



Analytical investigations of irradiated inert matrix fuel

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ABSTRACT

Yttria stabilised zirconia (YSZ) inert matrix fuel (IMF) fabricated at PSI and irradiated 3 years in the Halden Material Test Reactor (HBWR) since 2000, has been examined by Electron Probe Microanalysis (EPMA) and Secondary Ion Mass Spectroscopy (SIMS) after irradiation and compared with data gained for the unirradiated material. The examined pellet cross-section was estimated to have an equivalent burn-up of 22 MW d kg⁻¹. EPMA measurements demonstrate that the burn-up was rather flat over more than the half pellet radius. A Pu consumption of about 2.5 wt% has been measured with a higher rate in the fuel border zone. The high fuel temperature is responsible for a certain homogenisation of the mineral phases in the fuel centre region whereas the border zone has remained rather with an as-fabricated phase distribution. The central part was also characterised by a dense porosity distribution as well as a temperature and relocation driven depletion of the volatile fission products Xe and Cs. In addition, SIMS has been realised on the same specimen in order to determine the semi-quantitative distribution of different isotopes in the pellet.

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1. Introduction

The growing production of Pu in current LWRs is a general concern of the nuclear community. Different options have been proposed to reduce the proliferation risk or more to the point to reduce the Pu inventory by using it in the actual fleet of commercial nuclear reactors. One promising option is the implementation of Pu-containing inert matrix fuel (IMF) within a last fuel cycle. IMF can also be seen as an option to convert and thus reduce long-lived transuranium isotopes [1–4].

A major advantage of the IMF material would be that no fissile material with regard to energy production is left over after the end of irradiation. The conditioned assemblies can be sent in a once-through-cycle to direct waste disposal. Since the matrix is uranium free, the neutronic reactivity needs to be controlled by the addition of a burnable poison such as Er. Candidate fuels proved to be also very stable and practically insoluble [5] especially after irradiation and the low remaining actinide content is an important asset for the non-proliferation point of view.

PSI has been working on the IMF concept for more than a decade focusing on the yttria stabilised zirconia with dissolved Pu [6–8].

A batch of IMF was produced at PSI and irradiated in the Halden boiling water reactor (HBWR) within the IFA-651 experiment. The aim of this experiment in the Material Test Reactor was to measure the thermal behaviour of an yttria stabilised zirconia inert matrix

fuel under irradiation conditions similar to current LWRs and to compare the performance with MOX rods [9–11]. The present work focuses the post irradiation examination on the change in the fuel microstructure that has occurred during irradiation and the redistribution of the main constituents including the burning of plutonium as well as the behaviour of some fission products.

2. Material specification and irradiation

The IMF was made up of ZrO₂, Y₂O₃, PuO₂ and Er₂O₃ powders mixed and milled in a two stage attrition mill from KAERI (Korea Atomic Energy Research Institute). The precompacted granules were pressed to pellets and sintered. The characterisation of the fresh fuel pellets was reported in [7] together with the electron microprobe analyses of a non-resintered fuel piece of the same batch. The nominal composition of the fresh IMF after fabrication is given in Table 1.

After fabrication and characterisation the pellets were sent to IFE, Kjeller (Norway) for assembling and instrumentation of the rods. The irradiation took place in the IFA-651 rig starting in 2000 [12]. Rod 2 of the IFA-651 rig with 6 rods was discharged in the May–July 2003 shutdown. The equivalent burn-up of the rod reached about 21 MW d kg⁻¹. The rod piece sent to PSI for destructive examination had a burn-up of about 22 MW d kg⁻¹. IFE performed also the destructive (ceramography) and non-destructive post irradiation examinations [13]. The results of the first examinations are published in [9,10,13]. A neighbouring rod piece was sent to PSI for density, ICP-MS and electron microprobe analyses (EPMA).

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Table 1
Average concentration of elements in unirradiated attrition milled YSZ – IMF [7].

Element	O	Y	Zr	Er	Hf	Pu	Am
(wt%)	22.8 ± 0.5	9.1 ± 0.6	46.9 ± 1.5	4.7 ± 0.1	1.1 ± 0.1	14.6 ± 0.6	0.8 ± 0.1
(at.%)	66.6	4.8	24.0	1.3	0.27	2.8	0.14

The characteristic of the attrition milled YSZ–IMF material is that Y_2O_3 but also Er_2O_3 have a stabilising function in the zirconia based face centered cubic solid solution, whereas PuO_2 is assumed to be dissolved in the inert matrix with an expansion of the unit cell. Extensive analyses of the IMF material have been realised in PSI prior to irradiation. The major results have been published elsewhere [7] and are just very shortly summarised in the next paragraphs. These measurements are used as a reference state for the analysis of the irradiated specimens.

The XRD pattern confirmed a solid solution with varying composition but pure plutonia and almost pure zirconia particles on a micron range could not be ruled out. Unsatisfactory features of this fuel are the necessity to apply a high sintering temperature and the low thermal conductivity of the product, which at least is comparable to standard fuel at high burn-up [10].

