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# Manufacturing of zirconia microspheres doped with erbia, yttria and ceria by internal gelation process as a part of a cermet fuel

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**Abstract**

Zirconium oxide is an inert matrix candidate for the transmutation of plutonium in light water reactor (LWR). The thermal conductivity of cubic zirconia is however lower than the conductivities of $UO_2$ and MOX. Special designs are therefore necessary to avoid high peaking temperatures close to the melting point in the zirconia pellet. Cermet would be a favorable design to improve the thermal conductivity. The suggested cermet fuel consists of fine plutonium doped stabilized zirconia particles dispersed in a metallic inert matrix. Manufacturing tests on cubic zirconia microspheres were carried out by using the internal gelation process developed at the Paul Scherrer Institute. Gelation was conducted successfully and the sintered spheres had a homogeneous single cubic structure. The lattice parameter of the cubic zirconia was estimated as a function of the Er, Y and Ce atomic fraction using a simplified semi-quantitative formula. On the experimental side, it is necessary to further investigate the ideal fabrication conditions, because some gel spheres were opaque and fragile and most of the sintered spheres were cracked, nicked and porous.

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## 1. Introduction

Plutonium is produced during the operation of uranium-fueled reactors. This increases consequently the civilian plutonium stockpile. Over the last decades the amount of civilian plutonium was enlarged because of the development of nuclear power plants and the postponement or abandonment of fast reactor projects. Moreover, the dismantlement of nuclear weapons also increases the plutonium stockpiles larger [1]. Consequently some efforts are being made to reduce the plutonium stock. One method would be the transmutation of plutonium as mixed oxide (MOX) in light water reactor (LWR). The transmutation rate of plutonium from MOX fuel case, however, is not efficient enough because new plutonium is produced by the uranium neutron activation. An inert matrix based fuel must be used instead of MOX [2,3].

Zirconium oxide is one potential inert matrix candidate [2–4]. Cubic zirconia has a small neutron cross-section, a high melting point, is compatible with the Zircaloy cladding, and is stabile under irradiation. Its thermal conductivity is, however, lower than that of $UO_2$ and MOX. Special designs are therefore necessary to avoid high temperatures close to the zirconia melting point. One possibility is to use annular pellets. Another way would be to use heterogeneous matrices such as cercer (ceramic in an inert ceramic) or cermet (ceramic in a metallic inert matrix). The Japan Atomic Energy Research Institute (JAERI) proposed as specific consolidator so called the rock-like oxide fuel (ROX) which consists of a two-phase mixture of zirconia ($ZrO_2$) and spinel ($MgAl_2O_4$) [5]. Spinel is foreseen to act as a heat conducting media, since it has a higher thermal conductivity than $UO_2$ and MOX. Because metals have

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generally a superior thermal conductivity than oxides, cermet would be a better option to increase the thermal performance of pellet. The suggested cermet fuel consists of fine Pu doped zirconia particles dispersed in a metallic inert matrix. The fuel particles would be about only 400 μm in diameter to reduce its center temperature. It is necessary to apply and optimize a method to produce microspheres of cubic zirconia for cermet fuel fabrication. The internal gelation process developed at the Paul Scherrer Institute was used to fabricate microspheres of cubic zirconia in this study.

## 2. Experimental

### 2.1. Fabrication of spheres by internal gelation method

The fabrication of stabilized zirconia particle including plutonium was adapted to the production of microspheres with a diameter of around 400 μm. This size was selected to decrease the temperature difference between center and surface of the fuel particles in pile. Sol–gel or gelation methods are usually applied to fabricate fine particles. Here PSI's internal gelation process is applied, because the process seems to be well suited for this application. The process is based on the precipitation of metal oxi-hydroxides and the thermal decomposition of the precipitate [6]. The precipitation is achieved by the thermal acceleration of the nitric acid catalyzed decomposition of hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) and urea ($CO(NH_2)_2$). Ammonium hydroxide is formed in a heated droplet of a mixed solution of nitrates, HMTA and urea.

$$C_6H_{12}N_4 + 10H_2O \rightarrow 6HCHO + 4NH_4OH \tag{1}$$

$$CO(NH_2)_2 + 3H_2O \rightarrow CO_2 + 2NH_4OH \tag{2}$$

The ammonium hydroxide causes the precipitation of the metal hydroxides and gelation. Urea, $CO(NH_2)_2$, is also added into the feed solution to obtain good mechanical property of the gel spheres.

