ELSEVIER

Journal of Nuclear Materials 317 (2003) 226–233

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Oxidation of spent UO_2 fuel stored in moist environment

A. Leenaers *, L. Sannen, S. Van den Berghe, M. Verwerft

SCK • CEN, Reactor Materials Research, Boeretang 200, B-2400 Mol, Belgium

Received 9 September 2002; accepted 15 February 2003

Abstract

Spent fuel remnants, cut from BWR fuel rods were retrieved for microscopic investigations after 25 years of storage at ambient temperature. The storage atmosphere of the samples studied here was dry air for 10 years and a moist environment for the remaining 15 years. The comparison with earlier experiments conducted on samples that were stored in dry air for the full period demonstrates that moisture accelerates the oxidation process also at the low temperatures considered here. The composition of the atmosphere in contact with the fuel has been analysed by mass spectrometry and the microstructure of the samples has been investigated by optical and scanning electron microscopy. The microscopic observations evidence that grain boundaries are affected and different stages in grain boundary alteration could be evidenced. Oxidation first induces a weakened intergranular bond followed by increased sensitisation to chemical attack and finally decohesion and onset of bulk oxidation.

1. Introduction

Until its radioactivity has sufficiently subsided, spent fuel must be cooled in pools of water generally at the reactor site. After several years, the spent fuel can be removed and transferred either to be reprocessed (closed fuel cycle) or stored permanently in a geological repository (open fuel cycle). However, nowadays only a small fraction of the spent fuel is reprocessed and no final repository has been licensed yet. This deferral of decision has resulted in long-term intermediate storage of spent fuel. The spent fuel assemblies then either continue to be stored under water or in a dry gaseous environment (e.g. in storage casks) and are planned to be retrieved later, when decisions have been made for either direct disposal or reprocessing [1,2]. In either storage mode, the integrity of the fuel rods must be secured for a long period of time.

Oxidation of defective fuel during long-term storage is a concern, as it will lead to fuel swelling and eventual splitting of the cladding. In this framework, extensive studies on the oxidation of UO_2, concerning the storage of used fuel, have been conducted over the past decades [3–7; and refs. herein]. However, as the access to long term stored spent fuel is still not so evident, all of these studies are based on accelerated oxidation experiments (often at high temperatures) using intentionally damaged fuel elements. To simulate the conditions in the different storage modes, the fuel is exposed to atmospheres with various humidity and oxygen contents, ranging from inert gas to highly oxidising environments such as steam.

Remnants of fuel rods that were part of a post-irradiation examination (PIE) campaign and afterwards stored for 25 years, were available at the Belgian Nuclear Research Center (SCK • CEN). These were selected for a research program that aimed to investigate the slow degradation occurring under these storage conditions. This research program, funded by the Nuclear Fuel Industries (NFI), the Central Research Institute of Electric Power Industry (CRIEPI) and managed by the Belgian Mixed Oxide (MOX)

---

* Corresponding author. Tel.: +32-14 333044; fax: +32-14 321216.

E-mail address: aleenaer@sckcen.be (A. Leenaers).

0022-3115/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-3115(03)00104-1

fabrication and nuclear engineering company Belgonucleaire, was performed at SCK • CEN on MOX fuel remnants, stored for more than 20 years in dry air (air with H_2O content <0.02 vol.%) at ambient temperature. We previously reported that the MOX fuel degradation due to oxidation is very limited and is restricted to the UO_2 matrix only, while the Pu-rich zones do not show any observable effects [8]. It was furthermore calculated that only 0.02% of the UO_2 grains had reacted to a higher oxide. As this program involved only dry air storage conditions, and since experimental data involving long-term exposures of spent fuel are still relatively scarce, it was deemed essential to complement it with a study on fuel stored in a moist atmosphere (air with H_2O content >0.02 vol.%). The present paper reports on the investigation of spent UO_2 fuel stored for 25 years after unloading. During the first 10 years, the fuel was exposed to dry air but after ingress of water in the storage capsule, the storage ambient changed from dry air to a moist environment, in which the spent fuel remained for another 15 years.

The integrity of the spent UO_2 fuel remnants are compared to the fuel degradation observed in the MOX samples that were stored for the same period, but in dry air conditions. Detailed results on the latter samples have been presented elsewhere [8].

