INL/CON-16-39218-Revision-0

High Temperature Fuel Cladding Chemical Interactions Between Unirradiated TRIGA Fuels and 304 Stainless Steel

Emmanuel Perez, Dennis, D. Keiser, Jr., Bryan L Forsmann, Dawn E. Janney, Jody Henley, Eric Woolstenhulme, Jatuporn Burns, Steven Cook, Michael P Heighes

February 2016

The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

INL/CON-16-39218-Revision-0

High Temperature Fuel Cladding Chemical Interactions Between Unirradiated TRIGA Fuels and 304 Stainless Steel

Emmanuel Perez, Dennis, D. Keiser, Jr., Bryan L Forsmann, Dawn E. Janney, Jody Henley, Eric Woolstenhulme, Jatuporn Burns, Steven Cook, Michael P Heighes

February 2016

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy

Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

High Temperature Fuel Cladding Chemical Interactions Between Unirradiated TRIGA Fuels and 304 Stainless Steel

Emmanuel Perez, Dennis D. Keiser, Bryan Forsmann, Jatuporn Burns, Michael P. Heighes, Dawn E. Janney, Steven Cook, Jody Henley, Eric C. Woolstenhulme

www.inl.gov

Idaho National Laboratory

TMS 2017 146th Annual Meeting & Exhibition

THE WORLD COMES HERE. February 26 – March 2, 2017 • San Diego, California, USA

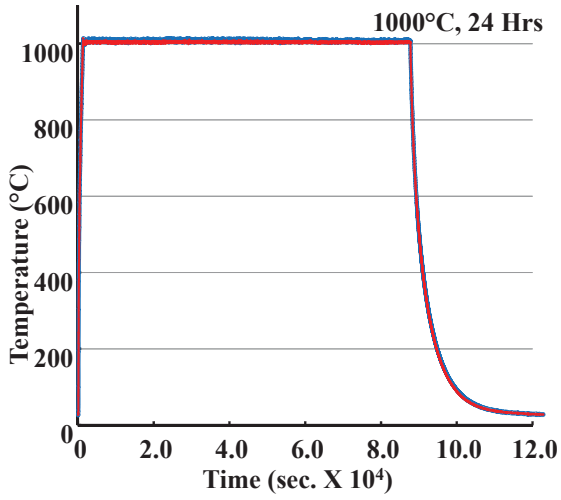
Introduction

- **High temperature chemical interactions between TRIGA (Training, Research, Isotopes, General Atomics) fuels and their type-304 stainless steel (304SS) claddings during irradiation and different TRIGA reactor transient scenarios are of interest from the standpoint of safe reactor operation.**
- **During irradiation and high temperature exposure, the fuel may come into close contact with the 304SS cladding, and an opportunity exists for interdiffusion to take place between fuel and 304SS.**
- **Annealing experiments using diffusion couples have been used to mimic this scenario.**
- **Interactions within the 304SS are given a priority.**

Experimental Details: Fuel

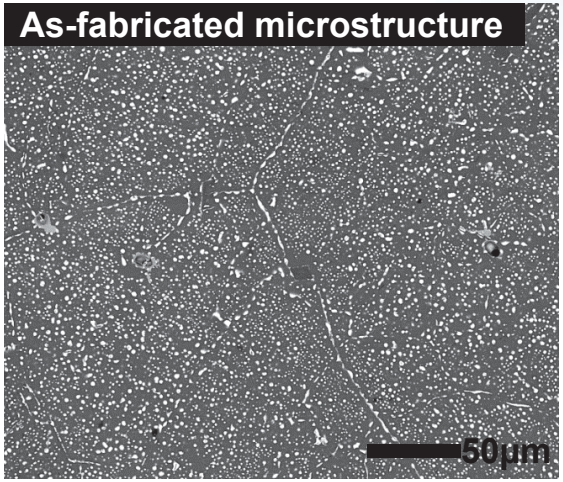
- Annealing experiments for this study were carried out in a furnace placed inside of a Ar-atmosphere glovebox.
  - Thermocouples monitored and logged temperatures.
  - A trickle flow (0.5 ft^3/hr) of high purity (<10ppb) Ar gas maintained low O_2 levels inside of the furnace.
  - Ta-foil was used to provide an additional O_2 barrier.
- TRIGA fuel samples, ¼" X ¼" X 1/8" pieces, and ¼" diameter rods of 304SS were used these experiments.

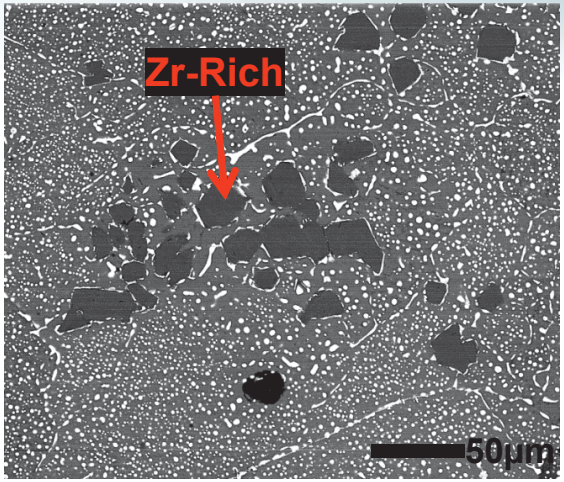
- Fuel samples were annealed at 950°C for 5, 16 and 24 hours to study the fuel evolution as a function of time.
- Diffusion couples of TRIGA fuel vs. 304SS were assembled and annealed at 1000°C for 5 and 24 hours.
- The microstructures of as-fabricated fuel, annealed fuels and the diffusion couples were examined by:
  - Scanning electron microscopy (SEM):
    - Secondary (SE) and backscatter (BE) electron imaging with compositional analysis by energy dispersive spectroscopy (EDS) and X-ray maps.
  - Transmission Electron Microscopy (TEM) and Scanning TEM (STEM):
    - Site-specific specimen preparation via Focused Ion Beam In-Situ Lift-Out (FIB-INLO)
    - Bright Field and High Angle Annular Dark Field (HAADF) imaging.
    - Selected Area Electron Diffraction (SAED).
  - X-Ray Diffraction (XRD)
    - Micro-XRD was used as a complementary characterization method.
- The presence of hydrogen was inferred from the crystallographic analysis.

