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Post-irradiation studies on LWR-MOX fuel fabricated by the optimized co-milling process

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Abstract

A LWR-MOX fuel pin cross-section irradiated up to 4.4% local burnup was examined by scanning electron microscopy and X-ray microanalysis. The fuel had been fabricated by the optimized co-milling process (OCOM) of UO_2 and PuO_2 powders of the final composition of $U_{0.7}Pu_{0.3}O_2$ and blending with UO_2 powder down to a typical LWR composition of $U_{0.949}Pu_{0.052}O_2$. The duplex structure of the highly burnt Pu rich agglomerates in the U rich fuel matrix remained. In the UO_2 matrix, 5.3% PuO_2 were observed at the fuel surface caused by the so-called rim effect. The cross-section averaged EOL PuO_2 concentration in the total fuel was 2.9% PuO_2. About 9% PuO_2 were measured in the dense areas of the high-porous agglomerates. Here, the burnup was calculated from the Nd concentration to be 19%. The cross-section averaged EOL Xe concentration in the total fuel was 0.29% Xe, resulting in a Xe release of 43% of the generated Xe. The oxidation of the inner Zircaloy-4 region attained a thickness up to 20 μm in direct contact with the Pu-rich agglomerates. The outer oxide layer had a thickness of 22 μm.

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1. Introduction

The fabrication of uranium–plutonium oxide fuel (MOX) for pressurized light water reactors (LWR) by ALKEM had started in 1972. UO_2 powder was mixed with about 5% PuO_2 powder. The amount was dependent on the fissile Pu fraction, and the PuO_2 grain diameter was limited to 0.1 mm. Fuel pins of this type were for the first time irradiated in the reactor Kernkraftwerk Obrigheim (KWO) up to about 4% burnup. Subsequent dissolution experiments in 1977 had shown that the fuel although irradiated to higher burnups, was not completely dissolvable in nitric acid. About 5% of the initial Pu content in the fuel remained undissolved [1]. As a consequence, advanced fuel fabrication methods were requested with higher rates of dissolution and less amounts of undissolved fuel already in the unirradiated state. One of these new methods considered recycled PuO_2 powder as a component of the initial product which was co-milled together with UO_2 in dry atmosphere. This optimized co-milling manufacturing process (OCOM) originally intended for the fabrication of fast reactor fuels resulted in an extremely fine-grained powder mixture. A continuous series of a solid $(U,Pu)O_2$ solution was obtained after sintering of the respective pellets. The Pu fraction corresponds typically to 25–30% PuO_2. This fuel was blended with UO_2 powder for use as LWR fuel. The final composition is about UO_2–5%PuO_2 depending on the fissile Pu fraction which is again contingent on the scrap fraction from the MOX fabrication for fast reactors [1].

The described LWR fuel type has a duplex structure, the full homogeneity is impaired by the presence of Pu rich mixed oxide islands in the UO_2 matrix [2] which survive the irradiation process at moderate linear heat ratings. However, the amount of Pu in the residues after dissolution of the irradiated LWR-MOX fuel in nitric acid is low and was measured to be 0.03% related to the initial Pu in the fuel [3].

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A high number of OCOM fuel pins with 15–30 vol.% $(U,Pu)O_2$ (OCOM-15 and OCOM-30) agglomerates in a UO_2 matrix was irradiated in KWO at moderate linear heat ratings [4]. A pin cross-section was investigated by ceramography and X-ray microanalysis for studies of the fuel homogeneity, local burnup behaviour, fission gas release and Zircaloy clad oxidation behaviour.

2. Experimental

The fuel, fuel pin and irradiation data of the OCOM-30 fuel type are given in Table 1 [4,5]. The fuel was fabricated in 1986, and irradiation in KWO started in 1987. Pin No. PN 19 was a segmented pin from the fuel element 17.42 and contained different short segments [4]; segment No. P 498 was selected for post-irradiation studies at Forschungszentrum Karlsruhe. For this purpose, a disk of 10 mm height cross-section was cut from the segment and was embedded into araldite resin, abraded, polished and examined using light-optical microscopy by the Hot Cell Staff of this Centre.

The analytical work was carried out by scanning electron microscopy and X-ray microanalysis with the radiation-shielded and combined JEOL instrument JRX50A/JSM6400. Step scans of the actinides U and Pu and of the prominent fission products were taken over night by a programmed method in two randomly preselected radial directions between fuel cross-section centre and surface using a step width of 100 μm or in picked-out positions for the measurements in the UO_2 matrix of the fuel. The X-ray intensities of all analysed elements were calibrated with element or compound standards of precisely known compositions and were converted to mass concentrations by a ZAF correction programme developed in this Centre. The measurements were done with 15 kV working voltage. A hypothetic Xe standard was used with 1% Xe in UO_2 by back-calculation of the ZAF-corrected Xe concentration to the respective Xe intensity of the Lα emission line.

