LA-UR-16-27390

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Title: FY2016 Ceramic Fuels Development Annual Highlights

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Intended for: DOE program deliverable
Report

Issued: 2017-01-24 (rev.2)

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FY2016 CERAMIC FUELS DEVELOPMENT ANNUAL HIGHLIGHTS

LA-UR-16-27390

Prepared for
U.S. Department of Energy
FCRD Program

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SUMMARY

Key challenges for the Advanced Fuels Campaign are the development of fuel technologies to enable major increases in fuel performance (safety, reliability, power and burnup) beyond current technologies, and development of characterization methods and predictive fuel performance models to enable more efficient development and licensing of advanced fuels. Ceramic fuel development activities for fiscal year 2016 fell within the areas of 1) National and International Technical Integration, 2) Advanced Accident Tolerant Ceramic Fuel Development, 3) Advanced Techniques and Reference Materials Development, and 4) Fabrication of Enriched Ceramic Fuels. High uranium density fuels were the focus of the ceramic fuels efforts. Accomplishments for FY16 primarily reflect the prioritization of identification and assessment of new ceramic fuels for light water reactors which have enhanced accident tolerance while also maintaining or improving normal operation performance, and exploration of advanced post irradiation examination techniques which will support more efficient testing and qualification of new fuel systems.

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ACRONYMS

AFC	Advanced Fuels Campaign
ANL	Argonne National Laboratory
ATF	Accident Tolerant Fuel
ATR	Advanced Test Reactor
BNL	Brookhaven National Laboratory
BU	Burn up
CEA	Commissariat à l’énergie atomique et aux énergies alternatives
CIAE	China Institute of Atomic Energy
CNWG	Civil Nuclear Energy Working Group
CTR-N	Carbothermic Reduction-Nitridization
DBA	Design Basis Accident
DOE	Department of Energy
EURATOM	European Atomic Energy Community
FAS	Field Assisted Sintering
FCRD	Fuel Cycle R&D
FOA	Funding Opportunity Announcement
FY	Fiscal Year
INERI	International Nuclear Energy Research Initiative
INL	Idaho National Laboratory
JAEA	Japan Atomic Energy Agency
KAERI	Korea Atomic Energy Research Institute
LANL	Los Alamos National Laboratory
LANSCE	Los Alamos Neutron Science Center
LFA	Laser Flash Analyzer
LHGR	Linear Heat Generation Rate
LWR	Light Water Reactor
MA-MOX	Minor Actinide – Mixed Oxide Fuel
MOX	Mixed Oxide Fuel
NDE	Non-Destructive Examination
NEA	Nuclear Energy Agency
NEUP	Nuclear Energy University Proposal
NSLS-II	National Synchrotron Light Source II

OECD	Organization for Economic Co-operation and Development
ORNL	Oak Ridge National Laboratory
PWR	Pressurized Water Reactor
PIE	Post Irradiation Examination
R&D	Research and Development
ROSATOM	Rosatom Russian Federation State Atomic Energy Corporation
SEM	Scanning Electron Microscopy
SET	Separate Effects Testing
SFR-AF	Sodium Fast Reactor – Advanced Fuels Arrangement
SPS	Spark Plasma Sintering
TD	Theoretical Density
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction
XPD	X-ray Powder Diffraction beamline

1. Introduction

Ceramic fuel development for FY16 focused on composite fuel and was a balance of effort seeking transformational R&D while also incrementally advancing fuel technology. The fundamental, science-based approach employed in this area relies upon close coordination of theoretical, experimental and modeling efforts.

Continued emphasis was placed upon increasing the ability to understand and improve the accident behavior of light water reactor (LWR) fuel. A range of material systems can offer enhanced oxidation resistance or fission product retention, but the challenge in deploying new fuel designs in existing or Gen III commercial reactors rests in the need to utilize the existing fuel fabrication infrastructure, meet existing licensing requirements, and retain fuel cycle and plant economy. Research is being conducted within the ceramic fuels technologies area for efficient development of accident tolerant fuels i) taking an evolutionary path based upon UO_2 fuels, ii) taking a revolutionary path based upon composite fuels, and iii) developing advanced fabrication and characterization technologies that can enable and accelerate development of the fuels with enhanced accident tolerance.

Development of fuels with enhanced accident tolerance involves exploration of advanced composite systems with the potential to improve the accident performance of light water reactor fuels as well as offer benefits to normal operation. Composite fuels have been of interest for many decades, as a wide range of both ceramic and metallic alloys can be envisioned that would surpass the performance of traditional LWR oxide ceramic fuels. However, when systems are explored within the constraint of use in existing commercial LWRs, the practical limit on uranium-235 enrichment creates significant challenges in the introduction of non-fissile second phases. Any inert second phase incorporated in a proposed fuel must be limited to extremely low volume fractions if reactor performance is not sacrificed and enrichment remains fixed. It is difficult for such concepts to achieve improvement in any of the critical metrics (e.g. thermal conductivity, mechanical properties, or thermochemical stability) when limited in such a way. One option that is being pursued to overcome this constraint is the use of uranium bearing second phases. Although they may not contain the uranium density of uranium dioxide or uranium nitride, a phase containing even half the uranium density of these reference ceramics may provide sufficient margin to retain reactor operation within a fixed enrichment. A wide range of uranium compounds have been investigated historically, many of which could be envisioned to offer intriguing benefits to accident performance as well as the overall fuel attributes. Also, changes of cladding and core materials to improve accident behavior can have a negative neutronic impact relative to current operations, but high uranium density fuels may compensate for some neutronic penalties and thus help enable change to core materials with enhanced accident tolerance.

Another critical area for more rapid and efficient development of ceramic fuels is development of advanced techniques for fuel fabrication and for characterization of irradiate fuels. Advanced sintering techniques can enable routes to model materials for separate effects testing, e.g. UO_2 pellets with nanometer grain sizes to simulate high burnup structure, and for composite fuel systems these techniques may enable fuel systems that can not be fabricated by conventional means. Also, the ability to fully nondestructively evaluate chemistry, phase distribution and structure of fresh and irradiated fuel will provide a greatly enhanced efficiency in fuel development by enabling direct comparison of individual test articles before and after irradiation. Detailed characterization of irradiated fuel pins/rodlets for composition, defects such as cracking, voids and second phases, as well as cladding interactions prior to conducting destructive post irradiation examination (PIE) is critical to informing modeling and simulation and provide more rapid and greater feedback on the effects of irradiation on the fuel and cladding. The non-destructive examination (NDE) also allows regions of interest in the irradiated fuel rod to be precisely probed and helps reduce destructive characterization work while generating large data sets. For example, if an unexpected or unidentifiable artifact is identified at a specific location in the test rodlet, destructive PIE can then be used to fully characterize only that region, as opposed to the expensive and time consuming serial sectioning that must be done in the absence of NDE characterization. This capability can then in turn allow for accelerated acceptance of new fuel forms and advance the fuel licensing process leading to more efficient fuels and safer reactors.

As noted earlier, key challenges for the Advanced Fuels Campaign (AFC) are the development of fuel technologies to enable major increases in fuel performance (safety, reliability, power and burnup) beyond current technologies, and development of characterization methods and predictive fuel performance models to enable more efficient development and licensing of advanced fuels. In support of addressing those key challenges, the ceramic fuel technologies development activities fell within areas of 1) National and International Technical Integration, 2) Advanced Accident Tolerant Ceramic Fuel Development, 3) Advanced Techniques and Reference Materials Development, and 4) Fabrication of Enriched Ceramic Fuels. Highlights from the FY16 ceramic fuel development R&D are provided in this document.

2. National and International Technical Integration

Advanced Fuels Campaign (AFC) researchers are very active in international collaborations with Korea, France, Japan, China, Russia, EURATOM, and OECD-NEA. These interactions and collaborations are managed through a combination of participation in Generation IV Global International Forum projects, International Nuclear Energy Research Initiative (INERI) projects, and participation in bilateral and trilateral government-to-government agreements. The ceramic fuels areas have collaborations primarily under the headings of Advanced Fuels within the US/Japan bilateral and the GenIV SFR. There is also collaboration on Field Assisted Sintering of Nuclear Fuels under a US/EURATOM INERI arrangement.

