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CY2013 Annual Report for DOE-ITU INERI 2010-006-E

J.R. Kennedy, V.V. Rondinella

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INTERNATIONAL NUCLEAR ENERGY RESEARCH INITIATIVE

State-of-the-Art Post-Irradiation Examination of Advanced Nuclear Fuels

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Collaborators: Colorado School of Mines, University of Central Florida, Massachusetts Institute of Technology, Los Alamos National Laboratory

Project Number: 2010-006-E

Program Area: FCRD

Start Date: January 2011

End Date: December 2014

Research Objectives

New concepts for nuclear energy development are considered in both the USA and Europe within the framework of the Generation-IV International Forum (GIF) as well as in various US-DOE programs (e.g. the Fuel Cycle Research and Development - FCRD) and as part of the European Sustainable Nuclear Energy Technology Platform (SNE-TP).

Since most new fuel cycle concepts envisage the adoption of a closed nuclear fuel cycle employing fast reactors, the fuel behavior characteristics of the various proposed advanced fuel forms must be effectively investigated using state of the art experimental techniques before implementation. More rapid progress can be achieved if effective synergy with advanced (multi-scale) modeling efforts can be achieved. The fuel systems to be considered include minor actinide (MA) transmutation fuel types such as advanced MOX, advanced metal alloy, inert matrix fuel (IMF), and other ceramic fuels like nitrides, carbides, etc., for fast neutronic spectrum conditions. Most of the advanced fuel compounds have already been the object of past examination programs, which included irradiations in research reactors. The knowledge derived from previous experience constitutes a significant, albeit incomplete body of data. New or upgraded experimental tools are available today that can extend the scientific and technological knowledge towards achieving the objectives associated with the new generation of nuclear reactors and fuels.

The objectives of this project will be three-fold: (1) to extend the available knowledge on properties and irradiation behavior of high burnup and minor actinide bearing advanced fuel systems; (2) to establish a synergy with multi-scale and code development efforts in which experimental data and expertise on the irradiation behavior of nuclear fuels is properly conveyed for the upgrade/development of advanced modeling tools; (3) to promote the effective use of international resources to the characterization of irradiated fuel through exchange of expertise and information among leading experimental facilities. The priorities in this project will be set according to the down selection procedure of U.S. and European development programs.

Research Progress

Experimental work in the US related to this collaboration during the 2013 timeframe was primarily directed towards development of high spatial resolution instrumentation for thermal conductivity and mechanical properties determination for eventual coupling with computational modeling and simulation efforts, atom probe tomography (APT) studies on fresh fuel samples from samples prepared with use of the focused ion beam (FIB), and higher spatial resolution microstructure studies of as-cast fuels from transmission electron microscope (TEM) studies for input into computational modeling and simulation efforts.

Topic 1: Investigation of properties and behavior of advanced fuels, with particular emphasis on high burnup, fast reactor irradiation behavior and effects associated with the presence of minor actinides. Topic 2: Synergies between the experimental and the modeling groups.

