INL/MIS-20-59025-Revision-0

Advanced Electron Microscope and Micro Analysis of TRISO coated Particles: FY2020 Overview

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Advanced Electron Microscope and Micro Analysis of TRISO coated Particles: FY2020 Overview

Isabella van Rooyen, Subhashish Meher, Karen Wright, Boopathy Kombaiah, INL
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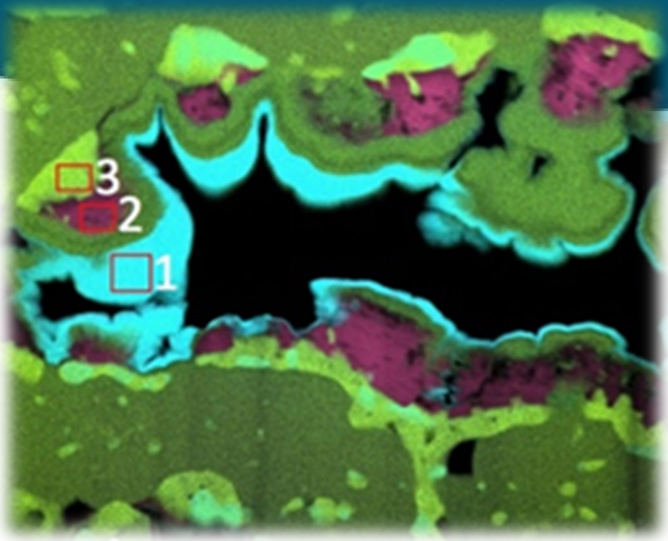
Presented at the Gas-Cooled Reactor Program Annual Review
July 14, 2020 via Videoconferencing from Idaho National Laboratory



ADVANCED REACTOR TECHNOLOGIES

ADVANCED REACTOR TECHNOLOGIES

Program Goals and Objectives

OBJECTIVES

- Understanding Effects of Irradiation on TRISO layers
- Fission product chemistry and behavior in UCO kernel
- Identify and Understand Fission Product Transport Mechanisms in TRISO Coated Particles

OUTCOMES and IMPACT

- Impact on Performance
- Improve Predictive Behavior Modeling
- Kernel Behavior: Release from kernel; release from whole particle
- Known Fission Product Transport Mechanisms

AGR-1 and AGR-2 Particle Irradiation History and Characterization

Particle	Ag Retention	Fuel Type	Burnup (% FIMA)	Kernel	SiC layer: FP Distribution and Microstructure				
					EPMA	FIB	STEM	PED	Radiation Damage
AGR1-632-034	0.65	Baseline	11.4						
AGR-523-SP01	0.16	Variant 1	17.4						
AGR1-131-066	0.39	Variant 3 ORNL Lab	15.3						
AGR1-433-001	0.66		18.6 Safety tested*						
AGR1-433-004	0.66		18.6 Safety tested*						
AGR1-433-003 AGR1-433-007	0.66		18.6 Safety tested*						
AGR2-223-R06 (Mount D07)	0.08	BWXT	10.8						
AGR2-223-R034 (Mount D06)	0.84		10.8						
AGR2-222-RS36 (Mount D25)	Not detectable Eu = 0.8		12.55 Safety tested*	FY2020					
AGR2-222-RS19 (Mount D26)	0.20 Eu = 0.54		12.55 Safety tested*	FY2020					
AGR2-222-RS27 (Mount D26)	0.11 Eu = 0.51		12.55 Safety tested*						
AGR2-633-RS28 (Mount D42)	<0.21		7.46	FY2020**	FY2020	FY2020	FY2020	FY2021	FY2021
AGR2-633-RS09 (Mount D43)	0.88		7.46		FY2020**	FY2020	FY2021	FY2021	
AGR2-633-RS01 (Mount D43)	0.76		7.46	TBD	TBD	TBD	TBD	TBD	
Unirradiated Baseline As-Fabricated	N/A	AGR1	N/A						
Unirradiated Baseline As Fabricated and Compacted	N/A	AGR2	N/A	FY2020**		FY2020	FY2021	FY2021	