This study reflects what happens to spent fuel in contact with a moist environment. Such a condition could arise if the cladding of a spent fuel rod, stored in a reactor pool or in a geological repository, would fail. It will be shown that even a very small leak is sufficient to severely change the atmosphere in contact with the spent fuel and as such to alter the microstructure of the spent fuel.

2. Experimental procedures and results

2.1. Fuel and storage history

The UO_2 fuel (2.5 wt% U^{235}) studied here, is made from IDR (Integrated Dry Route) [9] powder and was produced by British Nuclear Fuels (BNFL). It was loaded in the Dodewaard Boiling Water Reactor (BWR) for irradiation in April 1971 and remained in the reactor until April 1974 (four cycles). The fuel rods have undergone peak powers ranging from 220 to 320 W/cm and reached an end-of-life burnup of 23 GWd/tM.

After unloading, several of the fuel rods have been extracted from the assembly for an extensive PIE campaign (1975–1980) (Fig. 1). From these fuel rods, several samples have been cut and examined by different techniques. The remnants of the fuel rods were then stored in closed capsules (dry air filled), which themselves were put in a second, sealed canister which was kept in a storage pool. In the mid eighties it was observed that the canister, in which the capsules with the fuel segments under current investigation were stored, had a broken seal and contained water. The caps of the inner capsules were never meant to be airtight and ingress of water in the outer canister effectively changed the contact atmosphere from dry air ($H_2O < 0.02$ vol.%) to a moist environment ($H_2O > 0.02$ vol.%). The storage atmosphere of the fuel segments was thus ten years of dry air storage and fifteen years of moist storage. This storage history will be referred to as storage in a ‘moist atmosphere’.

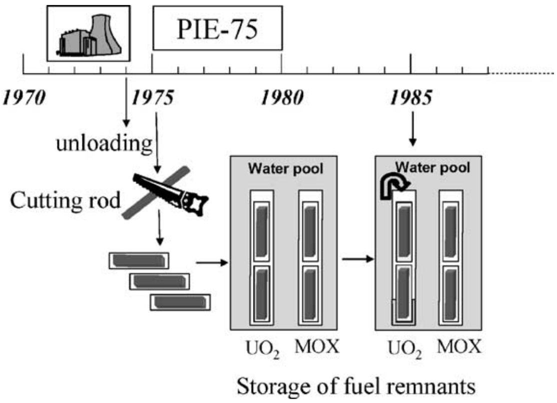

Fig. 1. Schematic overview of the fuel storage history.

As opposed to some accelerated oxidation experiments described in the literature, in the current study the fuel segments were not intentionally damaged by e.g. drilling a hole in the cladding. As it concerns remnants of fuel rods, i.e. open end fuel segments, the spent fuel is only in contact with the atmosphere through the gap between the cladding and the fuel pellets.

2.2. Puncture test

Even though the capsules were not gastight, the exchange between the atmosphere inside the capsule and the atmosphere outside the capsule is limited, allowing a faithful sampling of the contact atmosphere. First, a sleeve is put on the capsule’s cap and a small hole is drilled in the capsule. The gas is collected in an analytic volume and pumping continues until a vacuum of approximately 10^{-6} bar is obtained. In the present case, it was observed that vacuum could not be achieved. The pressure only went down to 27 mbar, which is the vapor pressure of water at a temperature of 23 °C, indicating that water indeed had ingressed in the inner capsule.

The collected atmosphere has been analysed by gas mass spectrometry. Table 1 gives the composition of normal air and the storage atmosphere of the current spent UO_2 fuel. For comparison, the atmosphere collected from the capsule containing the MOX fuel stored in dry air is also given [8]. The measured amount of H_2O (0.44 vol.%) in the moist atmosphere is less than what

Table 1
Puncture test results of the capsules and mass spectrometric analysis of the storage atmospheres

