



ZIRCONIA BASED INERT MATRIX FUEL: FABRICATION CONCEPTS AND FEASIBILITY STUDIES

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The internal gelation process has traditionally been applied to fabricate standard fuel based on uranium, typically UO_2 and MOX. To meet the recent aim to destroy plutonium in the most effective way, a uranium free fuel was evaluated. The fuel development programme at PSI has been redirected toward a fuel based on zirconium oxide or a mixture of zirconia and a conducting material to form ceramic/metal (CERMET) or ceramic/ceramic (CERCER) combinations.

A feasibility study was carried out to demonstrate that microspheres based on zirconia and spinel can be fabricated with the required properties. The gelation parameters were investigated to optimise compositions of the starting solutions. Studies to fabricate a composite material (from zirconia and spinel) are on-going. If the zirconia/spinel ratio is chosen appropriately, the low thermal conductivity of pure zirconia can be compensated by the higher thermal conductivity of spinel.

Another solution to offset the low thermal conductivity of zirconia is the development of a CERMET, which consists of fine particles bearing plutonium in a cubic zirconia lattice dispersed in a metallic matrix. The fabrication of such a CERMET is also being studied.

1 INTRODUCTION

Inert matrix fuel has been proposed in order to utilise plutonium in the most effective way and to reduce the amount of fissile plutonium in the spent fuel [1] which exceeds the current norm. By using existing fabrication technology in combination with so-called "inert matrix materials" like zirconia and spinel, disposal of spent fuel would become easier, and public acceptance of peaceful utilisation of plutonium for nuclear energy might be increased. PSI has used the internal gelation process [2] for many years to prepare small amounts of a variety of nuclear fuels like UO_2 , MOX and nitrides. This technology can also be used for the fabrication of uranium-free fuel. Concepts based on solid and annular pellets [1] and ceramic/ceramic (CERCER) and ceramic/metal (CERMET) material combinations have been proposed. By selecting an appropriate zirconia/spinel ratio, it is possible to overcome the low thermal conductivity of zirconia. Also the feasibility of a CERMET, which consists of fine particles bearing plutonium in a cubic zirconia dispersed in a metallic matrix is being investigated as a second option to offset the low thermal conductivity of zirconia. In the following paper a status report of ongoing work is given.

2 CONCEPTS FOR THE FABRICATION OF CERAMICS, CERCER AND CERMETS

Stabilised zirconium oxide as a carrier for fissionable material may include many additional components like yttrium or calcium as stabilising elements, erbia as burnable poison, with plutonium as fissile material. The solid solution might be prepared by a co-milling or a co-precipitation process. Different concepts for the fabrication of inert matrix materials, and also some effects of parameter changes, are outlined in the following text.