2.1 GenIV-Sodium Fast Reactor Arrangement on Advanced Fuels

K.J. McClellan, kmcclellan@lanl.gov, LANL

The Sodium Fast Reactor Advanced Fuel (SFR-AF) arrangement started in 2007 with a targeted duration of 10 years within the frame of the Generation IV Sodium Fast Reactor program. The primary objective is to investigate high burn-up Minor Actinide bearing fuels as well as cladding and wrapper materials capable of withstanding high neutron doses and temperatures. The project has been structured in 3 steps: evaluation of advanced fuels and materials options, Minor-Actinide bearing fuels evaluation, and assessment of high burn-up capability of advanced fuel(s) and materials. Participants in the arrangement include the DOE, CEA, JAEA, KAERI, EURATOM, China and Russia with the latter two having joined in December 2015. In FY16 program management board completed the Advaned Sodium Fast Reactor (SFR) Fuel Type Recommendation milestone which confirmed the prior Advanced Fuel Comparison report on fuel types and noted that the final SFR fuel type selection for each member country is dependent upon multiple domestic factors. The specifics of each country's experience, infrastructure and policies are critical determining factors in addition to the technical aspects in determining a preferred fuel type; the country-specific recommendation along with the reasoning was presented for each member country. Changes in the representatives and/or alternate representatives were made for EURATOM, France, and Russia in 2016.

2.2 US/Japan CNWG Collaboration on Advanced Fuels

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Cooperative research under the Advanced Fuels area of the Fuel Cycle R&D and Waste Management Sub-Working Group is performed under the general areas of properties, performance and analysis. The goal of this effort is to perform collaborative R&D for evaluation of basic properties and irradiation behavior of advanced fuels. The objectives of the collaboration are to expand the basic properties and performance data and to improve understanding of advanced fuels with an emphasis on employment of advanced experimental techniques. Through incorporation of new MA-MOX irradiation data the effort will also enable development and application of advanced modeling and simulation tools for design and performance analysis of oxide fuels. In FY16, technical expert meetings were held in Japan and in the US at INL to advance specific tasks on basic properties of fuels, development of PIE data, and modeling and simulation of irradiated transmutation MOX fuel. Several joint publications from the fuel properties activities were prepared during the period. A key accomplishment in FY16 was negotiation of a Bison license for JAEA which will allow the collaboration to advance in jointly developing a MA-MOX Bison model for fuel performance.

Another key aspect of the collaboration was a visiting JAEA scientist, Shinya Nakamichi, working at LANL on basic fuel properties. A highlight of the research by the current visiting scientist follows. For the near term, Mr. Nakamichi will be the last visiting scientist at LANL as the next CNWG visitors will reside at INL to support the Bison model development.

2.2.1 Sintering Behavior of U-Ce-O

J.T. White, jtwhite@lanl.gov, LANL; S. Nakamichi, JAEA-Tokai

Collaboration between the DOE and Japan on characterization of the properties of nuclear materials under the Civil Nuclear Energy Research and Development Working Group (CNWG) is essential to advancement of mutual capabilities in this area. CNWG targets to co-develop nuclear fuel technology by leveraging facilities and resources belonging to both Japan and the US. Japan Atomic Energy Agency (JAEA) research focuses on $(U,Pu)O_2$ as mixed oxide (MOX) fuel. Although current experimental work on MOX or other oxide transmutation fuels under DOE programs is minimal, the effect of Ce on the thermochemistry, thermophysical properties, and fabrication behavior of oxide fuel represent a common interest to both programs given the utility of Ce as a surrogate for Pu as well as its importance as a fission product.

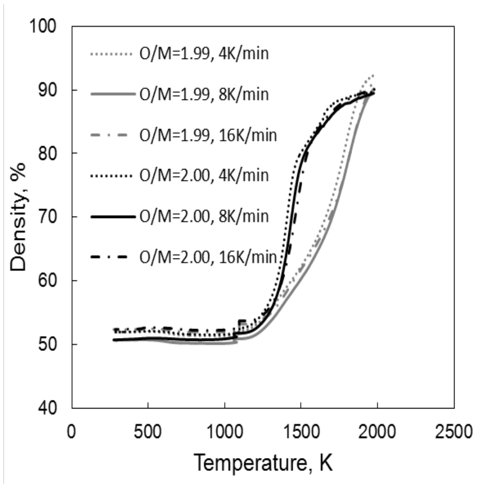

Figure 1 Densification of $(U_{0.8}, Pu_{0.2})O_2$ obtained as a function of stoichiometry.

Many studies have been reported on $(U,Ce)O_2$ as UO_2 with a fission product and a surrogate material of $(U,Pu)O_2$ since Ce is one of most prevalent fission products forming full solid solution over 1000°C. Furthermore, its 3+/4+ valence mirrors that of Pu, making it a suitable thermochemical surrogate. Fabrication of MOX remains an area of mutual interest given its status as the transmutation fuel of choice in Japan. No fuel form has been definitively chosen for US utilization, but MOX remains under consideration. The role of stoichiometry and specifically oxygen-to-metal ratio (O/M) on fuel properties such as thermal conductivity has been previously studied under the CNWG. However, recent work in Japan has identified O/M as a major contributor to the densification behavior of MOX. Further exploration of the role of O/M on densification of $(U,Ce)O_2$ was led by a Shinya Nakamich, a guest researcher stationed at LANL from March 2015 until March 2016.

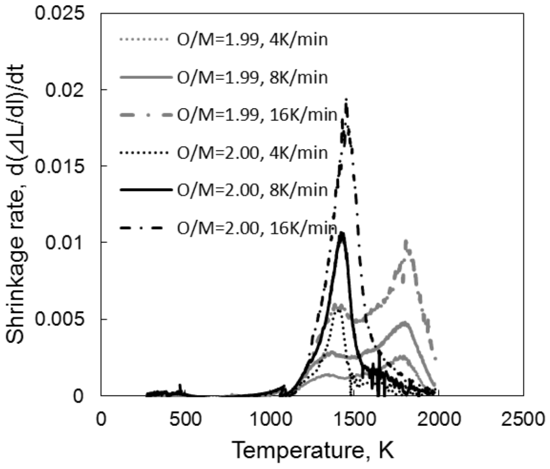

Figure 2 Densification rate of $(U_{0.8}, Pu_{0.2})O_2$ obtained as a function of stoichiometry.

Dilatometer experiments were performed at LANL and JAEA-Tokai to assess the shrinkage behavior of both $(U,Pu)O_2$ and $(U,Ce)O_2$ as a function of O/M. Dynamic gas atmospheres were used to adjust and maintain stoichiometric, hypostoichiometric, and hyperstoichiometric compositions. Thermogravimetric analysis was used to monitor and verify the O/M of each composition as a function of temperature. X-ray diffraction was also used to ensure that a solid solution was maintained as a function of both O/M and secondary cation content.

A strong dependence of shrinkage rate on O/M was found for both $(U,Pu)O_2$ and $(U,Ce)O_2$ compositions. Figure 1 illustrates the shrinkage of $(U_{0.8},Pu_{0.2})O_2$ on O/M as assessed by varying the heating rate. Figure 2 plots the shrinkage rate of these data. Feedstocks of UO_2, CeO_2, and PuO_2 were used in this study; it is hypothesized that the two disparate peaks observed in Figure 2 correspond to first reaction between the UO_2-UO_2 particles while the second corresponds to reaction between the UO_2 and PuO_2 particles. The same behavior is observed in UO_2-CeO_2. It is hypothesized that O/M plays a strong role in determining the point where UO_2 and the secondary cation specie begin to react to form a solid solution.

