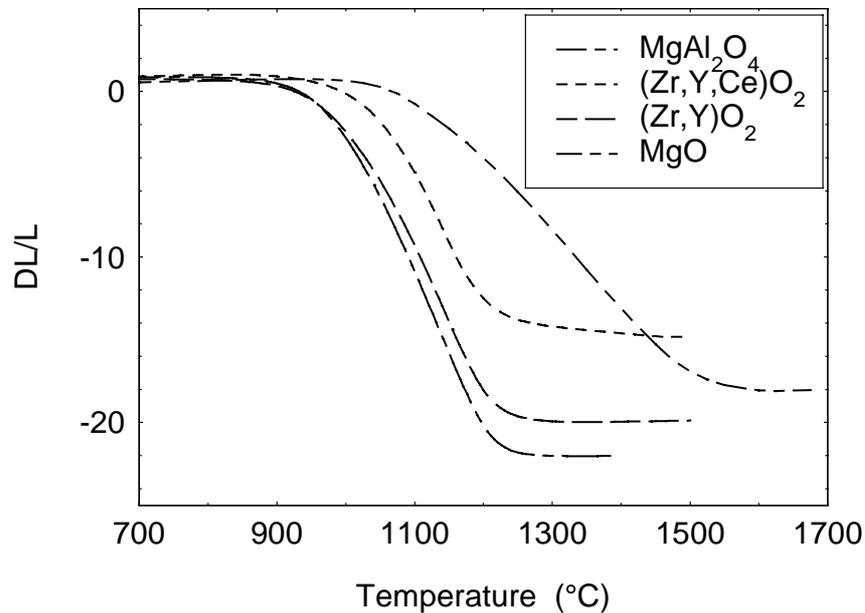


4. Ceramic-ceramic composite

CERCER composite pellets of $(\text{Zr,Y,Ce})\text{O}_2$ -MgO were fabricated by mixing $(\text{Zr,Y,Ce})\text{O}_2$ spheres with MgO granules, using Zinc stearate as lubricant. The pellets were sintered at 1923K for 6 hours in air. The $(\text{Zr,Y})\text{O}_2$ spheres were fabricated by the rotating cup, as described above, and the 80-90 μm and 125-140 μm fractions were selected, by sieving, for infiltration with a Ce-nitrate solution with a concentration of 400 $\text{g}\cdot\text{l}^{-1}$. A commercial MgO powder (CERAC M-1017) was granulated (size fraction 50200 – 80 μm) and either used directly or mixed with the original fine powder. Tests on MgO pellets without YSZ macrospheres showed that by pressing the different mixtures of granules, densities of greater than 95% of the theoretical value were obtained in all cases.

The resulting products in these experiments did not prove satisfactory, which is in contrast to previous work on $(\text{Zr,Y,Ce})\text{O}_2$ - MgAl_2O_4 composite pellets [7]. The $(\text{Zr,Y,Ce})\text{O}_2$ -MgO CERCERs always exhibit many cracks in the pellets, predominantly between the spheres (Figure 3). To understand this behaviour, dilatometer (Netsch DIL 402) measurements of the sintering behaviour of on $(\text{Zr,Y})\text{O}_2$, $(\text{Zr,Y,Ce})\text{O}_2$ spheres, MgO and MgAl_2O_4 were performed. The results shown in Figure 4 indicate distinct differences in the densification of the various materials. It is clear that MgO densifies much more (DL/L = 22.0%) than the $(\text{Zr,Y,Ce})\text{O}_{2-x}$ spheres (DL/L = 14.7%) and, moreover, the densification starts at a somewhat lower temperature. In contrast, the extent of densification of MgAl_2O_4 is significantly less (DL/L = 18.0%) and starts at temperatures above that of the $(\text{Zr,Y,Ce})\text{O}_2$ spheres. This implies that the sintering behaviour of the two powders in the $(\text{Zr,Y,Ce})\text{O}_2$ -MgO CERCER are so distinct so that cracks are difficult to avoid. This would require an extensive investigation to manipulate the properties of both powders to match another one. Tests on calcining the $(\text{Zr,Y,Ce})\text{O}_2$ at lower temperature proved unsuccessful, as it appeared that the organic additives were not sufficiently removed from the spheres. Preliminary tests on calcining the MgO granules at higher temperatures (up to 1273 K) were also unsuccessful as the sintered pellets show multiple cracks. A solution thus must be found by modification of the sintering properties of the MgO powder. Alternatively, one could consider the reduction of the size of the beads, which will reduce the stresses during sintering also. This will, however, have a penalty with respect to the undamaged volume fraction in the composite during its irradiation in a nuclear reactor.

Figure 4. Densification of MgAl_2O_4 , $(\text{Zr,Y,Ce})\text{O}_{2-x}$, $(\text{Zr,Y})\text{O}_{2-x}$, and MgO as a function of temperature.