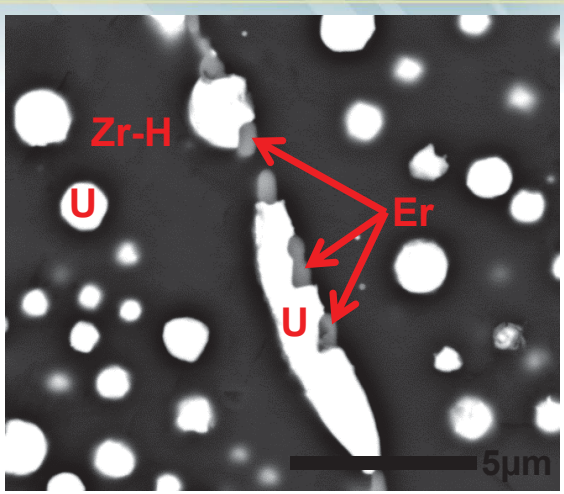


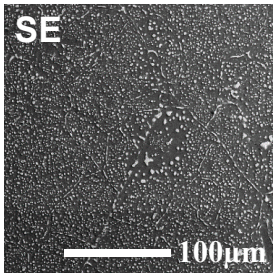
As-Fabricated TRIGA Fuel Microstructure

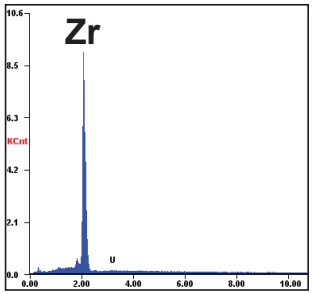
Idaho National Laboratory

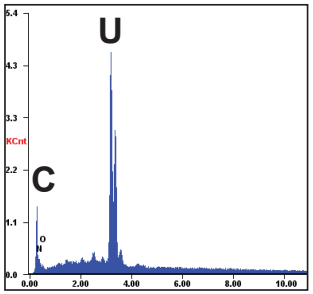


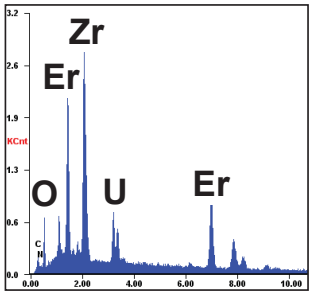




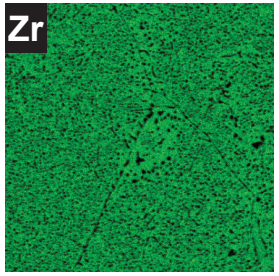


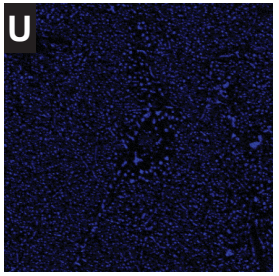


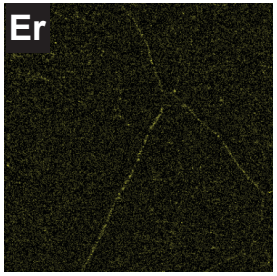


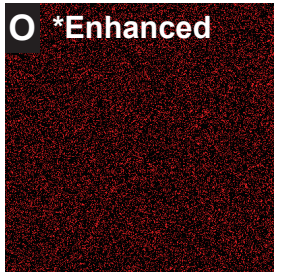


- TRIGA fuels are composed of U-particles dispersed in a Zr-H matrix.
- Analysis was carried out by EDS and X-ray mapping to validate the compositions of the fuel and the matrix.
  - The matrix was rich in Zr and did not contain U or other impurities.
    - Note: EDS cannot detect hydrogen.
  - The U-particles contained measurable concentrations of carbon.
  - Zr-rich grains were observed within the fuel matrix.
  - Er was observed within the grain boundaries.