EPMA showed a quite high heterogeneous elemental distribution of the fresh IMF on a 100 μm scale. Locally, the concentration of the main components varied strongly evincing thus a poor homogenisation of the material.

The large pores formed by surface preparation are mostly Pu, Er and Y rich indicating the locally poor integration of these phases (Fig. 1(a)). Also the incorporation of the Y and Er trivalent cations into the cubic zirconia lattice is different according to their size and it was demonstrated by the extremely large Er concentration range measured (Fig. 1(a)). However, for normal and low Pu content the complementarities of both Y and Er on one hand and Zr on the other hand has been evidenced and thus partially the homogenisation between these phases during the sintering process (Fig. 1(b)). But the scattering of Er and Pu concentrations indicates that this fuel is locally on a micron scale not throughout a single phase ceramic (Fig. 1(a)). Resintering at higher temperature of a batch of the same IMF improved the homogeneity significantly [7] but was not prepared for irradiation.

EPMA and SIMS analyses of the irradiated material from the 1st campaign are reported below.

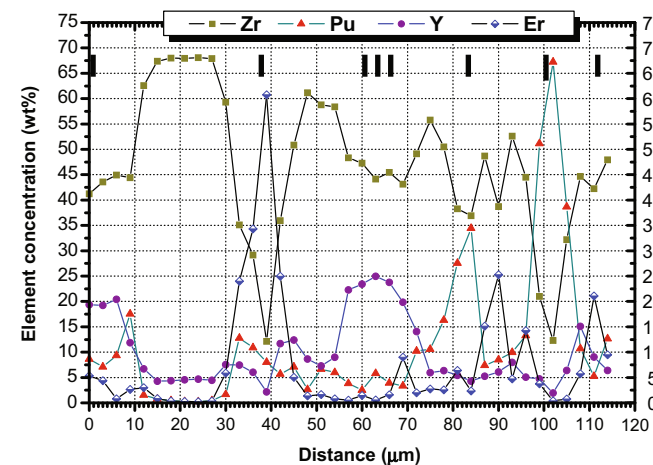


Fig. 1a. EPMA point area analysis ($3 \mu m \times 2 \mu m$) along a line on an unirradiated attrition milled YSZ–IMF pellet. Note the pore positions in the graph indicated by vertical bold bars.

3. Specimen preparation and analysis conditions

The fuel rod piece cut out at IFE Kjeller from rod 2 and sent to PSI was a sample adjacent to the pellet examined at IFE [13]. The pellet position was in the high burn-up region of the rod. The denomination IFA-651-2.2 refers to the rod number 2 and fuel piece 2. The EPMA sample was embedded a few times in a one inch steel sample holder with EPOFIX™ epoxy resin and ground to remove old embedding material and the subsequent damaged fuel surface. After the final polishing step with 0.25 μm diamond paste the sample had a thickness of about 1.6 mm. After decontamination of the sample surface by ultrasonic cleaning in ethanol the surface received a thin conductive carbon coating (20 nm). The same specimen has been used for the SIMS measurement after a very light repolishing to remove the coating layer.

The EPMA was performed on a shielded CAMECA SXR SX50 instrument with wave length dispersive spectrometers. A radial concentration profile of the main IMF elements and the fission products Nd, Cs and Xe was acquired. The preselected positions were analysed by a scanned beam of 20 keV, 160 nA (size of $12 \mu m \times 9 \mu m$ in the fuel periphery up to $55 \mu m \times 45 \mu m$ away from the border) avoiding pores as far as possible. The oxygen content was calculated by stoichiometry and the data points were normalised.

SIMS measurements were carried out on a shielded CAMECA Atomika 4000 instrument with a quadrupole mass analyser. $^{133}Cs^+$ primary ions of 10 keV, 435 nA and a beam diameter of 90 μm were applied on 17 measuring points across the fuel in steps of 0.5 mm. An electron gun was simultaneously applied for charge compensation on the insulating sample. In order to gain direct dependency for all detectable isotopes of plutonium, the unit parameters were optimised to ^{239}Pu . The SIMS parameters were fixed by normalising the peak intensities with the ^{133}Cs peak signals for each point [14].

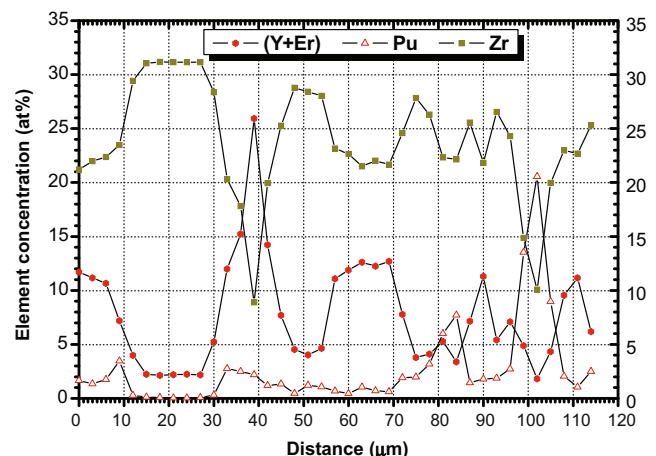


Fig. 1b. EPMA point area analysis ($3 \mu m \times 2 \mu m$) along a line on an unirradiated attrition milled YSZ–IMF pellet.