Atom Probe Tomography (APT) and Transmission Electron Microscopy (TEM) Studies

Advanced characterization techniques such as TEM and APT have been widely utilized for non-radiological materials; however, the extreme difficulty of working with radioactive samples has inhibited their application for nuclear applications. These advanced techniques provide the ability to obtain critical experimental data on the evolution of microstructure, dislocation density, grain size and orientation, and composition in irradiated materials from the atomic to the mesoscale. Atom probe tomography (APT) allows high resolution, "atom-by-atom" identification of element distribution in a sample. Dr. Melissa Teague at INL has used a focused ion beam (FIB) to produce site specific samples for the first ever APT studies of AFC transmutation fuels, performed at the Center for Advanced Energy Studies (CAES) facility at INL. Samples for APT were prepared using the hot FIB at the Materials and Fuels Complex and then transferred to CAES for analysis using the cutting edge LEAP 4000x HR atom probe. The first alloy studied was U-55Pu-20Zr in the annealed state. Due to instrumentation issues, an oxide layer formed on the outside of the samples. Figure 1 shows a reconstruction of an oxidized U-55Pu-20Zr sample. An interesting feature is the different oxidation behavior of the elemental components. The extent and depth of oxidation were element dependent with Zr having the thickest oxidation layer followed by U and then Pu. The presence of oxidized zirconium within metallic U/Pu is an interesting observation and further analysis is planned. A Pu/U rich and Zr depleted region was seen at the edge of the tip, which is hypothesized to be along a former grain boundary (Figure 2). Though preliminary in scope, the application of APT to transmutation fuels is an exciting advance and has great potential for helping to understand the complex behavior observed in both irradiated and unirradiated fuels. Further quantification of these type studies will be employed in conjunction with computational efforts (e.g. the MARMOT code at INL) to fully simulate the microstructure evolution in fuels under irradiation.

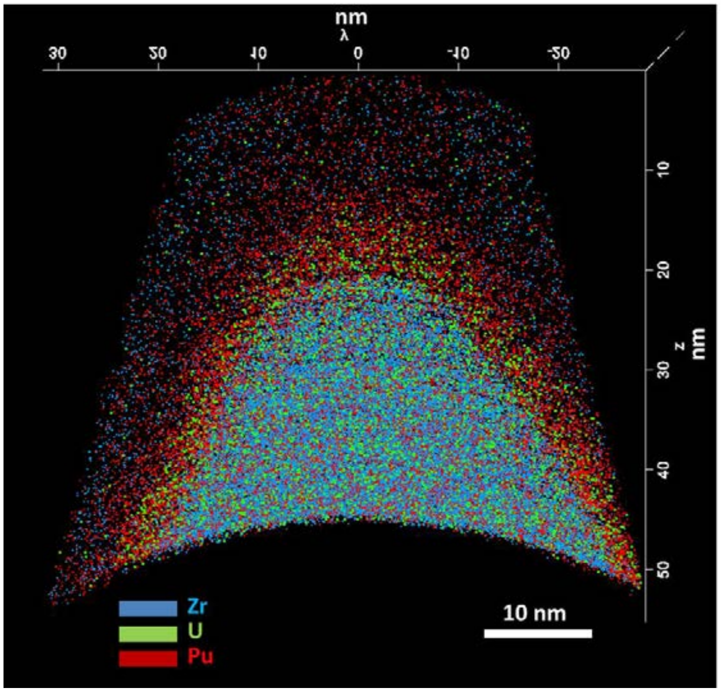


Figure 1. APT reconstruction of oxidized U-55Pu-20Zr sample showing the different oxidation depths of the components. Only the metallic ions of Zr, U, and Pu are displayed to highlight different oxidation behavior.