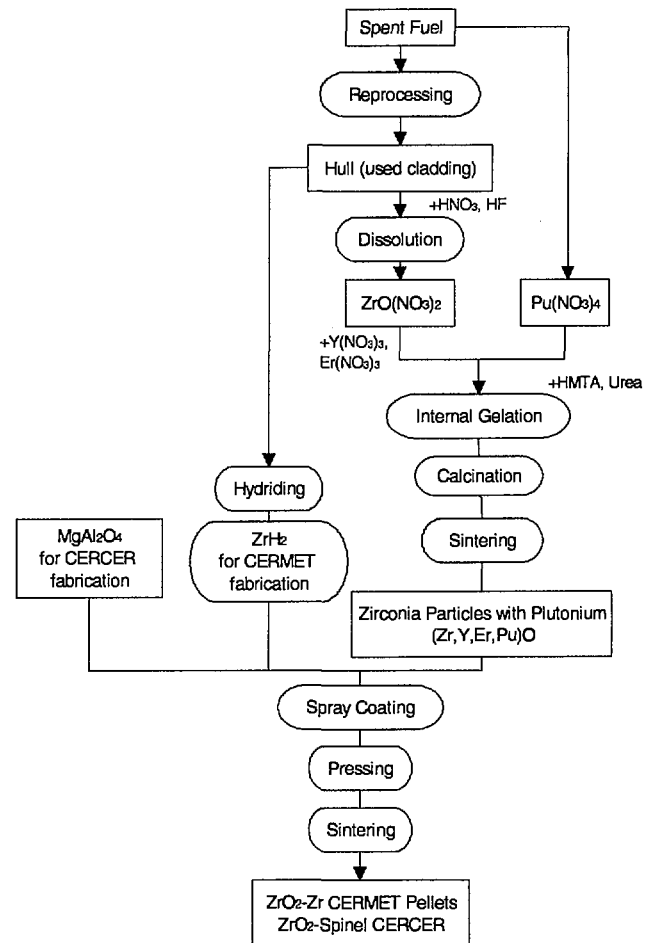


Fig. 1: Flow diagram for manufacturing of ZrO_2 -Zr CERMETS and ZrO_2 - $MgAl_2O_4$ CERCERS

2.1 Ceramics

Two possible fabrication procedures are recommended by PSI for the fabrication of homogeneous single phase material ceramics. Co-precipitated ceramics for classical pellets can be fabricated either from microspheres (internal gelation) or using a powder co-precipitation route. The experimental set-up for the gelation of microspheres has been already described elsewhere [2]. The process used here is one of several sol-gel type processes and is known as "internal gelation". The principle is conversion of a highly concentrated metal nitrate solution to a spherical particle of metal oxide with hexamethylenetetramine as the key reactant. The equipment in the PSI laboratories allows sphere fabrication with sizes varying from 800 μm down to 40 μm .

The standard procedure used at PSI for the fabrication of ceramic pellets of zirconia is based on co-precipitated powder which is afterwards milled, pressed into pellets, calcined and sintered [4].

The precipitation is performed with ammonia added drop by drop to the nitrate solutions until the precipitation is complete. Afterwards the precipitate is filtered on a glass filter and washed with Milli-Q-water until a pH-value of 8 is reached. Second a washing step with ethanol follows. The final result is a wet cake containing the hydroxides of the simulated fuel system. The wet cake is dried in a furnace at 120 $^{\circ}\text{C}$, and then the material is crushed.

The process is continued by milling (1.5 h, zirconia jar, Retsch), calcination (800 $^{\circ}\text{C}$, 5 h, air), another milling step (2.5 h) and final drying. The pelletising is carried out by using a hydraulic press with a pressure between 150 and 300 MPa for 10 seconds. Usually the powder is pressed to pellets with a diameter (d) of about 10mm and a height (h) in the range of $1.0 \leq h/d \leq 1.5$. The sintering is done in air at a minimum temperature of 1400 $^{\circ}\text{C}$. Similar low temperatures are applied for the microspheres prepared by gelation, and high densities could be obtained.

2.2 CERCER materials

Embedding zirconia microspheres in a spinel matrix is one CERCER concept which is being followed at present time in several institutes [5]. The flowsheet in Fig. 1 outlines the different steps for sphere fabrication and the compaction of a pellet based on spray coated microspheres, resulting in an optimal distribution of the spheres in the matrix. In this scouting experiment, a CERCER-material consisting of a zirconia/spinel combination in a very intimate mixture was also fabricated according to the internal gelation procedure. The fabrication parameters for a compound with 60% $(\text{Zr}_{.76}\text{Y}_{.12}\text{Ce}_{.12})\text{O}_2$ -40% MgAl_2O_4 (spinel) are given in Table 1, whereas cerium is used instead of plutonium. The result is a fine dispersion of the fissile material carrier in the conducting matrix.