	Storage atmosphere		
	Spent UO_2 fuel 10 years dry air + 15 years moisture	Spent MOX fuel 25 years dry air	Normal air
Puncture test results of storage capsules			
Free volume	49 cm^3	35 cm^3	
Gas pressure	$\simeq$1 bar	$\simeq$1 bar	
Amount of fuel	$\simeq$750 g	$\simeq$380 g	
Mass spectrometric analysis (in vol.%)			
N_2	53 ± 1	81 ± 2	78 ± 2
O_2	1.7 ± 0.1	18 ± 1	20 ± 1
Ar	0.5 ± 0.2	0.8 ± 0.2	1.0 ± 0.1
H_2	39.8 ± 0.8	0.12 ± 0.05	<0.02[a]
H_2O	0.4 ± 0.2	<0.02[a]	<0.02[a]
CO_2	3.5 ± 0.2	0.13 ± 0.05	0.08 ± 0.03
CH_4	0.08 ± 0.03	<0.02[a]	<0.02[a]
He	0.8 ± 0.2	<0.01[a]	<0.01[a]
Xe	0.5 ± 0.2	<0.01[a]	<0.01[a]

For the mass spectrometric analysis, the accuracy with which each component can be measured, is given.

[a] Below detection limit.

would be expected for an atmosphere at saturated humidity. The spectrometer, however, is designed for gas analysis only, and it is not possible to prevent adsorption and condensation of liquids. As a result, it is not possible to quantify the measured amount of water vapor but in qualitative terms 0.44% of measured H_2O corresponds to a highly humid atmosphere.

The elevated H_2 content (39.8 vol.%) is attributed to water corrosion of UO_2 to UO_{2+x} with production of gaseous hydrogen. Furthermore, based on the nitrogen-to-oxygen ratio of normal air ($p_{O_2}/p_{N_2} = 0.25$), a separate reaction involving oxygen depletion must have taken place (the measured contact atmosphere $p_{O_2}/p_{N_2} = 0.033$). There was no indication of corrosion of the aluminum capsule, but one notices an increased CO_2 concentration in the contact atmosphere, which suggests a partial consumption of oxygen by carbonaceous material. In case of the dry air stored MOX fuel, the only significant alteration of the atmosphere is a slight oxygen depletion. It was calculated directly from the composition of the atmosphere that this small amount of oxygen depletion caused only 0.02% bulk oxidation of the UO_2 matrix [8]. As a result of the above considerations, the oxygen depletion in the present case cannot be attributed to direct oxidation of the UO_2.

Even though the leak is small enough to reflect the oxidation processes in the gas composition of the capsule, containing the moisture exposed fuel, the amount of reacted fuel cannot be determined directly from this composition. The study on spent MOX fuel [8] has shown that long-term exposure to dry air does not lead to significant oxidation. As such, we can limit our attention in the current study to the period of moisture exposure (15 years) for further calculations.

Despite the high H_2 content, the measured pressure inside the capsule was found to be exactly 1 bar, which confirms that the capsule was not sealed. This leak allows the escape of gas in case of pressure build-up due to H_2 production. It would also allow eventual ingress of moisture to compensate a possible underpressure due to the direct reaction of UO_2 with oxygen. However, such an underpressure has never occurred, as can be deduced from the partial pressure evolutions calculated below.

According to the atmospheric composition, at least two oxidation mechanisms of the spent fuel are at play. A first one involves a reaction with water, resulting in a net production of gaseous H_2, and a second reaction leads to a net depletion of O_2 from the capsule's atmosphere. In moist environments, corrosion of UO_2 to higher oxidation states proceeds preferably through the reaction with hydrogen peroxide (H_2O_2) produced by radiolysis [3,10]. The balanced equation of this reaction reads as:

$$H_2O + 4UO_2 \rightarrow U_4O_9 + H_2. \tag{1}$$

There are no apparent indications for other corrosion reactions in the capsule (e.g. oxidation of the cladding, capsule), hence we can assume that the involved oxygen is entirely consumed by the UO_2. The oxidation of four moles of UO_2 to $UO_{2.25}$ is thus accompanied by the net production of one mole of H_2.

Given the low oxygen concentration in the atmosphere of the capsule, there must be a second reaction that involves the consumption of oxygen. The depletion of oxygen could be explained through the direct oxidation of UO_2 by capture of oxygen from the atmosphere:

$$O_2 + 8UO_2 \rightarrow 2U_4O_9. \tag{2}$$

However, it is known, that direct reaction of oxygen with UO_2 proceeds much slower than the reaction of UO_2 with H_2O_2 [3]. Another possibility is that the molecular hydrogen produced through the reaction in Eq. (1) is partly consumed by the atmospheric oxygen to produce again water molecules. This involves a chain reaction propagated by e.g. atomic oxygen or other radicals that are present as radiolysis products. The exact reaction path is not really important, but the net effect of both this indirect reaction and the direct reaction (Eq. (2)) is the oxidation of UO_2 with the consumption of oxygen and without the production of hydrogen.