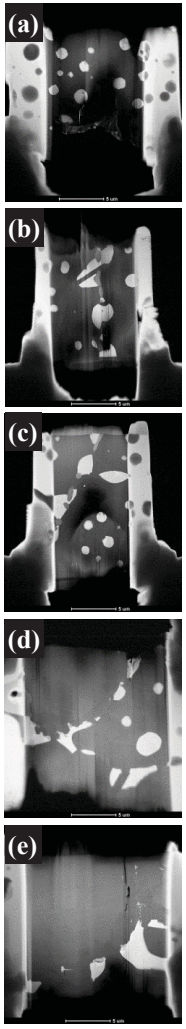


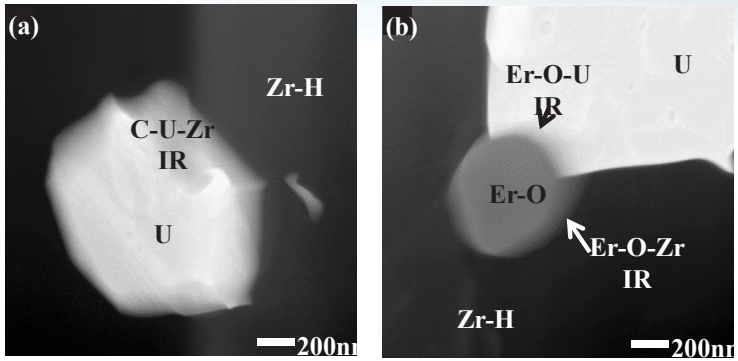




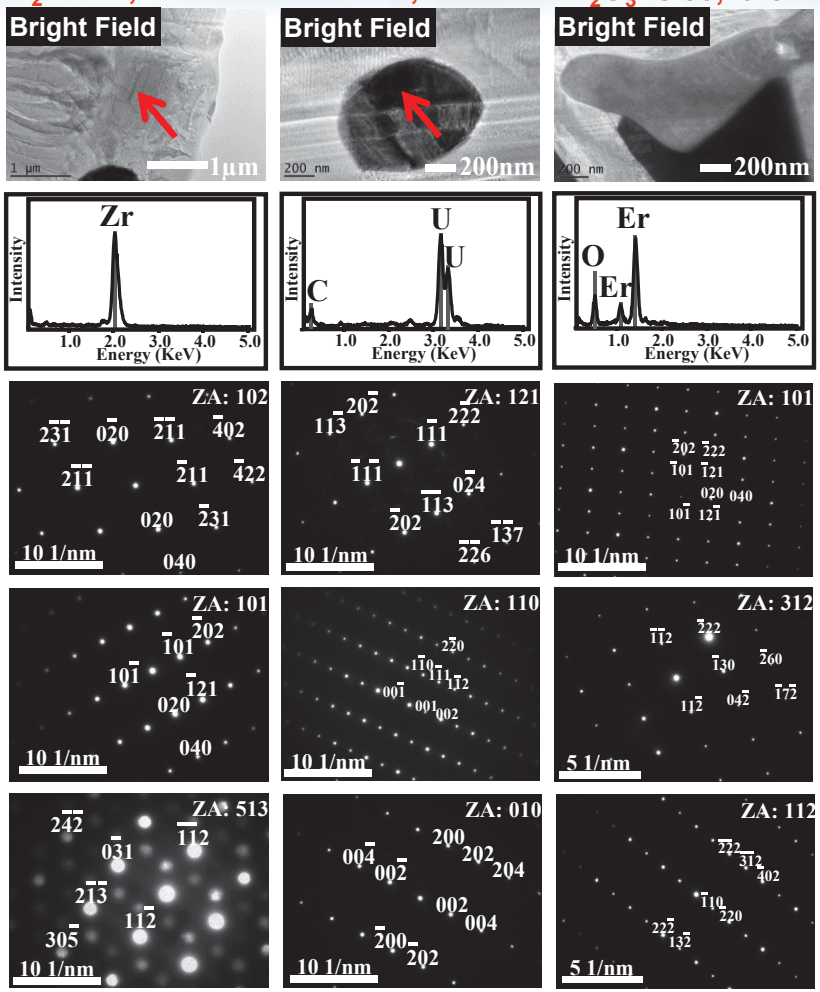


Fuel Characterization: TEM

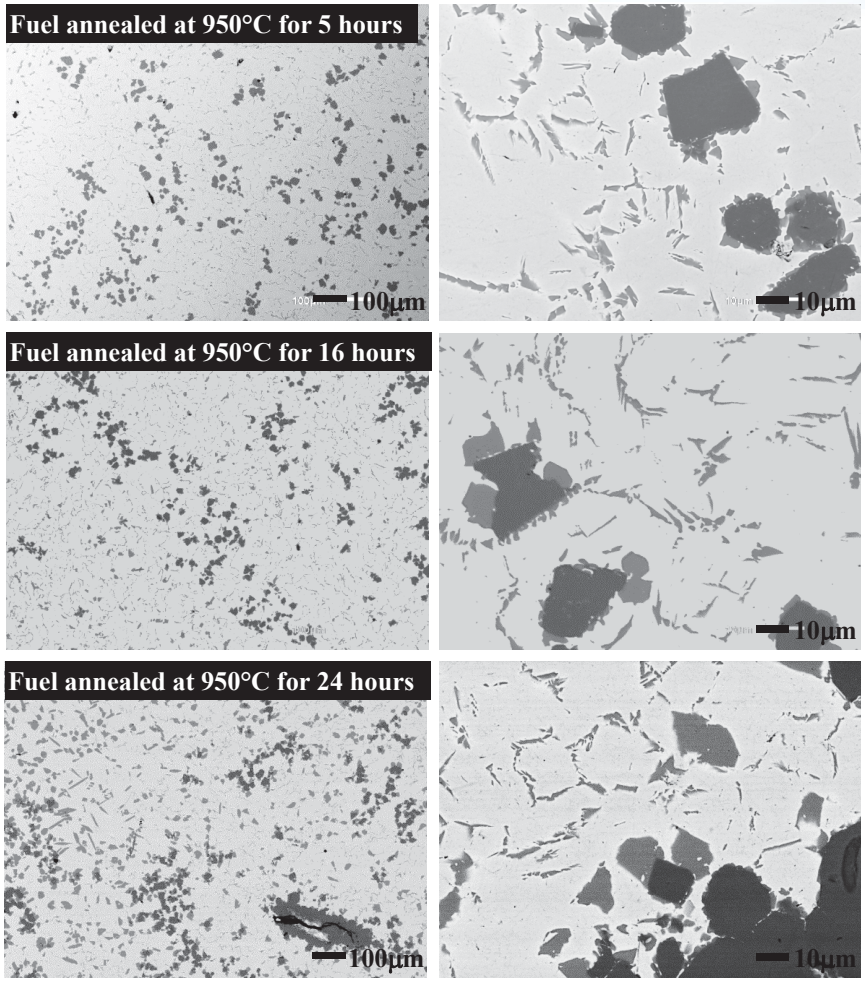


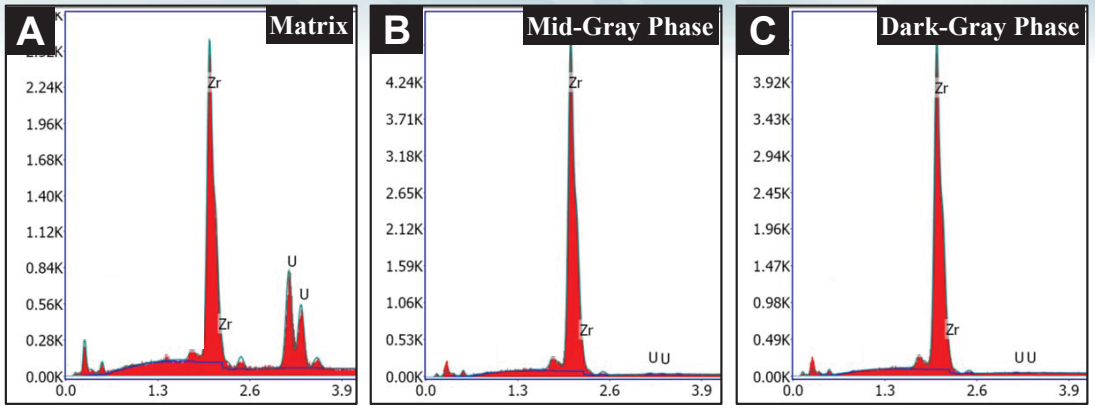


- Interaction regions (IR) were apparent between the Zr-H, U, and Er.
- The matrix was found to be composed of the tetragonal-H_2Zr phase.
  - The cubic-$H_{1.6}Zr$ phase did not present the best fit.
- The U-particles were composed of the expected orthorhombic-α-U phase.
- The Erbium additions were found to be composed of the cubic-Er_2O_3 phase.