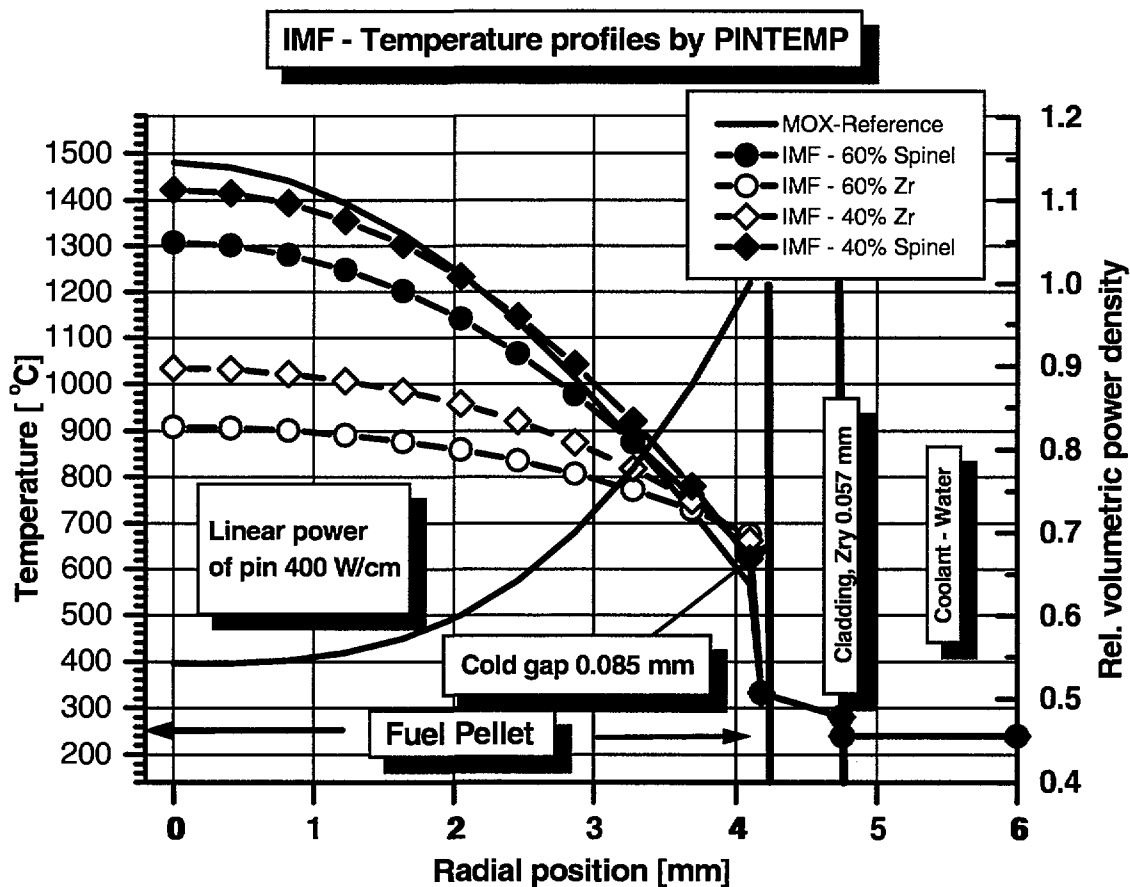


Fig. 2: Inert matrix fuel temperature profiles calculated with PINTEMP [3]

2.3 CERMETS

A further concept for producing a suitable inert matrix material with good thermal conductivity consists of fine particles bearing plutonium in a cubic zirconia matrix. It could be fabricated by the conversion of a $ZrO(NO_3)_2$ (+ $Y(NO_3)_3$ and $Er(NO_3)_3$ -solution) and a $Pu(NO_3)_4$ -solution (together with HMTA and urea as additives). After the gelation, washing and an appropriate thermal treatment plutonium bearing cubic zirconia particles would be obtained; by using a spray coating technique for adding ZrH_2 , followed by pressing, dehydriding and sintering it is feasible to fabricate ZrO_2 -Zr CERMET pellets (see Fig. 1).