The experimental conditions are shown in Table 1. The feed solutions were prepared by mixing the nitrate solutions of Zr, Y, Er and Ce according to the desired composition, HMTA and urea were added into the solution at the mole ratios of 1.20 as HMTA/metal and 1.05 as urea/metal. The feed solutions were dropped into silicon oil heated to about 373 K. The gel spheres were washed by kerosene to remove silicon oil surrounding the gel spheres, and then rinsed by 2 M of ammonium solution to remove by-products such as ammonium nitrate, formaldehyde. The gel spheres were dried at 333 K in air under stationary conditions. The dried gel spheres

Table 1
The experimental conditions and results for gelation of zirconia based materials

| Composition | $Er_{0.05}Y_{0.10}Zr_{0.85}O_{1.925}$ | | | | $Er_{0.05}Y_{0.10}$-$Ce_{0.10}Zr_{0.75}O_{1.925}$ | $Er_{0.05}Y_{0.10}$-$Ce_{0.20}Zr_{0.65}O_{1.925}$ |
|---|---|---|---|---|---|---|
| *Feed solution* | | | | | | |
| Weight (g) | 67.97 | 68.54 | 65.51 | 298.83 | 131.97 | 128.52 |
| Metal (mol kg$^{-1}$) | 0.71 | 0.35 | 0.49 | 0.40 | 0.69 | 0.68 |
| $NO_3$/metal (mol mol$^{-1}$) | 2.47 | 2.47 | 2.47 | 2.46 | 2.88 | 3.27 |
| HMTA/metal (mol mol$^{-1}$) | 1.19 | 1.19 | 1.20 | 1.19 | 1.20 | 1.20 |
| Urea/metal (mol mol$^{-1}$) | 1.04 | 1.04 | 1.05 | 1.04 | 1.05 | 1.05 |
| *Gelation conditons* | | | | | | |
| Temperature of solution (K) | 272 | 271 | 272 | 270 | 270 | 270 |
| Temperature of oil (K) | 375–379 | 376–378 | 375–376 | 373–375 | 373–376 | 376 |
| Gelation time (s) | 7 | 11 | 9 | 12 | 9 | 9 |
| *Drying conditions* | | | | | | |
| Temperature (K) | 333 | 333 | 333 | 373 | 333 | 333 |
| Time (h) | 24 | 240 | 240 | 120 | 40 | 40 |
| *Results* | | | | | | |
| Spheres weight (g) | 10.40 | 4.89 | 6.15 | 18.73 | 19.48 | 19.13 |
| Fraction of good spheres (wt%) | 48 | 50 | 64 | 30 | 86 | 93 |
| Fraction of opaque spheres (wt%) | 1 | 7 | 1 | 7 | – | – |
| Fraction of cracked or hollow (wt%) | 51 | 43 | 35 | 63 | 14 | 7 |
| Gelled sphere diameter (mm) | 1.30 | 0.94 | 1.01 | 0.85 | 1.18 | 1.14 |
| Opaque sphere diameter (mm) | 1.45 | 1.05 | 1.15 | 1.03 | – | – |

were calcined at 773 K to burn out all organic compounds in the spheres, and then sintered at 1873 K for 10 h in air.

### *2.2. Characterization of the spheres*

Thermogravimetry (TGA) and differential thermal analysis (DTA) were performed on the gelled spheres samples. Scanning-electron microscopy (SEM) and the energy dispersive X-ray spectroscopy (EDS) examinations were performed on sintered spheres. For SEM examinations, sintered spheres were embedded in an acrylic resin, and the specimens were cut. The surfaces for observation were mechanically polished with abrasive papers and then subsequently finished by alumina buffing. The polished samples were rinsed with water in an ultra-sonic bath. The surface of the observed section was covered with Au–Pd film to improve the electric conductivity. Photographs taken by SEM examinations were presented as back-scattering electron images (BEI). Furthermore, in order to measure the distribution of elements by EDS, characteristic X-rays of O–Kα, Zr-Kα, Y-Kα, Er-Lα and Ce-Lα were detected. The chemical compositions of these spheres were $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ and $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$.

The X-ray diffraction (XRD) measurements were performed not only to confirm whether the sintered spheres had a cubic structure, but also to investigate the relationship between the lattice constant and the amount of dopant. The sintered spheres examined by XRD and SEM measurements were produced in the same batch. In the present study, X-ray patterns from sintered spheres arranged closely to the glass plate were acquired using an X-ray diffractometer with Cu-Kα radiation operated at 40 keV and 40 mA. The diffraction angle 2$\theta$ was ranged from 20° to 100°, and the Miller indices of the fluorite cubic phase were determined.