We assume that Eq. (1) is a zero-order reaction and that H_2 is produced during the whole storage period at a constant rate, implying a steady-state regime of H_2O_2 concentration. Assuming furthermore that the reduction of O_2 is a first-order reaction (according to Eq. (2)), one may derive the evolution of the gas atmosphere in the capsule. The differential equations describing the evolution of the contact atmosphere due to the chemical reactions and the instantaneous pressure equilibration are conveniently written using partial pressures:

$$\frac{\mathrm{d}p_{O_2}}{\mathrm{d}t} = -k_1\frac{p_{O_2}}{p} - k_2 p_{O_2} + k_2 p_{O_2}\frac{\overset{\circ}{p}_{O_2}}{p}, \tag{3}$$

$$\frac{\mathrm{d}p_{H_2}}{\mathrm{d}t} = k_1 - k_1\frac{p_{H_2}}{p} + k_2 p_{O_2}\frac{\overset{\circ}{p}_{H_2}}{p}. \tag{4}$$

In this expression, p_{O_2} and p_{H_2} denote the partial pressure of O_2 and H_2; $\overset{\circ}{p}_{O_2}$, $\overset{\circ}{p}_{H_2}$, are the standard partial pressures of the same gases; p is the total pressure inside the capsule (1 atmosphere); k_1 is the rate constant for H_2 production (in units bar/s) and k_2 is the rate constant for O_2 depletion (in units 1/s). Using the boundary conditions: $p_{O_2}(0) = \overset{\circ}{p}_{O_2}$, $p_{H_2}(0) = \overset{\circ}{p}_{H_2}$, the set of differential equations can be solved straightforwardly:

$$p_{O_2}(t) = \overset{\circ}{p}_{O_2}\exp\left(-\left(\left(1-\frac{\overset{\circ}{p}_{O_2}}{p}\right)k_2 + \frac{k_1}{p}\right)t\right), \tag{5}$$

$$p_{H_2}(t) = p\left(1 - \mathrm{e}^{-(k_1/p)t}\right) + \frac{\overset{\circ}{p}_{H_2}}{1-\frac{\overset{\circ}{p}_{O_2}}{p}}\mathrm{e}^{-(k_1/p)t} \times \left(1 - \frac{\overset{\circ}{p}_{O_2}}{p}\exp\left(-\left(1-\frac{\overset{\circ}{p}_{O_2}}{p}\right)k_2 t\right)\right). \tag{6}$$

The rate constants k_1 and k_2 can then be calculated from the experimental values of the gas composition in the capsule. Putting the experimental values of the contact atmosphere composition in Eqs. (5) and (6), one obtains:

$$k_1 = 1.078 \times 10^{-9}\ \frac{\text{bar}}{s} \tag{7}$$

and

$$k_2 = 4.344 \times 10^{-9}\ \frac{1}{s}. \tag{8}$$

The total amounts of produced hydrogen and consumed oxygen over a period of 15 years is then obtained by integration over the period ($t_e = 15$ years), and taking the experimental conditions of storage ($T = 298$ K) and the free volume of the capsule ($V = 49$ cm^3):

$$[H_2] = \frac{V}{RT}\int_0^{t_e} k_1\,\mathrm{d}t = 1.02 \times 10^{-3}\ \text{mol}, \tag{9}$$

$$\begin{aligned}[O_2] &= \frac{V}{RT}\int_0^{t_e} k_2 p_{O_2}(t)\,\mathrm{d}t \\ &= \frac{V}{RT}\int_0^{t_e} k_2\overset{\circ}{p}_{O_2}\exp\left(-\left(\left(1-\frac{\overset{\circ}{p}_{O_2}}{p}\right)k_2 + \frac{k_1}{p}\right)t\right)\mathrm{d}t \\ &= 0.30 \times 10^{-3}\ \text{mol}.\end{aligned} \tag{10}$$

