

Thursday Morning, October 22, 2015

Actinides and Rare Earths Focus Topic
Room: 230A - Session AC+AS+MI-ThM

Nuclear Power and Waste Remediation

Moderator: David Shuh, Lawrence Berkeley National Laboratory

8:00am **AC+AS+MI-ThM1 Applications of Synchrotron Methods to f-Element Research in the Nuclear Fuel Cycle, Melissa Denecke**, The University of Manchester, UK **INVITED**

Celebrating 60 years of civil nuclear power generation offers an excellent opportunity to review synchrotron radiation (SR)-based techniques to characterize nuclear materials and elucidate processes relevant to the nuclear fuel cycle. The penetration capability of intense SR X-ray sources allows in situ investigations, including samples within radiological containments or specialized environments. The presentation will concentrate on application of X-ray spectroscopic techniques in studies related to the nuclear fuel cycle (fuel, cladding, recycle, waste disposal).

8:40am **AC+AS+MI-ThM3 Ab Initio Study of Advanced Metallic Nuclear Fuels for Fast Breeder Reactors, Alexander I. Landa**, Lawrence Livermore National Laboratory **INVITED**

The U-TRU-Zr and U-TRU-Mo alloys proved to be very promising fuels for TRU-burning liquid metal fast breeder reactors. The optimal composition of these alloys is determined from the condition that the fuel could remain stable in the bcc phase (γ -U) in the temperature range of stability of α -U phase. In other words, both Zr and Mo play a role of ' γ -stabilizers' helping to keep U in the metastable bcc phase upon cooling. The main advantage of U-Pu-Mo fuels over U-Pu-Zr fuels lies in much lower constituent redistribution due to the existence of a single γ -phase with bcc structure over typical fuel operation temperatures. The nucleation time for the decomposition of the metastable alloys, which controls the constituent redistribution process, is directly connected with the excess enthalpy of solution of these alloys. In the present study we perform KKR-ASA-CPA and EMTO-CPA calculations of the ground state properties of γ -U-Zr and γ -U-Mo alloys and compare their heats of formation with CALPHAD assessments. We discuss how the heat of formation in both alloys correlates with the charge transfer between the alloy components, and how the specific behavior of the density of states in the vicinity of the Fermi level promotes the stabilization of the U_2Mo compound. Our calculations prove that, due to the existence of a single γ -phase over the typical fuel operation temperatures, γ -U-Mo alloys should indeed have much lower constituent redistribution than γ -U-Zr alloys where a high degree of constituent redistribution takes place. The binodal decomposition curves for γ -based U-Zr and U-Mo solid solutions are derived from Ising-type Monte Carlo simulations incorporating effective cluster interactions obtained from the Screened Generalized Perturbation and Connolly-Williams methods. We also explore the idea of stabilization of the δ -UZr₂ compound against the α -Zr (hcp) structure due to increase of Zr d-band occupancy by the addition of U to Zr. Analogy with stabilization of the ω phase in Zr under compression is made. Though the U-Pu-Zr and U-Pu-Mo alloys can be used as nuclear fuels, a fast reactor operation on a closed fuel cycle will, due to the nuclear reactions, contain significant amount of MA (Np, Am, Cm). Calculated heats of formation of bcc Pu-U, Pu-Np, Pu-Am, Pu-Cm, Pu-Zr, Pu-Mo, Np-Zr, Np-Mo, U-Am, Np-Am, Am-Zr and Am-Mo alloys are also presented and compared with CALPHAD assessments. This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and was funded by the Laboratory Directed Research and Development Program at LLNL under project tracking code 12-SI-008.

9:20am **AC+AS+MI-ThM5 Shedding Light on Uranium Corrosion in Nuclear Waste Packages, Charilaos Paraskevoulakos**, University of Bristol, UK

Intermediate level waste (ILW) is encapsulated in grout and stored in stainless steel drums. A proportion of these have become a concern for the UK nuclear community, as significant distortion around the circumference of these drums has been observed. Distortion is ascribed to the generation of voluminous and potentially flammable corrosion products forming on uranium metal, e.g. uranium hydride. Thus potential oxygen influx caused by fracturing of canisters will threaten their suitability for waste disposal, potentially causing release of the encapsulated radioactive material or even ignition of the hydride. The association of the uranium corrosion mechanisms with the mechanical degradation of the encapsulants (stainless steel and grout), is the focus of the current project. Finite Element (FE)

Modelling, accelerated uranium corrosion tests as well as diffraction and tomography using synchrotron X-Rays/gamma rays could be employed to investigate the durability of the ILW packages.

9:40am **AC+AS+MI-ThM6 The Optical Properties of Uranium Carbide Measured by Spectroscopic Ellipsometry, Wigbert Siekhaus, A.J. Nelson, C.K. Saw**, Lawrence Livermore National Laboratory

Uranium carbide inclusions are common in metallic uranium, and uranium carbide itself is being used or being considered as a fuel in both gas-cooled, liquid metal cooled, and supercritical water-cooled reactors. To the best of our knowledge the only study of optical properties deals with high temperature radiance. [1] Here we first characterized a uranium carbide cube (supplied by Oak Ridge National Laboratory) with sides of approximately 3 mm length by X-ray diffraction and X-ray photo-electron spectroscopy and then measured its optical properties with an ellipsometer at angles of incidence between 65 and 75 degrees, and over an energy range from 1.26 to 3.2eV. The signal strength was low over that energy range, and too low to be useful above 3.2eV. The measured Δ and Ψ were converted to the dielectric constants ϵ_1 and ϵ_2 shown in the table below using a general oscillator model [2].