## 3. Results and discussion

### *3.1. Gelation and properties of gel spheres*

Gelation occurred successfully in all cases. Table 1 shows gelation time and average size of dried gel spheres for each experimental condition. The gelation-rate was enhanced by increasing the metal concentration in the feed solution. Some gel spheres were transparent and some were opaque. The opaque gel spheres were fragile and some of them were ever nicked. The opaque gel spheres were slightly larger than the transparent ones. These gel spheres were analyzed by TGA and DTA. The results of TGA and DTA are shown in Fig. 1. Endothermic reactions were observed below 473 K. Both gel spheres lost 10% of their weight by these endothermic reactions, probably evaporation of water. Exothermic

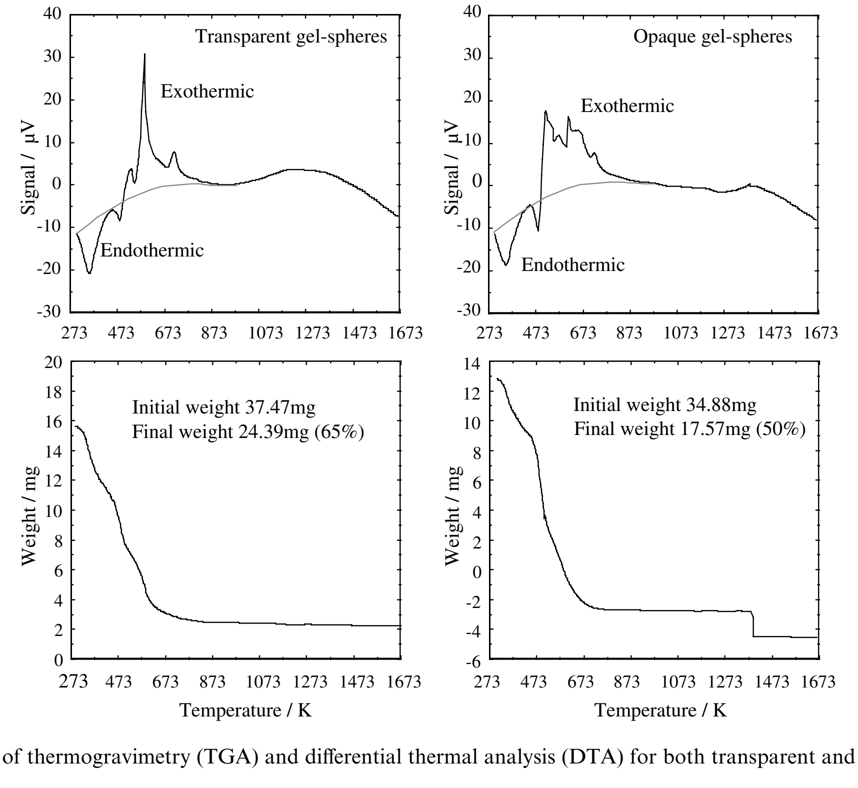

Fig. 1. The results of thermogravimetry (TGA) and differential thermal analysis (DTA) for both transparent and opaque gel spheres.

reactions were also observed in the temperature range between 473 and 873 K. These exothermic reactions were anticipated to be decomposition of by-products such as ammonium nitrate and formaldehyde. These reactions occurred more in the opaque gel spheres than in the transparent ones. The opaque gel spheres lost 35% of weight and the transparent spheres lost 25%. It thus appears that the opaque gel spheres included more burnable impurities than the transparent ones. Therefore, more careful rinsing must be considered to remove impurities from the gel spheres.

### *3.2. Ceramographic examination of sintered spheres*

Fig. 2 shows the cross sectional views of sintered spheres, (a, b) $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ and (c, d) $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$. These spheres were sintered at 1873 K for 10 h in air. As shown in Fig. 2, these spheres were well sintered. However, cracks, nicks and pores were observed from the back scattering electron images. The porosity of these spheres was estimated to be 20–40%. Other spheres produced in the same batch also had defects such as nicks and pores. These features might have been induced with volume shrinkage during calcination. Compared to the materials produced by the powder route, internal-gelation based spheres have a larger amounts of impurities before calcinations, such as organic components and water. Therefore, a more careful calcination must be considered, for example, using a more moderate temperature program up to the onset of calcination.

