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ORIGINAL PAPER

Characterisation of high burnup spent mixed oxide fuel after leaching at hyperalkaline pH in a reducing environment

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Abstract

Microstructural investigations of a *Zircaloy-4* clad mixed oxide fuel rod segment with a burnup of 50.3 GWd/t_{HM} after exposure to a synthetic young cementitious water at a hyperalkaline pH of 13.7(2) under reducing atmosphere for about 3.5 years were conducted. A deposit on surfaces exposed to the leachate was observed and attempts were made to identify its composition. Initial scanning electron microscopy/energy dispersive X-ray spectroscopy results indicate that it contains several leachate constituents, as well as Zr and Ti. The presence of Ti indicates corrosion of the autoclave liner during the leaching experiment. Surfaces which were not directly exposed to the leachate revealed additional features, such as distinct ε-particles. Remarkably, these could not be identified on surfaces exposed to the leachate, which may indicate that dissolution of the ε-particles took place as well.

Introduction

The disposal of spent nuclear fuel (SNF) in a deep geological repository (DGR) is regarded as the best practical waste management option in many countries. The long-term safety of a DGR over an assessment time frame of up to one million years necessitates a comprehensive understanding of the corrosion behaviour of SNF when coming into contact with near-field water once the waste canister is breached. Although various studies addressed this topic in the last decades [1–4], some of the processes contributing to the (radiolytic) matrix corrosion of SNF in the generally reducing repository environment are not fully understood. Furthermore, only limited efforts were deployed to study the corrosion behaviour of irradiated mixed oxide (MOX) fuels [5–7]. To examine the effects of environmental conditions on SNF corrosion, the SF-ALE project (Spent Fuel Autoclave Leaching Experiments) was initiated between the *Belgian Nuclear Research Centre SCK CEN*, the Belgian nuclear waste management organisation *NIRAS/ONDRAF*, and the *Forschungszentrum Jülich GmbH*.

Within SF-ALE, the corrosion behaviour of irradiated UOX and MOX pressurised water reactor fuels is studied. The irradiated fuel rod segments were leached in neutral bicarbonate solution (BIC) and in hyperalkaline young cementitious water (YCW) under reducing atmosphere in order to assess the release of various radionuclides and fission gases over a time frame of 3.5 years. First results on the leaching behaviour of these fuels have been published previously [8, 9]. Following the leaching phase, a post leaching characterisation of the MOX fuel rod segments was initiated in order to study the microstructural evolution and secondary phase formation. In this work, we present initial scanning electron microscopy (SEM) results of the post leaching characterisation of a MOX segment exposed to YCW.

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Materials and methods

Fuel rod segment

An autoclave leaching experiment was performed with a *Zircaloy-4* clad MOX fuel rod segment, having a burnup of 50.3 GWd/t_{HM}. Prior to irradiation, the pellets had a Pu metal fraction of 14 mol% and an oxygen-to-metal ratio of 1.99 [10]. The irradiation history and the burnup determination of the fuel rod are described elsewhere [8, 11]. The segment used in the leaching experiment had a length of 24 mm and a diameter ranging between 12 mm and 14 mm. It had a mass of 12.9 g and was cut from the fuel rod in such a way that it contained two half pellets and one full pellet in between [8].

Autoclave leaching experiment

The segment was subjected to an autoclave leaching experiment in YCW, which has a pH of 13.7(2) and contains Na, Ca, K, Al, Si, and CO_3^{2-} ions. The experimental set-up and the concentrations of the constituents in the leachates are described in a recent publication [9]. The experiment was conducted at room temperature in an autoclave with a Ti-coated stainless steel liner, which contained the clad segment mounted in a Ti holder, 200 mL of the YCW, and an Ar:H_2 gas atmosphere (96:4, $p = 40$ bar).

The leachate was renewed after 5 days and 734 days. Due to safety measures, the pressure was reduced to 4 bar 148 days prior to the second renewal. At the second renewal, the autoclave liner was also replaced by a new one and a pressure of 40 bar was maintained. The leaching experiment was stopped after a total duration of 1275 days. An alteration of the autoclave liner surface was visually observed after the leaching phase. The leached segment recovered from the autoclave was rolled over a non-woven polypropylene wipe to remove remains of the leachate and stored under argon atmosphere.