Completed previous years

Completed FY2020

Planned FY2020

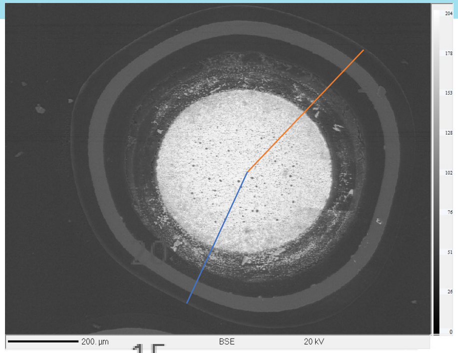
** in progress

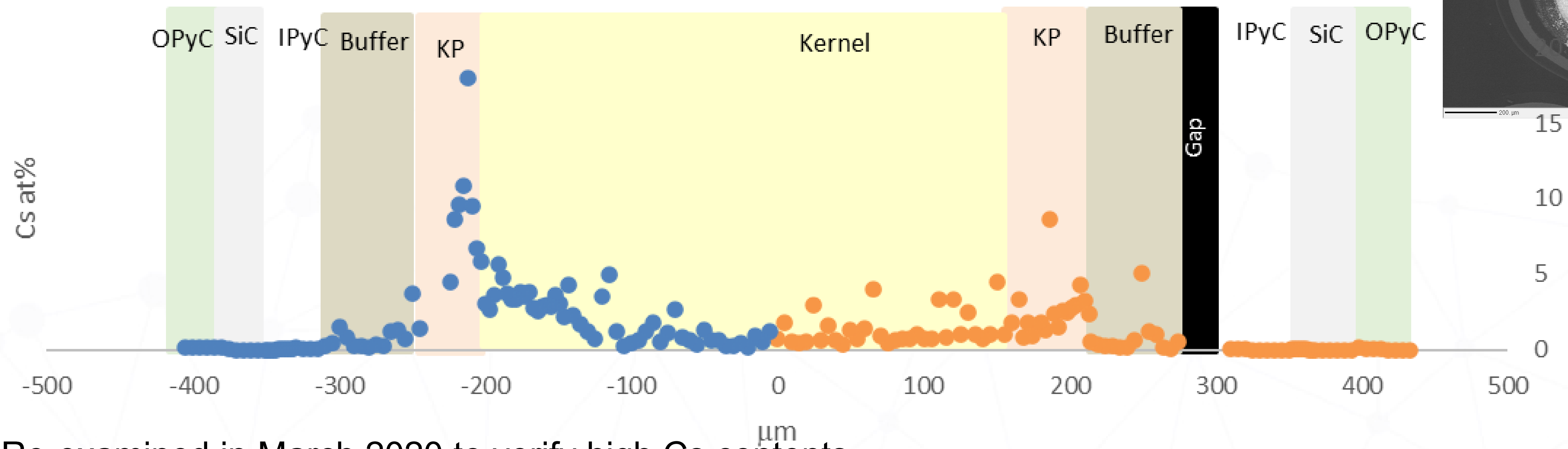
Planned FY2021

* 1600°C, 300h

Micro-Analysis Accomplishments FY2020

AGR2-633-RS28





Re-examined in March 2020 to verify high Cs contents.

- High Cs and Ba contents were verified (as high as 20 at% Cs, 1.3 at% Ba).
- Mass balance calculations show that this particle contains ~20x more Cs than predicted by ORIGIN modeling.
- Mostly likely this particle has surface contamination: source not identified yet.

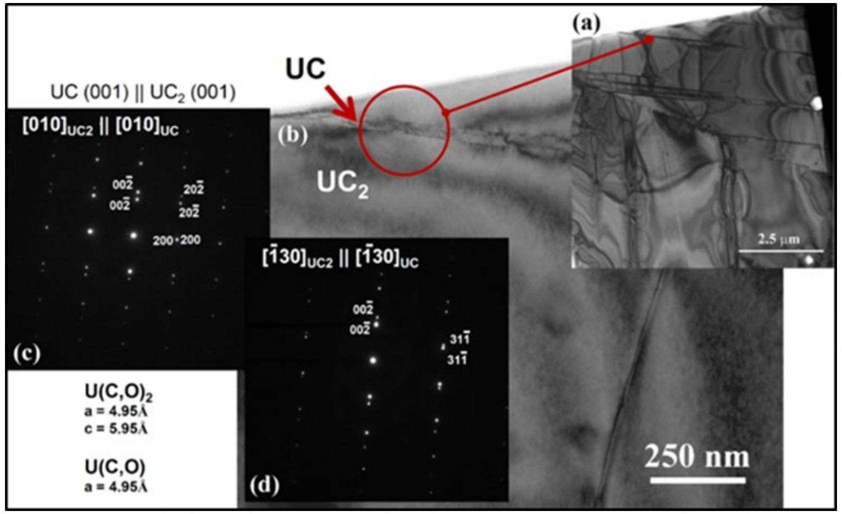
AGR2-633-RS09 EPMA analysis now in progress, surface cleaning