4. EPMA analysis

The sample surface showed a star like crack pattern with seven radial cracks (see also [13]). A few of them branched out within the outer half radius region.

4.1. SEM mode examination

Scanning electron microscopy images (SEM) with the EPMA in the relevant radial fuel positions were taken to investigate the porosity structure and also qualitatively through the bright–dark grey tone gradation (backscattered electron yield) the phase distribution. Phase patterns with the heavy elements (Pu, Er) and ‘light’

elements (Zr, Y) respectively are seen on the SEM images in Fig. 2(a) and (b). A series of images from the periphery to the centre along a pellet diameter were taken (Fig. 2(a)–(f)) for these purposes. From half radius towards the centre the brindle character of SEM images disappears. This part discloses a certain homogenisation of the above mentioned main mineral constituents (Fig. 2(d)–(f)).

After irradiation of this attrition milled IMF-fuel in the Halden BWR to a moderate burn-up of about 22 MW d kg⁻¹, the porosity in the border is low except at locations of high Pu concentrations with high local burn-up. The porosity within the outer one third of the radius is clearly reduced with respect to the fresh fuel (Fig. 2(a) and (b), [7,13]). Here small pores dominate although big pores are also present.

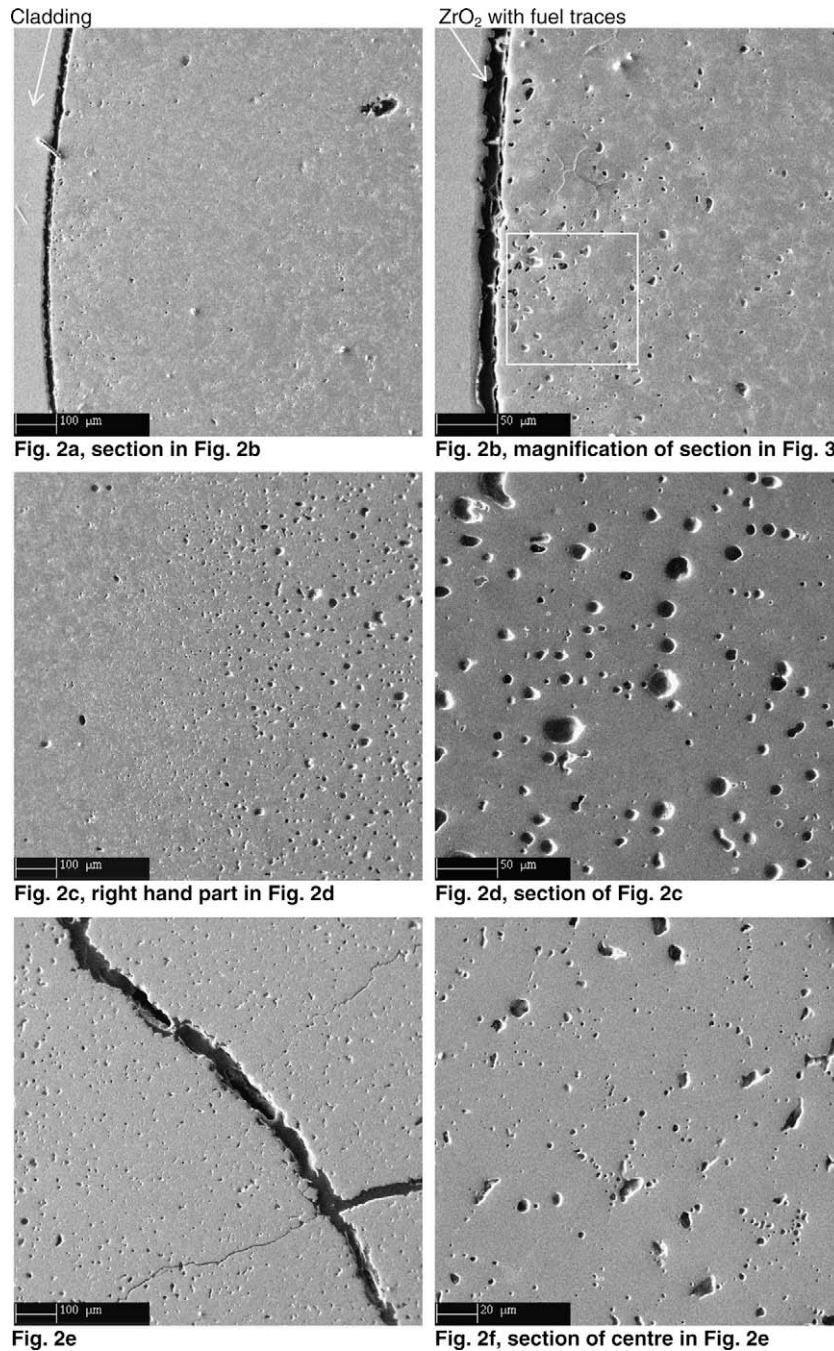


Fig. 2. SEM images showing porosity of irradiated YSZ – IMF. (a and b): at pellet periphery (note: bright field marks Pu and Er/rich positions. Dark fields are Y and/or Zr rich. Thin ZrO₂ layer with traces of fuel on cladding. c and d: position about 1.5 mm from pellet periphery (note porosity mainly from volatile impurities). d and e: position at pellet centre (note grain boundary pores).