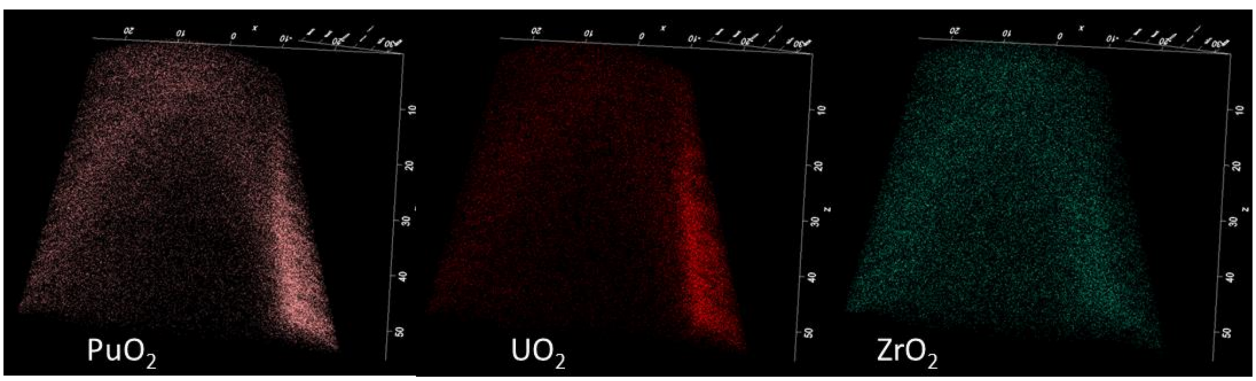


Figure 2. Reconstruction of U-55Pu-20Zr samples showing the Pu/U rich and Zr depleted region at the edge of the samples that is hypothesized to be a former grain boundary region.

In order to better understand the nature of the transmutation fuels and to better integrate experiment with computation and modeling, Dr. Dawn Janney initiated transmission electron microscopy (TEM) studies on various fuel types. These high spatial resolution microstructure studies are investigating a base U-Pu-Zr alloy in collaboration with Lawrence Livermore National Laboratory, a 52U-20Pu-3Am-2Np-8.0Ln-15Zr fuel composition that includes both minor actinides (MA) and lanthanides (Ln), and diffusion couples between U-Pu-Zr alloys and iron (Fe, representing cladding). These studies are the first of their kind with regard to use of the focused ion beam (FIB) for sample preparation of metallic transmutation fuels (TRU bearing fuel type materials) and the use of the TEM and its associated techniques (electron diffraction for single phase crystallite structure determination, energy dispersive spectroscopy for microchemical analysis) to investigate specific microstructural features of the fuel materials. Data from the U-Pu-Zr work and diffusion couple studies are still forthcoming but some very interesting and important results from the 52U-20Pu-3Am-2Np-8.0Ln-15Zr study given below.

Many Scanning Electron Microscopy (SEM) studies that do not allow the high spatial resolution possible with TEM have observed the as cast U-Pu-Zr fuels microstructure to appear as an undefined mixture of light and dark contrast phases but including also various shading of gray contrast material. It was speculated that this interesting feature could represent a nanosized grain structure composed of ζ-(U,Pu,Zr) and δ-(U,Pu)Zr_2 phases. Figure 3 shows a micrograph of a gray shaded area and reveals that indeed the as-cast microstructure is composed of nano-sized grains on the order of only a few tens of nanometers across. Electron diffraction analysis strongly suggests that one of the phases is in fact ζ-(U,Pu,Zr).

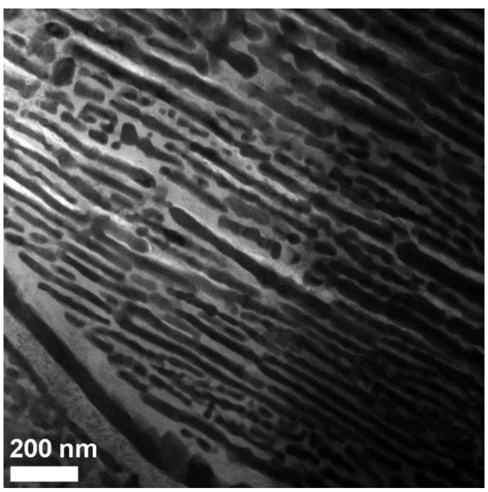


Figure 3. TEM micrograph obtained from an as-cast 52U-20Pu-3Am-2Np-8.0Ln-15Zr sample showing nano-sized light and dark contrast grain structure.