Post-leaching characterisation

SEM analyses of the segment cross-sections were performed using a *Jeol JSM 7100FA* field-emission electron microscope equipped with a secondary electron detector (SED) and a backscattered electron detector (BSED). The segment was clamped in a stainless steel hollow cylinder, which was inserted into the SEM chamber for the analyses. The working distance was about 10 mm and an accelerating voltage of 15 kV was employed.

Examinations were carried out on both sides of the fuel segment, which required the segment to be unclamped and removed from the holder, rotated by 180°, and clamped again. During this manipulation, fuel fragments dropped out of the segment, allowing to investigate surfaces not directly exposed to the leachate, as well as performing scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDS) analyses of the fragments to obtain information about the elemental composition of the phases observed by SEM imaging. Due to the high radiation of the full-size segment, the EDS detector was saturated and no SEM-EDS analyses could be carried out on the cross-sections of the segment itself.

SEM-EDS measurements on the recovered fuel fragments were performed, using a *XFlash®* system by *Bruker*, which is coupled to the aforementioned SEM. Data were acquired using the *Bruker* software *Quantax 400*. The fragments were fixed on specimen holders using carbon adhesive tape and SEM-EDS analyses were carried out employing accelerating voltages of 7 kV and 20 kV.

Results and discussion

Segment cross-sections

Figure 1 summarises some observations obtained by SEM on the cross-sections of the segment leached in YCW. Surface deposits consisting of spherical precipitates were observed (Fig. 1a–d) occurring either as larger single spheres with diameters in the range of about 5 µm to 7 µm (cf. Fig. 1d), or as agglomerates of smaller spheres with diameters between 1 µm and 3 µm (cf. Fig. 1b). The deposit was observed on the entire fuel surface, independent of the radial position and occurred also in regions with a high burnup structure (HBS), as shown in Fig. 1c, d. However, it was not found on surfaces of the fuel segment not directly exposed to the leachate (Fig. 1e, f), which suggests that the deposit is either a precipitate formed during the leaching periods, or a residue from the evaporation of leachate that remained on the segment surface after the leaching experiment.

Fragment surfaces exposed to leachate

SEM-EDS results of a fragment surface exposed to the leachate are presented in Fig. 2. The EDS spectrum of the MOX matrix, not covered by the surface deposit (Fig. 2a), shows the presence of U, Pu, and O as expected. An emission line around 677 eV was commonly observed in all measurements carried out, sometimes pronounced, other times less pronounced. This emission line would be associated to fluorine; however, the source of an F signal is not clear. Another possible explanation is that it is a convolution of multiple Fe L-edge emission lines, i.e. Fe L_l (615 eV), Fe L_n (629 eV), Fe $L_{\alpha1,2}$ (705 eV), and Fe $L_{\beta1}$ (719 eV). A possible source

