

Characterization of UO_2/Mo thin films as models for ϵ -particles in spent nuclear fuel

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Spent nuclear fuel (SNF) consists of 95% UO_2 and 5% is a mixture of radionuclides (RNs) and fission products, heterogeneously distributed throughout the fuel matrix in different phases, e.g.: gases (Xe, Kr, I), oxides (including transuranics Pu, Np, ...) and metallic precipitates or so-called ϵ -particles (Pd, Mo, Rh, Ru, ...)[1,2]. Systematic investigations of SNF matrix corrosion as an important source term for the mobilization of RNs are essential for evaluating SNF disposal safety.[3-4] We prepare UO_2/Mo thin films (TFs) for potential use as models to study the influence of ϵ -particles on the surface corrosion of SNF. The TFs provide a less complex system and lower radiation fields than actual SNF samples, which allows systematic mechanistic investigations even in non-radioactive laboratories.

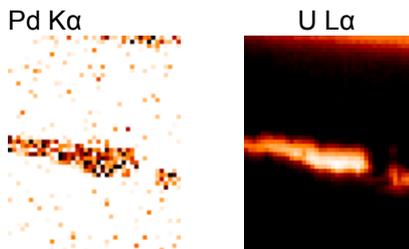
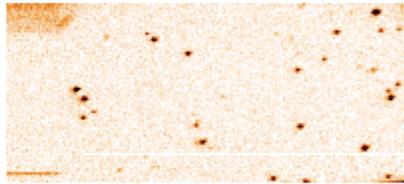


Figure 1: (top) Mo distribution measured in a $5000 \times 2100 \mu\text{m}^2$ area of sample I, $E_{\text{in}} = 23 \text{ keV}$. Increased Mo Ka intensity in 2-4 pixel areas is observed. (bottom) Pd and U distribution measured for sample B in a $450 \times 250 \mu\text{m}^2$ area covering a scratch, where UO_2 has been removed from the surface, $E_{\text{in}} = 24.5 \text{ keV}$. $25 \mu\text{m}$ step size and 0.5 s counting time for all images.

The first step in determining how well the SNF surface is mimicked by these TF models is to characterize their composition, structure and morphology. We use various methods to characterize samples prepared by in situ sputter co-deposition and subsequent heat treatment to ascertain if they provide ϵ -particle-like agglomerations of Mo in the UO_2 matrix. In previous investigations, XPS results indicate uranium to be present as UO_2 but metallic and oxide Mo was found in varying proportions, depending on the substrate (Si , SiO_2 or LaAlO_3) and the heating temperatures. In studies performed at the ESRF ID22Ni using a nanofocussed beam, we found that for TFs prepared on Si substrates tempered at 1000°C the UO_2 partially reacts with the substrate, forming USi_3 , with Mo localized as 100-400 nm nanoparticles in USi_3 grain boundaries. When SiO_2 is the substrate, this does not occur. Results of XRF tomography indicate that Mo is concentrated at the substrate surface for TFs prepared on LaAlO_3 . We use in this experiment μ -XRF to characterize

element distributions of these same samples (and one with Pd as dopant) over larger regions. With the focussed beam at selected regions, we record Mo K- and U L3-XANES to characterize oxidation state and coordination structure.

Measurements are performed at BL-L using a Si(111) double crystal monochromator and a polycapillary half-lens to focus the beam with maximum flux at the sample. Knife edge scans at 23 keV incident energy (E_{in}) indicate the beam spot dimensions to be $22 \mu\text{m}$ (V) \times $35 \mu\text{m}$ (H). TFs are prepared via co-deposition of U and Mo or Pd targets under $1.2 \cdot 10^{-6}$ mbar O_2 partial pressure and $4 \cdot 10^{-3}$ mbar Ar as sputter gas. The sample designations and descriptions are summarized in Table 1.

Table 1: Thin film samples, their dopant content and temper conditions.

