Microstructure of spent MOX and UO2 fuel stored for 25 years

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Abstract

In this paper, some results of microstructure analyses on spent MOX fuel with burnup of about 20 GWd/tM, stored for an extended period, are presented. The samples are taken from fuel that has been stored for 25 years either in intact cladding or exposed to dry air. The results of this investigation are compared to the microstructure observations made in the post-irradiation campaign, conducted on the same or sibling fuel rods shortly after reactor unloading (i.e. about twenty years ago).

The fuel from the long term stored intact rods demonstrated an identical behaviour, compared to its state shortly after reactor unloading. Segments of fuel rods that were exposed to dry air showed an alteration of the grain boundary cohesion of the UO2 grains, while apparently the Pu-rich zones were unaffected. These findings are coherent with the results found in accelerated ageing experiments. On the other hand, the formation of secondary phases with higher oxidation states of uranium, often observed during accelerated ageing experiments, could not be confirmed here.

Introduction

Extensive studies on the oxidation of UO2, concerning the storage of used fuel, have been conducted over the past decades [1-5 and refs. therein]. Most of these studies involve accelerated oxidation experiments, often at high temperatures and performed under different conditions (dry air, steam..). To the knowledge of the authors, little or no information can be found on the behaviour of Mixed Oxide fuel (MOX) during storage. Differences between the oxidation of MOX and UO2 fuel might be expected due to the higher energy deposition and decay heat of MOX fuel during storage. The non-similarities of the microstructure and chemistry could also have their influence on the oxidation behaviour.
This paper covers some results of the microstructure analyses on spent MOX fuel, stored for a period of more than 20 years at low temperature. Some of the observations of this study are compared to observations made during the PIE campaign conducted shortly after reactor unloading, more than twenty years ago.

Production of the MOX fuel used in this experiment consists of a granulation step performed on a UO2 powder, which is then mechanically blended with PuO2 powders. The resulting powder thus shows UO2 granules, surrounded by PuO2 rich zones containing, for some of them, up to 100% PuO2.
The fuel was loaded in the Dodewaard reactor (BWR) for irradiation in April 1971 and remained in the reactor till April 1974 (4 cycles). The fuel rods included in the present investigation programme have undergone peak powers ranging between 320 and 220 W/cm; their end-of-life burnups are given in Table 1.

Table 1. Average burn-up of the MOX rods subjected to current examination

	Sample ID	Average burn-up (GWd/tM)
P339	M26	21. 4
P354	M25	17.9
P355	M24	22.1

After unloading, several fuel rods had been extracted from the assembly, for an extensive post-irradiation examination campaign (PIE-75). The remaining segments of these rods (e.g. P354, P355) have been stored in sealed canisters (air filled), who themselves were put in a second sealed container, which was kept in a storage pool. The unexamined fuel rods (e.g. P339) of the original assembly have been stored in their intact cladding (standard inert atmosphere) in an open rack in the storage pool.

In 1999, a programme of non-destructive and destructive examinations planned and funded by NFI/CRIEPI and managed by BELGONUCLEAIRE, was performed at SCK•CEN on fuel from both remnants and intact rods (PIE-99) [10]. One series of observations is made on fuel from the intact rod P339 that was stored in the reactor storage pool. A second series focuses on fuel taken from short rod segments, which were remnants of fuel rods P354 and P355 studied in the PIE-75 campaign. These segments were exposed to dry air for an extended period of more than 20 years.
The microstructure evolution of spent fuel during storage is examined, by making extensive use of Optical Microscopy (OM) and Scanning Electron Microscopy (SEM). The samples are studied in the as-polished and grain etched states. In order to gather information on the grain boundary cohesion and structure, the samples are intentionally scratched to obtain the fractography of freshly exposed grain faces.

Storage atmosphere

During the PIE-75 the atmospheres of the fuel rods P354 and P355 have been analysed [7]. After storage (in 1999), the atmospheres in both capsules containing remnants of rod P354 and P355, and the atmosphere of the stored intact rod P339 have been measured. The results are summarised in table 2.

Table 2. Analysis of storage atmospheres .

(*)Remark : A small leak occurred when puncturing rod P354 and the capsule of P355.