At 1.5 mm ($r/r_0 \approx 0.65$) from the fuel periphery, a sudden porosity increase was observed with more spherical large pores that indicated gas occurrence and swelling driven by impurities contained in the feedstock (Fig. 2(c) and (d)). The porosity change for the adjacent sample investigated at IFE Kjeller (421 mm from rod bottom [13]) has been found to be around half radius position. In the mid radius toward pellet centre the pore shapes are spherical or elongated through coalescence. In the centre the porosity is again lower and a decoration of the grain boundaries with pores is observed (Fig. 2(e), (f)). The enclosed surface reflects a strong grain growth from a few microns up to 20 microns. The fuel gap was closed during irradiation as fuel residues stick at the inner cladding oxide (Fig. 2(b)).

4.2. X-ray mapping and quantitative analyses

Elemental distribution mappings have been acquired on the irradiated specimen in the different zones of the fuel pellet and compared to reference ones. The distribution patterns look very much the same in the outer half radius part as for the unirradiated fuel [7]. A typical example is presented in Fig. 3. In the periphery the average Zr content is about 47 wt% (24 at.%), the Pu average is 10 wt% (2 at.%) and the Er average is about 5 wt% (1.4 at.%). Although the element distributions look similar to the fresh fuel, the concentration ranges are slightly diminished and the bonding of Y and Er rich phases with the matrix is enhanced as only few pores have arisen from surface preparation with few of them

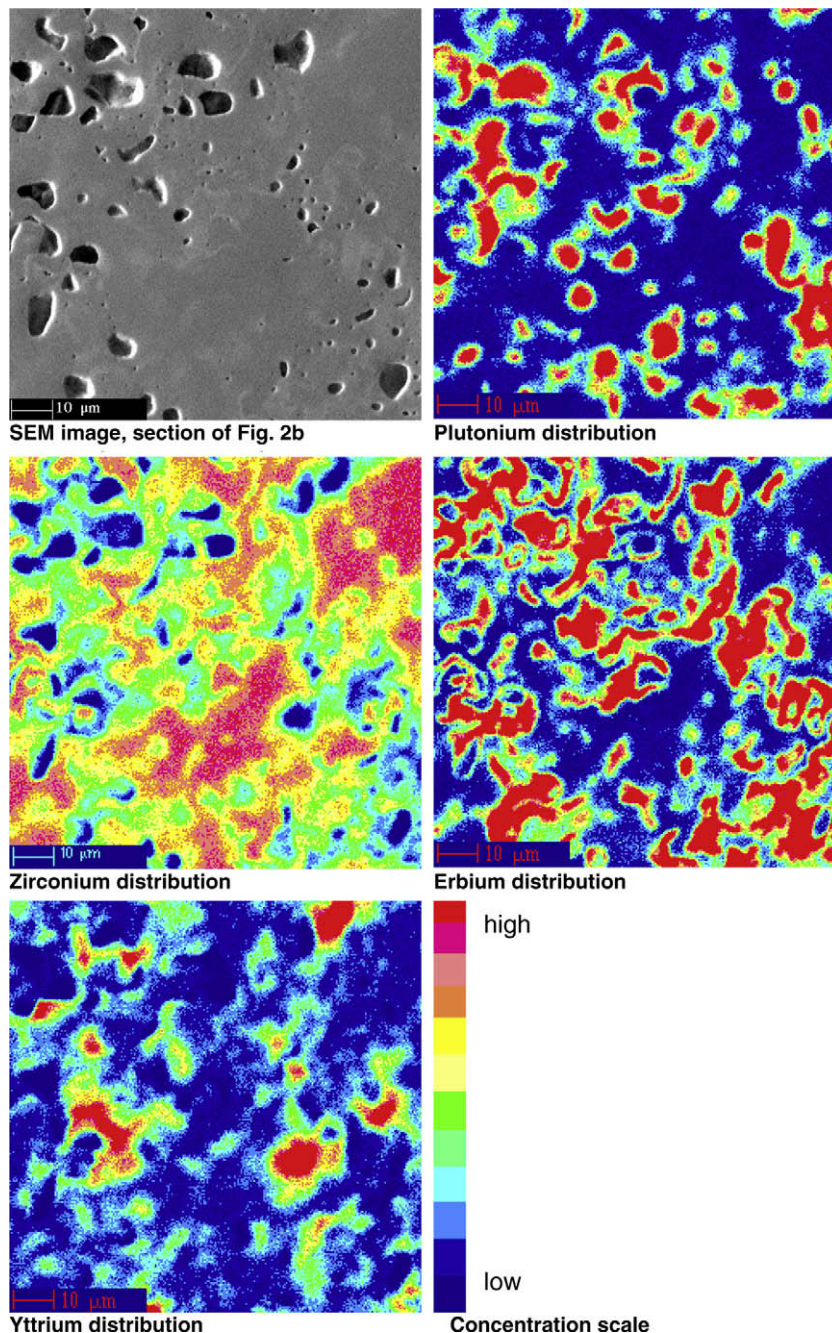


Fig. 3. Element mapping of irradiated YSZ – IMF at pellet periphery (section of Fig 2(b)). The content range (dark blue–red) are the following: Zr: 16–66 wt% (9–32 at.); Pu: 1–50 wt% (0.3–10.5 at.); Er: 1–40 wt% (0.3–13 at.%). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

having an Y or Er rich ground. Big Pu rich pores are formed at the fuel rim and probably represent sites with a high burn-up.