Table 1
Fuel and irradiation data of the pin segment P 498 [4,5]

Fuel data	
Fuel	UO_2–5.1%PuO_2
Fissile fractions	0.7% ^{235}U/U-total, 68.6% ^{239,241}Pu/Pu-total
Pu concentration in agglomerates	$Pu/(U + Pu) = 30\%$
Fuel stoichiometry	1.99
Fuel density	95% th. d.
Pellet diameter	9.13 mm
Fuel pin data	
Radial gap	0.085 mm
Fuel pin diameter	10.75 mm
Cladding thickness	0.725 mm
Cladding material	Zircaloy-4
Internal pre-pressure	22.5 bar at RT
Irradiation data	
Mean linear heat rating	18 kW/m
Mean outside cladding temperature	320 °C
Local burnup	4.4% (42 GWd/t metal)

3. Results

3.1. Ceramography

The ceramography of the cross-section revealed a duplex structure of the irradiated fuel containing highly burnt $(U,Pu)O_2$ islands in an interconnected UO_2 rich matrix. These agglomerates were preserved in the total area due to the low time-averaged linear heat rating of 18 kW/m. The diameters were below 100 μm and the fringes were poorly defined in the centre of the fuel for which the high concentration of burnt-out fuel and open Xe and Kr bubbles is demonstrated by a scanning electron image (SEI) in Fig. 1. The light-optical microstructure in Fig. 2 illustrates a 100 μm agglomerate at the position of about 0.6 r_0 (r_0 = fuel pellet radius) where the metallic fission product precipitates dominate and the open fission gas bubbles nearly disappear. The situation is again different in the fuel rim region. The electron-optical and the light-optical microstructures in Fig. 3 reveal a 140 μm agglomerate including the fabrication pore structure, smaller metallic fission product precipitates and the voids of the highly burnt fuel. The oxidized inner Zircaloy-4 clad wall presents an increased oxide

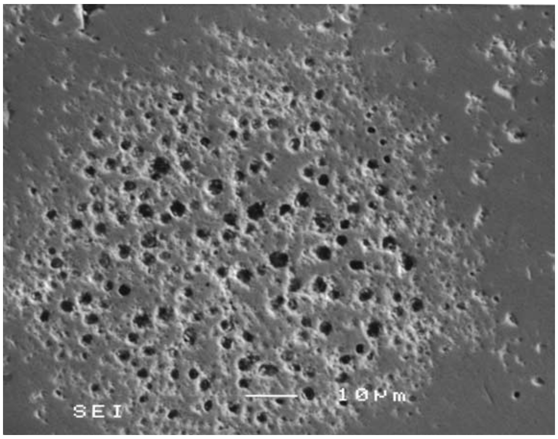

Fig. 1. Scanning electron image of a highly burnt $(U,Pu)O_2$ agglomerate in the fuel centre demonstrating the open fission gas bubbles and solid fission product precipitates.

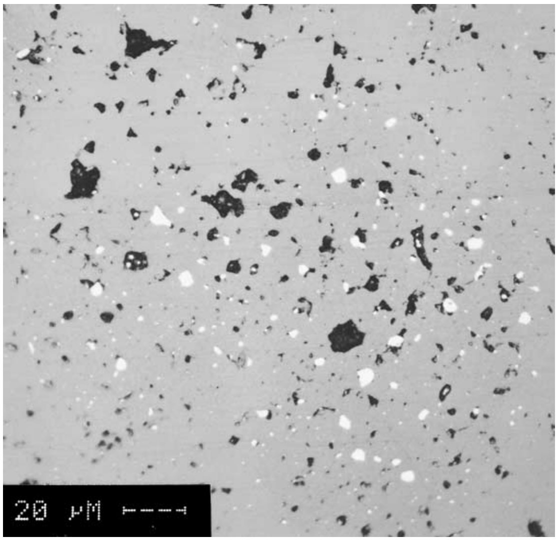

Fig. 2. Light-optical microstructure of a highly burnt $(U,Pu)O_2$ agglomerate at 0.6 r_0 (r_0 = fuel radius) accentuating the metallic fission product precipitates.

scale of 20 µm adjacent to the highly burnt $(U,Pu)O_2$ islands due to the higher local chemical potential of oxygen (higher oxygen partial pressure) which is caused by Pu fission. Because of that more oxygen is released than is bonded by the fission products. The oxide scale adjacent to the UO_2 matrix has an average thickness of 10 µm. An oxidized outer Zircaloy-4 clad wall was observed with a thickness of (23 ± 2) µm.