Vol%	P339	P354(*)	P355	P354 capsule	P355 capsule(*)	Normal Air
N_2	≤ 0.05	4.77	0.58	80 ± 2	81 ± 2	78.1
Ar	0.32 ± 0.05	0.39	0.37	0.75 ± 0.05	0.75 ± 0.05	0.93
O_2	≤ 0.04	1.13	0.01	18.8 ± 0.7	18.3 ± 0.7	20.9
H_2	≤ 0.02			≤ 0.05	0.12 ± 0.05	<0.02
CO_2	≤ 0.01	0.07	0.02	0.18 ± 0.05	0.13 ± 0.05	0.03
He	21.1 ± 1	25.30	20.06	<0.01	<0.01	<0.02
Xe	74.2 ± 1	64.23	74.10	<0.01	<0.01	<0.02
Kr	4.3 ± 0.2	4.11	4.81	<0.01	<0.01	<0.02

From the puncture test results it can be seen that the intact rod P339 has kept its inert atmosphere composition during storage for more than 20 years. The puncture results of the fuel capsules stored in dry air atmosphere show that during the long term storage, hardly any oxygen depletion has occurred in the capsules. Indeed, even though the O_2 concentrations is significantly lower in the capsules than in normal air (18.5 Vol% to 20.9 Vol%), the absolute amount of reacted oxygen is minute. A small fraction of the available oxygen has reacted with carbon (0.1 Vol%), and the remainder may have reacted with the fuel. With a capsule free volume of 35 cm^3, at atmospheric pressure and ambient temperature, the absolute amount of the reacted oxygen is of the order of 3.3 10^{-5} mol. Knowing that the amount of fuel in the capsules is 320 to 440 gram (about 1.2 to 1.6 mol metal), it can be calculated that the available oxygen is by far insufficient to

cause any observable bulk oxidation of the fuels (a maximum of 0.03 % of the UO_2 may have reacted to form U_4O_9 or 0.02% to form U_3O_7).
On the other hand, the amount of oxygen depletion should be sufficient to cause a grain boundary effect. Taken that the UO_2 fuel consist of ~7μm sized grains, the internal grain boundary surface fraction equals 2.9 10^5 m^2/m^3. The minute amount of reacted oxygen (3.3 10^{-5} mol) would be sufficient to oxidize the entire internal grain boundary surface to a higher oxidation state.

Optical Microscopy

Transversal samples M24, M25 and M26 were cut respectively from remnants of rods P354 and P355 and from intact rod P339. The samples were polished and examined by optical microscopy in the as polished and grain etched states. From literature it was learned that when partly oxidized UO_2 fuel is prepared for an optical ceramographic examination, grain pullout can occur in the oxidised regions during sample preparation.

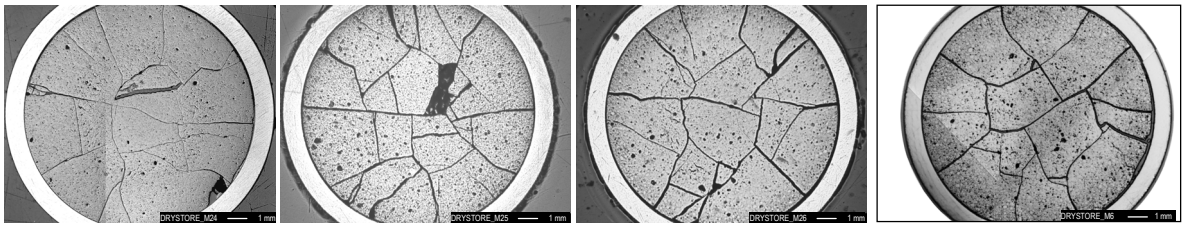


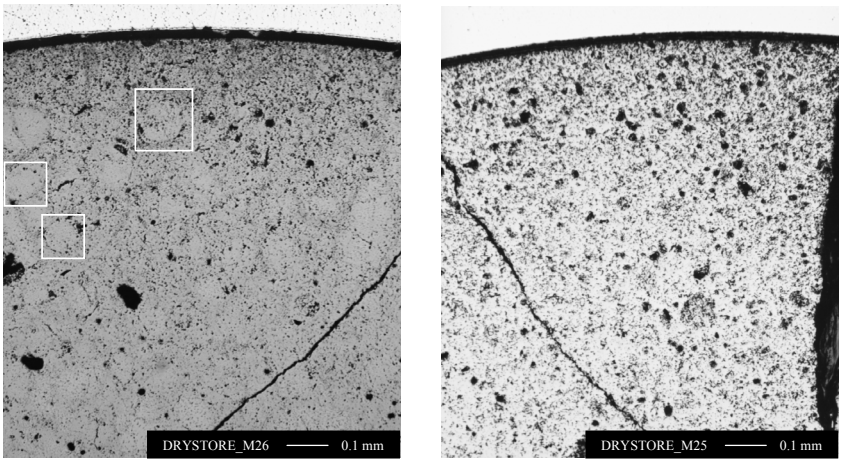
Fig.1. Macroview of respectively M24, M25 (both air exposed) and M26 (inert atmosphere stored) and a micrograph of a sibling fuel rod taken in PIE-75. All samples are in as-polished state.