Further study and assessment of this phenomenon will have significant implications in the ability to control sintering and microstructure of mixed oxide transmutation fuels. In addition to the effect on sintering rate, O/M control during densification was observed to strongly affect the final density and microstructure of both $(U,Pu)O_2$ and $(U,Ce)O_2$ pellets. Sintering under hypostoichiometric conditions was observed to limit grain growth; this allows porosity to remain located on grain boundaries where their elimination is possible. Excessive grain growth as occurs at higher O/M instead was observed to trap porosity at grain boundary interiors, thus limiting ultimate attainable densities

3. Advanced LWR Fuel Systems Analysis

3.1 Advanced LWR Fuel Concept Analysis

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The assessment of the impacts of advanced LWR fuels/cladding on reactor performance and safety characteristics is needed to identify potential issues associated with their viability/desirability for potential implementation in commercial reactors. In FY16 the major focus of BNL's activities in support of the Advanced Fuels Campaign (AFC) continued to be the evaluation of the impact of fuels with enhanced accident tolerance, aka "Accident Tolerant Fuels (ATF)", on reactor performance and safety characteristics. These assessments included assembly and core analyses to determine impacts on burnup/cycle length, and reactivity coefficients and control worths, and transient analyses for selected accident scenarios. The details of these analyses are described in the report/publications.

Several additional fuel/cladding concepts were analyzed to determine their impact on reactivity, safety coefficients, and cycle length/burn-up. The analyses were performed for a detailed/explicit model of a 17 x 17 PWR assembly with 4.9 w/o enriched ^{235}U using the TRITON neutronics lattice code. Example results for burnup/cycle length for UO_2 fuel with a molybdenum-based cladding, and a U+10w/o Mo metallic annular fuel with Zircaloy cladding are shown in Table 1. For both configurations the poisoning effect of the Mo with its high parasitic capture is seen.

Table 1 Three-Batch Cycle Length for UO_2 Plus Mo-based Cladding, and UMo Metallic Fuel

4.9%-enriched			
Fuel - Clad	UO_2-Zr	UO_2-Mo/Zr	U+10 w/o Mo-Zr
Discharge burn-up (GWd/t)	61.6	50.2	53.6
Cycle length (EFPD)	533	518	465

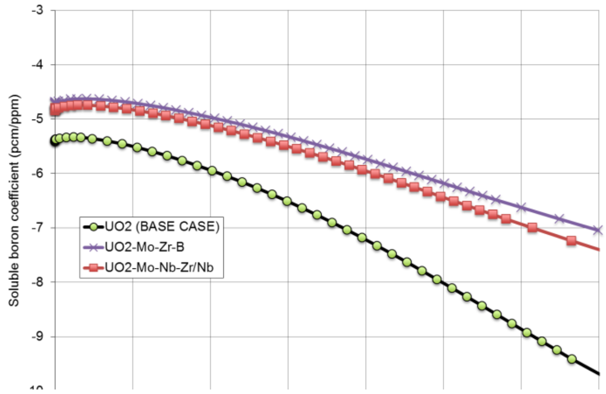

Figure 3 Soluble Boron Coefficient Mo-Based Cladding vs. Burnup

Figure 3 shows the soluble boron coefficient for the case with Mo cladding. The harder neutron spectrum for this configuration results in a reduced worth for the boron poison

Several Design Basis Accidents were evaluated with the TRACE systems code assuming a point kinetics representation of the reactor with reactivity feedback coefficients and control data from TRITON lattice or PARCS 3-D core models. An example of the results for a Reactivity Insertion Accident (RIA) with UO_2 fuel with Zircaloy and Kanthal APMT (a commercial FeCrAl) cladding, and U_3Si_2 fuel with SiC cladding is shown in Figures 4 and 5 for the normalized reactor power and fuel centerline temperature, repsctively. Similar analyses were also peformed for a Large Break Loss of Coolant Accident (LOCA).

A related activity in collaboration with INL compared fuel and cladding temperatures form TRACE and the fuel performance code BISON for a RIA, with good agreement.

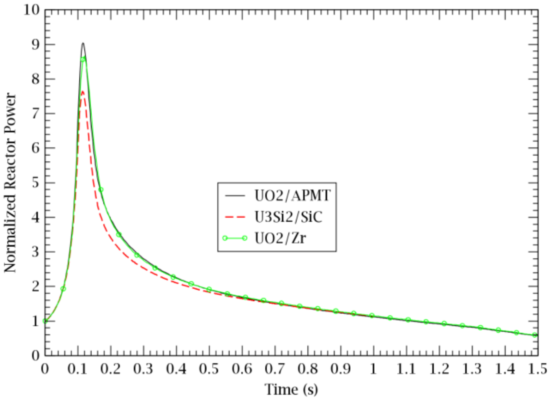

Figure 5 Normalized reactor power in a $1 RIA

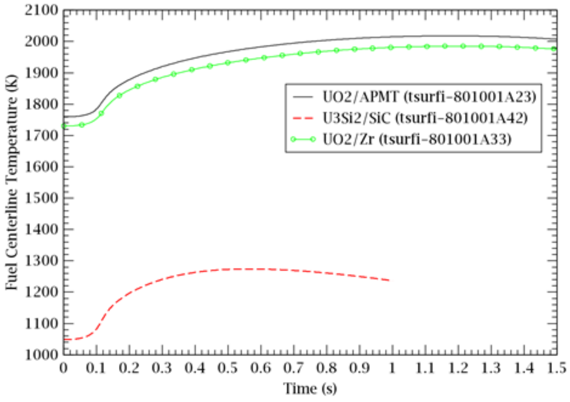

Figure 5 Comparison of Fuel Centerline Temperature

4. Advanced Accident Tolerant Ceramic Fuel Development

4.1 Corrosion Performance of High Density Ceramic Fuel Materials

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Application of uranium-silicon binary compounds in current or next generation light water reactors requires knowledge of how these proposed nuclear fuels will perform under various off-normal conditions. One such off-normal condition, a 'leaker,' occurs when the cladding is breached exposing the fuel to coolant in a localized region of the fuel rod. Simulation of this event is non-trivial given the high temperatures, pressures, and dynamic chemistries of a typical PWR or BWR are far from ambient conditions. Response of fuel and cladding materials to this condition is highly dependent upon the coolant chemistry, which can vary significantly depending upon the specific reactor design. Two such reactor chemistries are summarized in Table 2.

Table 2 Typical LWR coolant conditions

Parameter	Western PWR	BWR
Coolant	Pressurized H_2O	Boiling H_2O
Temperature (Inlet/Outlet) [C]	280/325	275/290
Pressure [bar]	156	70
Oxygen Content [ppb]	<0.05	200-400
Hydrogen content [ppm]	2-4	0.3
Additional Coolant Chemistry [ppm]	0-2200 H_3BO_3 0.5-3.5 LiOH	

FY16 work focused on assessment of U-Si compounds and U_3Si_2 in particular under PWR conditions. In general, PWR coolant chemistries are slightly reducing and may include boric acid as a means of reactivity control. A "Western PWR" is emulated although in practice the corrosion and autoclave tests can be adapted for either reactor coolant condition. Two separate test methods were used to assess fuel behavior. First, buffered autoclave tests were performed to analyze the response of samples to extended (weeks) exposures under relevant water chemistries. Water chemistry was controlled through use of solid state buffers. The buffers consisted of either oxide or oxide-metal compounds. Quartz tubes were introduced in the following buffered experiments to prevent galvanic corrosion. In this configuration, the sample was placed in the quartz tube above the water level within the pressure chamber. When heated to 300°C, the water level raised above the quartz tube, exposing the sample to pressurized water. Furthermore, either Ni/NiO or Co/CoO was placed in a separate quartz tube well above the water level that provide an atmosphere of $H_2(g)$ in the pressure chamber effectively buffering the deionized water with dissolved hydrogen or alternatively gettering excess oxygen from the pressurized water.