A typical example of the centre is presented in Fig. 4. An obvious homogenisation through interdiffusion has occurred which very much smoothed the concentration differences for Y, Er, Pu and Zr (decreasing order). Pu tends to concentrate at grain boundaries. Porous areas are generally Pu rich whereas in the grains Zr predominate. In the centre the average Zr content is always about 47 wt% (24 at.%), the Pu average reaches about 12.5 wt% (2.4 at.%) and the Er average is stable at about 5 wt% (1.4 at.%).

The main element but also the fission products distributions have been analysed using quantitative point area analyses. A general view is given by the diametrical profile presented in Figs. 5 and 6.

The smoothing of the element distribution in the centre is also visible in the diametrical profile analyses. The high Pu consumption on the pellet borders is also seen and the overall consumption is estimated to be around 2.5 wt% Pu, which is one sixth of the inventory.

Nd and Cs accumulations in Pu rich areas are observed in the outer fuel part. At around $r/r_0 = 0.7$ the Xe and Cs concentrations drop. Cs precipitates and Xe filled pores are observed in the inner part.

The burn-up represented by the fission product Nd is rather flat and increases at the periphery analogous to the Pu consumption.

The depletion of the volatile Cs and Xe fission products, for about two thirds of the pellet radius, stands for the effective migration out of the hot fuel centre. It is consistent with the fission gas