The macroviews of figure 1 show the typical cracked pattern of irradiated nuclear fuel with circumferential and radial cracks. One can also notice from this macro view that the width of the gap is not constant, but it is still open. One of the two air-exposed samples (M24, fig.1.a.), shows a tendency for crack healing, which is not observed in any of the other samples.

During grinding and polishing, it was observed by the hot cell operator, that there was considerably more grain pullout in the air exposed samples M24 and M25, while polishing of M26, the sample of the intact rod, was normal.

For this type of early LWR MOX production, pull-out of the Pu-rich agglomerates during grinding and polishing, is a normal observation. The very high local burnup inside the PuO_2 agglomerates results in high radiation damage and fission product concentrations, causing the PuO_2 agglomerate to restructure and develop a porous aspect. These porous zones are then easily broken during the mechanical manipulations (grinding and polishing) in preparation of OM. Detailed OM observations show that the aspect of the PuO_2 agglomerates was not different after 20 years of storage either in intact cladding or exposed to dry air.

However, increased pull-out is observed in the air exposed samples and seems to be related solely to the UO_2 matrix. The granulated UO_2 matrix is easily recognised on the polished cross-section of the intact rod (fig.2a).



a b

Fig.2. Micrograph of (a) sample M26 (inert atmosphere) and (b) M25 (dry air). Some of the UO_2 granulates are emphasised by a white square.

The micrograph of the fuel sample that was air exposed does not show that same morphology any longer (fig.2.b). This change in morphology is a direct consequence of the UO_2 grains pull-out, which obscures the details of the pellet morphology. Pull-out of the UO_2 grains was not observed in the PIE-75 campaign. The observed increase in UO_2 grains pull-out in the air exposed samples is attributed to a weakening of intergranular bonding and, by inference, for the oxidation of grain boundaries.

This weakening of intergranular bonding of the UO_2 matrix is even more apparent after etching. Grain etching was performed after irradiation (PIE-75) to identify irradiation related effects (e.g. grain growth at the pellet centre). In campaign PIE-99, grain etching was primarily performed to obtain ceramographic observations in conditions as close as possible to the results of the PIE-75 campaign. The essential outcome of the grain etching was a much more pronounced attack of the air exposed samples as compared to the fuel from the intact rod (fig.3.).

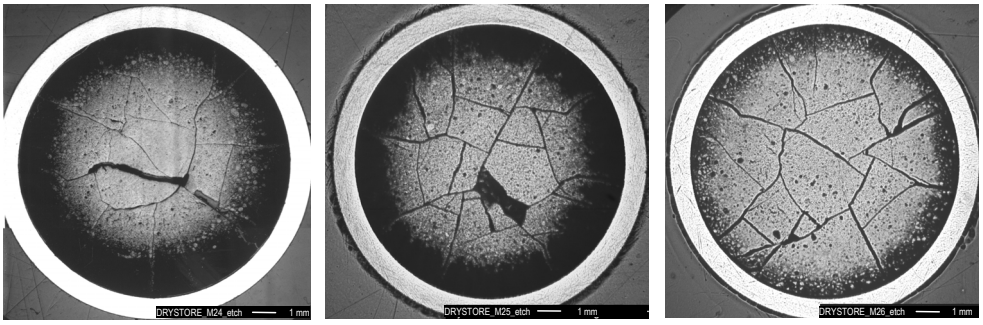
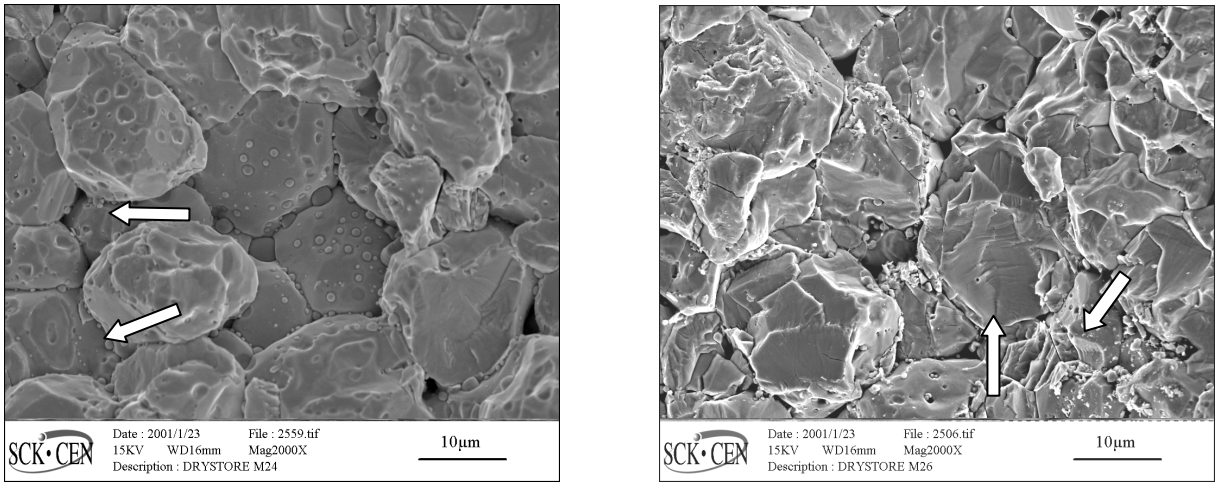