It is known that wet processes, e.g. coprecipitation and gelation, yield a better element homogeneity within the material than the dry processes. In order to confirm the material homogeneity, EDS and SEM examinations were performed. As a result, sintered spheres (see Fig. 2) showed a good homogeneity, whether pores were observed or not. Using non-standard ZAF correction, the atomic fractions were estimated to be Er: 0.04, Y: 0.14, Ce: 0.09, Zr: 0.72 and Er: 0.05, Y: 0.10, Ce: 0.18, Zr: 0.66 for $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ and $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$, respectively. The error on the atom fraction is around 10% and was found to be affected by the position of the electron beam in the analyzed microspheres.

### *3.3. Lattice structure of zirconia spheres*

Fig. 3 shows the XRD patterns for $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ and $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$. These XRD spectra are assigned to cubic fluorite structure, and the Miller indices correspond to each identified diffraction peak. Each diffraction peak splits into two corresponding Kα1 and Kα2. In this figure, diffraction peaks of $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$ shifted the position to lower diffraction angle $2\theta$, this was clearly observed at large angles. This means that the plane spacing expands as expected by increasing Ce content. From the relationship between plane spacing and corresponding Miller index, the lattice constants was calculated to be $515.8 \pm 0.5$ and $519.5 \pm 0.4$ pm for $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ and $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$, respectively. Lattice parameters of doped cubic zirconia reported in

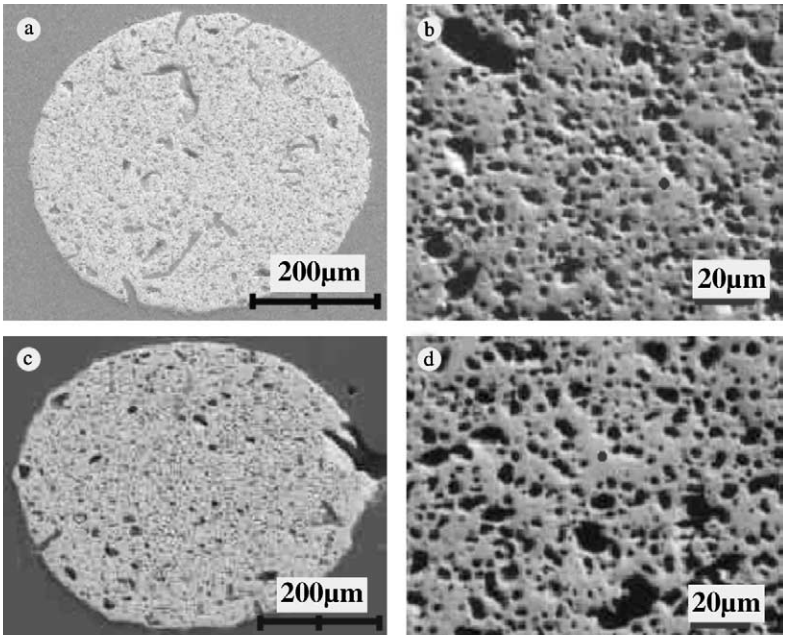

Fig. 2. Cross sectional views of sintered spheres, (a, b) $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ and (c, d) $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$.

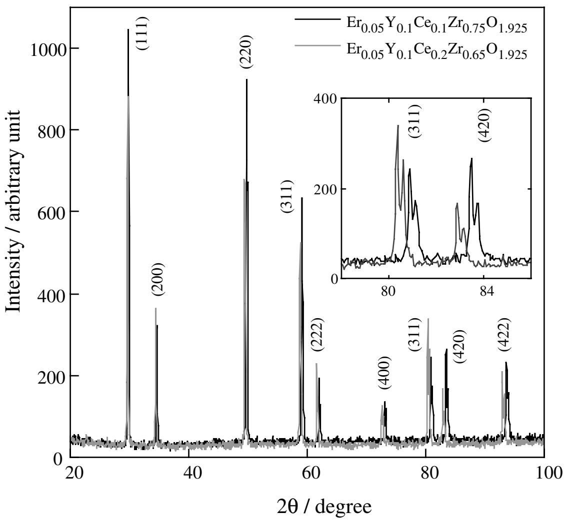

Fig. 3. X-ray diffraction patters from sintered spheres, $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ and $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$. Miller index of fluorite structure was corresponding with each diffraction peak.