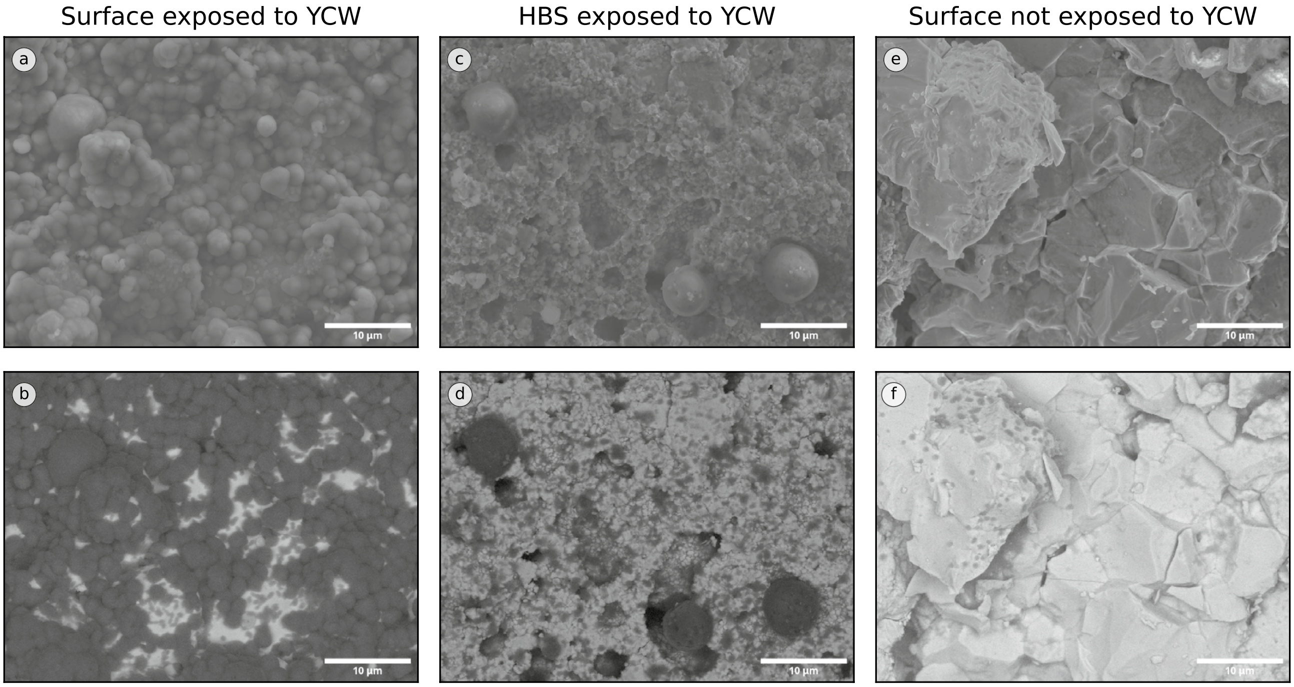

Fig. 1 SEM micrographs of segment surfaces exposed to YCW (**a–d**) and without contact to the leachate (**e**, **f**). For the first case, a regular region of the centre (**a**, **b**) and a region with a HBS (**c**, **d**) are shown (top row recoded by SED, bottom row by BSED)

