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The fabrication and irradiation of plutonium-containing inert matrix fuels for the 'Once Though Then Out' experiment

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Abstract

Seven plutonium containing inert matrix fuel (IMF) capsules were prepared for an irradiation experiment in the high flux reactor. In the irradiation experiment, named once-through-then-out, both spinel-based and zirconia-based targets are irradiated up to a plutonium burnup of about 200 GW d m^{-3}, corresponding to a Pu depletion of 50–60%. Both micro and macrodispersed spinel targets are tested, the zirconia targets are of the homogeneous type. In this paper, the fabrication routes of the IMF pellets for this irradiation are described in detail. The results of the dimensional measurements, density measurements, ceramographies and X-ray images of the samples are given. Some preliminary results of the irradiation are included.

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1. Introduction

For the incineration of excess plutonium using existing LWR's, inert matrix fuels (IMF) have been proposed for use in a once-through-then-out (OTTO) concept. The Pu inert matrices considered are uranium-free, and therefore have almost no Pu production during reactor-use, which gives Pu-IMF excellent possibilities for a very high net Pu incineration. The Pu-IMF can therefore be used to reduce Pu stockpiles and the associated radiotoxicity in an efficient manner. The Pu-IMF can be used for incineration of both reactor grade-Pu and weapons-grade Pu, where in both cases the proliferation risk is further reduced by a degradation of the plutonium vector.

Since the mid-nineties a large research effort has been devoted to Pu-IMF both in Japan and in Europe [1]. In Japan, the so-called rock-like fuels, consisting of yttria-stabilised zirconia ($(Y,Zr)O_{2-x}$, YSZ), spinel ($MgAl_2O_4$) and corundum (Al_2O_3) were proposed by the Japan Atomic Energy Research Institute (JAERI). In Europe, the zirconia-based Pu-IMF has been promoted by the Paul Scherrer Institute (PSI). Both spinel-based or zirconia-based Pu-IMF, are practically insoluble in water, which makes these fuels suitable for a once-through-then-out strategy.

At present different experimental programmes are focusing on IMF. An irradiation in the Halden Reactor is being performed on zirconia-based Pu-IMF [2]. JAERI has performed an irradiation experiment of different IMFs containing either spinel, corundum (Al_2O_3) or YSZ [3]. In addition, the European experimental feasibility of targets for transmutation (EFTTRA) group studies IMF concepts for the incineration of the minor actinides, which also are based on spinel [4,5].

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In this paper the fabrication of the fuels and some irradiation results for the OTTO experiment are discussed. The experiment is a collaboration between JAERI, PSI and the Nuclear Research and consultancy Group (NRG). The irradiation has recently been completed in the high flux reactor (HFR) in Petten.

2. Fabrication

In this chapter the fabrication of different types of IMF is described. In general one can distinguish solid solutions, such as the zirconia-based fuels, and composite fuels such as the spinel-based fuels. The composite fuels consist of a fissile phase dispersed in an inert matrix. These dispersions can be either micro or macrodispersions of fissile material, which are both studied in this experiment. An overview of the test matrix is given in Table 1.

In microdispersion or solid solution type of IMFs, the fission product damage is homogeneously distributed over the fuel. In macrodispersed fuels (fissile inclusions larger than about 100 μm), however, the fission products damage is concentrated in a small volume shell around the fissile inclusions. All designs (solid solution, micro or macro) have their advantages and disadvantages from the fuel behaviour point of view. In this project two inert matrices are studied, zirconia and spinel. Both materials are practically insoluble in water and have a good stability under neutron irradiation. In this experiment the feasibility of both inert matrices for plutonium burning is studied.

Removing the ^{238}U from the fuel, as is done in IMF, decreases the Doppler effect. In order to prevent safety problems in future large scale application of such fuels a small amount of erbia or urania is added. Therefore, each IMF in the OTTO experiment contains either erbia or urania.