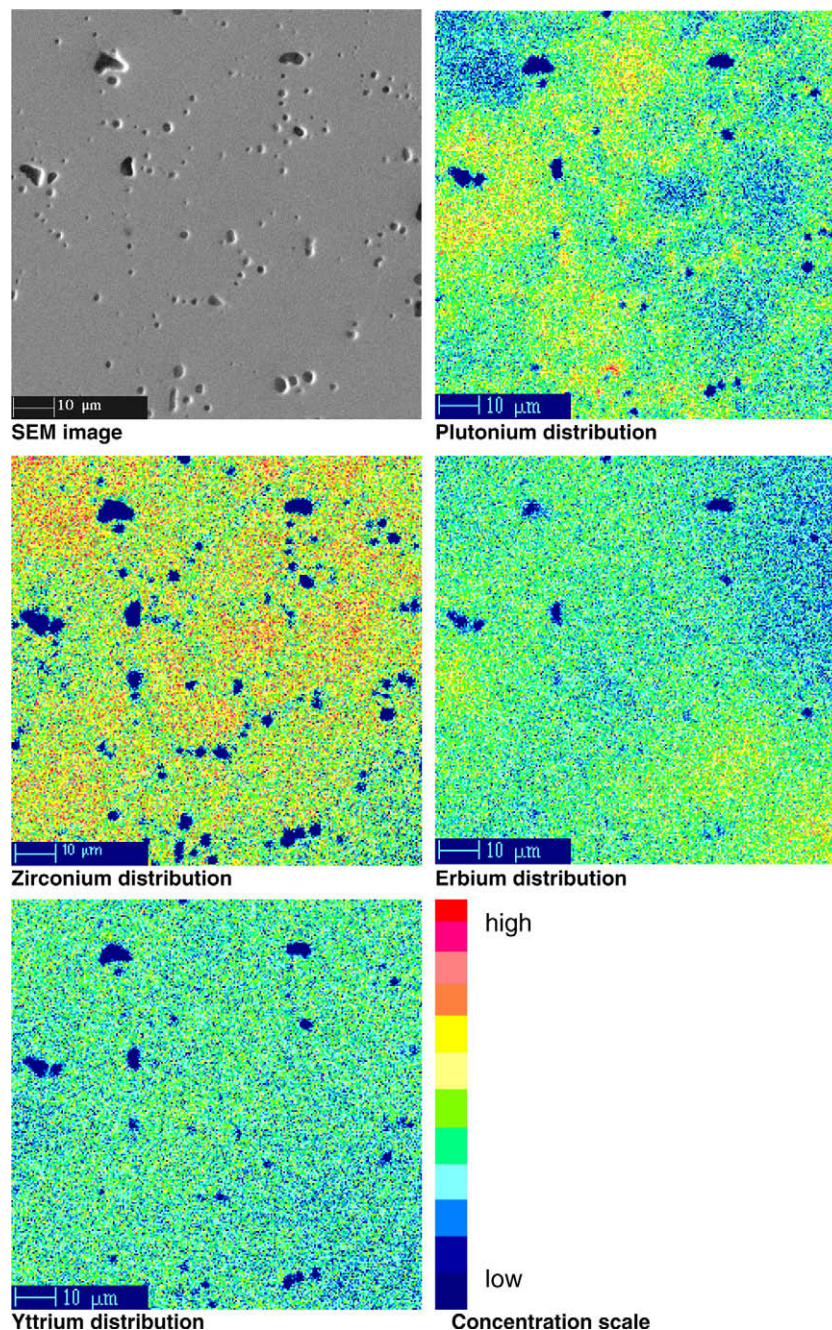


Fig. 4. Element mapping of irradiated YSZ – IMF at pellet centre. Position similar to Fig. 2(f). The content range (dark blue–red) is the following: Zr: 41–53 wt% (21–27 at.); Pu: 8–19 wt% (1.5–3.8 at.); Er: 4–6 wt% (1.1–1.7 at.%). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

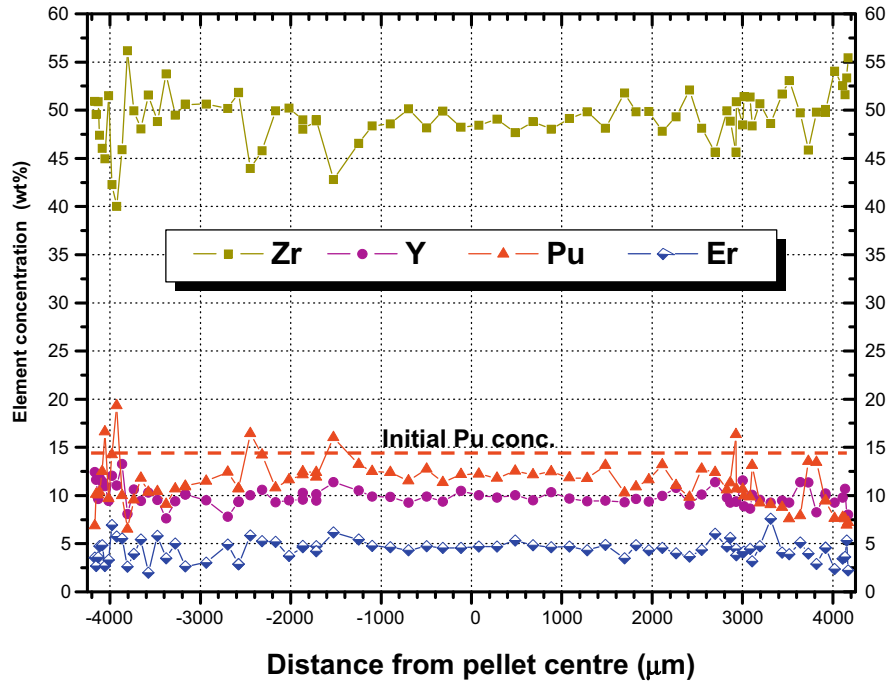


Fig. 5. Quantitative element point area analysis for the main constituents of the irradiated YSZ - IMF along a pellet diameter.

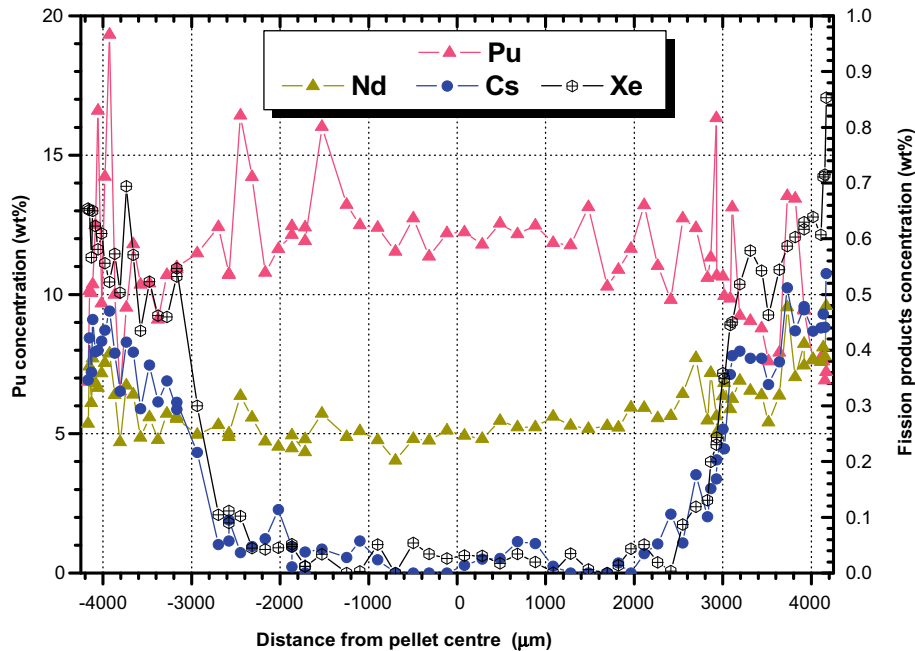


Fig. 6. Quantitative element point area analysis for Pu and three fission products in the irradiated YSZ - IMF along a pellet diameter.

release measured and fits with the sudden porosity change observed at this position on the scanning electron image (Fig. 2(c)).

