

Atomic-Scale Mapping of Pu Oxidation and Hydrogenation with Environmental Atom Probe Tomography

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Predicting the long-term stability of plutonium (Pu) requires mechanistic insight into how surface oxides and hydrides nucleate, grow, and evolve under storage-relevant environments. To address this knowledge gap, we have begun implementing the advanced Atom Probe Tomography capability of environmental-Atom Probe Tomography (eAPT) [1]. eAPT experiments were conducted on δ -Pu specimens to observe in real-time the interaction between native oxide and deuterium. Within the inherent electric field environment of the eAPT experiment, introduction of pure D₂ into the analysis chamber initiates hydrogenation and oxide-reduction events that were captured directly in reconstructed 3D atom distribution maps. This direct visualization provides quantitative insight into hydrogen uptake rates and reduction kinetics at the atomic scale, revealing strong crystal orientation dependences on hydrogenation behavior. Using PNNL's ball-model reconstruction tool we identified specific surface facets, particularly (111), (001), and (011) orientations that are observed as loci of increased reactivity. The facet-resolved maps also demonstrate grain-to-grain variability in the oxidation and hydride formation, underscoring the importance of microstructural context when considering corrosion susceptibility. Recent eAPT studies on iron [1] and associated quantum mechanical models on ruthenium [2] show that tens of V/nm electric fields (EFs) polarize and attract gas molecules, effectively increasing the local partial pressures at the specimen apex and lowering adsorption energy barriers. In this context, the PuO_x reduction observed under D₂ likely includes an EF contribution, making it necessary to develop field-ramp control and pulse-parameter sweeps to separate EF-driven effects from intrinsic reaction dynamics and enable facet-specific rate extraction. These eAPT results provide the first time-resolved evidence of plutonium oxide reduction and hydride formation by integrating atomic-scale composition mapping while recognizing EF-dependent effects. This framework is leading to an improved interpretation of aging behavior and supports the development of predictive models for long-term stability of plutonium materials.

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