2.1. Fabrication of microspheres

The fissile phase (74.2% fissile of total Pu at beginning of irradiation (BOI)) in all pellets is based on microspheres fabricated at PSI using the internal gelation method. After gelation, the microspheres were calcined in air at 673 K. The diameter of the calcined microspheres is in the range of 200–250 μm. For the fabrication of samples 1–6, batches of $(Er,Y,Pu,Zr)O_{2-x}$ and $(Y,Pu,U,Zr)O_{2-x}$ microspheres were prepared (see Fig. 1), each with two different zirconia concentrations: one concentration for samples 1 and 2, the other for samples 3–6. For sample 7, $(Pu,U)O_{2-x}$ microspheres were prepared.

2.2. Fabrication of pellets

2.2.1. Optimization of the fabrication process of the dispersed pellets

The pellets of samples 3, 4, 5 and 6 were produced by NRG. Before the final spinel-based pellets were produced, elaborate pressing and sintering experiments had to be performed. Several problems had to be solved before the final fabrication procedure was defined. The main problems are outlined below.

The dry mixing of the microspheres and the spinel powder resulted in inhomogeneous pellets. In order to achieve a homogeneous distribution of the microspheres in the pellets, it was necessary to make a slurry of spinel, microspheres and ethanol. During the evaporation of

Table 1
Irradiation test matrix for the OTTO experiment, including measured values for densities

Nr.	Composition[a]	Dispersion	Stack length[b] (mm)	Pu^{fis} (BOI) ($g\,cm^{-3}$)	Density[c]	
					$g\,cm^{-3}$	% TD
1	$(Er,Y,Pu,Zr)O_{2-x}$	Solid solution	67.7	0.37	5.76 (5.80)	91.0 (91.6)
2	$(Y,Pu,U,Zr)O_{2-x}$	Solid solution	67.0	0.34	6.00 (6.02)	92.7 (93.0)
3	$(Er,Y,Pu,Zr)O_{2-x}$ + $MgAl_2O_4$ (TC)	Microdispersion <25 μm	67.6	0.32	4.10 (4.13)	94.5 (95.0)
4	$(Y,Pu,U,Zr)O_{2-x}$ + $MgAl_2O_4$ (TC)	Microdispersion <25 μm	67.8	0.31	4.24 (4.23)	93.8 (94.5)
5	$(Er,Y,Pu,Zr)O_{2-x}$ + $MgAl_2O_4$ (TC)	Macrodispersion 200–250 μm	66.9	0.31	3.68 (3.98)	85.6 (92.4)
6	$(Y,Pu,U,Zr)O_{2-x}$ + $MgAl_2O_4$	Macrodispersion 200–250 μm	66.2	0.30	3.95 (4.12)	88.2 (92.0)
7	$(Pu,U)O_2$ (TC)	Solid solution	67.1	0.39	10.47 (10.57)	95.3 (96.2)

[a] (TC) means that this capsule is equipped with a central thermocouple.
[b] As determined from the X-ray image.
[c] This is the geometrical density, the value between brackets is the water immersion density.

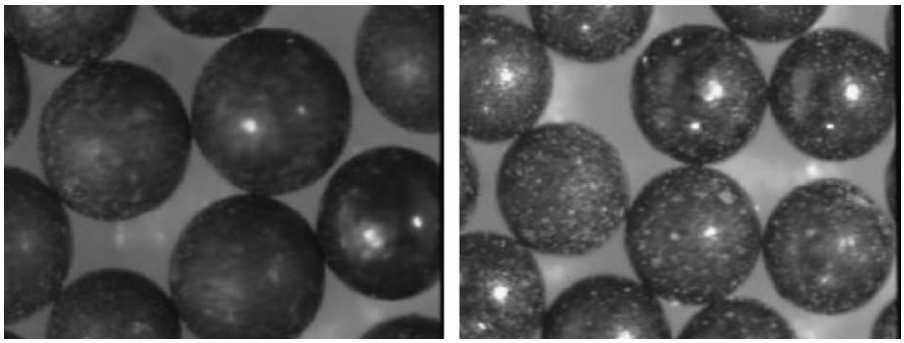

Fig. 1. External appearance of the $(Y,Pu,U,Zr)O_{2-x}$ microspheres (left) and the $(Er,Y,Pu,Zr)O_{2-x}$ microspheres (right).

the ethanol a good homogeneity was obtained by gently mixing and stirring the substance in a mortar.

