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Granulation and infiltration processes for the fabrication of minor actinide fuels, targets and conditioning matrices

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Abstract

The impact of Pu and Am, two elements that potentially pose a long term hazard for the disposal of spent nuclear fuel, can be abated by their reintroduction into the fuel cycle for transmutation. Such transmutation targets can be fabricated by a sol gel method for the production of porous inactive beads, which are then infiltrated by Am solutions. Following calcination, compaction into pellets and sintering, the product is obtained. At its heart, the sol gel process relies on an ammonia precipitation, so that it is not universally applicable. Therefore, an alternative is sought not just to overcome this chemical limitation, but also to simplify the process and reduce waste streams. The new concept utilises powder metallurgy routes (compaction, crushing and sieving) to produce porous, almost, dust free granules, which are infiltrated with the actinide nitrate. The method has been developed using yttria stabilised zirconia and alumina, and has been demonstrated for the production of Al_2O_3–AmO_2 targets for neutron capture investigations. The results are very promising and meet light water reactor fuel specifications. In addition, the process is ideally suited for the production of ceramic matrices for conditioning actinides for geological disposal.

1. Introduction

Processes for the fabrication of composite target materials for the transmutation of actinides or their conditioning for long term storage need to be developed. Due to the radiation hazard and high activity of the minor actinides, such fabrication processes pose particular requirements. Most importantly, they should not produce dust; they should be compatible with extensive automation and, only when necessary (e.g. intervention for maintenance), with remote operation. Finally, the wastes and scraps produced during fabrication should be minimal [1–3]. The infiltration method [4] is one of the most promising processes for the production of these materials. It is based on the preparation of porous precursor beads by a sol gel external gelation route [5], and their infiltration by an actinide nitrate solution. The sol gel beads, themselves, are sufficiently large and mechanically stable, that they can be handled without dust being produced. The infiltration method has the advantage that inactive precursors, such as porous yttria stabilised zirconia (YSZ) beads can be prepared in conventional laboratories or production plants. If PuO_2 or $(U,Pu)O_2$ beads are required, they can be produced using currently

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available technology in standard Pu gloveboxes. The minor actinide phase, e.g. Am, must be introduced by the infiltration technique in a special facility, with shielding beyond that prevalent in current MOX production plants. The recently commissioned Minor Actinide laboratory (MA LAB) at the JRC-ITU is such a laboratory scale facility. The fabrication facility must also have the capability to compact the infiltrated beads into pellets, and sinter them to give the final product, which can be a single phase solid solution, preferably with a cubic structure [3] or a multiphase composite material.

Although the infiltration process has been successfully deployed at the JRC-ITU, further process developments are not excluded. In particular, alternative processes for the production of the porous beads can overcome some disadvantages of the sol gel route. In particular, it produces liquid wastes, whose disposal today, even in standard inactive chemical laboratories, can be costly. Furthermore, the sol gel external gelation process is based on an ammonium hydroxide precipitation, and is therefore not compatible with all elements. This is perhaps a greater issue for the production of matrices for the conditioning of actinides for long term disposal, as many such compounds are based on silicates or phosphates [6]. To overcome these issues, a process based on the granulation of powders is being developed. This alternative granulation concept is based on powder mixing, compaction, and crushing to give granules, and is followed by a sieving step to yield particles with a size and mechanical stability, that do not produce dust. These granules are then introduced into the shielded facility and are infiltrated by the actinide nitrate solution. Following drying and calcination to convert the nitrate to oxide, the infiltrated granules are pressed into pellets, which are sintered to give the final product. Both production routes are compared in Fig. 1. In these investigations, the granulation process has been developed, and its limitations assessed and compared to the sol gel route in terms of dust produced, and most importantly, in terms of the quantity of actinide that can be infiltrated in a single infiltration step. In these tests, yttria stabilised zirconia (YSZ) sol gel beads and granules have been used. Ce has been employed as a surrogate for Am. Finally, the process has been demonstrated for the production of dedicated Al_2O_3–AmO_2 targets for the determination of neutron cross section data at JRC-IRMM.