3.2. X-ray microanalysis

3.2.1. Plutonium

The cross-section averaged end-of-life (EOL) PuO_2 concentration in the total fuel was measured by step scans in two pre-selected radial directions to be 2.9% PuO_2 (Table 2). About 5.3% PuO_2 were observed at the fuel surface of the UO_2 matrix (Fig. 4). The cross-section averaged PuO_2 concentration in the UO_2 matrix is (2.0 ± 0.2)% PuO_2. These concentrations in the UO_2 matrix are relatively high and are possibly also contributed by very small $(U,Pu)O_2$ particles from the agglomerates which were dissolved in the UO_2 matrix during burnup. By way of comparison cross-section averaged PuO_2 concentrations of LWR-UO_2 fuels generated exclusively by ^{238}U–^{239}Pu conversion gave only 1.2% PuO_2 after comparable burnup and 3% ^{235}U enrichment [6].

The measurements of the PuO_2 concentration in the highly burnt $(U,Pu)O_2$-MOX agglomerates were more difficult, (9 ± 2)% PuO_2 were obtained in the dense areas of the high-porous agglomerates (see Figs. 1 and 3).

3.2.2. Neodymium

Neodymium is a local burnup monitor of the fuel because it is dissolved in the fuel matrix and becomes mobile only at very high fuel temperatures above 2000 °C. The burnup can be calculated with the fission yield of 0.087% Nd per % burnup [7]. The cross-section averaged concentration was measured to be 0.38% Nd related to the total fuel which results in 4.4% burnup (Table 2). About 0.8% Nd was measured in the UO_2

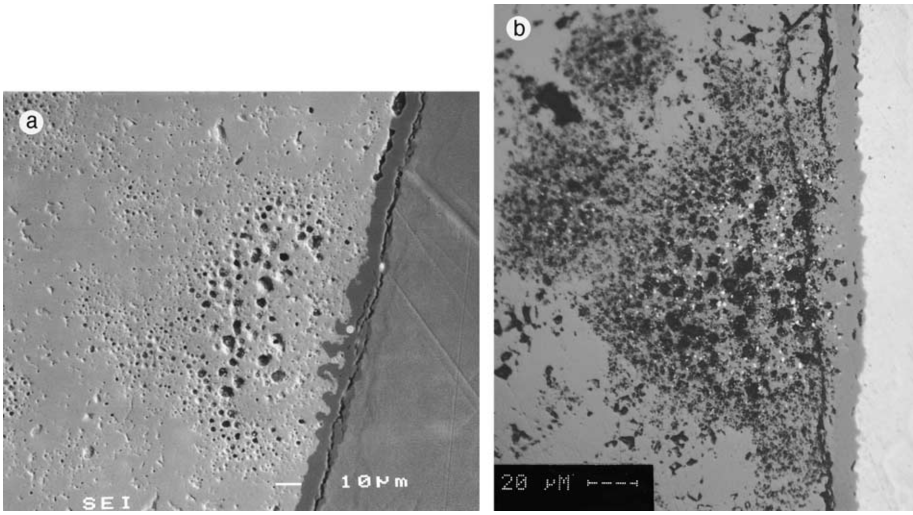

Fig. 3. Scanning electron image (SEI) (a) and light-optical microstructure (b) of a highly burnt $(U,Pu)O_2$ agglomerate in the fuel rim region demonstrating the fabrication pore structure, the metallic fission product precipitates, the fuel voids and the oxidized inner Zircaloy-4 clad.

Table 2
Cross-section averaged concentrations of actinides and dissolved fission products in the total fuel (agglomerates and fuel matrix)

Element	Mass%	Remarks
U	82.9	∧94.1% UO_2
Pu	2.6	∧2.9% PuO_2
Nd	0.38	Yield $Y = 0.087\%$ Nd per % burnup
Zr	0.22	Dissolved fraction only
Cs	0.42	Dissolved and submicroscopically precipitated
Ba	0.02	Dissolved fraction only
Xe	0.29	Submicroscopically precipitated, Xe release 43%
O	11.6	Bonded to the (U,Pu,f.p.) oxide solid solution