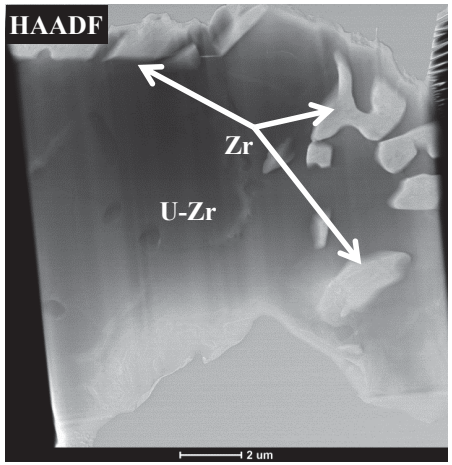
Annealed TRIGA Fuel Microstructure

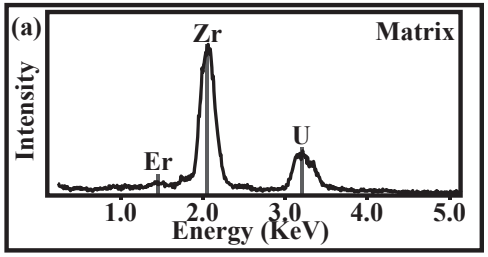


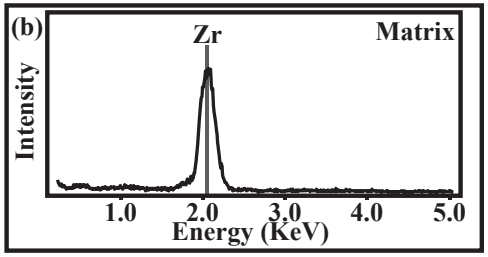


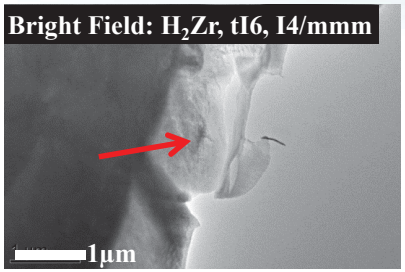
- After annealing, the U-particles fully interacted with the matrix.
  - U-particles were not observed in the annealed fuel.
- The Zr-rich phase regions remained within the matrix.
- Another Zr-rich phase appear to have developed.
- A phase with acicular microstructure developed throughout the matrix.
- EDS indicated that:
  - The matrix contained Zr and U.
  - Phase contrast in the BE micrographs suggest that the two Zr-rich phases contain differing compositions.
    - These phases may contain differing hydrogen concentrations.