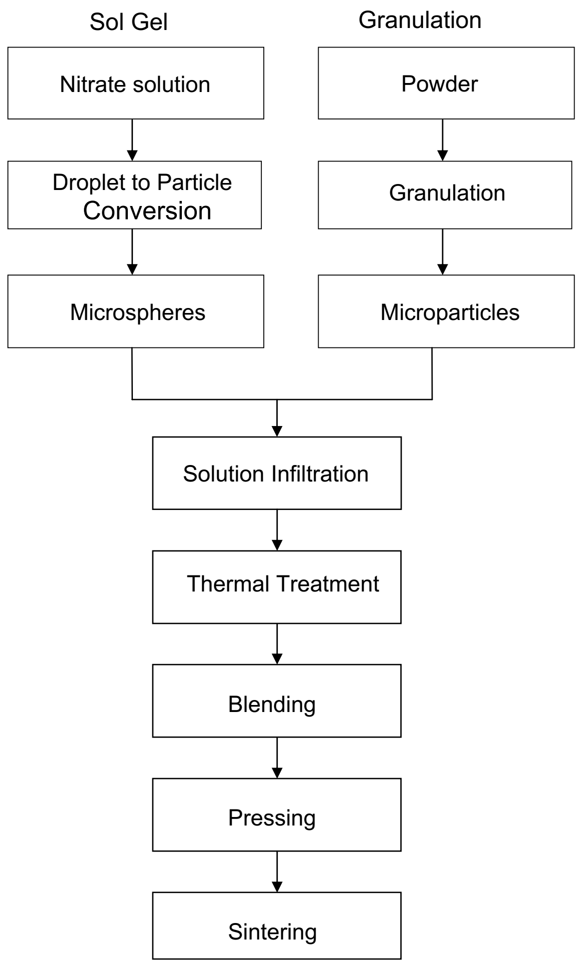

Fig. 1. Comparison of the sol gel and granulation fabrication processes.

2. Experimental, materials and equipment

The following starting materials were used in these experiments:

- Y_2O_3 (Alfa Aesar, 99.99% pure metal basis, <10 μm particle size).
- ZrO_2 (Alfa Aesar, 99.7% pure metal basis excluding Hf, Hf < 75 ppm).
- Nd_2O_3 (Alfa Aesar, 99.99% pure metal basis).
- Al_2O_3 (Baikowski Chimie, ultra high purity).
- YCl_3 (Alfa Aesar, 99.99% REO).
- $ZrOCl_2$ (Alfa Aesar, 99.9% metal basis).
- Methocel (Dow chemicals).

The oxide starting materials for the granulation process were prepared by manual mixing of the powders, or using a simple mill, referred to here as a ‘coffee mill’, as it consists of a container with a single internal rotor rotating at high speed. Powder compaction was performed using bi-directional hydraulic presses from P.O Weber and Laufer in the inactive laboratories and the actinide handling gloveboxes, respectively. Sintering was made in the 1873–1923 K range, with Ce and Am based samples being sintered under air and Ar/H_2, respectively.

YSZ porous beads were made using the sol gel external gelation method [3,5]. In this process, the Zr and Y chloride salts were dissolved in the required relative proportion in water, and then the viscosity was increased by the addition of the polymer methocel. This broth solution was atomised using a rotating cup disperser, and the droplets were collected in an ammonia bath, where gelation took place to form the hydroxide. Subsequent drying and calcination (1073 K) steps completed the conversion of the hydroxide to give porous oxide beads.

For the infiltration tests, the cerium solution was prepared from the nitrate salt, while the Am solution was prepared by dissolution of the oxide in 7 M nitric acid. Infiltration was always achieved by addition of the metal (Ce or Am) nitrate solution to the granules or beads until the incipient wetness point was reached. At this point, the solid has just transformed to a suspension, and no excess liquid is present.