KP: kernel periphery

Advanced Microscopy Examination of UCO Fuel Kernel

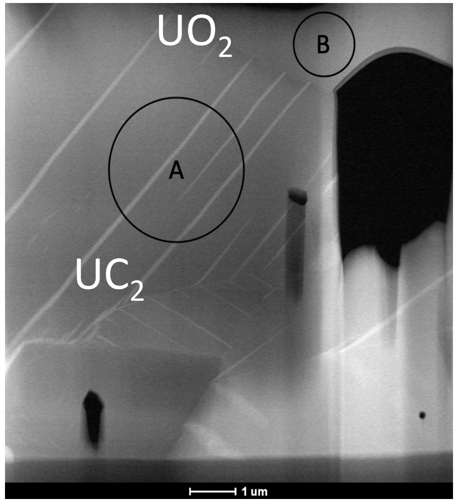
ADVANCED REACTOR TECHNOLOGIES

Fuel Kernel Microstructural Examination



As-Fabricated
AGR1 TRISO Fuel Kernel

I.J.van Rooyen, et al., HTR 2018, (2018) HTR 2018-3012.



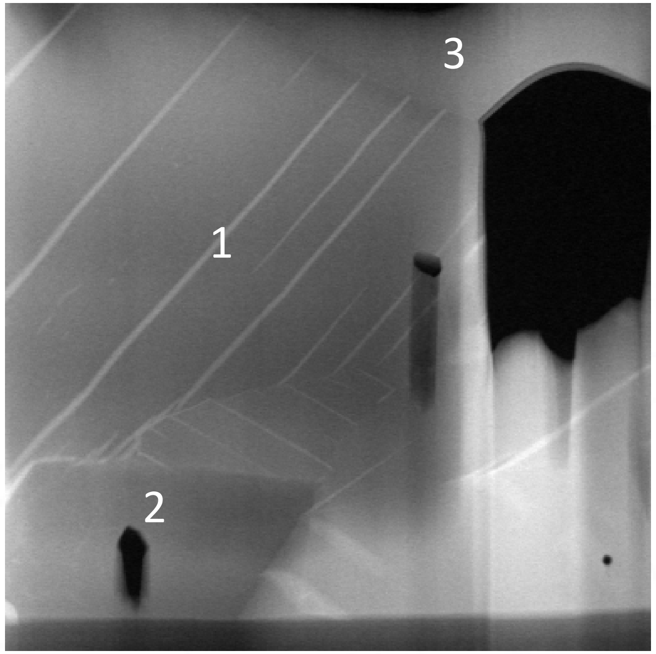
As Fabricated & Compacted
F51-LEU01-49T
AGR2 TRISO Fuel Kernel