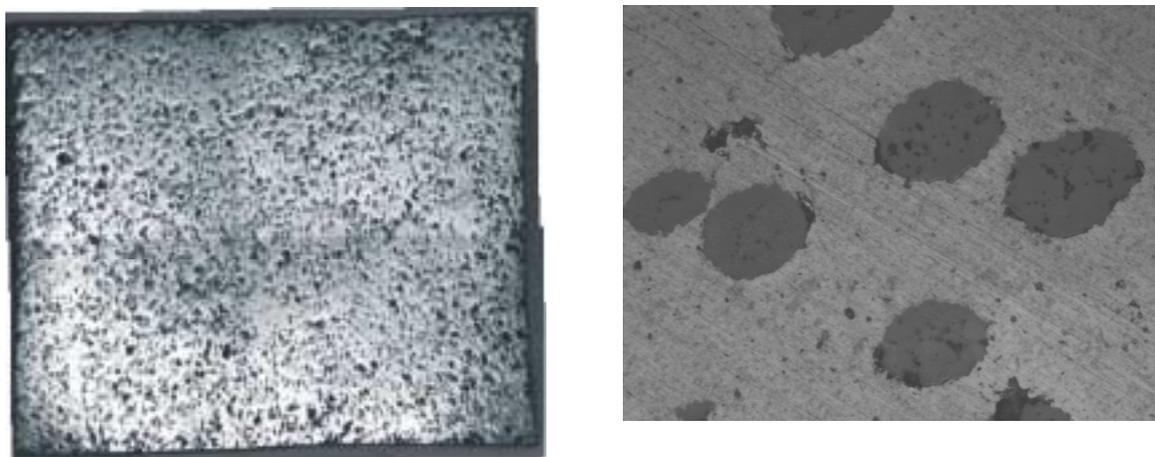


5. Ceramic-metal composite

CERMET composite pellets of $(\text{Zr,Y,Ce})\text{O}_2$ -Mo were fabricated by compaction of a mixture of the cerium infiltrated sieved fraction (112 – 125 μm) of the beads and commercial Mo powder (Merck) with addition of zinc stearate as lubricant. The pellets were sintered at 1923K in Ar/H_2 .

The densities of the $(\text{Zr,Y,Ce})\text{O}_2$ -Mo CERMETS were typically in the order of 90-92% of the theoretical value. Visual inspection of the pellet surface and the ceramographs of sectioned samples show that they have perfect cylindrical geometry and excellent integrity without macro or micro cracks (see Figure 6). Nevertheless due to the fact that there is a very distinct difference in hardness of the two materials, many spheres were pulled out of the matrix during polishing, resulting in “apparent” porosity in the pellet. A typical ceramograph of a $(\text{Zr,Y,Ce})\text{O}_2$ -Mo is shown in Figure 6. It should also be noted that there is excellent physical contact between the Mo matrix and the macrospheres so that the maximum benefit of the high thermal conductivity of the Mo is achieved.

Figure 6. Left: ceramograph of a(Zr,Y,Ce)O_{2-x}-Mo CERMET; the amount of (Zr,Y,Ce)O_{2-x} is about 20 vol%. Right: Detailed image of the sphere-matrix interface in a (Zr,Y,Ce)O_{2-x}-Mo CERMET.



6. Conclusions and outlook

The results presented in this paper have demonstrated the feasibility of the fabrication of homogeneous zirconia- and thoria-based fuels for transmutation of minor actinides, using liquid processes such as sol-gel and infiltration. Though our experiments have been made with cerium and plutonium as simulants of americium, the previous experience with these techniques obtained in the SUPERFACT and EFTTRA experiments [2,4] gives confidence that they can be extended to americium without difficulties. The sol-gel technique offers the highest flexibility with respect to the actinide content in the material, but it produces significant amount of active liquid waste, which could be recycled in an industrial process. The active liquid waste is minimal when the infiltration technique is used, but the actinide content that can be obtained is limited. Moreover, the properties of the infiltrated YSZ powder change with increasing amount of infiltrant, resulting in an increase of the porosity with increasing infiltrated metal content. Though this is favourable to manage the helium accumulation typical for MA fuels [8], it will lead to a decrease of the thermal conductivity. Especially for ZrO₂-based material, where the thermal conductivity is already a limiting factor for its application, this may be unacceptable. Experiments to investigate the cause of these low densities have therefore been started.

The results presented in this paper for the (Zr,Y,An)O₂-MgO composite fuels are not promising. It seems technically difficult, if not impossible, to obtain fault-free composite pellets when the dispersed phase consists of spherical particles with a size of greater than 100 μm, which is required, if the radiation damage to the matrix is to be minimised [9]. The effect of reducing the size of the dispersed particles on the fabrication process will be tested. Smaller particles would lead to greater damage of the matrix during irradiation, but this penalty could be tolerated, if the improvement of the thermal behaviour is the decisive requirement.

Promising results have been obtained for (Zr,Y,An)O₂-Mo composite fuels, but the Mo matrix is not the prime candidate for CERMET fuel. Therefore the study of steel-based CERMET fuels will be initiated.

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