The ubiquitous Zr inclusions observed in virtually all U-TRU-Zr fuels have generally been interpreted to form due to impurities such as oxygen, nitrogen, silicon, etc. introduced as part of the feedstock material or from the casting process and should exist in the α-Zr structure. Single-crystal electron diffraction analyses (Figure 4) on these inclusions show this isn't necessarily true and, in fact, the high-Zr inclusions have a face-centered cubic (fcc) structure that haven't been reported previously in the literature. This study was recently published (D. E. Janney, J. R. Kennedy, J.W. Madden, T.P. O'Holleran "Crystal structure of high-Zr inclusions in an alloy containing U, Pu, Np, Am, Zr and rare-earth elements", J. Nucl. Mater. 448 (2014) 109–112)

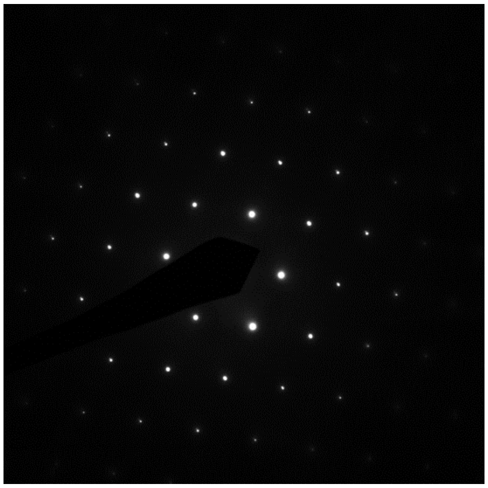


Figure 4. Electron diffraction pattern from a Zr rich inclusion along the [110] axis revealing it to be in the, to date, unreported face-centered-cubic structure.

Additional interesting findings show that, as previously reported in SEM data, there are two kinds of RE inclusions: high-Nd ("dark") and high-Am ("light"). Although all of the RE inclusions are high in Nd, proportions of other elements differ. High Nd content inclusions can have significant concentrations of oxygen and low concentrations of actinides. High Ce content inclusions are also high in Am and have significant concentrations of Pu. Interestingly, all of the observed high Zr inclusions are adjacent to high Ce inclusions, but not all high Ce inclusions are adjacent to high-Zr inclusions (Figure 5). The implications of these observations are still under consideration.

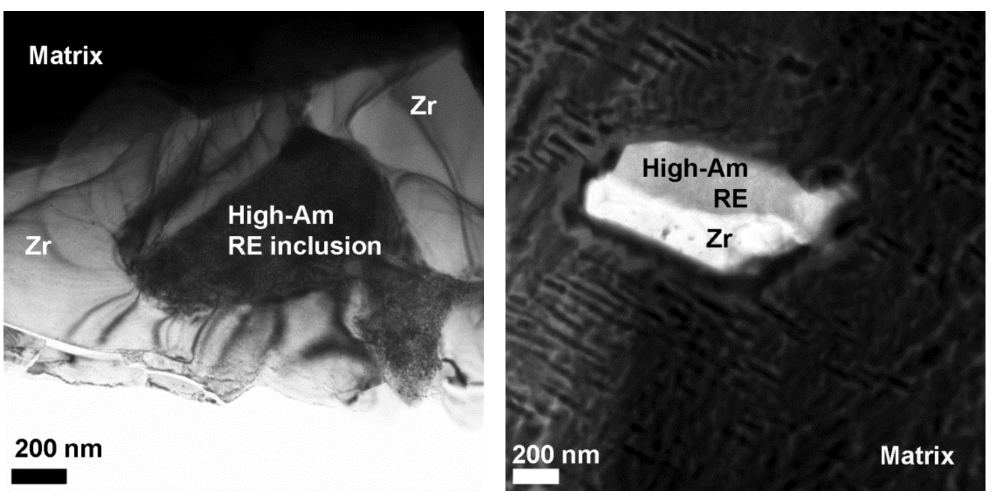


Figure 5. Left: high Am content RE inclusion surrounded by high Zr content inclusion. Right: combined high Zr content and high Am content inclusion.

Thermal Conductivity Studies and Modeling Developments

Thermal conductivity studies in ITU have continued; during the reporting period, the cause for thermal conductivity decrease associated with increasing fractions of Pu in MOX fuel has been investigated. The results of this study are published in [Staicu and Barker, *Thermal conductivity of heterogeneous LWR MOX fuels*, J. Nucl. Mater. 442 (2013) 46-52].