The local quantitative linescans demonstrate the perpetuation of the phase distribution in the fuel border as seen for the as-fabricated fuel and shown above with the X-ray mapping. It means an insufficient homogenisation of the main elements and thus strong concentration variations and even Zr rich areas with hardly any Pu present. Otherwise in the centre, the Zr and Pu concentrations change normally rather smoothly and for Y and Er change only little. Cs and Nd follow the Pu variation according to the higher local burn-up. Xe is often peaked beside the maximum Pu content.

Intermetallic precipitates were not examined in detail; they are however well documented in the ceramography of an adjacent fuel sample at IFE [13]. X-ray spectra of the intermetallic precipitates in the centre revealed Ru and Rh as major elements with minor amounts of Pd and Tc but scarcely any Mo.

5. SIMS analysis

On the same fuel pellet cross-sections secondary ion mass spectrometry analysis (SIMS) was performed using a cesium primary

ion source (^{133}Cs) [14]. The analysis results presented here are semi-quantitative with respect to the isotope ratios and the isotopic composition respectively. Measurements on an unirradiated specimen with comparison and subsequent quantification are intended in a further step. The results are basically consistent with the EPMA data.

For Pu an increased relative consumption towards the border of the fissile ^{239}Pu against all other Pu isotopes can be seen (Fig. 7) also against the isotopes that are mainly consumed either by neutron capture (^{238}Pu) and/or fission (^{241}Pu). All of them are relatively enriched towards the border by the enhanced neutron reactivity moderation there. The relative isotope amounts can also be retrieved from the plot.

Er acts as a burnable poison. The ^{167}Er isotope is consumed due to the high neutron capture cross-section of this isotope compared to the other Er isotopes. ^{168}Er is thus produced with a higher rate in the border zone. Fig. 8 shows the profile of isotopic abundance ratio $^{167}\text{Er}/^{166}\text{Er}$ and $^{168}\text{Er}/^{166}\text{Er}$ and the correspondingly pronounced rim effect.

The Cs isotope concentrations (^{134}Cs , ^{135}Cs , ^{137}Cs) are lower in the centre due to their diffusion out of this hot fuel part (Fig. 9). This is quite discernible even on the logarithmic scale. The daugh-

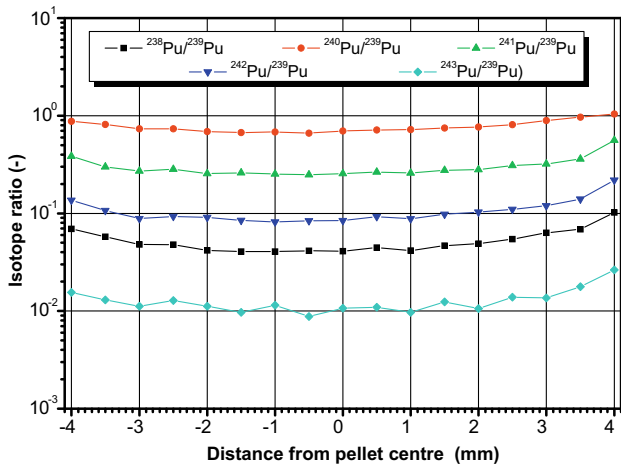


Fig. 7. SIMS analysis of the irradiated YSZ – IMF along a pellet diameter. Pu isotope abundance ratios relative to the fissile ^{239}Pu .

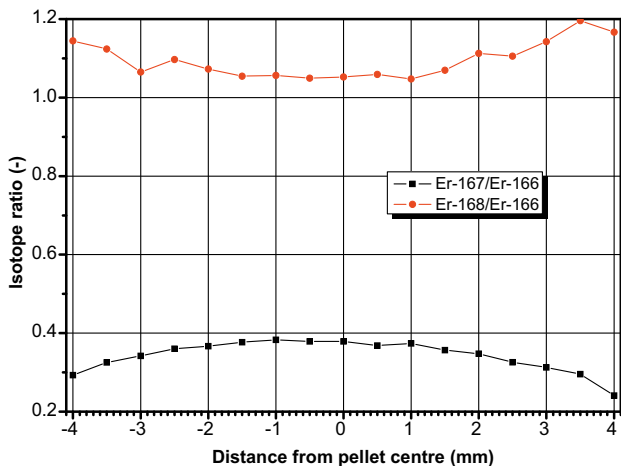


Fig. 8. SIMS analysis of the irradiated YSZ – IMF along a pellet diameter. Er isotope abundance ratios showing different neutronic behaviour.