X-ray powder diffraction (XRD) was performed on samples produced by both methods to determine the crystalline phases present and their lattice parameters. Measurements on granulation and sol gel samples were made using Phillips PW1050/70 Bragg–Brentano and Siemens D500/501 diffractometers, respectively. The incident irradiation was provided in both cases by CuK_α X–ray sources. The diffraction patterns were systematically analysed by a Rietveld-type profile refinement method using the ‘Fullprof’ [7] or ‘Powder cell’ [8] software packages.

3. Results and discussion

3.1. Yttria stabilised zirconia prepared by sol gel and granulation

The YSZ granules were prepared from the appropriate relative quantities of the oxide powders to give the desired Y/(Zr + Y) molar ratio. The powders were mixed either by simple manual blending or milling (20 times) with the ‘coffee mill’ for intervals of 20 s. The milling procedure is the more efficient of these two methods, as it produces finer particles. It is certainly not as efficient in the production of micronised powders as either ball or attrition mills. The latter mill systems require very large powder quantities, and should be considered for a larger scale demonstration of the granule production method.

The blended or milled powders were compacted in the bidirectional press at pressures between 100 and 600 MPa. The resulting disks were crushed to give granules and then calcined at 1073 K under air for 2 h, to remove moisture and other impurities that might have been incorporated in the granulation process. Granule fractions between 40 and 120 μm were selected by sieving the main batch. This size range is also typical of beads produced by the sol gel method, and generally is suitable for pellet pressing, and minimising dust generation. Sol gel YSZ beads were produced by the external gelation method for comparison. Solutions of the yttrium and zirconium chloride salts were mixed in the appropriate quantities and the Y/(Y + Zr) ratio was determined by IC/ICPMS. The beads produced by this method were also in the 40–120 μm size range. They were used without sieving.

Samples produced by the granulation and sol gel routes were taken, and the incipient wetness point measured. For this purpose water was infiltrated into a given quantity of the granules or beads. The quantity of water infiltrated until the incipient wetness point is reached provides a measure of the porosity of the material. It is this porosity that ultimately determines the quantity of an actinide, which can be infiltrated into the material. When the actinide, or its Ce surrogate, is infiltrated, the material is allowed dry overnight and then calcined at 1073 K to convert the infiltrated nitrate into the oxide.

The porosities of the beads produced by the granulation blending and milling methods are given in Table 1. The measurements indicate that the powder blending method does not dramatically influence the porosity of the granules, though those prepared by the milling procedure were about 15% more porous than those prepared by manual blending of the powders. In addition, the compaction pressure appears to have had little influence on the porosity in either case.

A comparison of the amount of Ce that can be infiltrated into the granules and sol gel beads is shown in Fig. 2. Again, it was noted that the Ce

Table 1
Porosity of the granules determined by the normalised volume of water infiltrated to reach the incipient wetness point

Compaction pressure (MPa)	Manual blending ($ml\ g^{-1}$)	Blending by coffee mill ($ml\ g^{-1}$)
100	0.30	0.37
200	0.32	0.34
400	0.30	0.32
600	0.32	0.35

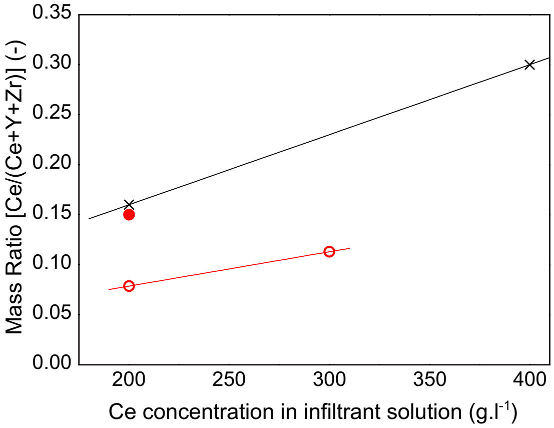

Fig. 2. Ce infiltration into YSZ sol gel beads (**x**) and granules (○) as a function of Ce concentration in the infiltrant solution. A second infiltration into the granules is also shown (●).