Thermal conductivity degradation of LWR MOX fuel compared to that of pure UO_2 is usually attributed to the substitution of U atoms by Pu. However, Duriez and Philiponneau indicate that the thermal conductivity of MOX is independent of the Pu content in the ranges 3 - 30 wt. % PuO_2. In fact, heterogeneity in the plutonium distribution in the fuel causes a variation in the local O/M ratio. This feature has a strong impact on the thermal conductivity. A model quantifying this effect was defined and validated using a new set of Laserflash measurements on homogeneous and heterogeneous MOX fuels. The stoichiometry perturbations are sufficient to explain the lower thermal conductivity of heterogeneous MOX fuel when compared to UO_2. The effect due to the presence of Pu in heterogeneous MOX is thus overestimated in the correlations available in literature.

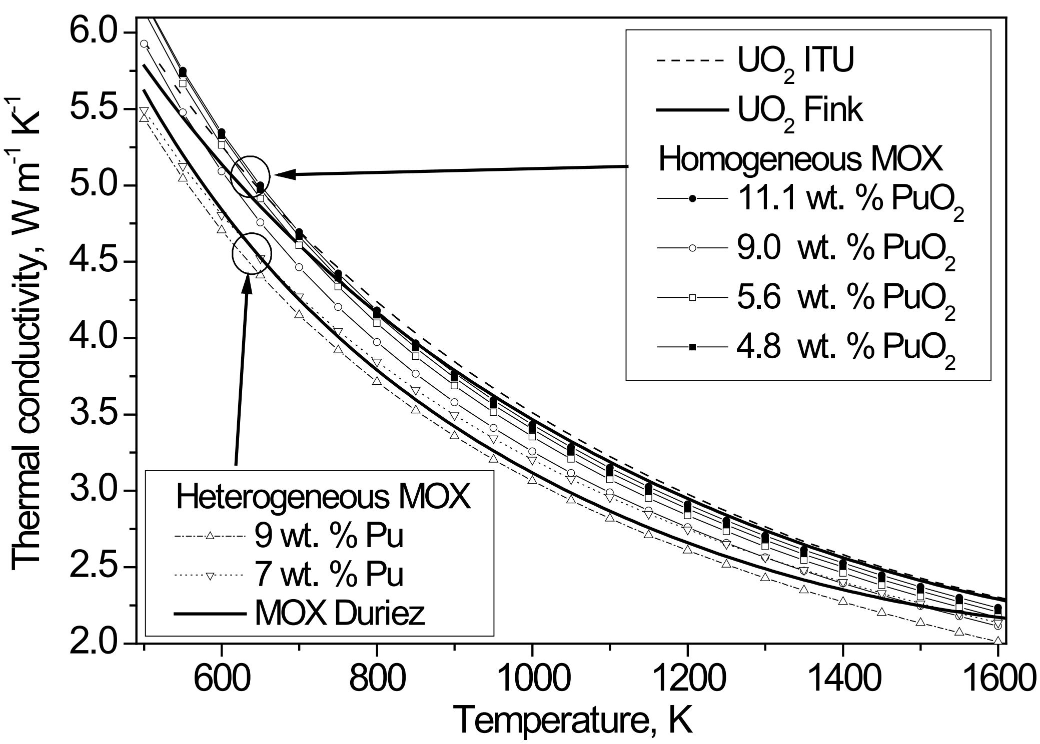


Figure 6. Experimental thermal conductivity of homogeneous and heterogeneous MOX compared to UO_2 (95 %TD) [from Staicu & Barker, 2013].