3 RESULTS

Experimental investigations on this topics are in the early stages. The emphasis is at the present time on (a) the calculations performed to characterise the temperature distribution in a ZrO_2 - $MgAl_2O_4$ CERCER and ZrO_2 -Zr CERMET fuel compared to ZrO_2 and MOX fuels and (b) on the application of the internal gelation process.

3.1 Calculations of the temperature distribution in a fuel pin

As a result of the low thermal conductivity of zirconium based inert matrix fuel, the centreline temperature of a solid pellet calculated for a standard LWR geometry and with linear power (of the fuel pin) of 400 W/cm is about 320 °C higher than that of MOX, see Ref [1]. Figure 2 shows the temperature distribution for two different ratios of CERMET and CERCER fuel pellets, again calculated with a linear power of 400 W/cm. The calculations were performed with the programme PINTEMP and SPACON [3]. Calculations for MOX are added for comparison. The lowest temperatures (<1000 °C) are obtained for the pellet IMF-60 % zirconium metal (IMF means *Inert Matrix Fuel*), while for the IMF - 40 % zirconium metal the temperatures are also even lower than for MOX and CERCER materials. In general, the higher the metal composition is, the lower the centreline temperature of fuel.

3.2 Gelation studies

To prepare the starting solutions for fabricating zirconia spheres (stabilised with Y_2O_3 for the cubic modification and CeO_2 as simulant material for Pu), oxide powders of ZrO_2 , Y_2O_3 and CeO_2 were dissolved in nitric acid.

Typical compositions of the solution used for the preparation of ceramic microspheres are shown in Table 1 for the oxide compound $(Zr_{.80}Y_{.10}Ce_{.10})O_2$. The effects of the variation of the key parameters during the gelation procedure were evaluated in small scale experiments and are described as follows:

Metal concentration

A high metal concentration exhibits a high gelation tendency, which leads to more uniform spherical structures with a high density and crystallinity after the temperature treatment. However, the low solubility of the different metal nitrates limits the maximum concentration of the feed solution.

Hexamethylenetetramine content

HMTA decomposes into an amino and hydroxyl group at elevated temperature; an excess HMTA content therefore ensures the complete precipitation of metal hydroxide, but there is the drawback that increases the possibility of previous gelation of the feed solution at low temperature. A high HMTA content leads to an amorphous material after calcination. Residual HCOH left inside the spheres is undesirable as it increases the porosity of spheres during the heat treatment.

Acid content

The acid content strongly inhibits the gelation process by shifting the pH of the solution far from the so-called PZC (**P**oint of **Z**ero **C**harge). Consequently, a polymer network within the gel spheres will be lost to some extent. The structure will contain more NH_4^+ and organic groups, which result in a high porosity after heat treatment. Also inorganic Cl^- or NO_3^- -ions are not easy to wash off, except by using water (which is not recommended here). Against that, the acid has a catalytic effect on the decomposition of HMTA.

Table 1: Fabrication parameters for microspheres (internal gelation procedure)

Composition of oxides	Concentration of metal [mol/kg solution]	HMTA*/metal	HNO ₃ / (urea+metal)	Remarks
$(Zr_{.80}Y_{.10}Ce_{.10})O_2$	0.621	1.00	0.158	about 200g materials were fabricated (size fractions: 800 μm and 250 μm)
60% $(Zr_{.76}Y_{.12}Ce_{.12})O_2$ - 40% $MgAl_2O_4$ (spinel)	0.800	1.12	0.242	only the coarse fraction (diameter 800 μm) was fabricated

*hexamethylenetetramine

Urea content

A low urea content helps to stabilise the feed solution at low temperature. However, it contains also unwelcome organic components. Urea will lightly hydrolyse into a NH_4^+ and OH^- group, tending to induce premature gelation slowly. A very high urea content seems to produce more rigid spheres (urea works as a binder in the gel network), provided it is accompanied by more acid in the feed solution in order to prevent early gelation.