For each mole of produced hydrogen gas, four moles of UO_2 are oxidised to form one mole of U_4O_9. According to Eqs. (9) and (1), 4.08×10^{-3} moles of UO_2 may have reacted to U_4O_9. In addition, there is the direct or indirect consumption of atmospheric oxygen. Taking into account that part of the oxygen reacted with carbonaceous material to form CO_2, the amount of oxygen that reacted with UO_2 is slightly lower than given by (10) and amounts to $[O_2] = 0.23 \times 10^{-3}$ mol. One mole of oxygen yields the oxidation of eight moles of UO_2 and the reduction of atmospheric oxygen thus corresponds to the oxidation of 1.84×10^{-3} moles of UO_2. In total 5.92×10^{-3} moles of UO_2 could react to U_4O_9. In the capsule, we had 2.8 moles of UO_2, which means that about 0.21% of UO_2 should have been oxidised.

Further analysis of the mass spectrometric data, shows the release of helium (0.8 vol.%) and xenon (0.5 vol.%) in case of the spent fuel stored in a moist atmosphere. Helium is used as filling gas of the fuel rods, and it can get trapped in the fuel during irradiation. Xenon is a fission gas which can mostly be found on the fuel grain boundaries. It was observed that the Xe isotopic composition in the current study is consistent with the ratio generally found in irradiated fuel. The release of both He and Xe in spent fuel stored in a moist atmosphere, would therefore indicate that the grain boundaries have weakened.

2.3. Optical microscopic observations

After the puncture analysis, cross sections of the fuel elements were cut and prepared for ceramographic

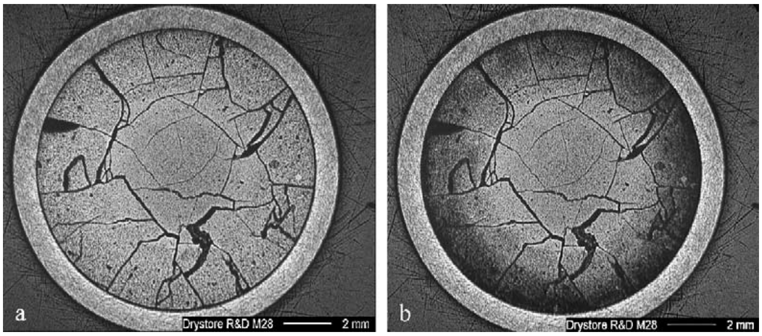

Fig. 2. Macroview of the spent fuel in as-polished state (a) and etched state (b). The dark region in the grain-etched state shows the progression of the oxidation front from the gap towards the center of the pellet. There is no indication of preferential oxidation at the radial cracks.

observation. The samples are examined by optical microscopy in the as-polished and grain etched state.

The overview of the fuel pellet in the as-polished condition (Fig. 2(a)), shows the typical crack pattern of irradiated nuclear fuel. During grinding and polishing for ceramographic examination, considerable grain pullout was observed by the hot cell operator. The region of increased grain pull-out was limited roughly to the outer quarter of the pellet. This observation is attributed to a weakening of intergranular bonding and, by inference, to the oxidation of grain boundaries [4,5].

To reveal the UO_2 grain structure, the as-polished samples are etched in a mixture of 5% sulphuric acid and 15% hydrogen peroxide. The samples are immersed in the solution only for a few seconds, rinsed in distilled water and checked. This procedure is repeated until a good contrast of the grain boundaries is obtained. If the fuel has altered, grain etching would lead to a much more pronounced attack than in as-irradiated fuel. Such an enhanced grain boundary etching in the case of oxidation induced grain boundary weakening has been reported earlier [4,8]. The optical micrographs in the grain etched condition show a radial, non-uniform progression of the oxidation starting from the fuel clad gap inwards (Fig. 2(b)). From Fig. 2(a) it is noticed that the gap between cladding and fuel is open but the width of the gap is not constant. Detailed images of the fuel clad gap at different azimuthal positions show a gap width at 0° (top of Fig. 2(a) and (b)) of 30 μm while at 180° (bottom of Fig. 2(a) and (b)) the width is 70 μm. This clearly indicates that the fuel clad gap is the pathway by which the gas in the capsule is supplied to the fuel. At the position where the gap is the widest (at 180°, bottom of Fig. 2(b)), we observe the most pronounced grain boundary attack. The depth of penetration of rapid grain boundary attack extends from the periphery to about mid-radius. There is no indication of enhanced oxidation starting from the radial cracks, which could also serve as pathway for access of oxygen to the fuel [4].