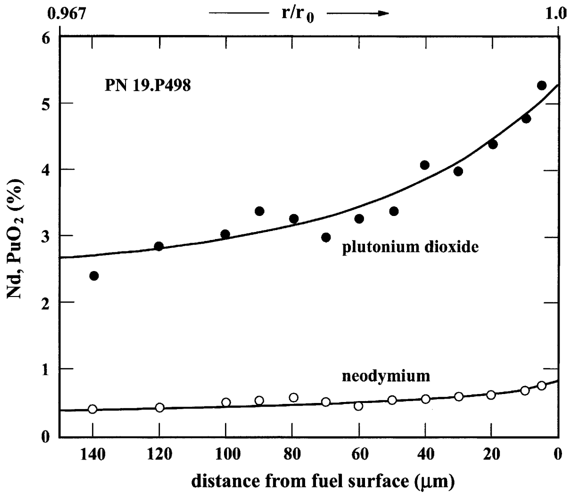

Fig. 4. PuO_2 and neodymium concentrations in the rim region of the UO_2 matrix as a function of the distance from the fuel surface.

matrix at the fuel surface (Fig. 4) which corresponds to a local burnup of 9%. The cross-section averaged Nd content in the UO_2 matrix was measured to be 0.22% Nd which gives a burnup of 2.5%. Within the high-burnup $(U,Pu)O_2$-MOX fuel islands, however, the Nd concentration was measured with less precision to be (1.7 ± 0.2)% Nd which corresponds here to (19 ± 2)% burnup. This result and the EOL concentration of (9 ± 2)% PuO_2 yield a concentration of (28 ± 3)% PuO_2 that includes also the fraction of Pu which was formed by ^{238}U–^{239}Pu conversion during irradiation.

3.2.3. Caesium

About 0.42% fuel-averaged Cs was found which is deposited in submicroscopic precipitates, probably in form of Cs uranates (Table 2). Only 0.07% Cs is soluble in UO_2 [8]. Cs zirconates were not observed in the fuel-clad gap. This phase has not yet been established. Small amounts of Cs were implanted by direct recoil into the ZrO_2 layer of the oxidized inner Zircaloy-4 clad.

3.2.4. Metallic fission product precipitates

The metallic fission product precipitates near the fuel centre ($r/r_0 = 0.2$) consist of 26% Mo, 7% Tc, 28% Ru, 8% Rh and 31% Pd. In the near-surface fuel region ($r/r_0 = 0.98$), the following compositions were observed: 16% Mo, 7% Tc, 34% Ru, 8% Rh and 35% Pd. The compositions are located in the hexagonal ε-phase field of the quinary Mo–Tc–Ru–Rh–Pd system. The decrease of the Mo content with increasing relative fuel radius r/r_0 points to an increasing oxygen partial pressure of the oxide in the surface-near fuel region [7].

3.2.5. Xenon

Xenon is precipitated in gas bubbles, in grain boundaries of the fuel and in negligible amounts in the fuel lattice. Substantial fractions are released to the free pin volume depending on fuel temperature and burnup. The bonded Xe fraction in the agglomerates and the fuel matrix is presented as a function of the relative fuel radius r/r_0 in Fig. 5. Programmed step scans were used in two pre-selected radial directions at equal intervals of 100 μm. In addition, 20 point analyses were made at the fuel surface and different azimuthal angles. The cross-section averaged concentration is 0.29% Xe (Table 2). A small Xe loss from the gas bubbles during cross-section polishing cannot be excluded. Using a fission yield of 0.115% Xe per % burnup [7] the released Xe after 4.4% burnup was calculated to be $R_{Xe} = 1 - 0.29/(0.115 \cdot 4.4) = 43\%$ of the generated Xe. The cross-section averaged burnup was calculated to be 2.5% in the fuel matrix resulting also in 0.29% Xe. The calculation

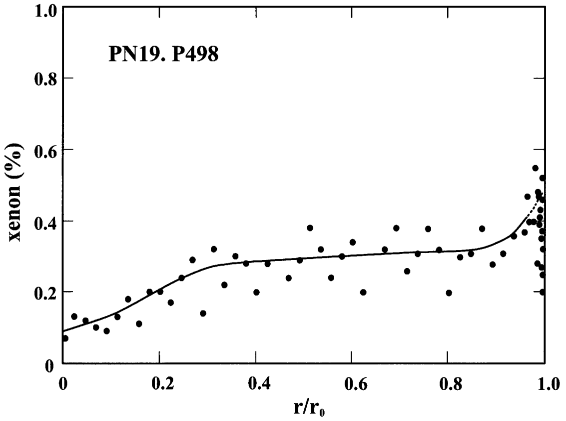

Fig. 5. Bonded xenon in mass% of the total fuel as a function of the relative fuel radius r/r_0. No distinctions were made between $(U,Pu)O_2$ agglomerates and UO_2 matrix in the equidistant step scans.

and Fig. 5 imply nearly no Xe release from the fuel matrix with the exception of the fuel centre region at $r/r_0 < 0.25$ which corresponds to less than 7% of the total fuel cross-section. The predominant Xe release originates from the high-burnt $(U,Pu)O_2$ agglomerates.