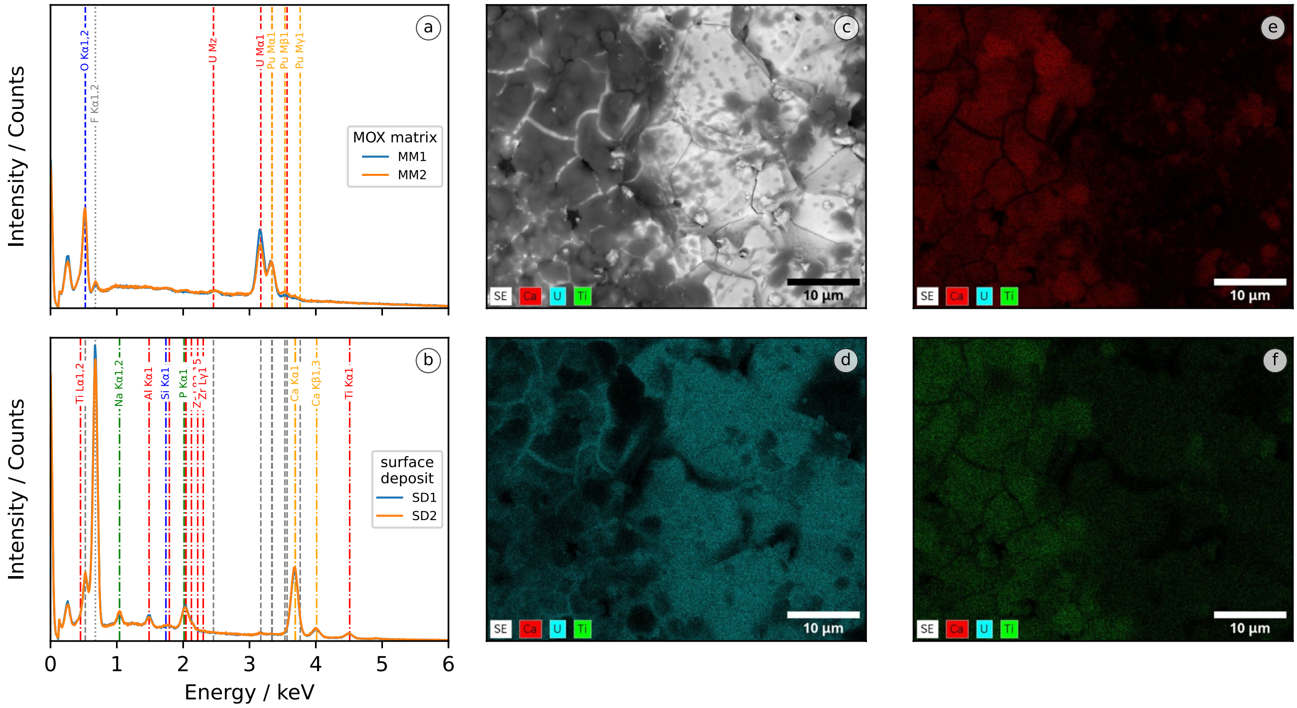

Fig. 2 SEM-EDS results of a surface exposed to YCW: Spectra of MOX matrix (**a**) and surface deposits (**b**), SED micrograph (**c**), as well as the distribution of U, Ca, and Ti (**d–f**). The measurements were carried out using an accelerating voltage of 7 kV and the emission lines in grey (**b**) correspond to those introduced in (**a**). Measurements (**a, b**) performed in regions not part of (**c–f**)

for Fe is the autoclave liner, which is fabricated from stainless steel but coated with Ti. During SEM-EDS analyses performed at 20 kV accelerating voltage, the Fe $K_{\alpha 1}$ line at 6.4 keV was present in addition to the aforementioned low-energy emission lines.

Signals of the MOX matrix were also observed in SEM-EDS analyses of the surface deposit with an accelerating voltage of 20 kV. These signals did not occur in measurements performed with an accelerating voltage reduced to 7 kV (Fig. 2b, MOX matrix: dashed vertical grey lines). Since the latter results in a smaller sample volume subjected to the electron beam, we assume that the surface deposit is free of U and Pu. However, it clearly contains Na, Ca, K, Al, and Si (cf. Fig. 2b), which are constituents of the YCW. Additionally, a broad emission line with a maximum at 2 keV is observed, which is likely associated to Zr based on the asymmetric shape of the peak. Zr originates most likely from the *Zircaloy-4* cladding. The low-energy emission line around 677 eV (dotted vertical grey line), likely associated to Fe rather than F, appears with a significantly higher intensity as compared on the MOX matrix. Moreover, the occurrence of Ti is also clearly apparent in the surface deposits. The existence of Ti points to a corrosion of the autoclave liner and the segment holder, which were in contact with the YCW during the leaching experiment. Furthermore, it explains the visually observed alteration of the surface of the autoclave liner after the leaching experiment. These results are supported by mappings of the U, Ca, and Ti distribution (Fig. 2c–f), representing (i) a fuel matrix element, (ii) a leachate constituent, and (iii) a corrosion product of the leaching equipment, respectively.

Autoclaves equipped with Ti-liners are/were used in several SNF leaching studies [12]. A recent publication reported a high sorption affinity of uranium on Ti-coated liners in YCW and BIC under reducing atmosphere [9], which we also observed in our leaching experiments. Moreover, we demonstrated that not only radionuclide sorption on Ti is a problem, but also corrosion of metallic Ti when exposed to hyperalkaline media.

If the surface deposit originates from precipitation, it can be assumed that this process occurred during the entire leaching phase since no increase in the concentrations of the YCW constituents in the leachate is anticipated. Another explanation of the deposit origin is that it is a residue from the leachate which evaporated from the segment surface after the leaching experiment.