Fig.3. Macroview of M24, M25 (both air exposed) and M26 (inert atmosphere stored) after respectively 180, 210 and 210 seconds of etching.

The formation of oxygen-rich uranites phases (e.g. U_4O_9 , U_3O_7) visible as a thin layer around a UO_2 grain core in the vicinity of the pellet periphery or radial cracks [4], could not be observed in either samples.

SEM observations



a b

Fig.4. Fractography of sample M24 and M26 at mid radius, indicating an almost complete intergranular fracture mode in M24 (a) and a more transgranular fracturing in M26(b) .

To study the grain boundary structure in more detail, the samples were intentionally scratched to obtain a fractography of freshly exposed fuel grains.
Since this type of examination was not performed in the PIE-75 campaign, only results of the long term stored samples can be presented. The most striking difference between the air exposed and intact rod fuel fractography is the difference in fracture mode. The air exposed fuel shows a predominant intergranular decohesion (fig.4.a). The fuel from the intact rod shows transgranular cleavage (fig.4.b) or sometimes mixed cleavage mode. This observation again confirms the weakening of intragranular bonding.
The present analysis included also backscattered electron observations, but these could not reveal the formation of separate second phases on the grain boundaries. Considering the limited consumption of oxygen, the formation of well-defined second phases of a higher oxidation state of Uranium was not really expected.

The effects of reactor irradiation were still readily apparent in both samples. Fission gas bubbles and tunnels, decorated with five metal particles were identified near and at the center of the pellet (fig.4.a,b).

Discussion

Although direct evidence for changes in the MOX composition or morphology could not be obtained, there was very convincing and systematic evidence for the modification of the coherency of the matrix as a result of prolonged exposure to the air.
The puncture test on the fuel capsules stored under dry air atmosphere reveal a small amount of oxygen depletion. Observable bulk oxidation of the fuel could therefore not be expected. It can however be calculated that the small fraction of oxygen depletion, could be sufficient to oxydize the entire internal grain boundary surface of the UO_2 grains to a higher oxidation state.
During preparation of the samples for OM, severe pull-out in the air exposed samples is observed in the UO_2 matrix. As a consequence of increased pull-out of UO_2 grains, a change in morphology (the UO_2 granulates are no longer optical visible) is witnessed in the long term air exposed

samples. The increased pull-out is interpreted in terms of weakening of intergranular bonding due to oxidation of the grain boundaries. This effect is even more pronounced during etching of the samples.
Pull-out of the PuO_2 zones has also been witnessed. This, however can be related to the irradiation history. Compared to archived images of PIE-75, the structure of the PuO_2 agglomerates is unaltered.
SEM observations confirm the OM and puncture test results. Fractographic analysis of freshly exposed grains, reveal a striking difference in fracture mode between the long term air exposed samples and the sample of the intact stored rod. While the sample stored in inert atmosphere shows a more transgranular, sometimes mixed cleavage mode, the air exposed samples reveal a predominantly intergranular decohesion. This confirms a weakening of the grain boundary of the UO_2 matrix attributed to long term exposure of the fuel to air.
Neither the OM, nor SEM or Back Scatter electron analysis indicate the formation of well defined secondary phases of higher oxidation state of uranium. This is in agreement with the conclusion drawn from the puncture analysis, stating only a limited consumption of oxygen.