The above testing provides a method to assess fuel response to prolonged exposure to oxidizing (or reducing) test environments. However, the increased electrical conductivity of U-Si compounds compared to conventional ceramic fuels suggests that galvanic corrosion may be a concern for these materials. This was assessed through measurement of the corrosion potential and execution of a Tafel analysis for U-Si compounds. Samples were mounted in specially designed epoxy mounts that featured threaded rod to facilitate electrical contact between the sample and the potentiostat. Boric acid was dissolved in deionized water to create a 2000 ppm electrolyte solution, which was heated to 80°C and degassed with Ar to remove dissolved oxygen from the solution. A voltage was then varied between the sample and graphite electrode and resulting current was measured.

Use of both methods in conjunction illustrates a means of fully assessing the response of novel nuclear fuel materials to coolant exposure. The basic experimental configuration and resulting Tafel plot for the four compounds investigated are shown in Figures 6 and 7. Fitting the data using a complex non-linear Tafel analysis provides the corrosion potential and corrosion current, which are used to calculate the corrosion rate. It is seen that the corrosion potential is more negative (less noble) when the U-density is increased in the U-Si binary compounds. Furthermore, UO_2 is the most noble of the compounds measured in this study and displays symmetric peaks around the open circuit corrosion potential.

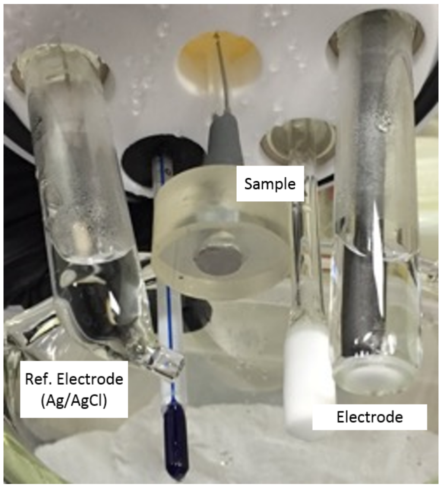

Figure 6 Experimental test rig used to measure corrosion potential of ATF fuel concepts.

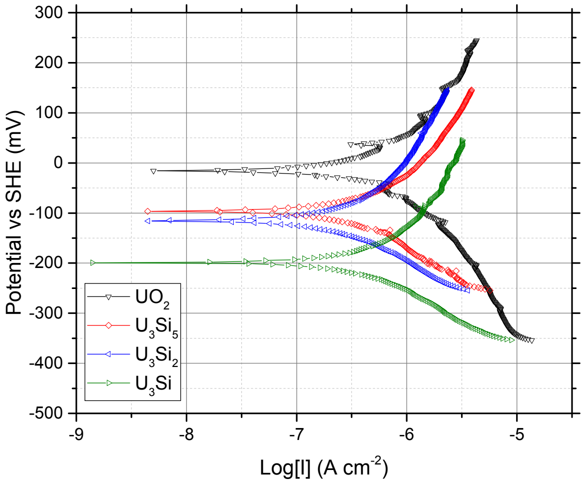

Figure 7 Tafel analysis of U-Si binary compounds as measured in 80°C DI water containing 2000 ppm boric acid.

Results of two extended series of buffered autoclave testing performed on U_3Si_2 are shown in Figures 8. Temperature and pressure conditions for these tests are constant at 300°C and 85 bar. The three different water chemistry conditions plotted illustrate the strong role of oxygen content in the response of this material. The 'static autoclave' tests are simply sealed with no attempt to control water chemistry. While sealing is performed under inert cover gas, oxygen levels within the sealed capsule are far higher than any reactor water chemistry. The 'oxygen getter' tests included only metallic iron used to remove residual oxygen but retain a slightly oxidizing environment as provided by the water alone. Finally, the 'buffered' solution matches the reducing environment of a typical PWR. The results of extended testing highlight the importance of water chemistry in dictating the response of U_3Si_2. Pulverization weight loss occurred monotonically during static testing, and full pulverization was observed following seventy days. Far less weight loss was measured

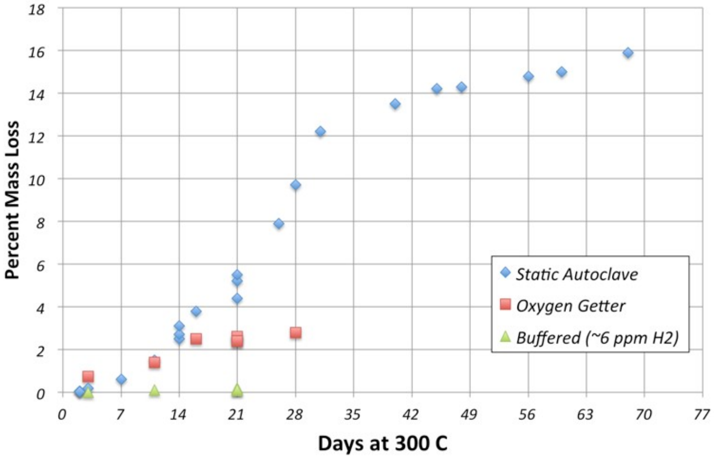

Figure 8 Weight change as determined following autoclave testing of U_3Si_2 performed at 85 bar and 300°C under a range of water chemistries.

when trapped oxygen was removed from the system, and essentially no weight change is observed when a reducing environment is imposed.

These tests will continue into FY17 in order to fully assess the behavior of accident tolerant fuel candidate systems as well as exercise the methodology to develop modified high density fuels and fissile composites with improved performance under off normal operating conditions.

4.2 Development of U-Si-X Compounds for Improved Oxidation Performance

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The Advanced Fuels Campaign is investigating novel high density uranium compounds to both enable new cladding materials and improve economics. Uranium-silicide fuels provide higher thermal conductivity than UO_2 allowing for a lower centerline temperature in the case of a transient or accident scenario. In addition U_3Si_2 fuel provides a higher U density, facilitating longer cycles to higher burnup and/or more extensive modification of the cladding. However, U-Si compounds are known to display poor oxidation resistance in both O_2 containing atmospheres and steam. This challenges both fabrication and performance. Alloying of U-Si compounds with ternary elements appears to be a promising means of improving this liability.

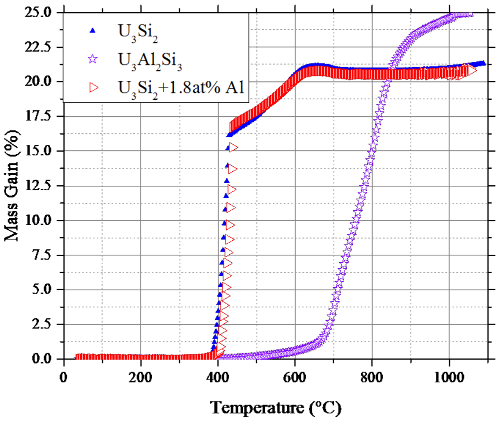

Figure 9 Thermogram displaying the onset of breakaway oxidation for U_3Si_2, $U_3Al_2Si_3$, and U_3Si_2 + 1.8at%Al.

In FY16 oxidation resistance screening tests were performed on U-Si-Al and U-Si-B compositions synthesized in late FY15. The four compositions, nominally U_3Si_2+1.8at%Al, $U_3Al_2Si_3$, U_3BSi_4, and U_3Si_5+1.5at%B , were exposed to synthetic air (Ar-O_2, 80-20%) up to 1000 °C under thermal ramp conditions. Al additions to U_3Si_2 facilitated a delay in the onset of breakaway oxidation as shown in Figure 9, however B provided no increase in oxidation resistance of U3Si5 during air testing. The onsets of breakaway oxidation for U_3Si_2 and Al containing compositions are 402 °C for the low Al composition and 678 °C for $U_3Al_2Si_3$, both increased from the U_3Si_2 onset at 384 °C.