other studies [7,8] are listed in Table 2 for comparison with our data. Kim [7] proposed an empirical formula for the lattice parameters of doped zirconia. According to the formula the lattice parameter of doped cubic zirconia is a function of the stoichiometric coefficients of the dopants and the differences of ion radius and charge difference between each dopant ion and tetravalent zirconium. Shannon and Prewitt [9] reported that for the coordination number of 6–8, the ionic radii of $Er^{3+}$, $Y^{3+}$, $Ce^{4+}$ and $Zr^{4+}$ were 88.1–100, 89.2–101.5, 80–97 and 72–84 pm, respectively. The coordination number is ideally 8 for cations in cubic zirconia, and decreases with increasing yttria content [10] because the trivalent dopants, such as $Er^{3+}$ and $Y^{3+}$, substitute for $Zr^{4+}$ ions in the cation sub-lattice, thereby creating one oxygen vacancy for every two replaced tetravalent ions [8]. To estimate the lattice parameter of doped cubic zirconia, the used ion radii were 88.1, 89.3, 92.0 and 79.0 pm for $Er^{3+}$, $Y^{3+}$, $Ce^{4+}$ and $Zr^{4+}$, respectively [11]. Consequently, the lattice parameter, $a$ (pm), may be estimated as follows;

$$a = 512.0 + 17.1\xi_{\mathrm{Er}} + 19.6\xi_{\mathrm{Y}} + 27.6\xi_{\mathrm{Ce}}, \tag{3}$$

where $\xi_i$ is the stoichiometric coefficients of dopant $i$. The first term of the formula (3), 512 pm, is a hypothetical lattice parameter of pure cubic zirconia (extrapolated to zero dopant concentration) at 298 K [12]. The estimated values of the lattice parameter by Eq. (3) are in good agreement with the experimental values as shown in Table 2. They correlated within 0.3%.

## 4. Summary

This study covered the preparation of $ZrO_2$-based IMF by a sol–gel method developed at PSI. Gelation of Zr, Y, Er and Ce nitrate mixtures was conducted successfully, though there were some opaque gel-spheres, which were fragile and included more organic impurities than the transparent spheres. The gelation rate depended on the metal concentration of the feed solution. Several spheres were broken during the drying and calcination processes. Therefore, more careful rinsing and calcination must be considered, for example, moderately rising the temperature until calcination initiates. The sintered spheres consisted of a uniform cubic phase. The lattice parameter of cubic zirconia doped with Er, Y and Ce could be estimated using a Kim [7] equation within 0.3% of error. Most of the sintered spheres had cracks, nicks, and small pores. More efforts are required to produce high quality materials being usable in cermet fuel.

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Table 2
Lattice parameters experimentally determined and calculated for cubic zirconia doped with erbia, yttria and ceria

| Materials | Ref. | Lattice parameter $a$ (pm) | | $a_{\mathrm{calc.}} - a_{\mathrm{exp.}}$ (pm) | $(a_{\mathrm{calc.}} - a_{\mathrm{exp.}})/a_{\mathrm{exp.}}$ |
|---|---|---|---|---|---|
| | | Exp. | Calc. | | |
| $ZrO_2$ | [7] | 512.0 ± 0.5 | 512.0 | 0.0 | 0.000 |
| $Er_{0.05}Y_{0.10}Zr_{0.85}O_{1.925}$ | [8] | 513.6 ± 0.2 | 514.8 | 1.2 | 0.002 |
| $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.85}O_{1.925}$ | This work | 515.8 ± 0.5 | 517.6 | 1.8 | 0.003 |
| $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ | [8] | 517.4 ± 0.7 | 517.6 | 0.2 | 0.000 |
| $Er_{0.08}Y_{0.09}Ce_{0.16}Zr_{0.65}O_{1.915}$ | [8] | 520.3 ± 0.5 | 519.5 | −0.8 | −0.001 |
| $Er_{0.05}Y_{0.10}Ce_{0.20}Zr_{0.65}O_{1.925}$ | This work | 519.5 ± 0.4 | 520.3 | 0.8 | 0.002 |
| $CeO_2$ | [7] | 541.3 ± 0.3 | 539.6 | −1.7 | −0.003 |

and XRD analysis. The author thanks Dr C. Degueldre, PSI, for useful exchange of information, Mr G. Ledergerber, PSI for the very constructive discussions.

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