infiltrated into the granules was independent of the blending or milling route used in their production. In contrast, however, the quantity of Ce that can be infiltrated into the sol gel beads is at least a factor of two higher than that infiltrated into the granules. Nevertheless, about 8% by weight (wt%) of Ce can be infiltrated into the granules using a Ce infiltrant solution of $200\ g\ l^{-1}$, which is entirely compatible with the processing of both Pu and Am nitrate solutions. The results in Fig. 2 also show that repeating the infiltration of the granules following an intermittent calcination step results in a Ce content of ca 16 wt%. This is identical to that achieved by infiltration of sol gel beads in a single infiltration step. When these results are extrapolated to actinide compounds, such quantities (8–16 wt%) are within the range necessary for the production of homogeneous fuels for Pu disposition in light water reactors.

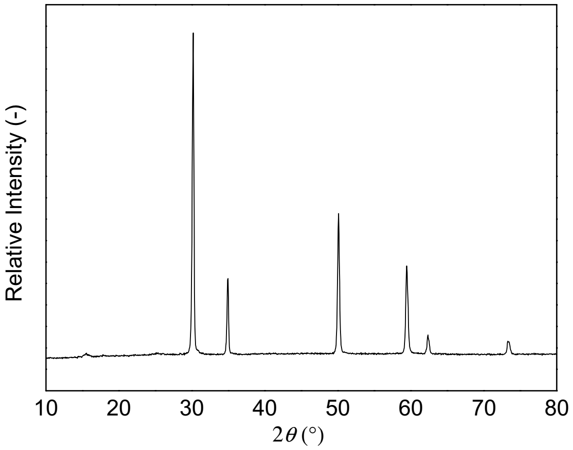

Fig. 3. X-ray diffraction pattern from sintered Ce infiltrated YSZ granules.

X-ray diffraction measurements on products manufactured by the infiltration of Ce, Nd, Pu and Am into YSZ beads produced by the sol gel method all exhibit a single phase cubic structure, which follows the Vegard law as a function of composition [3]. The XRD pattern (see Fig. 3), characteristic of the sintered samples produced from powders prepared by the infiltration of granules, also exhibits a single phase cubic structure.

Preliminary tests on the sintering qualities of these granules have been initiated. The results thus far show that the density of pellets, produced by the compaction of the granules and subsequent sintering, is about 80% of the theoretical density (TD). Further process improvements are required to increase the pellet density beyond 90%TD, which is the typical specification to license a fuel for irradiation in commercial reactors. In a similar pioneering work in this area made at PSI, densities greater than 90%TD for similar inert matrix fuels (IMF) were achieved by attrition co-milling of zirconium, yttrium erbium and plutonium oxides [9,10]. The disadvantage of co-milling the powders lies in the very fine particles produced, and their concomitant dispersal as dust throughout the glovebox facilities. For this reason, such a process is excluded for minor actinide IMF fabrication.

3.2. Production of Al_2O_3–AmO_2 composites by granule infiltration

The ultimate aim in the development of this process is its application to transuranium elements. This has been tested and demonstrated by the infiltration of Am nitrate solution into Al_2O_3 granules. Alumina is not a material considered for IMF, but its low neutron absorption cross section makes it an ideal support material for minor actinides in dedicated experiments to determine neutron cross section data. The samples produced here will be sent to JRC-IRMM in Geel, Belgium, for such measurements.

A series of pre-tests were performed to determine the best means to granulate the Al_2O_3. The powder was compacted using three different compaction pressures (100, 250 and 500 MPa) before being crushed. The resulting granules were sieved to obtain a size fraction between 100 and 500 μm, and were then calcined for 2 h at 1073 K. The incipient wetness point was determined by water and Ce nitrate solution addition. The results (see Fig. 4) show there is a small but significant dependence of the porosity of the granules on the compaction pressure. Using higher pressures results in granules that are less porous. When the incipient wetness point is determined by Ce nitrate addition, a lower porosity of the granules is found. The difference between the results for water and Ce nitrate solution addition is attributed to the higher viscosity of the latter. Table 2 shows the Ce content, in the form of oxide that was infiltrated into these granules. The same trend is observed, though there is some scatter, basically due to the errors introduced in handling the samples between infiltration, calcination and gravimetric steps. Roughly 5.6 wt% of Ce can be infiltrated using a cerium nitrate solution with a concentration of approximately 65 g l^{-1}. This is slightly less than desired quantity, as set in the specifications for the production for the samples for JRC-IRMM, indicating the need for an additional infiltration step, when this metal concentration is used.