| E, eV | ϵ_1 | ϵ_2 | E, eV | ϵ_1 | ϵ_2 | E, eV | ϵ_1 | ϵ_2 |
|-------|--------------|--------------|-------|--------------|--------------|-------|--------------|--------------|
| 1.26 | -1.96 | 5.07 | 1.95 | -0.30 | 2.73 | 2.61 | 2.61 | 1.32 |
| 1.33 | -1.69 | 4.77 | 2.02 | -0.21 | 2.55 | 2.68 | 2.68 | 1.21 |
| 1.40 | -1.47 | 4.45 | 2.10 | -0.12 | 2.34 | 2.75 | 2.75 | 1.07 |
| 1.47 | -1.25 | 4.14 | 2.18 | -0.03 | 2.18 | 2.83 | 2.83 | 0.94 |
| 1.54 | -1.06 | 3.87 | 2.25 | 0.04 | 2.02 | 2.91 | 2.91 | 0.85 |
| 1.61 | -0.89 | 3.63 | 2.32 | 0.12 | 1.87 | 2.98 | 2.98 | 0.76 |
| 1.69 | -0.73 | 3.44 | 2.40 | 0.20 | 1.73 | 3.05 | 3.05 | 0.67 |
| 1.76 | -0.60 | 3.23 | 2.47 | 0.28 | 1.59 | 3.12 | 3.12 | 0.58 |
| 1.84 | -0.48 | 2.95 | 2.54 | 0.35 | 1.43 | 3.20 | 3.20 | 0.51 |

Prepared by LLNL under Contract DE-AC52-07NA27344, LLNL-ABS-670149

[1] D. Manara, F. De Bruycker, K. Boboridis, O. Tougait, R. Eloiardi, M. Malki, High temperature radiance spectroscopy measurements of solid and liquid uranium and plutonium carbides, J Nucl Mater, 426 (2012) 126-138.

[2] R. Synowicki, J.A. Woollam CO. Inc. 645 M Street, Suite 102, Lincoln, NE 68508-2243, USA

11:00am **AC+AS+MI-ThM10 Uranium Wet Oxidation in the Presence of Hydrogen Overpressure, Antonios Banos**, University of Bristol, UK

The radioactive intermediate level (IL) and high level (HL) waste have been accumulated in the UK's legacy ponds and silos for over 60 years. There is a great need for these wastes to be retrieved to follow long term storage. Uranium hydride (UH₃) has been identified as a reaction product of the corrosion process. Hydride formation occurs due to the increasing concentration of hydrogen gas, generated from the reaction of uranium, Magnox (MagnoxAl80) and other metals. The highly pyrophoric and unstable nature of UH₃ in air poses considerable environmental risks, due to potential radionuclide release. In this work we will try to simulate the corroding conditions by immersing an initially polished uranium sample in water under vacuum and introducing hydrogen gas overpressure to the system. The ternary system will be investigated in different temperatures and pressures with two main questions awaiting to be answered: 1. Is UH₃ identified? For this reason post-examination of the reacted surface will be conducted using Secondary Ion Mass Spectrometry (SIMS), Focus Ion Beam (FIB) milling. 2. If UH₃ is identified, on which part of the reaction is it produced and how this affects the overall reaction? The kinetics will be monitored using a specifically designed set-up comprised from a stainless steel pot and a pressure controller attached on one end and logged to a computer in order for the whole reaction to be recorded and the rate of corrosion through gas generation to be evaluated.

11:40am **AC+AS+MI-ThM12 Resolving the Issues of 5f Covalency and Ionicity in UO₂ and UF₄, James Tobin**, Lawrence Livermore National Laboratory

Building upon our recent work, a concerted effort to isolate and understand covalency and ionicity in uranium compounds has been pursued. Specifically, the isoelectronic formal charge systems, uranium dioxide and uranium tetrafluoride, have been investigated with a novel mixture of both soft and hard-x-ray spectroscopies. The results to be discussed will include the following: (1) the use of soft X-ray O1s/F1s X-ray absorption spectroscopy (XAS) and U4d X-ray emission spectroscopy (XES) to follow

the 2p/5f bonding via the unoccupied density of states; (2) the utilization of hard X-ray U L3 extended X-ray absorption fine structure (EXAFS) to trivially distinguish the ordering in each; and (3) the use of hard X-ray L3 resonant X-ray emission spectroscopy (RXES) to distinguish 5f occupation/covalency effects in UO₂ and UF₄. Collaborators include CH Booth, DK Shuh, T. Tyliczszak, G. van der Laan, D. Sokaras, T.-C. Weng, D. Nordlund, S.-W. Yu, W. Siekhaus and P.S. Bagus.

Authors Index

Bold page numbers indicate the presenter

— B —

Banos, A.K.: AC+AS+MI-ThM10, **1**

— D —

Denecke, M.A.: AC+AS+MI-ThM1, **1**

— L —

Landa, A.: AC+AS+MI-ThM3, **1**

— N —

Nelson, A.J.: AC+AS+MI-ThM6, **1**

— P —

Paraskevoulakos, C.: AC+AS+MI-ThM5, **1**

— S —

Saw, C.K.: AC+AS+MI-ThM6, **1**

Siekhaus, J.: AC+AS+MI-ThM6, **1**

— T —

Tobin, J.G.: AC+AS+MI-ThM12, **1**