Fragment surfaces not directly exposed to leachate

Results of SEM-EDS analyses of a fragment surface not directly exposed to the leachate are summarised in Fig. 3. Here, the surface deposits seem to be largely absent (Fig. 3a, b). The bulk material is the fuel matrix, which was confirmed by SEM-EDS measurements. The resulting spectra

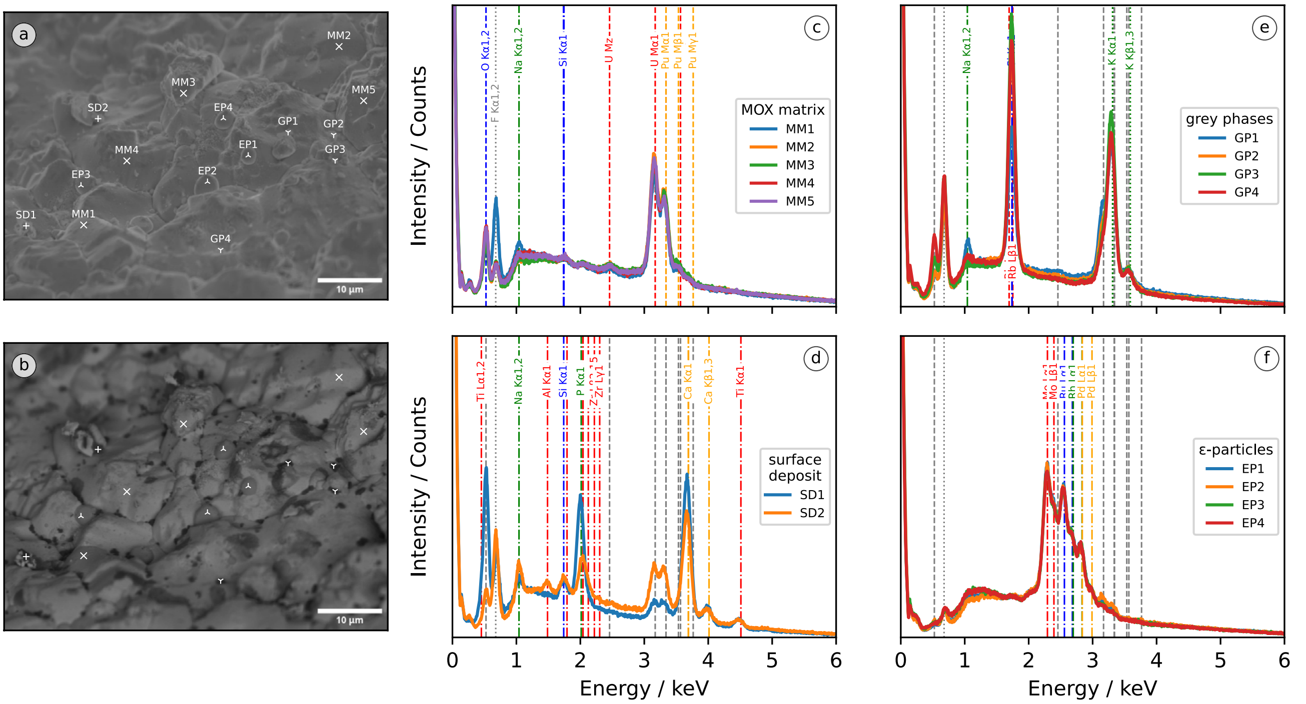

Fig. 3 SEM-EDS results of a surface not directly exposed to leachate: SED (**a**) and BSED (**b**) micrographs, as well as spectra of the fuel matrix (**c**), surface deposits (**d**), possible grey phases, (**e**) and ε-particles (**f**). The measurements were performed using an accelerating voltage of 7 kV and the emission lines in grey (**d–f**) correspond to those introduced in (**c**)

are shown in Fig. 3c and are similar to those of the MOX matrix described previously (cf. Fig. 2a).