The design diameter of the pellets was specified to be 8.00 mm. The Zircaloy-4 cladding has an inner diameter of 8.22 mm and an outer diameter of 9.5 mm. For the homogeneous samples (nr, 1, 2, 7), which were fabricated at PSI, a centerless grinder was used to achieve the design diameter. The average diameter of these pellets is 8.002 ± 0.002 (sample 1), 8.001 ± 0.001 (sample 2) and 7.999 ± 0.003 (sample 7) mm. For the composite pellets (samples 3, 4, 5, and 6) fabricated at NRG, no centerless grinder was available such that the diameter of the sintered pellets must be within the specification. During the optimisation of the mixing, pressing and sintering process parameters like die diameter and pressing force were varied. Each of these parameters influences the sintering characteristics of the pellets and as a result also the final diameter. The diameter of these spinel based composite pellets is 8.003 ± 0.010 (sample 3), 8.013 ± 0.011 (sample 4), 8.054 ± 0.020 (sample 5) and 7.982 ± 0.018 (sample 6) mm. It is interesting to note that the spinel shrinks more than the fissile inclusions during sintering. Therefore, the microspheres 'pop out' of the pellet after sintering (Fig. 3). This is also reflected in the histograms of the diameter distributions (Fig. 2), which shows that the macrodispersed pellets show a somewhat wider diameter distribution than the homogeneous (micro)-dispersed pellets.

A lubricant (0.6% Zn-stearate) was added to the powder mixture and a die with a conical push-out part was used to prevent end-capping or disk-cracks in the pellets. The densification of the microspheres during sintering is less than that of the spinel powder, as a result of which small cracks between the microspheres are observed.

Several tests were performed in order to find a spinel powder, which matches the densification of microspheres such that mechanical stresses during sintering are minimal. Unfortunately, such optimal spinel powder could not be found.

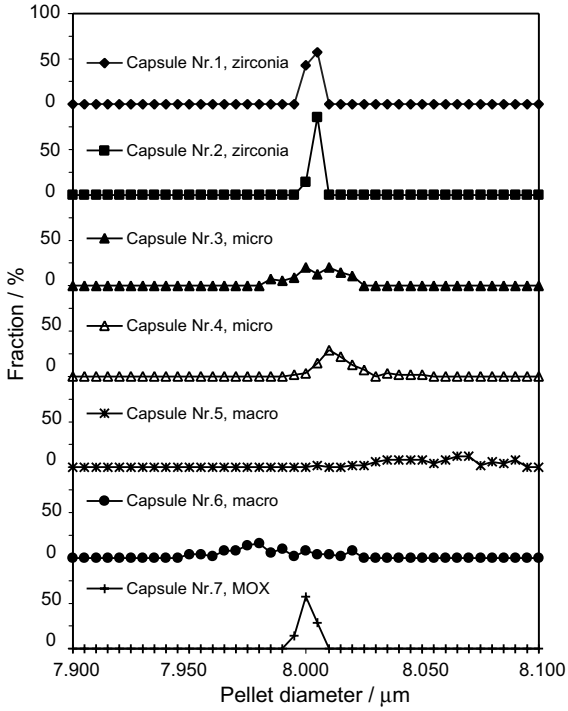

Fig. 2. Diameter distribution of pellets of samples 1–7. The scale for each of the sample runs from 0% to 100%. The difference between the ground sample (samples 1, 2, 7), the macrodispersed (samples 5, 6) and the microdispersed pellets (samples 3, 4) can be clearly observed.