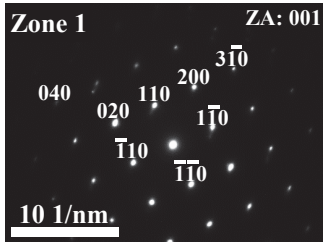
Annealed Fuel Characterization: TEM

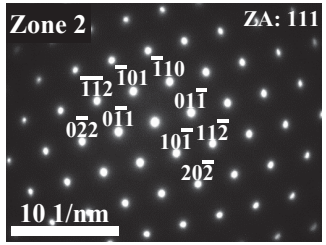


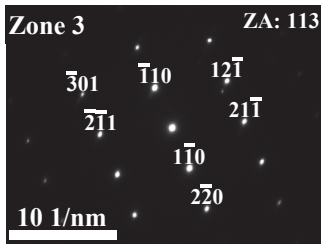


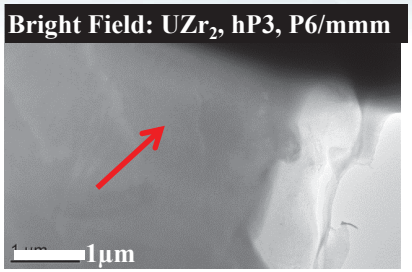


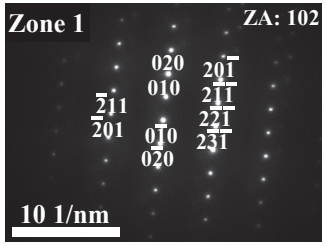


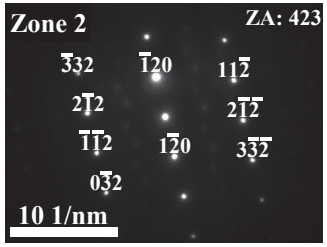


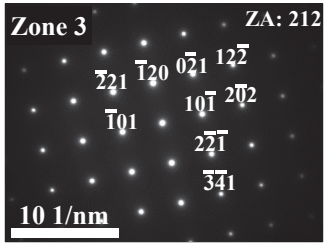






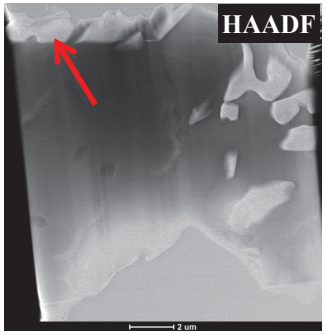




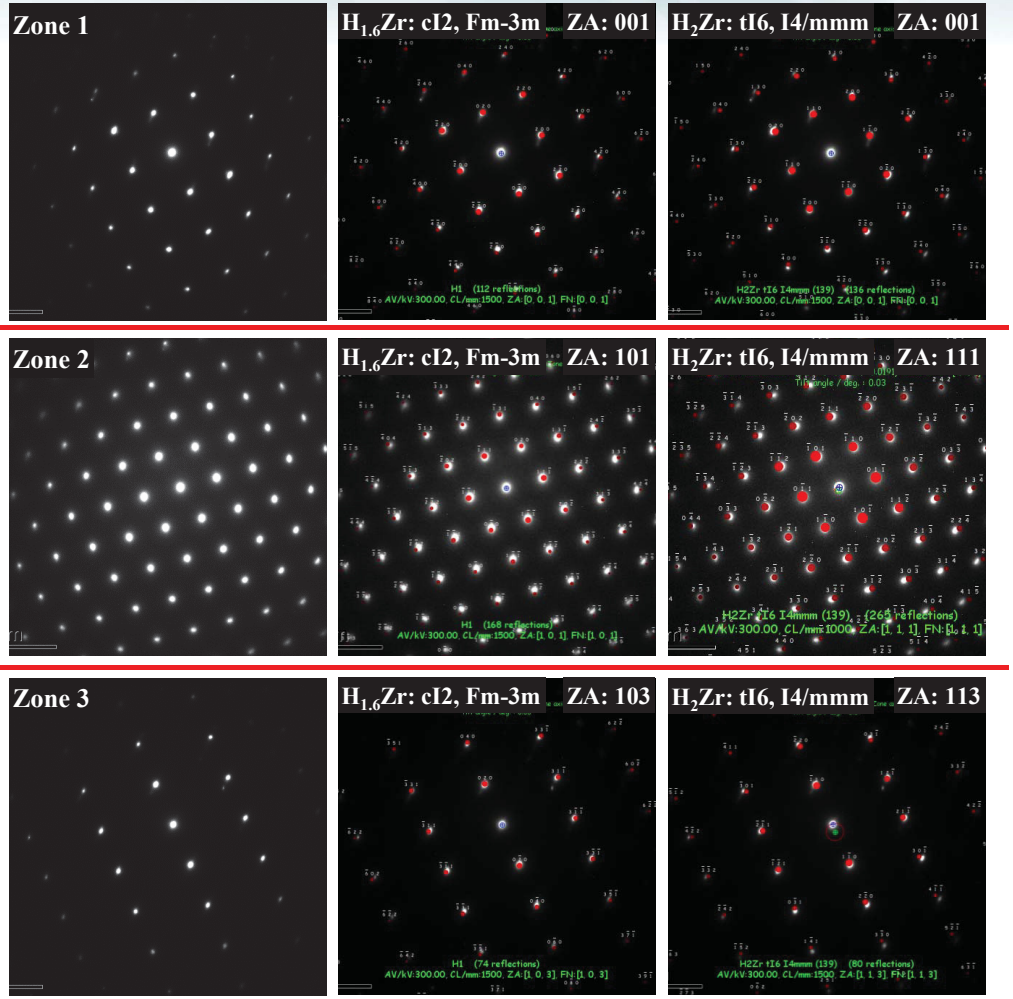


- One sample was prepared for characterization from the fuel annealed at 950°C for 24 hours.
- The sample captured the matrix and acicular phases.
- The dark-gray contrast phases were not captured.
- EDS verified that the matrix was composed of U-Zr, and contained localized small concentrations of Er.
- The acicular phase was Zr-rich and did not contain Er or U.
- The matrix consisted of the hexagonal-UZr_2 phase.
- The Zr-rich particles likely contained the tetragonal H_2Zr phase.
  - The cubic-$H_{1.6}Zr$ phase did not present the best fit.

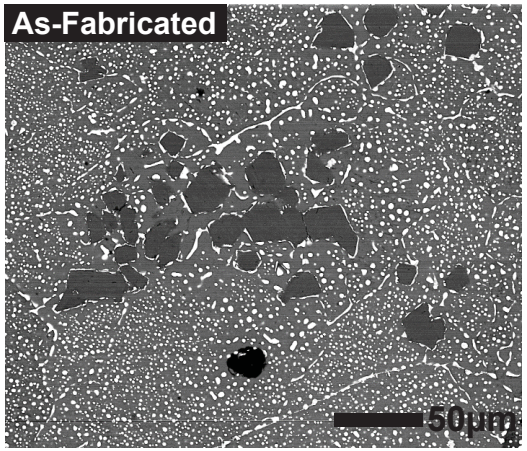
Annealed Fuel Characterization by TEM

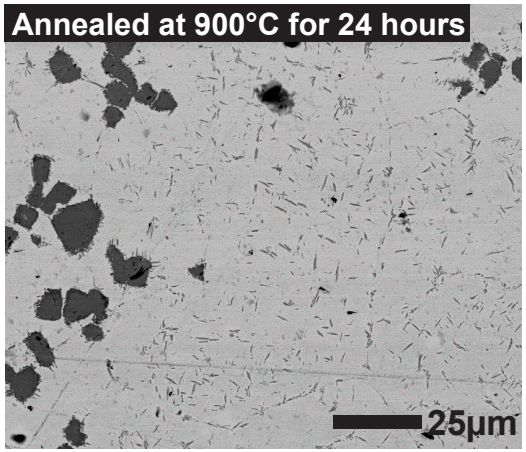


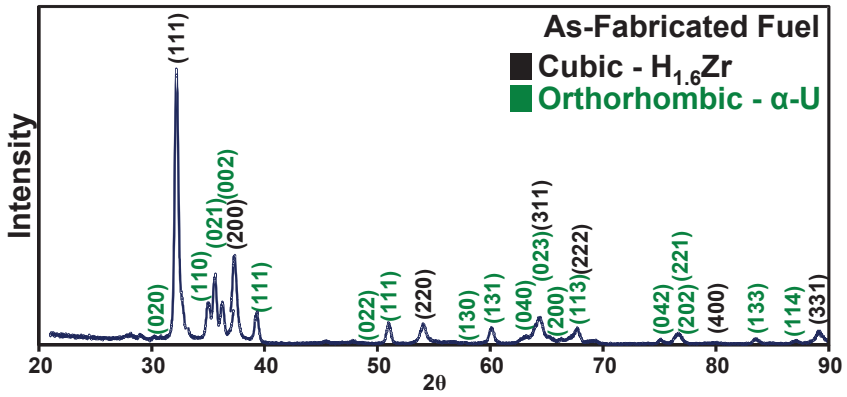
- Diffraction analysis was facilitated by the JEMS electron microscopy software package version 4.3905U2016.
- Characterization analysis of the Zr-hydride phases was complicated by close similarities in the spot patterns of the cubic-$H_{1.66}Zr$ and tetragonal-H_2Zr phases.
- The spot patterns did not reliably differentiate between the two phases.