At the fuel–clad gap, the gradual transformation of UO_2 to higher oxides is observable. Fig. 3 shows a high magnification micrograph of a region with severe grain pull-out and the formation of grains consisting of a core of UO_2 and an envelope of a higher oxide [4]. To the right side of the image, all grains are wrapped in a higher oxide scale, while at the left side of the image, the grains are only partially oxidised (top left), or not visibly oxidised at all (lower left part of the image).

2.4. Scanning electron microscopic observations

After the optical microscopic observations, the samples were repolished for scanning electron microscopy (SEM). The grain boundary alteration occurring at the sample periphery is confirmed by backscattered electron imaging observations. Near the pellet–clad gap, back-

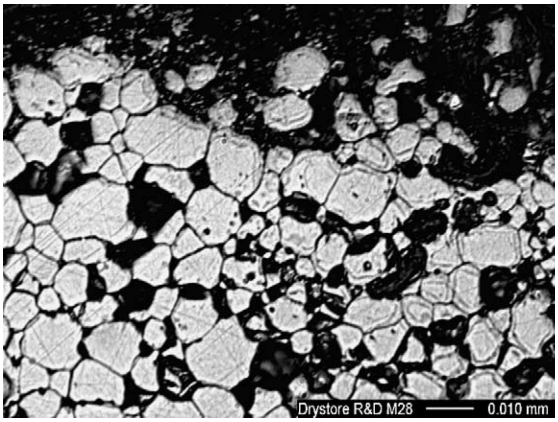

Fig. 3. Etched condition of the UO_2 fuel at the fuel–clad gap, showing grains consisting of a core of UO_2 and an envelope of a higher oxide (right side of the image), partially oxidised UO_2 grains (top left side) and UO_2 grains with no visible oxidation (lower left side).

scattered electron images clearly show grain boundary delineation (Fig. 4(a)) which disappears closer to the centre of the sample (Fig. 4(b)). Higher oxide phases, supposedly formed on grain boundaries, could not be observed directly.

To study the grain boundary structure in more detail, the samples were intentionally scratched to obtain a fractography of freshly exposed fuel grains (Fig. 5(a) and (b)). In the present case, the predominant fracture mode all along the pellet radius is intergranular cleavage (Fig. 5(a)). In as-irradiated fuel, the fracture mode is predominantly transgranular cleavage, with a very limited intergranular component (Fig. 5(b)). This indicates that even in central areas where grain boundary alteration is not yet observable directly by backscattered electron imaging or evidenced indirectly by more pronounced etching, the slow oxidation did affect the intergranular bonding. Similar observations of cleavage mode alteration have been reported for dry air exposed spent fuel [5,8]. This observation again points to a weakening of the intergranular bonding.

3. Discussion

The exposure of spent fuel to successively 10 years of dry air and 15 years to a moist environment at ambient temperature (this history is referred to as 'moist atmosphere') shows a limited, but clearly observable oxidation process. The oxidation mainly affects and progresses along the UO_2 grain boundaries. It results in weakened intergranular bonding, sensitization for grain boundary chemical attack and the onset of grain boundary decohesion. The different microscopic observations indicate that the oxidation progresses gradually from the periphery inwards and develops several loosely defined fronts of oxidation evolution. In contrast to the experiment of Wasywich et al. [4] there is no evidence that the radial cracks play any role as fast routes for oxidation.

A decreased intergranular bonding is the first aspect induced under the current conditions of oxidation. It is reflected by a change in cleavage mode from transgranular to intergranular. The decreased intergranular