3.2.6. Zircaloy-4 oxidation

A gap between the fuel and the oxidized inner Zircaloy-4 clad was not observed (Fig. 3). Caesium compounds in the interface were not identified. The Zr, Sn and O concentrations of the inner surface region of the alloy were measured by step scans as a function of the distance from the inner clad surface and are presented in Fig. 6. The oxide layer attains the maximum thickness of 20 μm in direct contact with the $(U,Pu)O_2$ agglomerates. The composition is 33.5 at.% Zr, 0.28 at.% Sn and 66.2 at.% O which results in $(Zr,Sn)O_{1.96}$. Furthermore, up to 0.03 mass% Cs were measured in the oxide layer which were implanted by direct fission product recoil. The Zr, Sn and O concentrations below the surface oxide layer (Fig. 6) indicate a two-phase region in this position. This is followed by the Zr–Sn–O alloy containing oxygen down to the initial concentration after further 20 μm distance. The oxide scale on the outer clad side had a thickness of 22 μm.

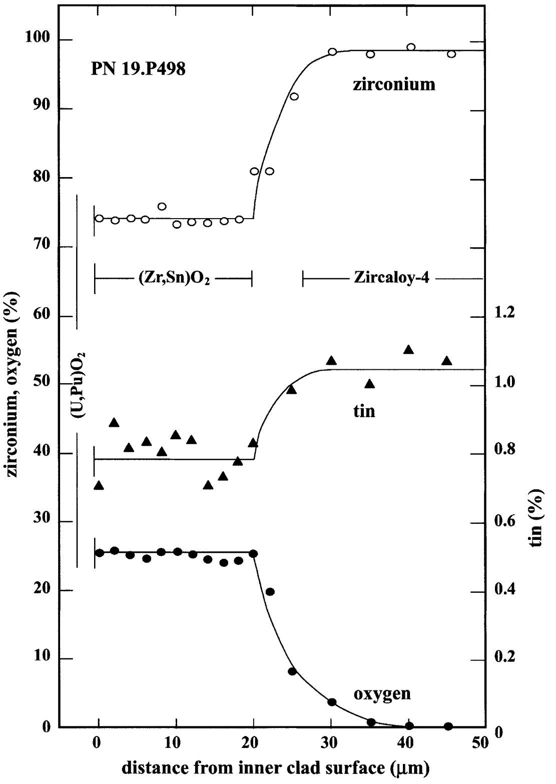

Fig. 6. Zirconium, tin and oxygen concentrations in $(Zr,Sn)O_2$ and Zircaloy-4 as a function of the distance from the inner clad wall.

4. Discussion

The optimized co-milling method (OCOM) for the fabrication of LWR-MOX fuels is an improved version of the previous so-called mastermix mixed-granules method [2]. A duplex structure of the unirradiated fuel appears in both cases which is characterized by isolated $(U,Pu)O_2$ agglomerates in a UO_2 matrix. The Pu inhomogeneities are clearly represented in the autoradiographs [2]. The duplex structure is preserved after irradiation at the moderate linear heat ratings of 18 kW/m in this fuel pin. The Xe release from the total fuel is 43% of the generated Xe. Fig. 5 implies that Xe is only slightly released from the UO_2 matrix. Earlier PIE work on UO_2 fuel enriched by 3.1% ^{235}U and irradiated to about 4% burnup resulted in an EOL cross-section averaged PuO_2 concentration of 1.13% $PuO_2/(U,Pu)O_2$ [6]. As the PuO_2 concentration in the examined UO_2 matrix is 2.0% of the fuel, the ^{238}U–^{239}Pu conversion and the presence of small $(U,Pu)O_2$ inclusions dissolved in the UO_2 matrix during irradiation are obvious. A special feature of this fuel type is the random position of agglomerates in direct contact with the clad. The thickness of the oxidized Zircaloy-4 layer is here doubled. The reason for this is the higher local chemical potential (partial pressure) of oxygen that is released during Pu fission. Only part of the resulting fission products are able to form oxides whereas the remaining oxygen is gettered by the Zircaloy clad.

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