We observed only a negligible fraction of the surface deposit on the surface not directly exposed to the leachate, its spectra are summarised in Fig. 3d. Signals of MOX matrix elements were observed as well in these spectra (dashed vertical grey lines), but the deposits observed here are much less spread out on the surface, leading to a higher probability that information from the surrounding matrix is acquired. This contamination could be debris of the deposit that occurred during handling or reached the fragment surface due to cracks in the MOX matrix.

Moreover, non-unambiguously identified phases containing Na, K, Rb/Si, and O were observed, and their spectra are presented in Fig. 3e. They occur quite frequently but are very small in size (about 0.5 µm to 2 µm; Fig. 3b) and exhibit also signals of the MOX matrix elements (dashed vertical grey lines). The origin of these phases is not entirely clear, the latter could point to secondary phases, but the signals are most likely caused by the surrounding fuel matrix and the fact that these phases were only found on surfaces that were not directly exposed to the solution suggests otherwise. They might be associated to the so-called grey phases (i.e. oxide phases containing various fission products), if the presence of Rb can be verified. This will require additional SEM-EDS analyses using a higher accelerating voltage to assess the Rb $K_{\alpha 1}$ line (13.4 keV). However, the incorporation of the YCW constituents (Na, K, Si) rather contradicts this. Grey phases are usually associated with Rb, Cs, Sr, Ba, Zr [13], but other alkali metals and alkaline earth elements, such as Na and K, may also have an affinity for incorporation.

Metallic precipitates (ε-particles), which were not noticed on fuel surfaces in contact with the leachate were observed here as well. Figure 3f shows spectra of such ε-particles, consisting of Mo, Tc, Ru, Rh, and Pd in variable proportions. Some ε-particles were found to contain a significantly higher amount of Pd and less Mo, Tc, and Ru. The composition of the ε-particles was not quantified, but corresponds to those observed in ε-particles studied by Cui et al. [14].

The mentioned study addressed also the dissolution of ε-particles in synthetic ground water under Ar:CO_2 atmosphere, where a congruent dissolution behaviour of Mo, Tc, and Rh was observed. Further investigations were carried out in Ar:CO_2:H_2 atmosphere, which revealed lower metal concentrations in the leachate [14], pointing to an inhibition of dissolution due to the reducing atmosphere. García-Gómez et al. [15] investigated the oxidation behaviour of Mo in high burnup SNF and observed that more than 60 % of the initially metallic Mo oxidised to its hexavalent oxidation state after an exposure to a solution with a pH of 13.2 in air; the oxidised fraction was significantly smaller in solutions with a lower pH. Due to the hyperalkaline nature of the YCW used in our work, a similar effect might explain the absence of ε-particles on surfaces exposed to the leachate in this study, even though reducing conditions were maintained during the leaching experiment.

Conclusions

The initial results of the post leaching characterisation of the clad MOX fuel rod segment with a burnup of 50.3 GWd/t_{HM} leached in YCW and an reducing environment for a duration of 3.5 years show that a dissolution of ε-particles likely occurred on surfaces exposed to the leachate. A phase possibly containing Rb together with Na, K, Si, and O was observed on surfaces not directly exposed to the leachate. Additional EDS analyses are needed to verify if these correspond to the so-called grey phases. Moreover, deposits containing constituents of the YCW, as well as Zr originating from the cladding, and Ti resulting from the corrosion of the autoclave liner material were observed on surfaces exposed to the leachate, whereas surfaces not directly exposed to the leachate did not exhibit this deposit. Further efforts are required to determine whether the deposit is a precipitate formed during the leaching experiment or whether it is a residue from evaporation of leachate remaining on the surfaces after termination of the leaching experiment. Moreover, it was demonstrated that not only radionuclide sorption is a problem on Ti-coated liners used in leaching experiments, but also that Ti corrosion occurs when exposed to hyperalkaline media. Consequently, the usage of liners and sample/segment holders made of alternative materials, e.g. polyether ether ketone (PEEK), is recommended, especially if a hyperalkaline leachate is used. Future characterisations of segments exposed to BIC will depict whether Ti corrosion occurs also in leachates with lower pH.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability The data of the current study are available from the corresponding author on reasonable request.

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