The oxygen local distribution effect can be expected to disappear in irradiated fuel, as the concentration of irradiation-induced defects, including oxygen defects, is much higher than the oxygen defects due to non-stoichiometry. In irradiated fuel both fission and the temperature gradient in the pellet cause oxygen redistribution, as shown by Lassmann [Lassmann, K., J. Nucl. Mater., 1987. **150**: p. 10-16.] and Sari [Sari, C. and G. Schumacher, J. Nucl. Mater., 1976. **61**: p. 192-202]. Therefore, under irradiation a rapid thermal conductivity convergence between heterogeneous MOX and UO_2 can be predicted, due to the overall oxygen sub-lattice evolution with burn-up. This interpretation is consistent with previous out-of-pile thermal diffusivity measurements at ITU [see e.g. Cozzo, C., et al., *Thermal diffusivity of homogeneous SBR MOX fuel with a burn-up of 35 MWd/kgHM.* J. Nucl. Mater., 2010. **400**: p. 213-217. 6. Staicu, D., et al., *Thermal conductivity of homogeneous and heterogeneous MOX fuel with up to 44 MWd/kgHM burn-up.* J. Nucl. Mater., 2011. **412**: p. 129-137].

Positive developments of the collaboration between INL and ITU have occurred in the domain of modeling and code applications. Such effort has resulted in a paper with joint INL, ITU and University Politecnico di Milano authorships: G. Pastore, L.P. Swiler, J.D. Hales, S.R. Novascone, D.M. Perez, B.W. Spencer, L. Luzzi, P. Van Uffelen, R.L. Williamson, "*Uncertainty and sensitivity analysis of fission gas behavior calculations in engineering-scale fuel modelling*", J. Nucl. Mater., submitted.
The paper reports about a sensitivity analysis on parameters related to a physics-based model coupling fission gas release and swelling performed using the BISON fuel performance code.

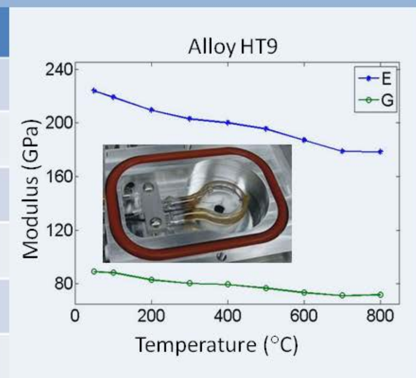
Topic 3: Advanced Instrumentation

Two key areas of instrument development at INL in the advancement of laser-based techniques are to determine mechanical and thermal properties of nuclear fuel and these are the Mechanical Properties Microscope and the Thermal Conductivity Microscope. These developments come out of the group of Dr. David Hurley.

The Mechanical Properties Microscope (MPM), shown in the left pane of Figure 7, is being designed to operate in a radiation hot cell environment via remote control manipulation. The MPM provides micron-level mechanical property information that is commensurate with microstructure heterogeneity. The development of the MPM connects closely with INL's larger PIE effort to provide new validation metrics for fundamental computational material science models. Currently in stage I mockup, the MPM is being used to provide important data on surrogate fuel samples. One example includes measuring the elastic anisotropy resulting from deformation texture in UMo fuel surrogates. Another example involves measuring the elastic constants of the UZr system as a function of composition (data presented in units of GPa in the left-middle pane of Fig. 7).

MPM | Mechanical Properties Microscope Developed at Idaho National Laboratory

% Du	E	G
0	93	35
20	124	49
50	130	51
80	144	56
90	164	65
100	196	81



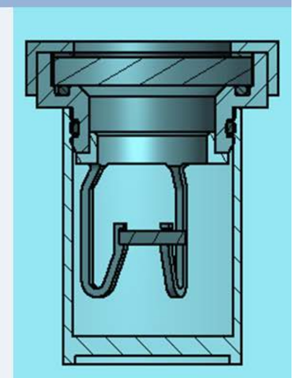


Figure 7. Left: Photograph of MPM, Left-middle: Elastic constants of UZr system vs. composition (values reported in GPa), Right-middle: Elastic constants of HT9 vs. temperature (inset: heating furnace), Right: Sample loading capsule.