Gelation temperature

The influence of the gelation temperature is usually considered prior to other parameters, from the point of view of conservative sol-gel science. Here it is expected that the gelation temperature would affect both the gelation kinetics and the decomposition rate of HMTA or urea, and it will have in addition a catalytic effect of acid on HMTA. The choice of gelation temperature will also be limited later by the plutonium content of the inert matrix. Up to now the gelation temperature on the lab scale is between 100 °C and 105 °C.

Heat treatment

The cracking of spheres is usually caused by high surface tensions and a large capillary pressure of liquid inside the structure. The choice of the sintering parameters is therefore important, in particular when regarding the high densification and phase transformations.

Drying of the spheres is usually done in air at 80-100 °C. A constant atmosphere will avoid the huge difference between capillary force and pressure outside the pores.

During the calcination, a temperature chosen according to the TGA-results (Thermo Gravimetric Analysis) for the transformation of the amorphous zirconia to the cubic structure is applied; a slow heating rate and long holding time in air will help the transformation to oxide. During sintering there is a competition between densification and crystallisation. The process should be controlled, so that the former takes place earlier than the latter. Due to the fact that the crystallisation is a relatively time consuming process, a previous fast sintering at a temperature lower than the sintering temperature, followed by a slow crystallisation procedure at the sintering temperature is recommended.

As a main result, the gelation technology has been demonstrated successfully for both zirconia and zirconia/spinel. Fig. 3 and 5, respectively, show the gelled products after drying. The zirconia spheres appear very homogeneous, whereas, the zirconia/spinel spheres still have to be optimized concerning their shape and size (work on this is still ongoing). The zirconia spheres were calcined (500 °C, 4h, air) and afterwards sintered (1350 °C, 4h, air). Fig. 4 shows a scanning electron microscopy photo of small zirconia

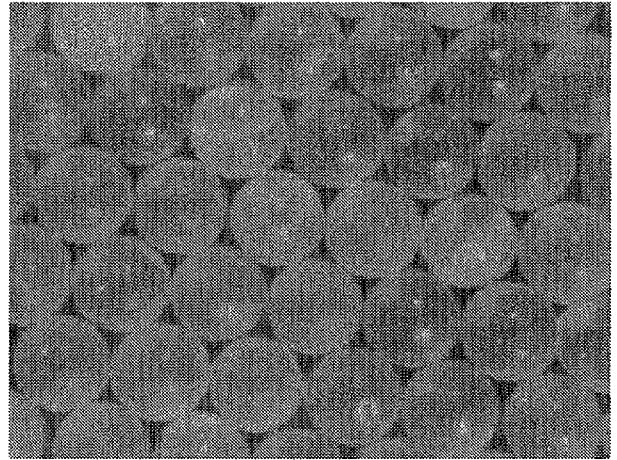


Fig. 3: *G-80Zr-10Y-10Ce* - microspheres of zirconia (after drying), photo taken from light microscope; spheres about 800 μm

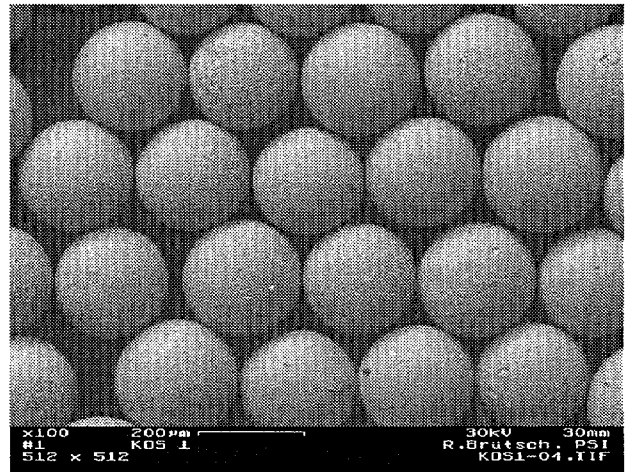


Fig. 4: *G-80Zr-10Y-10Ce* - microspheres of zirconia (after sintering), SEM photography, diameter of spheres about 250 μm