The $U_3Al_2Si_3$ composition displayed no oxidation after a 10 hour hold at 400 °C, and after 30 minutes at 500 °C had formed a multi-phase surface oxide. It was determined via scanning electron microscopy that Al_2O_3 oxidized on the surface, though a uniform layer did not form. Figure 10 displays an EDS line scan of Al_2O_3 formed on the surface as revealed during cross sectional electron microscopy. The formation of Al_2O_3 indicates that passivation is possible in this material. The multiphase nature of the composition could inhibit the formation of a uniform Al_2O_3 layer as could the simultaneous formation of UO_2. The next steps in this study will be to assess whether or not homogenization of the material can allow for a more uniform Al_2O_3 layer to form, facilitating passivation. In addition, lower concentrations of Al additions will be investigated to retain the high U density benefit to U_3Si_2 while promoting passivation by the Al additions.

4.3 Mechanical Properties of U-Si Compounds

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The mechanical properties of nuclear fuels are not necessarily primary design criteria, but knowledge of the elastic modulus, hardness, and other properties are essential for fuel performance assessments. Pellet cracking during normal operation, possible pellet-cladding interaction, and possible defects induced by handling during manufacturing and transportation are dictated by mechanical properties. Novel fuels such as many considered under Accident Tolerant Fuel development often contain minimal data regarding these properties. Uranium silicide fuels in particular exhibit a range of attractive material properties for nuclear fuel applications, but no data is available regarding their mechanical behavior.

Nanoindentation and Resonant Ultrasound Spectroscopy (RUS) have seen limited use for evaluation of the mechanical properties of nuclear fuel materials. The mechanical properties of nuclear fuels, and ceramics in particular, can be challenging to assess through conventional mechanical testing methods. The structure of nuclear fuels at high burnup can prove to be especially difficult given the significant changes in both chemistry and microstructure caused by fission products. Furthermore, the volume of material available following test irradiations can be limited. Destructive analysis of irradiated fuel material to obtain gross information on the mechanical behavior is not likely to be a high priority. Thus, nanoindentation may therefore prove to be a valuable addition to post irradiation examination. The present focus is assessment of the room temperature modulus and hardness of a series of U-Si materials. This preliminary work will aim to provide baseline mechanical properties for these fuels in the unirradiated state to lay the groundwork for future extension to both elevated temperatures and ion beam irradiations.

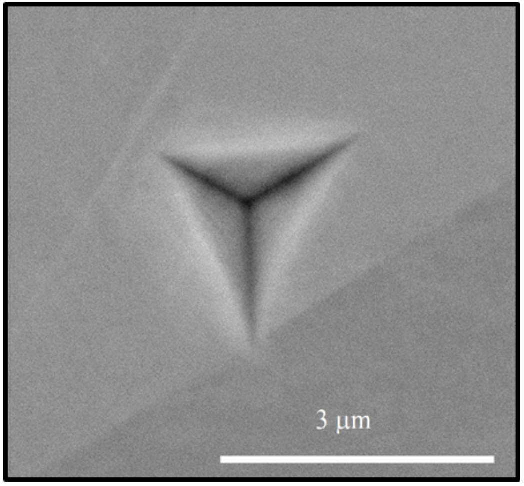

Figure 10 SEM image of indent produced by nanoindentation.

High purity, high density uranium silicide samples were prepared using established powder metallurgy processes and tested for hardness using a Hysitron™Triboindenter™ dual mode with a diamond Berkovich tip. Tip-shape function for the Berkovich indenter was obtained after calibration with aluminum, quartz and polycarbonate standards and machine compliance. The surface of the sample was scanned with the Scanning Electron Microscopy (SEM) and with the low load tip to obtain an estimate of the roughness of the sample (between 0.5 and 8 nm). The hardness tests were performed

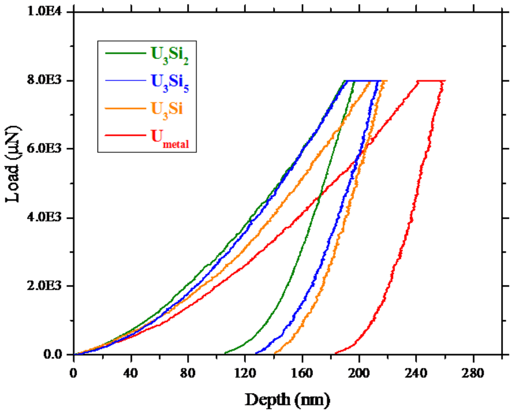

Figure 11 Plot of nanoindentation force versus indenter displacement obtained from tests at room temperature.

by making average of ten indents per sample under a load-control cycle in quasi-static and continuous stiffness measurement (CSM) modes with a low load head. The load used was 8 and 18 mN. Figures 10 and 11 shows typical indent and load displacement curves on U_3Si_5.The load was then held constant for a specified period (30 seconds), and finally decreased at a constant rate over 10 seconds. The hardness was then calculated for Quasi-static and CSM mode and using an average of points which showed a change in the values of the hardness and the Young's Modulus (Figure 12).

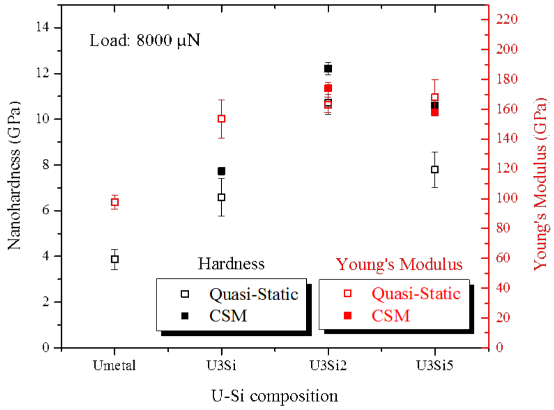

Figure 12 Nanohardness and Young's modulus of U-Si compounds tested as determined using both nanoindentation and resonant ultrasound spectroscopy.

For the samples included in this study, the Young's modulus, shear modulus and Poisson's ratio were measured using RUS with a commercial unit (RUSpec, Quasar International, Albuquerque, NM, USA) with a two transducer configuration. The RUS technique provides a dynamic measurement of the elastic moduli. In a RUS experiment, the ultrasonic driving signal is swept through a range of frequencies so that for each RUS measurement, a series of mechanical resonance peaks are recorded as a function of frequency. For the U_3Si_2 and U_3Si_5, the driving frequency ranged from about 50 to 500kHz. Each of the resonance peaks corresponds to a distinct vibrational mode of the samples. Elastic properties were calculated using the resonant frequencies, mass, shape and dimensions of the samples by a commercial software package (RPModel, Quasar International, Albuquerque, NM, USA). Considering the specimens isotropic, the elastic stiffness components, C_{11} and C_{44}, were used to calculate the uncertainties in the Young's Modulus and Poisson's ratio. For the samples included in this study, 15 to 20 peaks in each ultrasonic resonant spectrum were included in the RUS analysis, obtaining a value of 85 and 125GPa for U_3Si_5 and U_3Si_2 respectively, resulting RMS errors ranging between 0.25% and 0.45%.

These data will be used as baselines for initial fuel performance modeling and initial post irradiation examination of U_3Si_2 and U_3Si_5 that is anticipated to begin in FY17.