2.2.2. Fabrication of composite macro and microdispersed pellets

The fabrication routes of the pellets are outlined in Fig. 4. Samples 5 and 6 were prepared at NRG by mixing microspheres with a slurry of $MgAl_2O_4$ with 0.6 wt% lubricant (Zn-stearate) and ethanol, similar to the route described in Ref. [3]. The substance was gently mixed and stirred in a mortar. After the evaporation of

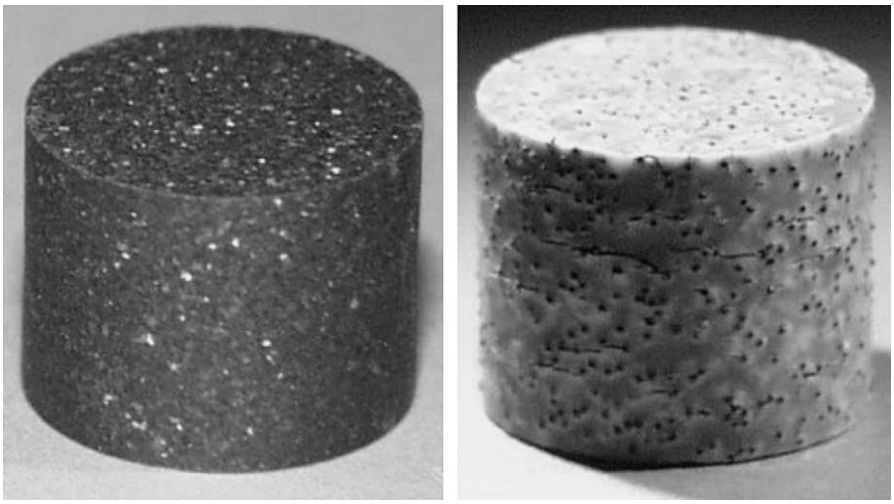

Fig. 3. Representative pellet of sample 4 (left). Representative pellet of sample 6. Visible are small cracks and microspheres partly popping out of the pellet surface (right).

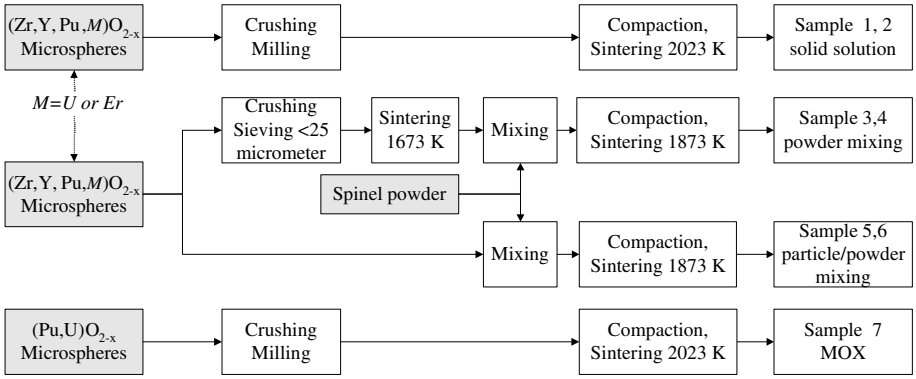

Fig. 4. Flow diagram for the fabrication of pellets for the OTTO irradiation.