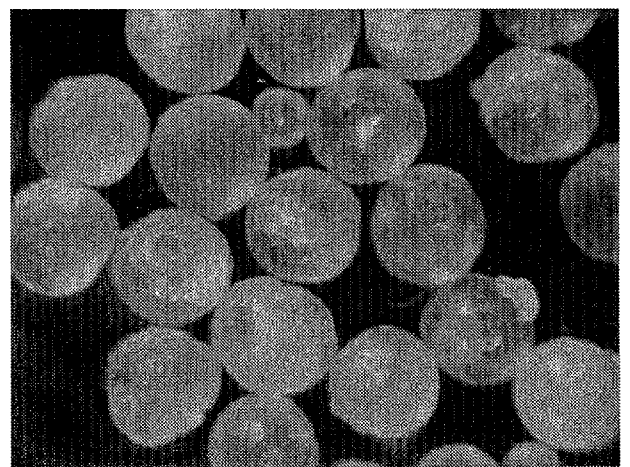


Fig. 5: *G-48Zr-6Y-6Ce-40MgAl₂O₄* microspheres of zirconia/spinel (after drying), photo taken from light microscope, diameter of spheres about 800 μm

spheres (diameter about 250 μm) after sintering. The X-ray diffraction results confirm that we obtained a cubic single-phase material with a lattice parameter $a=0.5168$ nm. The density of the sintered zirconia product was measured with a helium pycnometer and found to be 5.898 g/cm³ (> 95% of the theoretical density value).

4 DISCUSSION AND OUTLOOK

The motivation for the investigation of inert matrix materials is mainly the reduction of fissile plutonium in the spent fuel. To show that the fabrication of ceramics for this purpose is feasible, spheres of zirconia (doped with ceria and yttria) and spinel were gelled, dried, calcined and sintered. The products were examined by X-ray analysis, chemical analysis, ceramography and technological characterization. The influence of the gelation parameters (gelation time, temperature conditions, pH-value of the solution) and the influence of nitric acid, HMTA (hexamethylenetetramine) and urea contents on the gelation process were investigated in detail.

A concept combining microsphere fabrication followed by spray coating and sintering has been proposed for the CERMETS (ZrO₂ in Zr-matrix) and for the CERCERS (ZrO₂ in spinel matrix). Temperature profile calculations demonstrate that the thermal conductivity is significantly increased above that of "pure" zirconia by combining it with metals or other ceramics.

Future work at PSI will consist of the preparation of plutonium containing inert matrix fuels and of further characterization of the IMF-fuel (ceramics, CERCER and CERMET), with emphasis on the irradiation behaviour.

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6 REFERENCES

- [1] C. Degueldre, U. Kasemeyer, F. Botta, G. Ledergerber, "Plutonium incineration in LWR's by a once-through cycle with a rock-like fuel", Mat. Res. Soc. Symp. Proc. Vol. 412, Materials Research Society 15-23 (1996).
- [2] G. Ledergerber, H.P. Alder, F. Ingold, R.W. Stratton, "Experience in preparing fuel by the gelation method", ECN '86, Fourth International ENS/ANS Conference, Geneva, 1-6 June 1986, Transactions Vol. 4, 225-232.
- [3] F. Botta, K. Bakker: "Computations on thermal conductivity of Sphere-pac unit cells", (to be published in *Nuclear Science and Engineering*).
- [4] M. Pouchon: Private communication. Paul Scherer Institut, Switzerland.
- [5] G. Ledergerber (PSI, Switzerland), T. Ohmichi (JAERI, Japan), R.J.M. Konings (ECN, Netherlands): Private communication.

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