Characterization of UO₂/Mo thin films as models for ε-particles in spent nuclear fuel

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Spent nuclear fuel (SNF) consists of 95% UO₂ 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 UO₂/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.

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 UO₂ matrix. In previous investigations, XPS results indicate uranium to be present as UO₂ but metallic and oxide Mo was found in varying proportions, depending on the substrate (Si, SiO₂ or LaAlO₃) 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 UO₂ partially reacts with the substrate, forming USi₃, with Mo localized as 100-400 nm nanoparticles in USi₃ grain boundaries. When SiO₂ is the substrate, this does not occur. Results of XRF tomography indicate that Mo is concentrated at the substrate surface for TFs prepared on LaAlO₃. 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 (Eₗ) indicate the beam spot dimensions to be 22 µm (V) x 35 µm (H). TFs are prepared via co-deposition of U and Mo or Pd targets under 1.2*10⁻⁶ mbar O₂ partial pressure and 4*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.

<table>
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<tr>
<th>Sample ID</th>
<th>Description</th>
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<tr>
<td>I</td>
<td>8% Mo, SiO₂ substrate, 1000 °C (10h)</td>
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<tr>
<td>H</td>
<td>20% Mo, Si substrate, 1000 °C (10h)</td>
</tr>
<tr>
<td>B</td>
<td>12% Pd, LaAlO₃ substrate, 1000 °C (10h)</td>
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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 beampot 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 beampot 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 Kα 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).

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 3d5/2 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.

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