5. Reference Material and Technique Development

5.1 Onset Conditions for Flash Sintering of UO_2

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Thousands of tons of uranium dioxide fuel pellets are fabricated each year for use in the world's nuclear reactors.[1] Sintering is one step in the fabrication process where powder compacts are brought to a high temperature in order to create high-density ceramic fuel pellets. Conventional sintering of pellets typically takes anywhere from 4-6 hours in a furnace at temperatures as high as 1750°C. There have been numerous attempts to lower the sintering temperature in order to improve the efficiency of fuel production, but any improvements made in temperature reduction still require long sintering times.[2]

Field assisted sintering (FAS) describes a group of novel sintering methods that use an electric field and/or current in order to provide powder densification. These techniques have proven to produce a higher level of densification on much shorter timescales compared to conventional sintering. The feasibility of using FAS techniques to fabricate nuclear fuel is gaining recognition due to the potential economic benefits and improvements in material properties. Methods like spark plasma sintering (SPS) have already demonstrated the ability to sinter fuel pellets with controlled microstructure by using the combination of pressure, temperature, and an applied electric field/current.[3]

Flash sintering is one type of FAS technique that uses only an applied electric field/current and temperature to provide densification of materials on very short time scales. The characteristic behavior of flash sintering is a current runaway, which occurs sometime after a critical field is applied across a sample. During the runaway, the current exponentially increases until reaching a pre-defined current limit. The bulk of sintering can occur in a matter of seconds under the application of a increased field and temperature.[4] The general trend observed so far is that the critical field required to flash a sample decreases with an increase in temperature. Additionally, the temperatures required to sinter with flash sintering are lower than those used in conventional sintering. Material behavior during flash sintering has been linked to applied and material parameters, but the underlying mechanisms active during flash sintering have yet to be identified. However, there is now a general agreement that thermal runaway from joule heating is largely responsible for the current runaway, with recent studies showing good agreement between experiment and model.[5]

The objective of this study was to demonstrate flash sintering on uranium dioxide, highlighting some trends in the onset of flash sintering according to a variation in stoichiometry. Preliminary experimental results for $UO_{2.00}$ and $UO_{2.08}$ are shown in Figures 13 and 14, respectively, where the trend observed is that the increase in oxygen content causes a decrease in the field required for flash. These experimental results are being analyzed against an existing thermal runaway model for comparison and to provide further model validation. The results therefore act as an initial study on flash sintering of uranium dioxide, which will be expanded upon with future optimization of the process. Furthermore, the possibility of using flash sintering to fabricate various advanced composite fuels will be investigated, including UO_2 composites. The premise is that the shorter sintering time may delay reactions between constituents that would otherwise occur during conventional sintering of composite fuels.

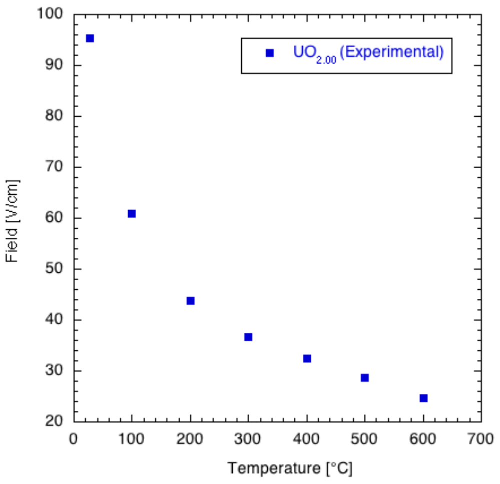

Figure 13 Critical field at flash as a function of temperature for $UO_{2.00}$

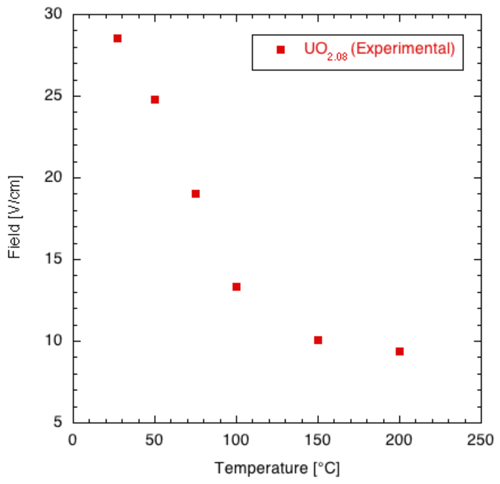

Figure 14 Critical field at flash as a function of temperature for $UO_{2.06}$

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[2] X.-d. Yang, J.-c. Gao, Y. Wang, X. Chang, Low-temperature sintering process for UO2 pellets in partially-oxidative atmosphere, Transactions of Nonferrous Metals Society of China (English Edition) 18 (1) (2008) 171–177.

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5.2 In Situ Synchrotron characterization of the Field Assisted Sintering of UO_2 at the National Synchrotron Light Source-II

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During Field Assisted Sintering (FAS) it is important to understand the densification mechanisms that are activated by the applied electric field. FAS techniques employ electrical fields in combination with heat and pressure, to reduce sintering times and temperatures. FAS-induced densification is difficult to control and the rate controlling mechanisms are not yet understood. In situ techniques such as X-ray diffraction were used to identify the phase changes, microstructure and defects present in UO_{2+x} during the application of electric field at room temperature. The data generated by the in situ experiments will provide information for theoretical models. The ultimate goal is to develop a more controlled, optimized densification process for UO_{2+x}.

The in situ experiments were performed at the X-ray Powder Diffraction (XPD) beamline at the National Synchrotron Light Source-II (NSLS-II). High energy (66keV) x-rays were used to probe UO_{2+x} samples as a function of stoichiometry and applied voltage. The experimental set up included a spring loaded sample holder encapsulated in a double quartz cell, fitted with gas feed lines, electrical leads and thermocouple. The collection of the diffraction patterns (over 100,000 in total) was performed in transmission mode with 1.0s acquisition time with a Perkin Elmer flat panel detector. The sample to detector distance calibration and instrument response were determined using a NIST LaB_6 standard. The Rietveld analysis of the diffraction patterns and extraction of the lattice parameters was performed using dedicated high-throughput python scripts that interface with TOPAS (Bruker).

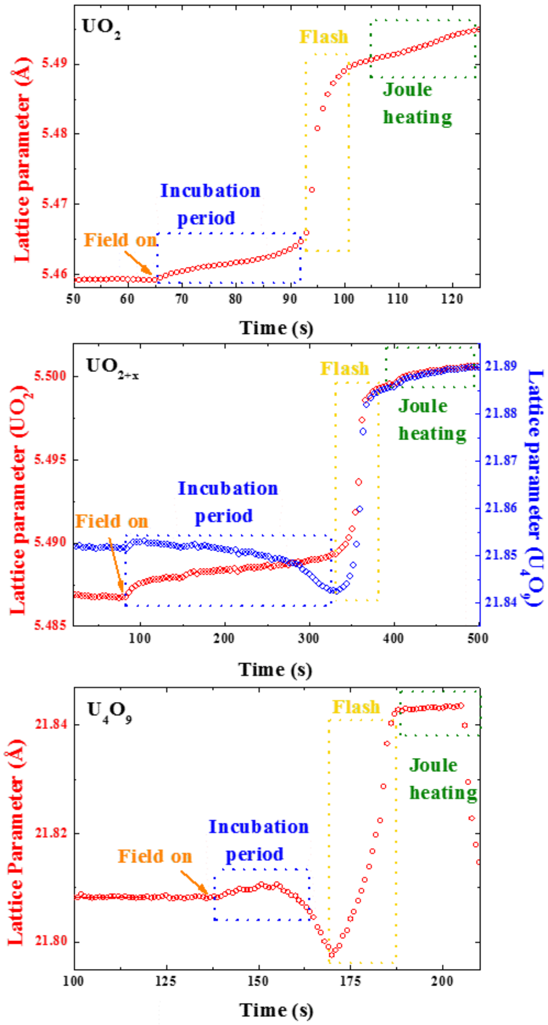

Figure 15 Lattice parameter as a function of time for three different UO_{2+x} samples. The behavior in the different regions are described in the text.

The lattice parameters were determined for three different UO_{2+x} sample compositions (UO_2, U_4O_9 and a ~50/50 mixture of UO_2 and U_4O_9) during the flash experiments and are shown in Figure 15. The time when the field was applied is also shown. The in situ behavior of the samples at room temperature show that that there is an incubation period prior to the flash event. The incubation period is characterized by an initial increase in the lattice parameter. The samples are not highly conductive during this time and length of the incubation period is related to the applied voltage. The incubation period was observed in all samples, with minimal (to no) increase in the temperature. Such structural changes are indicative that the number of lattice defects increases prior to the onset of the flash event and may be composition independent. Figure 15 also shows that following the incubation period there is a very-rapid increase in the lattice expansion during the flash event for all compositions[1]. This expansion coincides with an increase in conductivity and an increase in the measured temperature. After this rapid expansion there is another region where there is steady increase in the lattice parameter due to joule heating.