Sample ID	Description
I	8% Mo, SiO_2 substrate, 1000°C (10h)
H	20% Mo, Si substrate, 1000°C (10h)
B	12% Pd, LaAlO_3 substrate, 1000°C (10h)

In Mo distributions reconstructed from large area XRF scans of sample I (Figure 1, top), 500-150 μm sized Mo hot spots are revealed. These were not observed in scans using a nano-sized beamspot at the ESRF, as the Mo hot spots are distributed randomly and widely spaced. The U and Mo distribution in sample H (not shown) appears homogeneous as expected, as the beamspot size is much larger than the observed Mo nanoparticles. In areas of sample B recorded at a scratch on the surface visible in light microscope images, the highest Pd K α counts are observed where the UO₂ has been removed (Figure 1, bottom). Similar to observations for UO₂/Mo on LaAlO₃ substrate, this result indicates that a Pd layer at the substrate interface forms and its fluorescence emission is higher in areas void of UO₂ (no absorption).

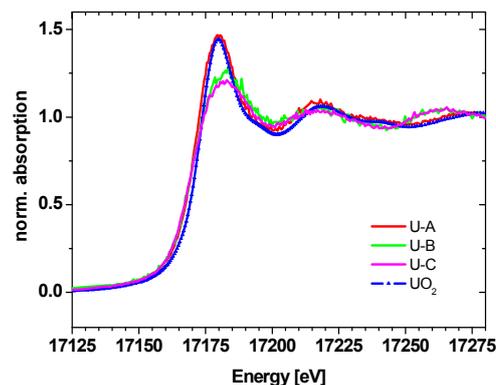


Figure 2: U L3 XANES measured at different positions of sample H and compared to a UO₂ reference. See test for details.

Mo K edge XANES of Mo hot spots in sample I and of sample H at different areas known to be composed of UO₂, USi₃ and a mixture of these two phases are recorded (indicated as A, B and C, respectively). Uranium L3 edge XANES are recorded for sample H at the same positions. The results are depicted in Figures 2 and 3 and compared to spectra from Mo foil and UO₂ references. The U L3 XANES U-A strongly resembles that for the UO₂ reference. A broadening of the strongest absorption feature (white line at ~ 17180 eV) is observed, as well as indication of a lengthening of the average U-O distance (shift of the first EXAFS resonance at ~ 17216 eV to lower energy). The U-B spectrum recorded where USi₃ is present is dissimilar; the white line is reduced and the first two visible EXAFS oscillations are significantly different. The U-C spectrum measured at the mixed phase area of sample H resembles U-B, suggesting that U is mostly present as USi₃. All Mo K XANES differ from that for Mo(0); the edges observed for sample H are shifted comparably to lower energy, that for sample I to higher (see Figure 3, inset). The edge energy of the sample I Mo hot spot lies between edge energies for MoO₃ and MoO₄. [5] This is in agreement with Mo 3d_{5/2} binding energies determined for sample I in XPS studies. The Mo-B XANES recorded at the same position as U-B differs from the spectra measured where UO₂ or a phase mixture is present in the sample. In contrast to the U L3 results, the Mo-C XANES in the mixed phase region is more similar to the Mo-A XANES recorded in the UO₂ region.

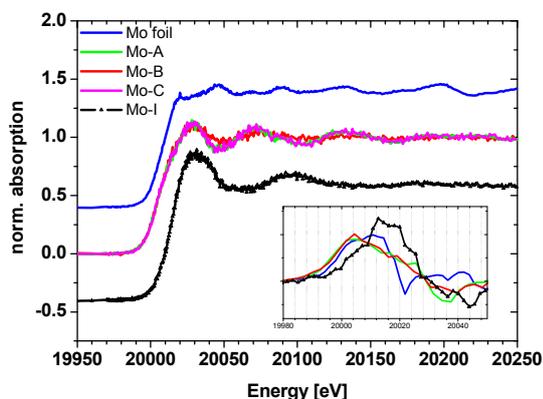


Figure 3: Mo K-edge XANES recorded at position in a USi₃ area (Mo-B), in a UO₂ area (Mo-A) and in mixed phase area (Mo-C) of sample H, compared to the XANES of a Mo hot spot in sample I and a Mo foil. Inset: 1st derivative spectra.

These results show that none of the substrates or temper program used produce viable SNF ϵ -particle models. Nano- (sample H) and micron-sized (sample I) Mo particles form but are either not embedded in the desired UO₂ substrate or are in oxide form.

References

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