Although to the knowledge of the authors, little or no information exists on similar experiments (i.e. >20 years of storage of MOX samples at low temperatures and in different atmospheres), the observations are not unexpected. Concerning the UO_2 matrix, it has indeed been inferred from literature [1] that oxidation of UO_2 grains, as a result of exposing the fuel to unlimited air, is in early stages restricted to very thin oxide films on the grain boundary. This oxidation results in weakening of the grain boundary, causing increased pull-out of the UO_2 grains and more intergranular fracturing due to the mechanical manipulation of the fuel [4].
On the oxidation of irradiated PuO_2, literature is very scarce. One could assume that the high concentration of fission gases in the Pu rich zones could have an influence on the oxidation rate. On the other hand, oxidation experiments on non irradiated UO_2 and MOX fuel indicate a slower oxidation rate of MOX fuel [6,8]. Recent studies [9] also imply the existence of a higher oxidation state of Pu (Pu6+). The present experiment, shows that the structure of PuO_2 agglomerates, clearly visible in the OM observations at the pellet periphery, is not altered compared to archived micrographs taken shortly after unloading of the reactor. Exposure to air for an extended period, seems not to lead to further oxidation of the pure PuO_2 agglomerates for the storage conditions studied here.

Conclusion

The present study on spent MOX fuel with a burnup of about 20 GWd/tM, stored for more than twenty years in low temperature condition, show a general good behaviour. The samples investigated come from an intact spent fuel rod with an internal inert atmosphere or from closed capsules containing spent fuel segments in dry air environment. It has been shown that the spent MOX fuel from the intact rod shows no alteration due to storage. In the capsules containing the air exposed spent fuel, limited air consumption has taken place. Here, oxidation of the UO2 grain boundaries does occur, resulting in weakening of the intergranular bonding of the UO2 matrix.
This was expected from accelerated experiments and is now confirmed. On the other hand, formation of secondary phases, often observed in accelerated experiments is not found.
Contrary to the UO2 matrix, the PuO2 zones in the investigated MOX fuel (low burnup), show no indication of further degradation when stored in limited air and low temperature conditions.
More detailed experiments especially focussing on grain boundary evolution are necessary to confirm the present observations and to help identifying mechanisms of grain boundary oxidation.

Acknowledgements

The authors like to thank A. Gys, G. Cools, H. Van Eyck and L. Sannen for their participation in the sample preparation, puncture analysis and ceramographic observations.

References

[1] McEarchern, R.J., and Taylor, P., "A review of the oxidation of uranium dioxide at temperatures below 400°C", J. Nucl. Mater. 254 (1998) 87-121.

[2] W. H. Hocking, R. Behnke, A.M. Duclos, A.F. Gerwing and K.M. Wasywich, "Grain-Boundary oxidation of used CANDU fuel exposed to dry air at 150 °C for a prolonged period", Fourth International CANDU Fuel Conference, 6B-20 to 6B-38, 1995

[3] J. Nakamura, T. Otomo, T. Kikuchi and S. Kawasaki, "Oxidation of fuel rods under Dry storage conditions", J. Nucl. Sience and Techn., 32(4), pp. 321-332 (1995).

[4] K. M. Wasywich, W. H. Hocking, D. W. Shoesmith and P. Taylor, "Differences in oxidation behaviour of used CANDU fuel during prolonged storage in moisture-saturated air and dry air at 150 °C", Nucl. Techn., Vol. 104, p. 309 (1993)

[6] D.W. Shoesmith, "Fuel corrosion processes under waste disposal conditions", J. Nucl. Mater. 282 (2000) 1-31

[7] J. van de Velde, "Post-Irradiation examinations of rods of the Pu-assemblies B200, B201 and B301 of the Dodewaard core – Punction and Fission gas collection", TEC/39.218.4/17/JVDV/fq (1979).

[8]| V.J. Tennery and T.G. Godfrey, "Oxidation properties of (U,Pu)O2 Solid Solutions", J. Am. Cer. Soc., Vol.56, No. 3 (1973)

[9] J. M. Haschke, T.H. Allen and L.A. Morales, "Reaction of Plutonium Dioxide with water : Formation and Properties of PuO2+x", Science, Vol 287, 285 (2000)

[10] A. Sasahara and T. Matsumura,"The Post Irradiation Examinations of Twenty-years Stored Spent Fuel", ATARNTE2000, Avignon, (2000)

Oxidation of spent UO2 fuel stored in moist environment

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Submitted to Journal of Nuclear Materials