These in situ experiments readily show that significant changes in the atomic structure ensue during field assisted sintering. The next step in this work is to compare the experimental results directly to theoretically predicted behavior. Analysis of the lattice parameter as a function of distance between the electrical contacts and time will facilitate determining if there are any spatial

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[1] We note that the U_4O_9 sample displays an initial lattice contraction, and then lattice expansion

changes in the samples with flash conditions. Finally, the beamline and analysis capabilities presented here are by no means limited to FAS, but could be applied to other material systems where structural information is needed to develop a deeper physical understanding of material dynamics.

5.3 Progress in Advanced NDE Development and Demonstration at LANL

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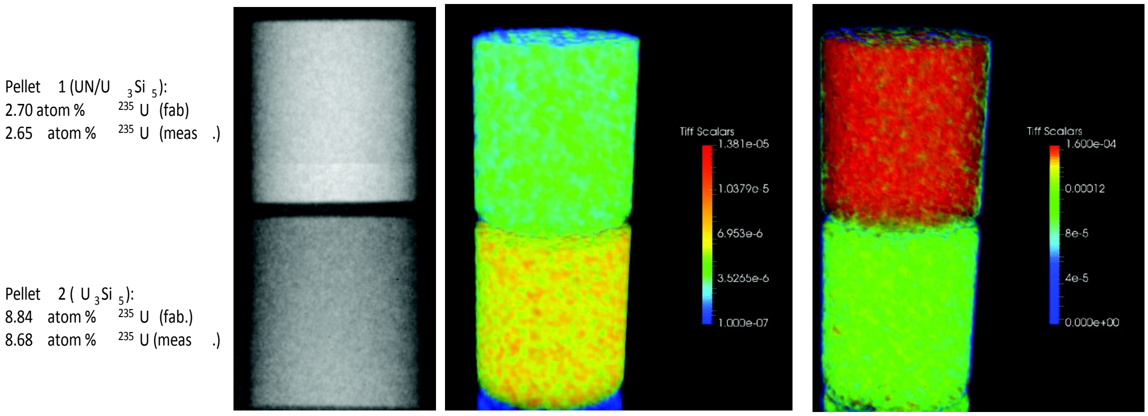
Imaging and diffraction measurements of ceramic and metallic nuclear fuels have been completed at the Los Alamos Neutron Scattering Facility. The measurements are non destructive and provide insight about phase composition, defects, enrichment, microstructure and texture. A series of UN / U-Si pellets of varying stoichiometry and isotopic enrichments were examined this year. The techniques span length-scales from the crystal cell to the microstructure to macroscopic features. The goal of the measurements is to provide insight on fabrication, document the pre-irradiation condition of test samples and to develop techniques that could be applied to irradiated fuel. Imaging and spectroscopic measurements are performed at the LANSCE pulsed spallation neutron source using a pixilated time-of-flight neutron imaging detector that can record thermal and epithermal energies simultaneously. Isotopic enrichment is determined from fitting absorption resonances and tomographic reconstructions provide 3D distributions of features and isotopics.

The technical objective of this project is the development and improvement of a suite of neutron based non destructive characterization tools that can be applied to fresh and, potentially, irradiated nuclear fuel formulations. Energy-resolved neutron imaging and absorption resonance spectroscopy measures isotope distributions. By performing multiple measurements tomographic characterization is possible. When combined with neutron diffraction the data provide non-destructive multi-lengthscale characterization opportunities. Current objectives include improving the sensitivity of measuring neutron absorption resonances to provide spatially resolved characterization of isotopic enrichment. Opportunities for neutron induced prompt gamma analyses are being assessed as is the development of laser-driven pulsed neutron sources which would enable deployed application of these techniques rather than requiring the neutron production infrastructure at Los Alamos.

The techniques are being applied to composite Accident Tolerant Fuel (ATF) candidates that are fabricated in the Fuels Research Laboratory at Los Alamos. For example crystallographic unit cell dimensions indicate whether mixing occurs between the composite constituents. The formation of U(N,Si) compounds in UN/U_3Si_5 composites is apparent from changes in lattice parameters of the constituent phases. Texture measurements indicate whether preferred orientation is introduced during sintering (which influences thermal stresses and crack formation). Tomography verifies homogeneity of pellets as well as measuring gaps between pellet and cladding or between rodlet and capsule (which determine the thermal conditions experienced by pellets in reactor).



Thermal ^{235}U density ^{238}U density

Figure 16 Neutron radiographs and tomographic reconstructions of two pellets with different ^{235}U enrichment; Thermal radiographs (left) ^{235}U tomographic reconstruction (center) ^{238}U tomographic reconstruction (right) Pellets are 9.4mm long and 8 mm in diameter.

By maximizing the insight obtained from irradiation testing this work contributes to the accelerated certification of new fuel formulations. The current activity is focused on documenting the pre-irradiation condition of fuels before irradiation in the Advanced Test Reactor. However the unique probe characteristics of neutrons mean that the same techniques could be applied to irradiated fuels to provide pre- and post-irradiation characterization of exactly the same material. This could provide unique insight on microstructural evolution that takes place during irradiation and guide the application of destructive techniques to representative and atypical regions of behavior.

Neutron tomography and neutron diffraction characterizations were performed on nine pellets; four UN/ U-Si composite formulations (two enrichment levels, Figure 16), three pure U3Si5 reference formulations (two enrichment levels), and two reject pellets with visible flaws (to qualify the technique). The ^{235}U enrichments ranged from 0.2 to 8.8 wt. %. The nitride/silicide composites are candidate compositions for use as Accident Tolerant Fuel (ATF). The monophase U_3Si_5 material was included as a reference. Pellets from the same fabrication batches will be inserted in the Advanced Test Reactor at Idaho during 2016.

Analysis of neutron resonance measurements (averaged over the centerline of 8 mm diameter pellets and with 45 minutes of data collection enrichment levels) yielded enrichment levels that agreed with the nominal fabrication levels to within 0.1 wt%. Tomographic reconstructions of the ^{238}U and ^{235}U isotopic components demonstrated homogeneity of the pellets to at least 100 microns. Thermal neutron tomography demonstrated the ability to measure dimensions of pellets and the rodlet capsule gap double-encapsulated in ATR irradiation capsules. Spatially resolved microstructural analysis by neutron diffraction complemented the imaging and provides archival characterization of the pre-irradiation state. Advances in the analysis of the neutron imaging relied on the ENDF\B-VII.1 database, in conjunction with the ORNL nuclear cross-section analysis code SAMMY.

6. Fabrication of Enriched Ceramic Fuels

6.1 Fabrication of U_3Si_5 and UN/U_3Si_5 Fuels for the LANL-1/ATF-1 Test

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The ATF-1, LANL-1 irradiation test in the Advanced Test Reactor (ATR) consists of Kanthal (FeCrAl) clad U_3Si_5 and UN-U_3Si_5 fuels. This fuel-clad system was selected after initial screening evaluations consisting of fuel material reaction couples, thermophysical property measurements [1], thermodynamic analysis [2], and neutronic performance and safety calculations [3] of several composite fuel concepts.