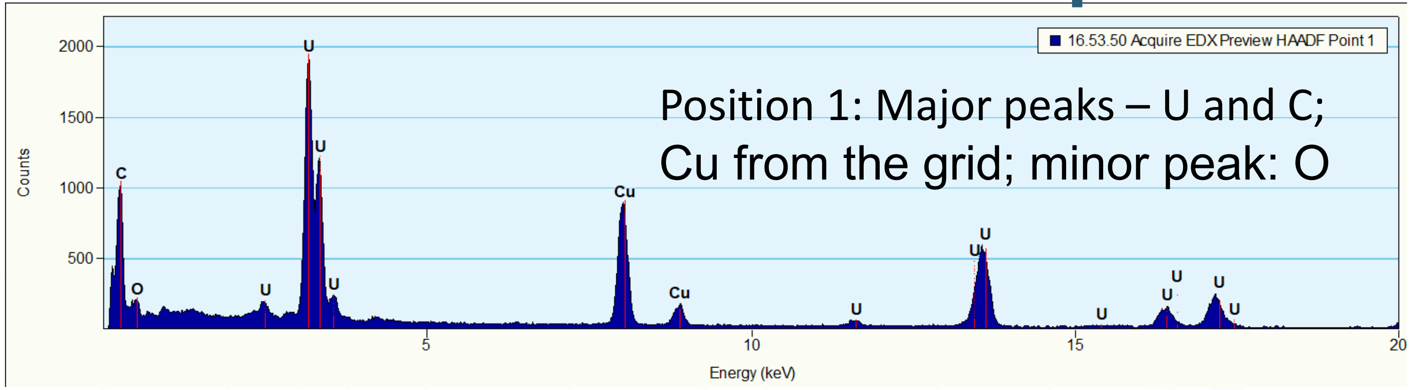
In Progress

As Fabricated & Compacted & Irradiated AGR1/AGR2 TRISO

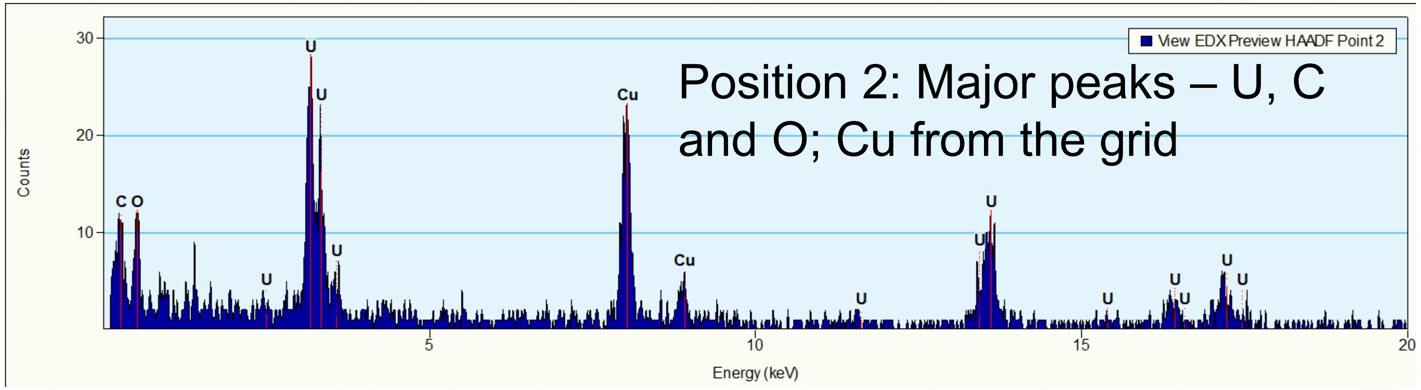
- AGR1-632-034
- AGR1-433-001
- AGR1-131-066
- AGR2-223-RS06
- AGR2-222-RS36
- AGR2-222-RS19
- AGR2-222-RS27
- AGR2-633-RS09
- AGR2-633-RS28