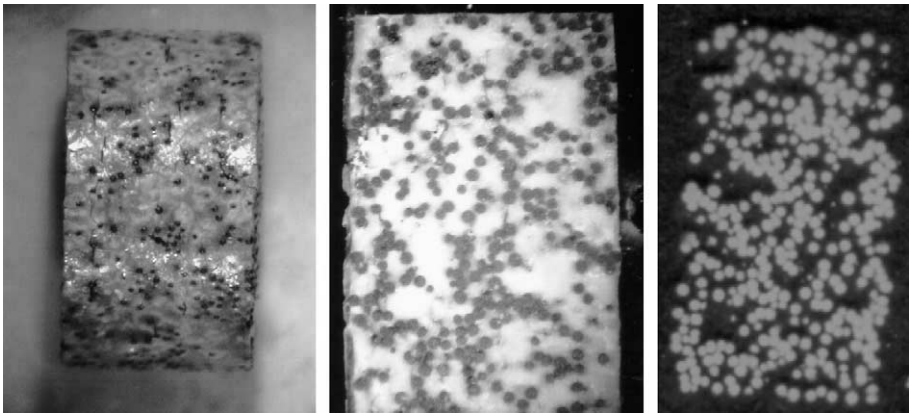

Fig. 5. External appearance (left), internal appearance (middle) and alpha-autoradiography of a representative pellet (pellet 32) of sample 5, a macrodispersion of $(Er,Y,Pu,Zr)O_{2-x} + MgAl_2O_4$ spinel, sintered at 1873 K.

the ethanol a good homogeneity of the mixture was obtained. The mixture was pressed to pellets in a 10.0 mm diameter die at a pressing force of 150 MPa. The pellets were dewaxed for 2 h at 773 K and sintered for 5 h at 1873 K in an atmosphere of argon with 5% hydrogen. An example of a macrodispersed pellet is shown in Fig. 5. The calculated volume fraction of the microspheres, is 19.7 vol.% for the sintered pellets of both capsule nr. 5 and 6.

Samples 3 and 4 were prepared at NRG by mixing crushed, sieved and calcined microspheres with a slurry of $MgAl_2O_4$ with 0.6 wt% lubricant and alcohol, similar to the route for the fabrication of the macrodispersed pellets. The microspheres were crushed in a mortar and sieved through a 25 μm sieve to obtain small fissile particles. These particles were calcined for 1 h at 1673 K in an atmosphere of argon with 5% hydrogen. The calcination of the particles before mixing it with spinel, resulted in more dense and uniform pellets. The mixture was pressed to pellets in a 9.7 mm diameter die at a pressing force of 260 MPa. The pellets were dewaxed for 2 h at 773 K and sintered for 5 h at 1873 K in an atmosphere of argon with 5% hydrogen. An example of a homogeneous pellet is shown in Fig. 6. The calculated volume fraction of the fissile phase (crushed microspheres), is 20.8 vol.% for the sintered pellets of capsule nr. 3 and 20.7 vol.% for the sintered pellets of capsule nr. 4.

2.2.3. Fabrication of homogeneous pellets

Samples 1, 2 and 7 were prepared at PSI by crushing and attrition milling of the microspheres. After adding 0.2 wt% of lubricant and subsequent mixing, the powders were pre-compacted and granulated. Another 0.2 wt% lubricant was added to the granulate after which the mixture was pressed to pellets in a 9.9 mm diameter die at a pressing force of 600 MPa. The pellets were dewaxed for 2 h at 673 K and sintered for 6 h at 2023 K in an atmosphere of nitrogen with 8% hydrogen. The sintered pellets were ground to a diameter of 8.000 ± 0.005 mm with a centerless grinder.

2.2.4. Drilling holes in pellets

Four of the capsules are equipped with a central thermocouple. For this reason a central hole is drilled in a number of pellets. The drilling device ('Metabo T6 electronic') is equipped with a hollow diamond drill (outer diameter 1.8 mm) which is operated at 2200 rpm. The pellets were mounted in a brass sample-holder, placed on a translation table, in order to centre the pellet under the static drill. A drop of water is added on top of the pellet for cooling of the drill. The vertical displacement of the drill and the applied amount of force is adjusted manually by a lever. Little force is exerted and small movements are made with the lever, during drilling. After a few mm of progress, the inside of the drill is 'cleaned' by a steel wire. In this way, approximately 15 min are required for a hole to a depth of 7 mm. The last part of each pellet needs extra care and time (smaller force). The bottom of the pellet is supported on a plastic (PVC) round plate, in order to prevent damage ('breakout') of the pellet in the last phase of the drilling.