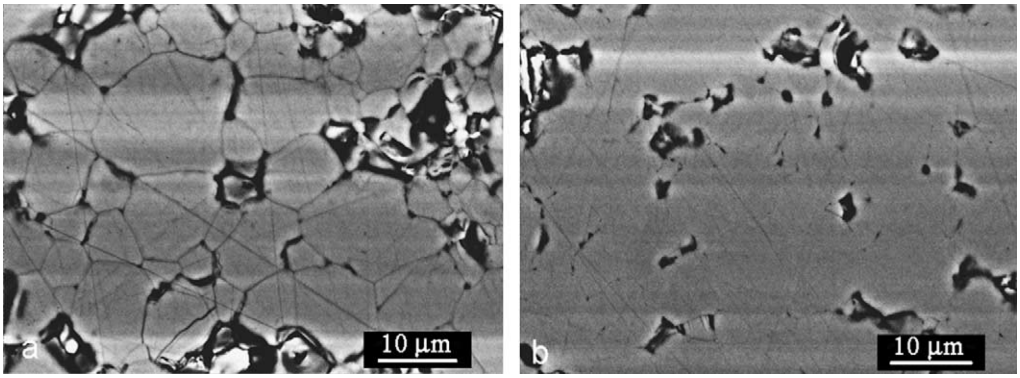

Fig. 4. Comparison of the backscattered electron image (a) at the pellet periphery ($R/R_0 = 1$) and (b) at a quarter radius ($R/R_0 = 0.75$). In (a), the image shows a clear delineation of the UO_2 grains, which is not present in (b).

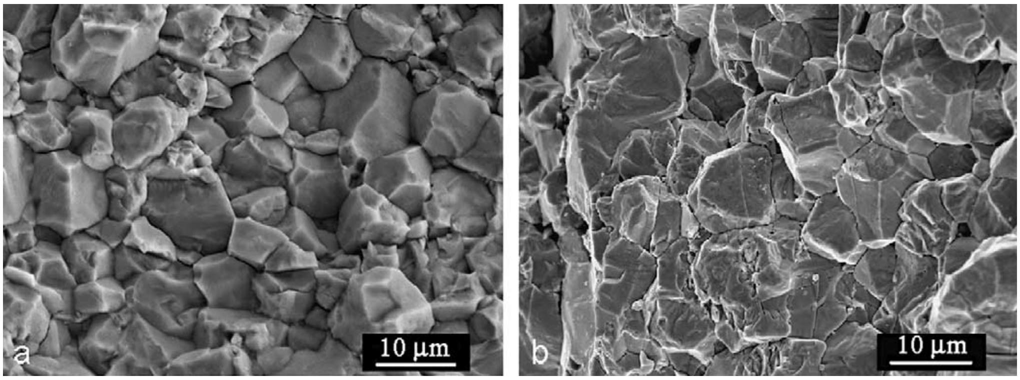

Fig. 5. (a) Fractography of exposed fuel grains from the current study indicates an almost complete intergranular fracture mode, showing the crystalline nature of the grains with a smooth texture. (b) At the same radial position in an as-irradiated fuel pellet, the fracture mode is predominantly transgranular. This is characterized by river patterns on the fractured grain surfaces, secondary cracks, grainy or faceted texture.

bonding is observed throughout the entire pellet and we assume that it reflects the first stage of grain boundary oxidation. The next step is an increased sensitivity to chemical attack of the grain boundaries. The etching of the present samples shows that this front progressed to about mid-radius. The decohesion of the individual grains occurs close to the periphery and extends about one quarter of the radius into the sample. It is evidenced both by an increased grain pull-out during sample polishing and the grain boundary delineation in backscattered imaging. At a few locations adjacent to the gap, the oxidation was not limited to the grain boundaries and the onset of bulk oxidation of UO_2 grains could be observed.

The large oxygen depletion observed in the moist atmosphere opposed to only a slight oxygen depletion in the 25 years dry air storage, indicates that the oxidation of spent fuel apparently progresses much slower in a dry air than in a moist atmosphere. The contribution of 10 years in dry air storage to the oxidation of the fuel in the current experiment could therefore be considered minimal compared to the oxidation due to storage in a moist environment for the last 15 years.

At least two oxidation mechanisms are needed to explain the observed changes in the contact atmosphere. Since the capsule was not sealed, the amount of reacted UO_2 could only be derived after making some simplifying hypotheses on the reaction mechanisms. The derived fraction of 0.2% of reacted UO_2 should thus be regarded as an approximate value.

Still, it is clear that with about 0.2% of reacted UO_2, the oxidation proceeds much faster in a moist atmosphere than in dry air alone, where the amount of reacted UO_2 was less by about one order of magnitude (approximately 0.02% [8]). This observation confirms other findings of oxidation experiments, conducted at higher temperatures [4].