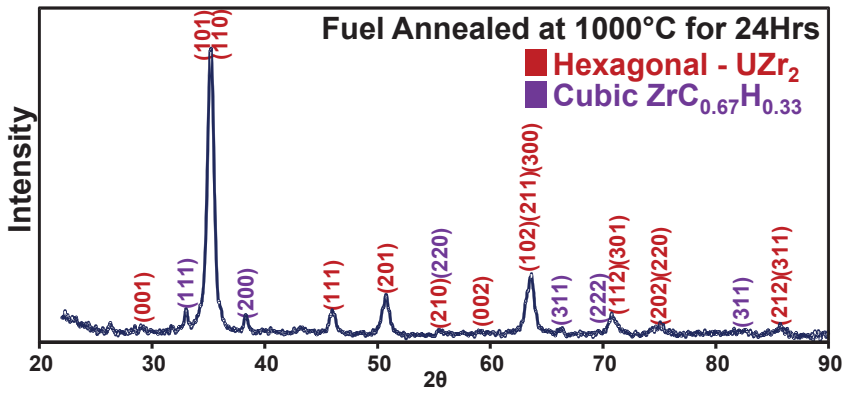


As-Received vs. Annealed Fuel Microstructures



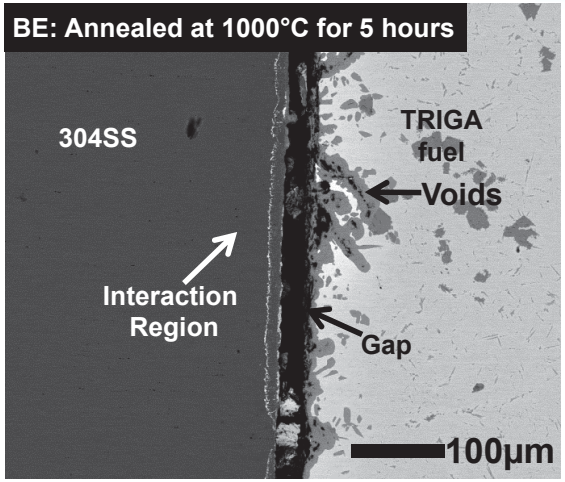


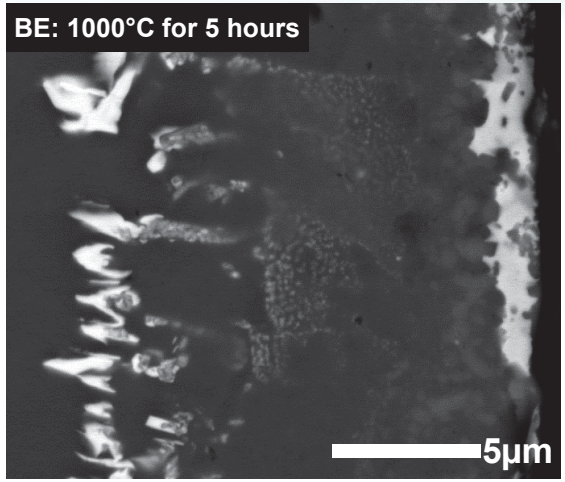


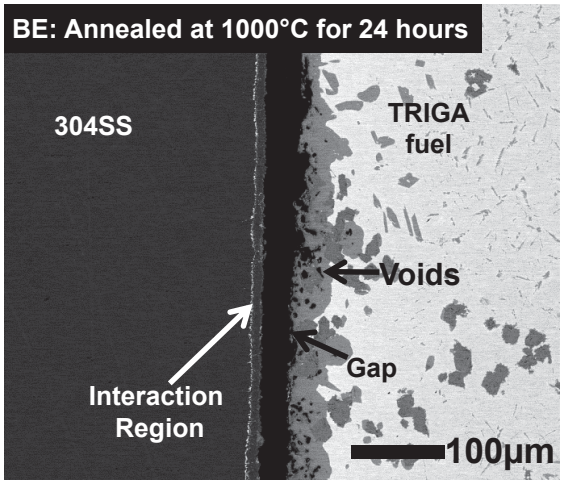


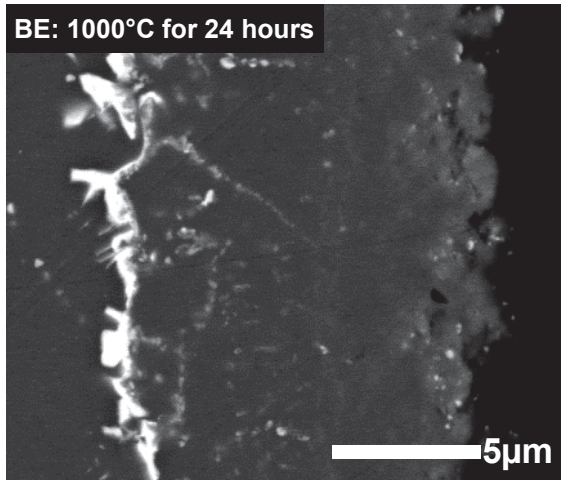
- Significant microstructural changes were observed between the as-fabricated and the annealed microstructures of the TRIGA fuel.
- XRD shows significant changes in the phases present within the microstructure of the matrix.
- As-received:
  - Cubic $H_{1.6}Zr$
  - Orthorhombic α-U
  - Tetragonal H_2Zr (TEM)
- Annealed:
  - Hexagonal UZr_2
  - Cubic $ZrC_{0.67}H_{0.33}$

Diffusion Couples Annealed at 1000°C for 5 and 24 hours





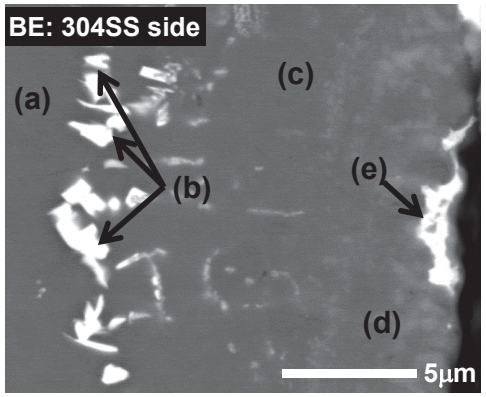


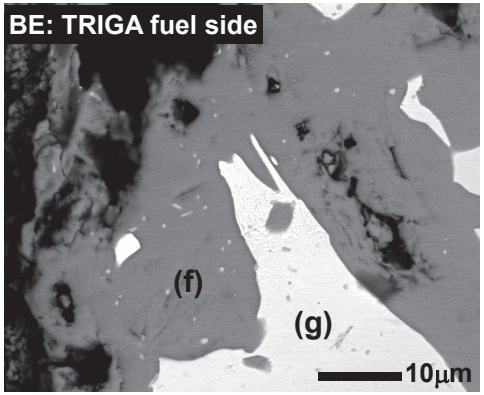


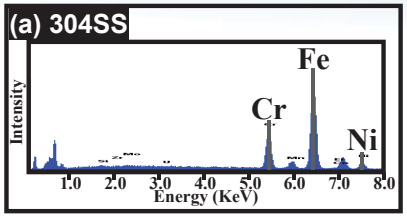
- Diffusion couples of TRIGA fuel vs. 304SS were assembled and annealed at 1000°C for 5 and 24 hours.
- Interaction regions developed within the 304SS side of the diffusion couple and contained multiple phases.
- Typically voids were observed in the TRIGA fuel side of the couple next to the interaction region.
  - Voids were not observed where interaction regions did not develop.
- During annealing, the couples generally experienced failure at or near the interdiffusion interface between the fuel and the 304SS after some time.
  - Volumetric change of the fuel is suspected to cause the interface failure.
- Both diffusion couples developed interaction regions of similar thickness.
  - This result suggests that the couple failure occurred at approximately the same annealing time.

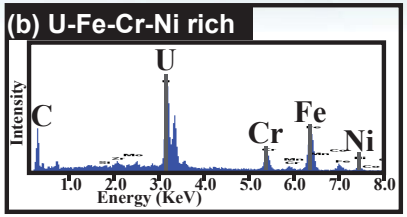
Interaction Regions

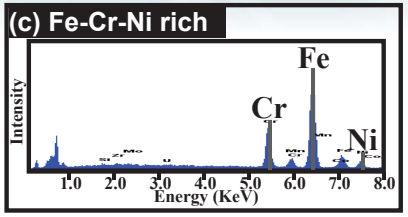
Diffusion Couple Annealed at 1000°C for 5 hours

