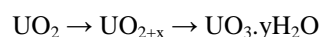


The Composition of Oxide Films on Gd-doped Uranium Dioxide (UO₂)

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Abstract

Spent nuclear fuel is doped with rare earth elements as a consequence of the in-reactor fission process. This doping influences both the composition and lattice structure of the fuel making it essential to determine its influence on the chemical/corrosion reactivity of the fuel under permanent disposal conditions. The aim of this study is to elucidate the influence of rare earth doping on fuel reactivity using Gd-doped UO₂. Electrochemical experiments are being conducted on stoichiometric UO₂ pellets uniformly doped with Gd^{III} (6 weight %) and characterized by Scanning Electron Microscopy (SEM)/Energy-dispersive X-ray spectroscopy (EDX) and Raman spectroscopy. A combination of electrochemical experiments in chloride solutions with/without carbonate/bicarbonate followed by X-ray photoelectron spectroscopy (XPS) shows that surface oxidation occurs in stages



While this general reaction scheme is similar to the anodic oxidation behavior observed on slightly non-stoichiometric UO₂ and SIMFUEL [1, 2] (UO₂ containing 11 dopants to simulated spent nuclear fuel), the extent of oxidation is sensitive to the degree of non-stoichiometry and the extent of Gd^{III} doping, the pH of the solution and the presence/absence of carbonate/bicarbonate. The overall inhibiting effect of Gd-doping on film formation/dissolution can be attributed to the high doping level (6 wt%) which Raman spectroscopy shows reduces the availability of the oxygen vacancies (O_v) required to accommodate O²⁻ during oxidation by forming RE^{III}-O_v defect clusters. This is in contrast to non-stoichiometry which leads to the formation of U^V-oxygen interstitial (O_i) clusters which facilitate a deeper oxidation of the surface. The influence of carbonate/bicarbonate, which complexes and solubilizes the U^{VI} state, confirms that the thin U^{VI} surface layer formed at positive potential on the Gd-doped surface is more readily dissolved than that on the more deeply oxidized SIMFUEL and non-stoichiometric UO_{2+x}.

References

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- [2] B. G. Santos, H.W. Nesbitt, J.J. Noël and D.W. Shoesmith, *Electrochimica Acta* **49** (2004) 1863-1873