Further evidence for an enhanced oxidation rate in a moist atmosphere, is the presence of helium and xenon in the atmosphere. Both gases are usually located on the grain boundaries. Weakening of the grain boundary due to oxidation, has caused the release of the trapped helium filling gas and the fission gas xenon. Both these gases could not be traced in the dry air atmosphere in contact with the spent MOX fuel, indicating that oxidation has not proceeded as fast in that case.

Similar to the moist atmosphere experiments conducted by Wasywich et al. [4], our findings apply to a condition with limited air supply, but the evolution of the contact atmosphere in our experiment differs substantially from the results obtained at more elevated temperatures and shorter duration. While the experiments of Wasywich et al. showed complete oxygen starvation (less than their detection limit of 0.02 vol.% O_2) and only limited H_2 production (about 4 vol.% H_2), our results show a much higher H_2 production (the atmosphere contains 40 vol.% H_2) and the oxygen did not yet completely react (slightly less than 2 vol.% O_2 remained). In view of the elevated hydrogen content of the contact atmosphere, one might furthermore argue that the oxidation of the UO_2 is not progressing further. It may be that the elevated concentration of H_2 impeded the suggested oxidation mechanism. Oxidation of UO_2 proceeds much faster via hydrogen peroxide reduction than through direct reaction with O_2 [3]. On the other hand, reaction of H_2O_2 with H_2 competes with this reaction and at elevated H_2 concentrations, even when H_2O_2 continues to be produced by radiolysis, it may be effectively scavenged before it can react with UO_2. If this happens, the proposed reaction effectively stops. Whether the measured composition of the contact atmosphere reflects the termination condition or instead a condition in evolution, can of course not be derived from a single analysis.

4. Conclusion

We have reported the observations made on the oxidation of spent fuel stored successively for 10 years in dry air and 15 years in a moist environment. Even though oxidation has occurred, the spent fuel still shows a generally good condition.

Based on the microscopic observations and (semi-quantitative) calculations of the amount of reacted UO_2 in spent MOX fuel stored for 25 years in dry air and the spent UO_2 fuel in the current study, it is found that moisture enhances the oxidation rate, also at ambient temperatures. The oxidation affects first the grain boundaries, and several stages could be identified. First, the grain boundary bonding is weakened, followed by an enhanced sensitivity to chemical attack, grain boundary decohesion and finally the onset of bulk oxidation of the UO_2 grains.

Acknowledgements

The authors like to thank F. Swinnen, G. Cools and H. Van Eyck for their participation in the sample preparation, puncture and mass spectrometry analysis.

References

[1] P. Dyck, M.J. Crijns, Rising needs: Management of spent fuel at nuclear power plants, IAEA Bull. 40 (1998) 1.

[2] M. De Valkeneer, C. Dierick, Nucl. Eur. Worldscan 5–6 (2001) 24.

[3] D.W. Shoesmith, J. Nucl. Mater. 282 (2000) 1.

[4] K.M. Wasywich, W.H. Hocking, D.W. Shoesmith, P. Taylor, Nucl. Technol. 104 (1993) 309.

[5] W.H. Hocking, R. Behnke, A.M. Duclos, A.F. Gerwing, K.M. Wasywich, Grain-boundary oxidation of used CANDU fuel exposed to dry air at 150 °C for a prolonged period, Fourth Intern. CANDU Fuel Conf., 1995, p. 6B-20.

[6] R.J. McEarchern, P. Taylor, J. Nucl. Mater. 254 (1998) 87.

[7] J. Nakamura, T. Otomo, T. Kikuchi, S. Kawasaki, J. Nucl. Sci. Technol. 32 (1995) 321.

[8] A. Leenaers, M. Verwerft, D. Boulanger, N. Itagaki, T. Matsumara, Microstructure of spent MOX fuel stored under dry air for 25 years, Eighth Intern. Conf. on Radioactive Waste Management and Environmental Remediation, ICEM '01, Brugge (Belgium), September 30 October 4, 2001, Proceedings published in ASME.

[9] IAEA-TECDOC-1087.

[10] T. Lundström, H. Christensen, K. Sehested, Radiat. Phys. Chem. 61 (2001) 109.