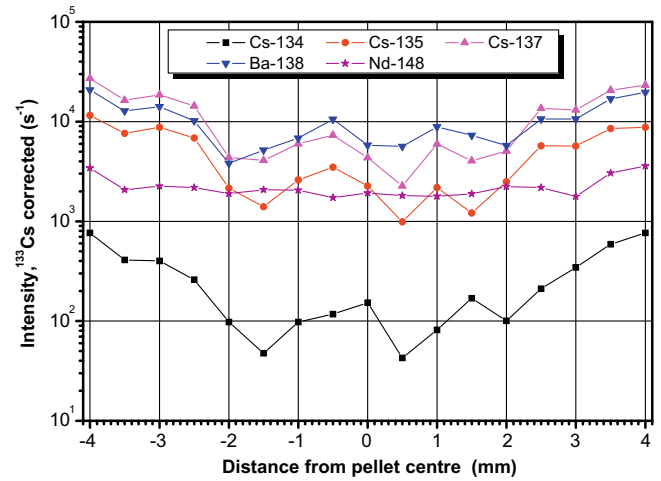


Fig. 9. SIMS analysis of the irradiated YSZ – IMF along a pellet diameter. Relative concentrations of Cs isotopes and burn-up monitor ^{148}Nd .

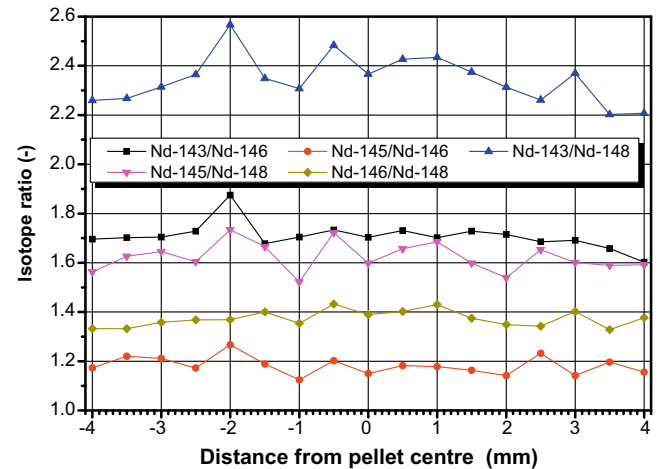


Fig. 10. SIMS analysis of the irradiated YSZ – IMF along a pellet diameter. Nd isotope abundance ratios.

ter nuclide ^{138}Ba from ^{138}Cs precipitates and defies the diffusion so that its concentration drops less. The ^{148}Nd burn-up monitor was found to be rather flat over the diameter (Fig. 9) giving thus proof of the even radial fission rate at this relatively moderate burn-up.

Nd-isotopes formed by fission show their different neutronic behaviour through the individual, subsequent neutron capture as for ^{143}Nd and ^{145}Nd relative to ^{148}Nd . It entails in the border zone a higher consumption rate of the first two isotopes (Fig. 10). Congruent with the higher neutron capture cross-section this effect is more distinct for ^{143}Nd .

6. Leaching tests

Finally, the leachability of the irradiated IMF material was tested. Neither the classical wet-chemical dissolution procedure (boiling under reflux) nor the microwave pressure digestion technique using a mixture of concentrated nitric acid, hydrofluoric acid and hydrogen peroxide yielded a complete dissolution of the fuel sample. This strong inert behaviour is in contrast to non-irradiated material [15], which can be dissolved completely with the described techniques [16].

7. Summary and conclusion

The analysis results presented showed a rather good fuel behaviour under irradiation up to a burn-up of 22 MW d kg⁻¹ despite some heterogeneity in the feed mixture, the disturbing impurities and the insufficient sintering conditions for the attrition milled YSZ–IMF [7,10].

A low porosity is observed in the outer IMF-fuel region but with a broad pore size distribution depending on the local Pu content. A sudden and strong porosity increase is observed at $r/r_0 = 0.65$ with peak around $r/r_0 = 0.35$ partly due to gas forming impurities (swelling). Finally, in the centre a distinctive grain growth with intergranular small bubbles is observed.

The observed porosity change at $r/r_0 = 0.65$ is clearly related to the volatile fission products Xe and Cs distribution with an effective depletion in the hot fuel part. A rather high fission gas release is thus confirmed and attributed to grain growth and high temperature in the centre (low thermal conductivity and high linear heat rate up to 35 kW m⁻¹). It must however be noted that at higher burn-up the gas release is comparable to MOX fuel as observed in the 2nd part of the irradiation campaign [11].

The burn-up distribution (Nd) is rather flat through the pellet diameter but shows local variations at the periphery that are related to the Pu local concentration as usual. The Pu burning is evaluated from the EPMA measurements at about 2.5 wt%. Also, homogenisation of all mineral constituents is observed in the pellet centre and is due to the high temperature of this region.

First SIMS fuel analysis using Cs primary ion bombardment have been realised on the EPMA specimen and are consistent with the EPMA data. The neutronic effects could be demonstrated by the determination of the relative isotopic composition of different elements across the pellet diameter.

The analyses attest the fuel integrity and thus the stable irradiation behaviour of YSZ–IMF fuel and *the material proved to be also chemically inert*.

It can be concluded that apart from the good fuel behaviour the optimisation of the fabrication process is necessary and achievable.

The destructive examination of the rods after the 2nd part of the campaign is recommended to gain further insight in the microstructural development and elemental repartition at higher burn-up.

Acknowledgements

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