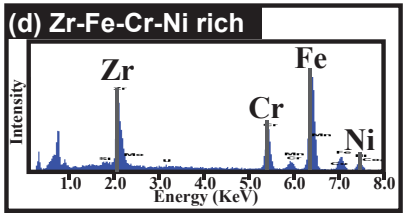


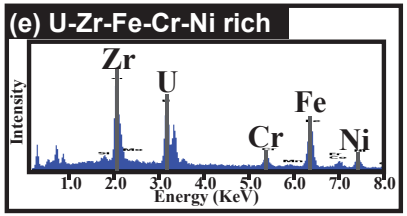


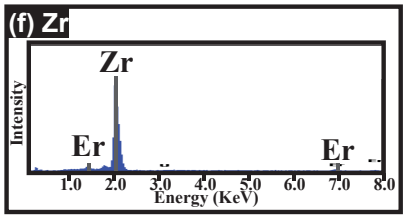


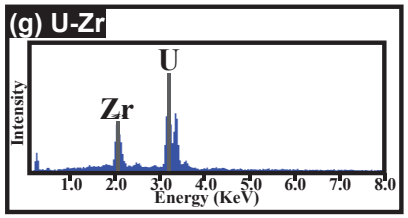






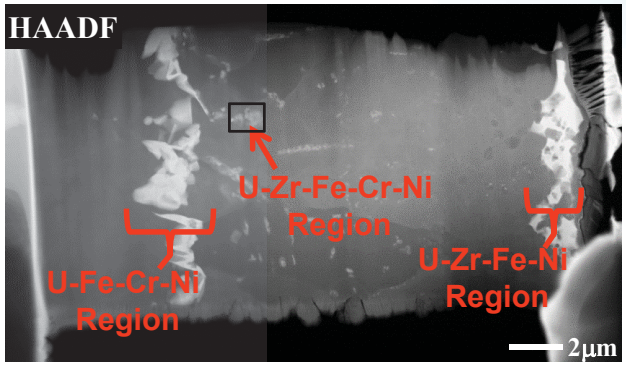


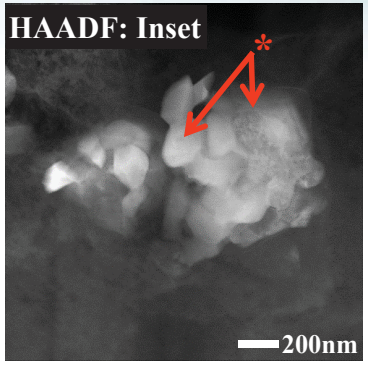




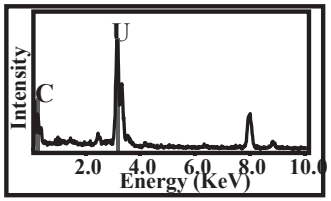
- An interaction region developed within the 304SS.
  - It contained four distinct phase regions with measurable compositional differences:
    - U-Fe-Cr-Ni
    - Fe-Cr-Ni
    - Zr-Fe-Cr-Ni
    - U-Zr-Fe-Cr-Ni
- The TRIGA fuel side of the diffusion couple did not show any elements from the 304SS.
- A Zr-rich layer was observed within the TRIGA fuel near the interdiffusion interface.
- Some of these regions may contain multiple finely distributed phases.
- Due to the interaction volume of the electron beam some of the measured regions contained more than one phase.