3. Characterization

Prior to irradiation, the fabricated pellets were characterized. The density was measured, and ceramographies and X-ray images were taken for inspection of the homogeneity and integrity of the samples. Before

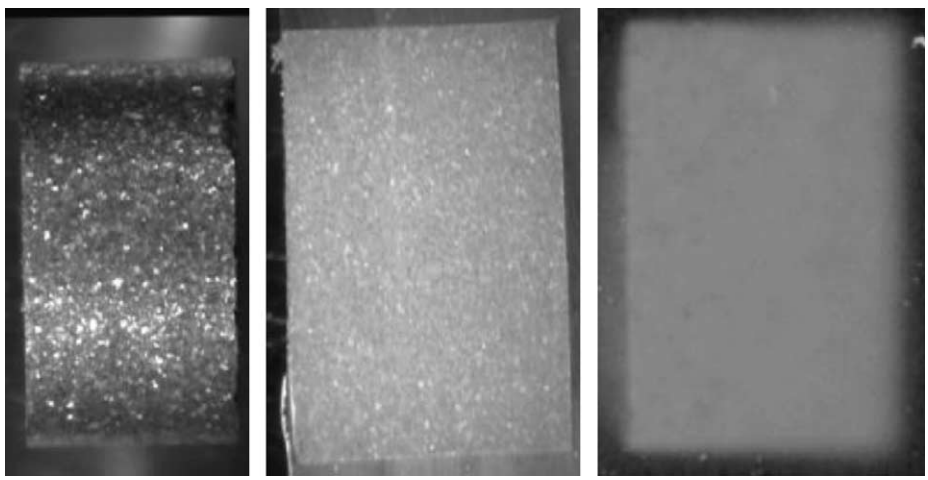

Fig. 6. External appearance (left), internal appearance (middle) and alpha-autoradiography of a representative pellet (pellet 41) of sample 4, a microdispersion of $(Y,Pu,U,Zr)O_{2-x} + MgAl_2O_4$ spinel, sintered at 1873 K.

Table 2
Properties of the microspheres used for sample 3, 4, 5, and 6, for different thermal treatment temperatures

Characterization			
$(Y,Pu,U,Zr)O_{2-x}$ microspheres used for sample 4, 6			
Product code	C-48Zr-12Y-20U-20Pu-O33	O-48Zr-12Y-20U-20Pu-903	O-48Zr-12Y-20U-20Pu-905
Thermal treatment temperature/K	673	1273	1673
Sphere size/μm	270 ± 14	224 ± 35	221 ± 28
Density/g cm^{-3} [a]	7.41	7.45	8.16
XRD a [b]/nm	0.54523	0.5274	0.5287
(Er,Y,Pu,Zr)oxide microspheres used for samples 3, 5			
Product code	C-58Zr-14Y-8Er-20Pu-O32	O-58Zr-14Y-8Er-20Pu-903	O-58Zr-14Y-8Er-20Pu-904
Thermal treatment temperature/K	673	1273	1673
Sphere size/μm	233 ± 18	217 ± 18	213 ± 18
Density/g cm^{-3} [a]	6.88	6.80	7.33
XRD a [b]/nm	[c]	0.5205	0.5208

[a] Density measured by He-immersion method.
[b] Lattice parameter.
[c] Could not be measured, because of lack of crystallinity.

the fabrication of the composite spinel fuels the microspheres were characterized. The microspheres that are used for the production of samples 3, 4, 5 and 6 (see Fig. 1) were fabricated by PSI. These microspheres are calcined in air at 673 K. The characteristics of these microspheres are listed in Table 2 for three different calcination temperatures.

An overview of the densities of the seven samples prepared for the OTTO experiment is presented in Table 1. The density, as measured by water immersion, is higher than 90% TD for all samples. Due to popping out of the microspheres and crack formation, the geometrical density is smaller than the water immersion density which is clearly reflected in the results for sample nr. 5 and 6 in Table 1.