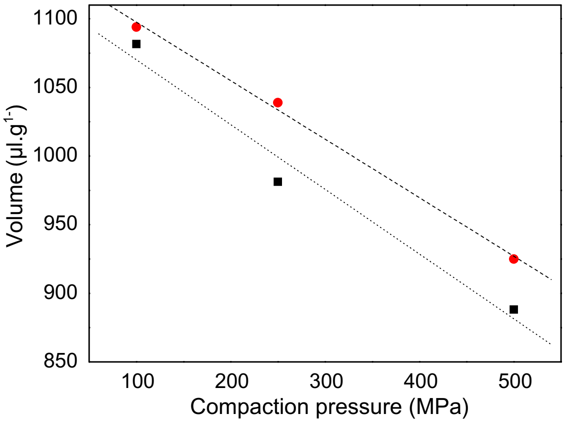

Fig. 4. Normalised volume of water and Ce nitrate solution required to reach the point of incipient wetness in Al_2O_3 granules as a function of compaction conditions.

Table 2
Cerium content (as oxide) following infiltration of alumina granules

Compaction pressure (MPa)	Ce content (wt%)
100	5.98
250	5.62
500	5.80

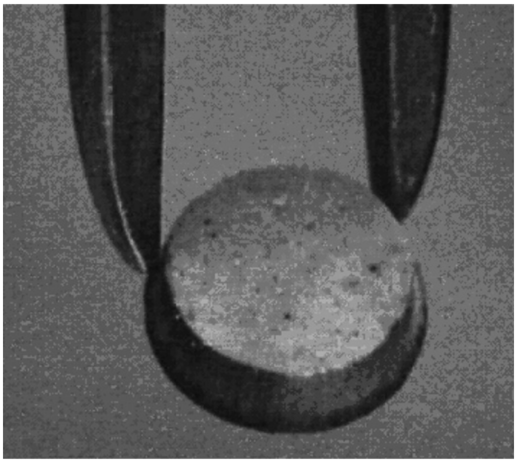

Fig. 5. Sintered Al_2O_3–AmO_2 pellet.

For the production of the Am composites, the Al_2O_3 granules were introduced into the MA LAB, and were infiltrated with an Am nitrate solution (47 g l^{-1}). Following calcination at 1073 K to convert the nitrate to the oxide, the Am content was 4.7 wt%. The material was infiltrated a second time with the same Am nitrate solution and calcined a second time. The Am content was determined by calorimetry and the final Am content was 9.7 wt%. From this powder batch a pellet was pressed and sintered (see Fig. 5). The densities of the green and sintered pellets were 51% and 72% TD, respectively. For these applications, such sintered densities are adequate, but for fuels and conditioning matrices, higher densities are required. The improvement of the process to reach higher densities is the subject of ongoing investigations.

4. Conclusions and outlook

A variation of the infiltration method based on porous granules rather than sol gel beads has been developed and tested. The results demonstrate that the process can be applied both for LWR fuels and for matrices for the conditioning of actinides for long term storage. The granules have a lower porosity than their sol gel counterparts, but their production is easier and less costly. An increase in their porosity could be achieved with alternative processing, such as high energy milling to micronise the powder [10], and possibly the co-milling of a pore former, which should be pyrolysed in a calcination step prior to the infiltration. Such improvements will be tested in the future. These studies will also be extended to conditioning matrices, such as substoichiometric Zr pyrochlores, phosphates and other materials.

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