The nominal irradiation test parameters are shown in Table 3 where highest priority was placed on understanding the relationship between fuel phase enrichment, fuel centerline temperature, and burn-up (BU) for a fixed linear heat generation rate (LHGR). The ^{235}U enrichments for the two fuel phases in first three rodlets were chosen so that the ^{235}U atoms/cm^3 would be the same across the composite. For these rodlets, the volumetric heat generation should be the approximately the same across the pellet whereas the damage accumulation in the U_3Si_5 should be greater than in the UN. The fuel centerline temperatures for Rodlets 1 and 2 are 1000ºC and 700ºC respectively with a target BU of 10 GWd/MTU. Rodlet 3 is a 700ºC test with BU extended to 20 GWd/MTU. Rodlet 4 is a U_3Si_5 fuel test with no UN. While monolithic U_3Si_5 is not being advocated as a stand alone fuel concept, due to the relatively low uranium density of 7.5 g/cm^3, the silicide-only rodlet is being irradiated as an efficient way to collect irradiation behavior data for this composite constituent phase. The fuel phases in Rodlet 5 will have the same ^{235}U enrichment. As a result, the UN should have a greater heat flux and more radiation damage than the U_3Si_5 phase. This rodlet will be tested at 700ºC to 10 GWd/MTU BU for comparison with Rodlet 2.

Table 3 ATF-1/LANL-1 nominal test design parameters.

Rodlet Number	UN Enrichment (wt.%)	U_3Si_5 Enrichment (wt.%)	LHGR (W/cm)	Centerline Temp (°C)	Cladding Material	Target Burnup, GWd/MTU
1	4.95	8.84	228	1000	Kanthal AF	10
2	4.95	8.84	223	700	Kanthal AF	10
3	4.95	8.84	232	700	Kanthal AF	20
4	-	8.84	237	700	Kanthal AF	10
5	2.7	2.7	240	<700	Kanthal AF	10

Previously determined feedstock synthesis routes and processing parameters from [4] were adopted for use in the fabrication campaign to produce fuel for the ATR irradiation. The process to fabricate UN-U_3Si_5 and U_3Si_5 fuel can be generally divided into three steps: (1) feedstock synthesis, (2) pellet fabrication, and (3) pellet characterization.

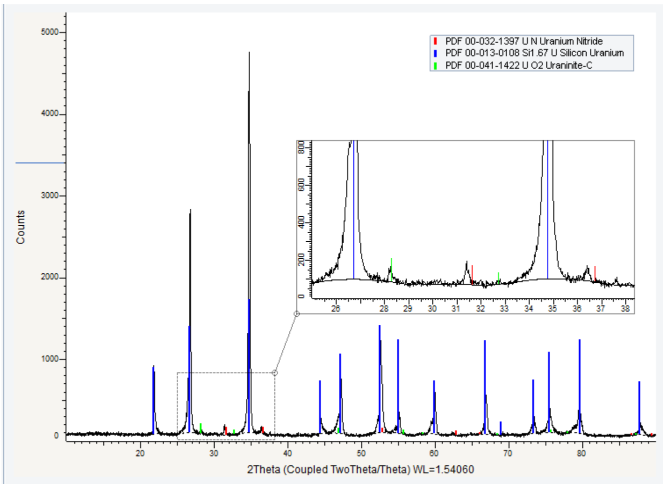

Figure 17 X-ray diffraction pattern of a sample taken from a low-enriched U_3Si_5 pellet showing peaks indicating UO_2 and UN impurity phases.

Depleted and low-enriched uranium nitride feedstock was produced using the historical carbothermic reduction nitridization process developed in the 1980's at the Los Alamos National Laboratory (LANL) and optimized for this fuels campaign. Milled and sieved depleted UN powder was shown to be phase-pure, as indicated by X-Ray Diffraction (XRD), and combustion analysis produced oxygen and carbon results of 426 ppm and 237 ppm respectively. XRD of low-enriched UN powder indicated trace amounts of impurity UO_2. XRD of the depleted and low-enriched UN powder indicated trace amounts of an unidentified impurity U-Si phase. The result from combustion analysis for oxygen was 542 ppm therefore the amount of oxide phase in the depleted U_3Si_5 is negligible. XRD of the low-enriched U_3Si_5 showed trace amounts of UO_2 and UN with the latter being cross contamination for preparation (Figure 17).

Fabrication of the ATF-1, LANL-1 fuel began in FY15 with the depleted UN-U_3Si_5 composite pellets. The average of the pellet densities for the batch was 95.2% of theoretical and few physical defects were observed. The XRD pattern contained unambiguous UN and U_3Si_5 phases with no secondary phases observed. Figure 18 shows an example centerless-ground depleted UN-U_3Si_5 and the microstructure of the ~95%TD composite pellet.

Ground pellets of depleted and low enriched U_3Si_5 and UN/U_3Si_5 were shipped to INL for fabrication into rodlets for fabrication into ATF-1/LANL-1 test articles. Encaspulated rodlets ATF-L41 and ATF-L45, corresponding respectively to rodlets #1 and #4 in Table 3, were fabricated, inspected and inserted into the ATR at the beginning of cycle 160-A. Fabrication of rodlet ATF-L44 (Table 3, rodlet #5) was not completed in time for the 160-A cycle and so is scheduled for insertion in the 160-B cycle. Fabrication and irradiation of the remaining LANL-1 rodlets has been deferred indefinitely as additional ATF-1 irradiation tests have been deprioritized relative to ATF-2 tests.

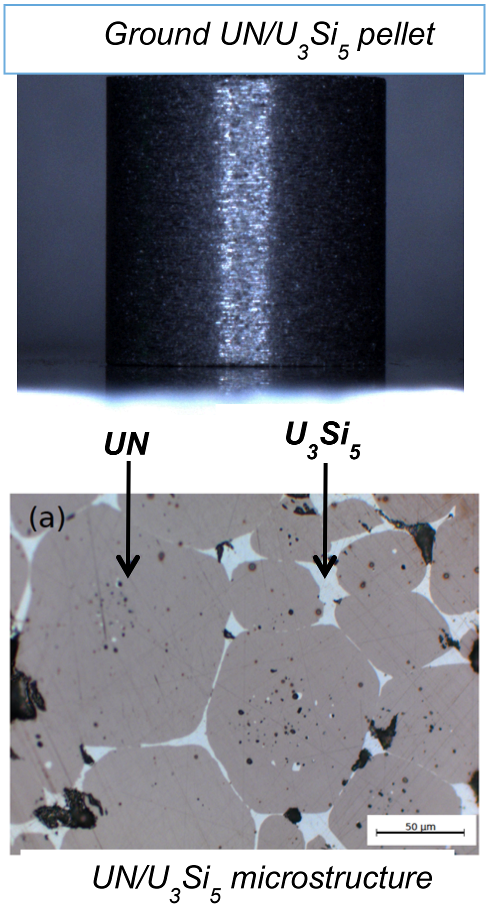

Figure 18 : Centerless ground depleted UN-U_3Si_5 composite pellet (Top) and associated optical image of the microstructure (Bottom)

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7. FY16 Ceramic Fuels Publications

- L-Y Cheng, A. Cuadra, M. Todosow, K. Gamble (INL), P.Medvedev (INL), *Performance of U_3Si_2 Fuel in a Reactivity Insertion Accident,* Top Fuel 2016.
- L-Y Cheng, A. Cuadra, N. Brown (ORNL), M. Todosow, *Transient Performance of Accident Tolerant Fuel in Design Basis Accidents*, Top Fuel 2016.
- Reiche, Vogel, Tang, "In situ synthesis and characterization of uranium carbide using high temperature neutron diffraction", J. Nucl. Material 471, pp. 308-316, 2016.
- Aydogan, Maloy, Vogel et al., "Effect of tube processing methods on the texture and grain boundary characteristics of 14YWT ODS steels", Materials Science and Engineering: A 661, pp. 222-232, 2016.
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- Losko, Vogel, Bourke et al., "Energy-Resolved Neutron Imaging for Interrogation of Nuclear Materials", Proceedings Advances in Nuclear Nonproliferation Technology and Policy Conference (ANTPC), Santa Fe, NM, September 25-30, 2016
- Losko, Vogel, Bourke, "Characterization of Fresh Nuclear Fuel using Time-Of-Flight Neutrons ", Proceedings ANS Annual Meeting 2016, New Orleans, LA, June 12-16, 2016