The ceramographies of the spinel based samples 3 and 5 are shown in Figs. 5 and 6. The homogeneity of the fissile material in the matrix is very good, as can be seen from the alpha-autoradiographs.

Before irradiation, detailed X-ray imaging of the capsules was performed. In Fig. 7 X-ray images of the fuel stack in each capsule is shown. These images show the proper alignment of the fuel stacks, the isolating spinel pellets, and the Hf plugs (Fig. 8).

3.1. Chemical compatibility of spinel with fissile phase

During the sintering tests in the pre-fabrication stage of the spinel based fuels, chemical interaction was found between the fissile phase and the spinel matrix. The spinel-containing pellets 3–6 are prepared by sintering the green pellets in a chamber furnace for 5 h at 1873 K in an Ar/5%H_2 atmosphere. The first sintering test of sample 6 at a temperature of about 1973 K (the uncertainty in the measured temperature is at least 30 K) revealed chemical interaction and melting-like behaviour of the pellet during sintering. These results were found for both $(Y,Pu,U,Zr)O_{2-x}$ and $(Er,Y,Pu,Zr)O_{2-x}$

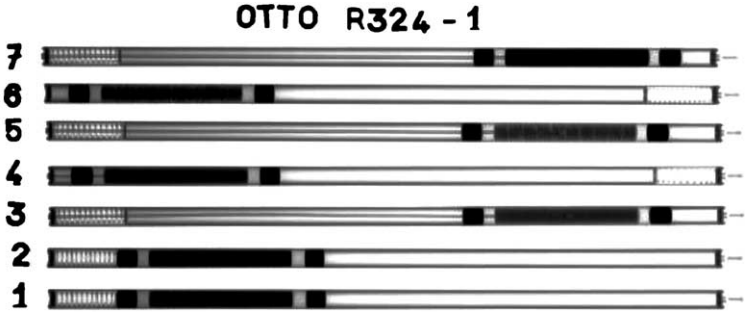

Fig. 7. X-ray image of the seven capsules before irradiation.

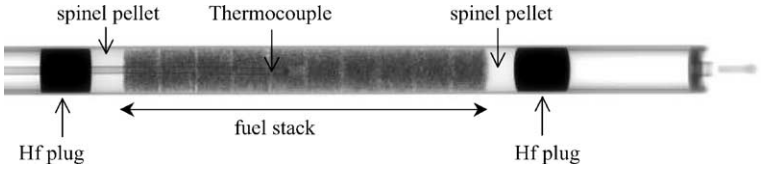

Fig. 8. Detail of the X-ray image of capsule nr. 5, explaining the capsule inventory.

microspheres. The chemical interaction did not occur when the sintering temperature was 1873 K and therefore this sintering temperature was used in the fabrication stage. These phenomena are discussed in more detail in [6], and it was concluded that the interaction of spinel with the fissile phase occurs at temperatures above 1973 K.

4. Irradiation

4.1. Description of the irradiation

The OTTO experiment has been irradiated in the HFR Petten. The irradiation duration is 22 HFR cycles, which corresponds to 548 full power days (FPD). The irradiation started on 27 October 2000, and was completed on 30 December 2002.

During the irradiation the fuel and the cladding temperature were monitored by means of 24 thermocouples. Four central thermocouples measured the temperatures of capsule nr. 3, 4, 5 and 7. In Fig. 9 the central temperatures are shown for the complete irradiation. Unfortunately, the temperature signal of capsule 4 was lost during the fourth HFR irradiation cycle (after about 80 full power days). The other thermocouples monitored the cladding temperature at various axial positions. The computed power and burn-up, including the central temperatures are listed in Table 3.