A high temperature furnace was designed and constructed that can heat samples to 1000 °C. The furnace, which utilizes radiative heating, is shown in the inset of the middle-right pane of Figure 7. To minimize heat transfer to the environment, the sample chamber is evacuated, which increases the maximum sample temperature and reduces optical lensing issues. As shown in right-middle pane of Figure 7, the functionality of the furnace has been demonstrated by measuring the elastic constants of a Ferritic-Martensitic alloy (HT-9) up to 800 °C.

The MPM requires optical access to both the top and bottom surfaces of a sample. Irradiated samples also require preparation and loading in a remote environment. To meet these requirements, a sample capsule along with a sample loading technique have been developed (right pane of Fig. 7). The sample is held in place by four thin “J” shaped legs. A notch on the short side of each leg supports the sample. The legs deflect to allow the sample to be loaded into position. With the sample held captive in the sample holder, the holder is sealed under vacuum to a quartz tube with a quartz window in the bottom. This sealed capsule containing the sample can then be transported to the MPM for high temperature measurements. The long thin legs minimize thermal conduction away from the sample and allow maximum exposure of the sample to the IR radiation from the heating element.

A similar laser-based instrument, used to measure thermal conductivity, is also being developed. The optical access requirements for the Thermal Conductivity Microscope are similar to the MPM. As a consequence, some system components have dual-platform utility. For instance, a similar heating furnace as described above is being developed for the TCM. Minor changes to the existing furnace will include moving the sample closer to the front window to enable strong focusing with a microscope objective and removal of the backside window. Moving the sample closer to the front window will raise issues concerning uniform heating and uniform sample temperature. These issues are currently being addressed.

Additional activities

The exchange of information and sharing of knowledge between INL and ITU continues as, for example, with the exchange of know-how on EPMA nuclearization and operation. In addition to regular email communication and meetings at conferences, dedicated visits were organized. The exchange of information covers all EPMA related topics such as adaptation of devices to the nuclear environment (e.g. application of coating and decontamination procedures for sample preparation, hot cell – EPMA lab transport containers and shielded connections for sample introduction in the device), EPMA related software, reference materials, sample preparation and analytical methodology. Karen Wright (INL) will visit ITU (P. Poeml, S. Brémier) for 2 weeks in April 2014. Karen will observe how EPMA of irradiated fuels is performed at ITU. The objective is also to share tips and compare the daily practices of the 2 laboratories. The specific case of EPMA on metallic fuel alloys is a topic of interest for ITU whereas INL benefits from the general experience of handling irradiated materials developed in ITU. INL participates in the informal group of shielded microprobe users that ITU launched some years ago. INL and ITU participate in the forum of users of the "Probe for EPMA" software that both laboratories use.
INL and ITU will co-organise a nuclear related symposium at the next Microscopy and Microanalysis conference in Hartford, US in 08/2014.

The exchanges on the EPMA are considered as a fruitful example by the researchers involved. This type of collaboration will be extended to the FIB. In this case, INL is already operating a FIB on irradiated fuel whereas ITU is still at an installation stage. Another area where technical exchanges and synergies are envisaged is the thermal transport characterization of irradiated fuel using techniques that cover different scale ranges (from micron to millimetre).

Planned Activities

Continue to find resolution to the issues associated with sample sharing transport of higher level radioactive materials, including fuels. The identification of a viable transport solution to exchange samples between INL and ITU is essential for the deployment of the full scope of the present collaboration program. Until a solution is found, the scope of the joint work will remain forcibly limited.

Continue interactions related to post irradiation examinations with emphasis on operation of EPMA as well as advanced technique development such as micro X-ray diffraction, focused ion beam (FIB), thermal conductivity measurements, and mechanical property measurements.