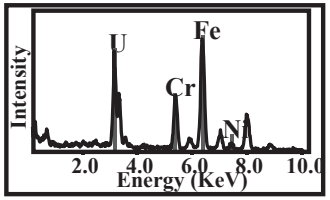
Characterization by TEM



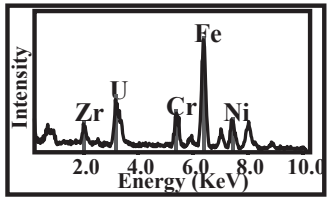


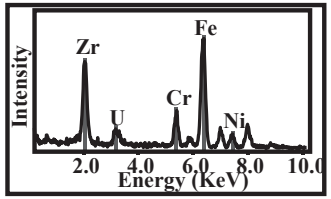
U-Fe-Cr-Ni Region

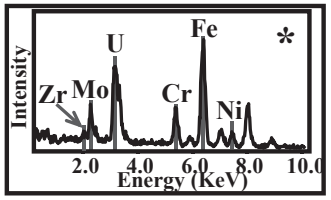




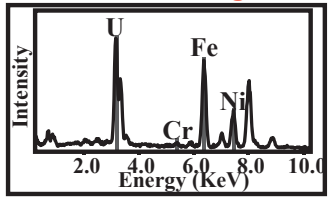
U-Zr-Fe-Cr-Ni Region

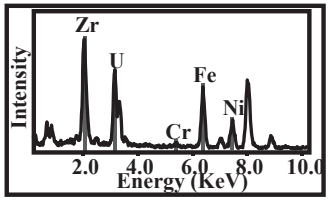




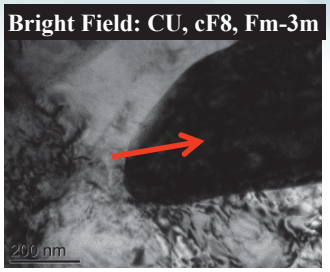


U-Zr-Fe-Ni Region

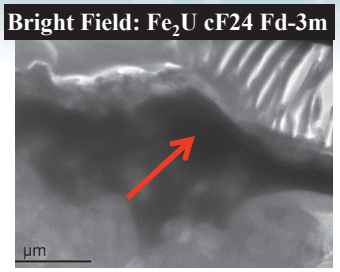


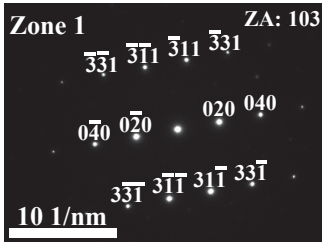


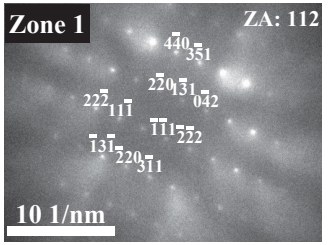
Bright Field: CU, cF8, Fm-3m

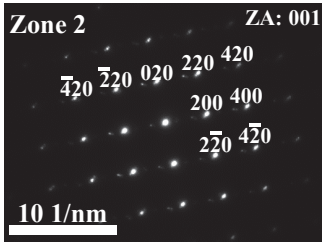


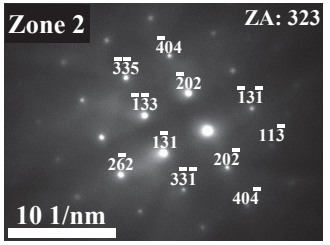
Bright Field: Fe_2U cF24 Fd-3m

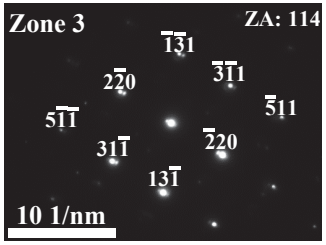


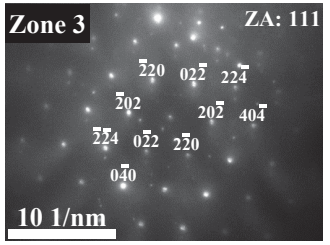






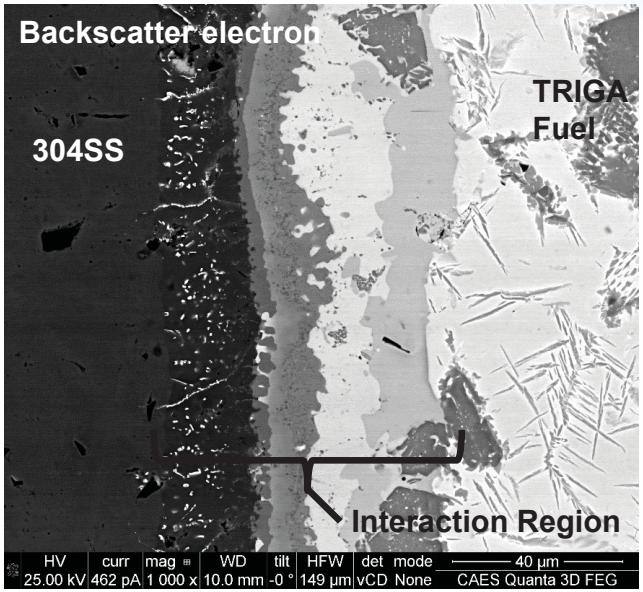


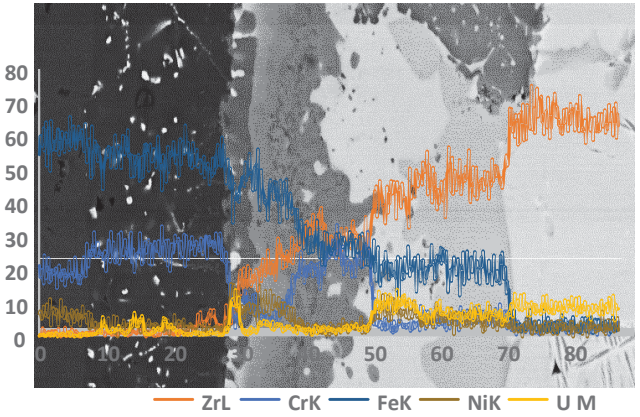




- TEM analysis confirmed observations made by SEM.
- The interaction region developed grains with significant (U,Zr)-(Fe-Cr-Ni) compositional variations.
- *Mo was observed in some grains within the region containing U-Zr-Fe-Cr-Ni.
- To date, the cubic-Fe_2U, cF24, phase has been identified in the U-Zr-Fe-Ni rich region.
- The cubic-uranium-carbide (CU), cF8, phase was found in the U-Fe-Cr-Ni region.
- EDS results suggest that several other phases may be present within the interaction region.

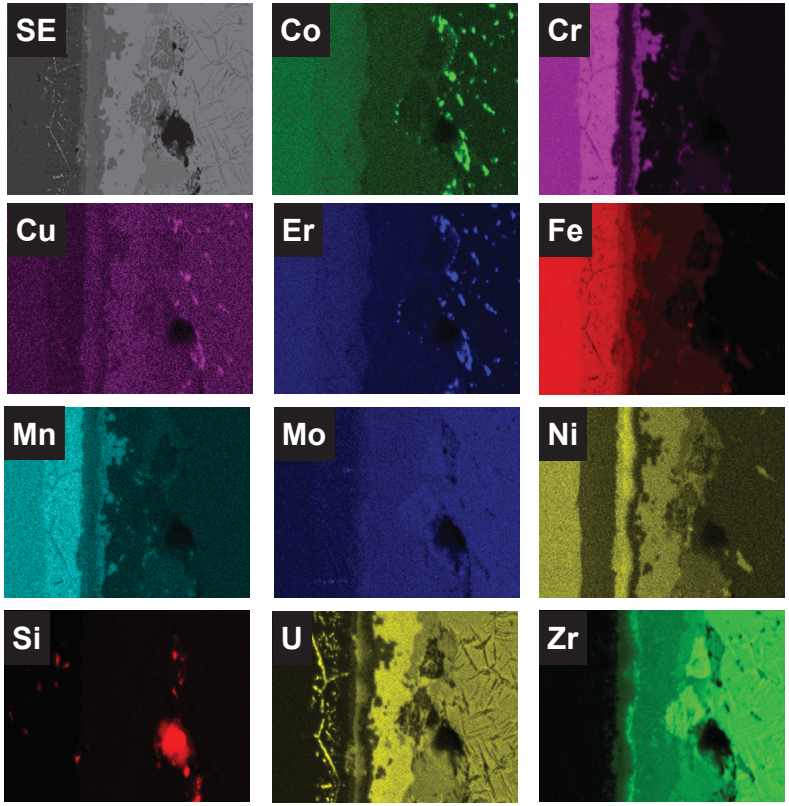
Current and Future Work





TRIGA Fuel vs. 304SS Diffusion Couple Annealed at 900°C for 24 hours

- X-ray maps have been collected from the interaction at locations of interest.
- SEM analysis showed that the interaction region developed a layered microstructure.
- The maps showed that different layers differed in composition. Layers enriched-in and depleted-in Cr and Ni and vice versa were observed. U showed similar behavior.
- Concentration profiles generated by EDS correlated well with the observations made from the X-ray maps.
- Because the diffusion couple was cooled in the furnace over a period of several hours, cooling effects on microstructural development cannot be ruled out at this time.
- Detailed characterization by TEM is planned.



Summary

- **TRIGA fuels in the as-fabricated and annealed conditions were characterized by SEM and TEM to identify the constituents phases in the fuel.**
  - **The TRIGA fuel matrix is composed of α-U particles dispersed in a $H_{1.6}Zr$ matrix with Er_2O_3 additions concentrated within grain boundaries. Some H_2Zr was observed by TEM.**
  - **After annealing at 950°C, the U-particles fully interacted with the matrix to develop a UZr_2 matrix with $ZrC_{0.67}H_{0.33}$ and H_2Zr secondary phases.**
- **Diffusion couple experiments of 304SS vs. TRIGA were carried out at 1000°C for 5 and 24 hours.**
  - **The couples developed interaction regions within the 304SS.**
  - **U-Fe-Cr-Ni, U-Zr-Fe-Cr-Ni, and U-Zr-Fe-Ni regions developed within the interaction region.**
  - **The UC and Fe_2U phase were identified in the microstructure.**
  - **Other phases may be present.**