The thermal behaviour of OTTO is in line with the model calculations, as becomes clear from Table 3. The central fuel temperature is typically 1273–1373 K at the maximum flux position (capsules 3 and 5). The

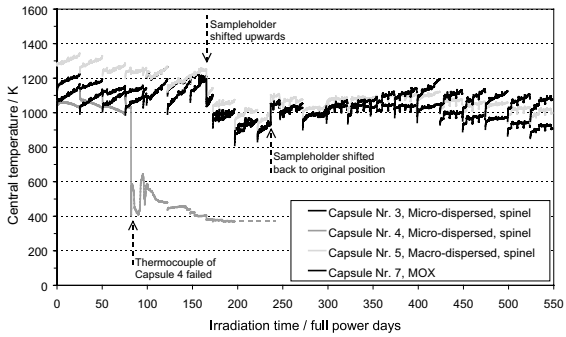

Fig. 9. Central temperature and control rod position during the OTTO irradiation.

zirconia solid solution capsules 1 and 2 have a higher (computed) central temperature of about 2173 K at BOI, due to the low thermal conductivity of zirconium oxide. No central thermocouple was present in these capsules.

4.2. Results of neutrography

At various stages during the irradiation neutrographic images were taken; before irradiation, after 1 cycle (25 d (FPD)), 7 cycles (172 d), 14 cycles (347 d) and after irradiation (548 d). From the neutrographic images the swelling and crack behaviour can be observed during irradiation.

Image analyses was performed on the neutrographic images, showing that:

- The axial swelling of the fuel stacks of the capsules is limited to 2%, except for capsule nr. 4. The fuel stack

Table 3
Irradiation parameters of the OTTO irradiation

Capsule	Fission power/W cm^{-1}		Burn-up/GW d m^{-3}	Central temperature/K at BOI	
	BOI	EOI		Calculated	Measured
1	280	112	200.1	2173	–
2	288	119	208.7	2173	–
3	220	100	166.8	1240	1226
4	202	106	162.7	1155	1032
5	218	99	164.7	1207	1345
6	199	105	161.0	1298	–
7	217	166	207.5	1306	1168

of capsules 1 and 2 seems to show very slight shrinkage. The macrodispersed spinel based samples (capsules 5 and 6) show less axial swelling than the microdispersed samples (capsules 3 and 4). This is in accordance with earlier observations from spinel/UO_2 irradiations, which were performed within the EFTTRA framework [6].

- The radial swelling is difficult to measure quantitatively, but the gap between fuel pellets and cladding still exists. This indicates that also the radial swelling is limited.
- Capsules 1 and 2 show a clear crack structure. From the other capsules the neutrographic images did not reveal any cracks, but they are also more difficult to distinguish (because spinel is invisible on the neutrograms), especially in the macrodispersed images.
- The cladding of capsule nr. 4 appears to be damaged, which is in agreement with the failure of its central thermocouple. The exact nature of the damaging of capsule nr. 4 is difficult to assess, but it appears the diameter of the cladding tube has increased slightly.

More detailed quantitative results of the image analyses will be prepared.

5. Conclusion

For the OTTO experiments, two basic types of Pu-containing pellets were fabricated, composite pellets and homogeneous pellets. The composite pellets contain spinel as an inert matrix, the homogeneous pellets are based on a zirconia matrix. For the composite spinel fuels, both macro (250 μm inclusions) and microdispersed (25 μm inclusions) fuels were fabricated. Each fuel contained either uranium or erbium dopant, which gives four spinel fuels and two zirconia based fuels. For reference, a MOX sample was fabricated. In total seven capsules were prepared for the OTTO irradiation.

The fabrication of the pellets for the OTTO experiment was completed successfully. The fabrication of the composite pellets containing spinel required considerable optimization in order to minimize cracking. After optimisation, good quality pellets were obtained with densities higher than 90% TD. The zirconia pellets were fabricated from crushed sol–gel spheres and have a very high density.

The OTTO irradiation was completed on December 30, 2002 and extensive post irradiation examinations are to be performed in 2003. The neutrographs made during the irradiation show limited axial swelling (<2%) of the fuel stacks, except for capsule 4. This capsule, which contains a microdispersed spinel-based sample, appears to be damaged. The on-line analysis of the thermocouples show good agreement with design calculations.

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