Unirradiated Fuel Kernel : As-Fabricated and Compacted STEM-EDS spectra

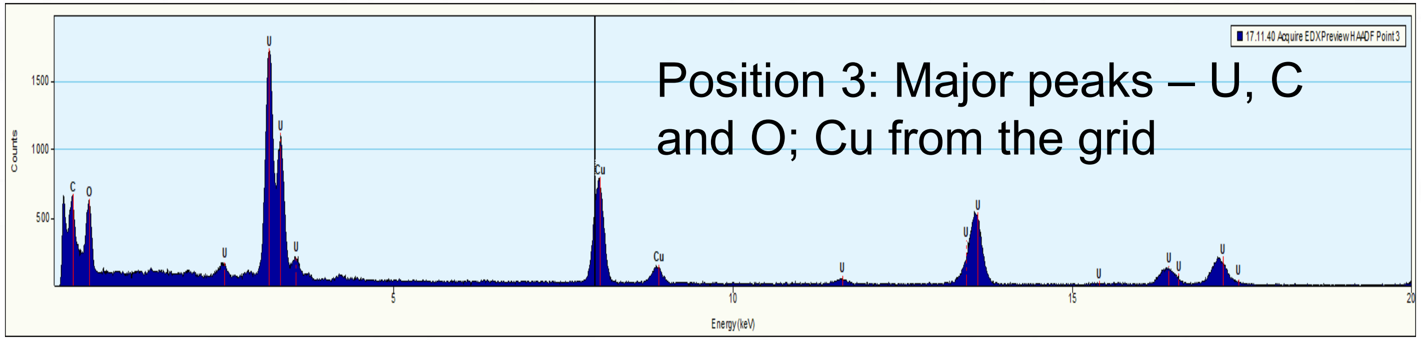




Position 1: Major peaks – U and C; Cu from the grid; minor peak: O

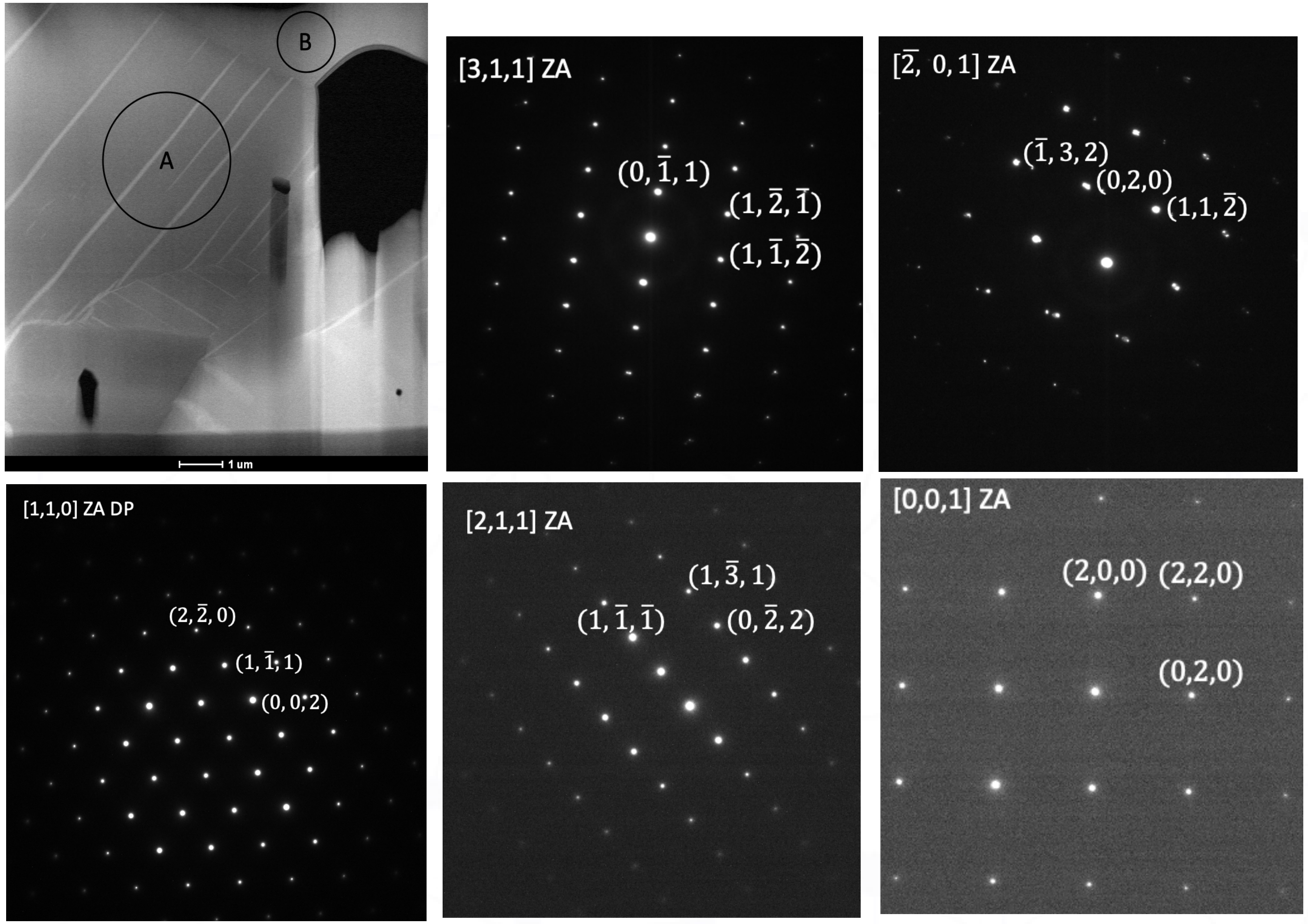


Position 2: Major peaks – U, C and O; Cu from the grid



Position 3: Major peaks – U, C and O; Cu from the grid

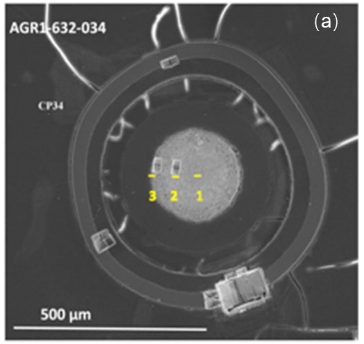
Unirradiated Fuel Kernel : As-Fabricated and Compacted Diffraction pattern indexing and phase identification

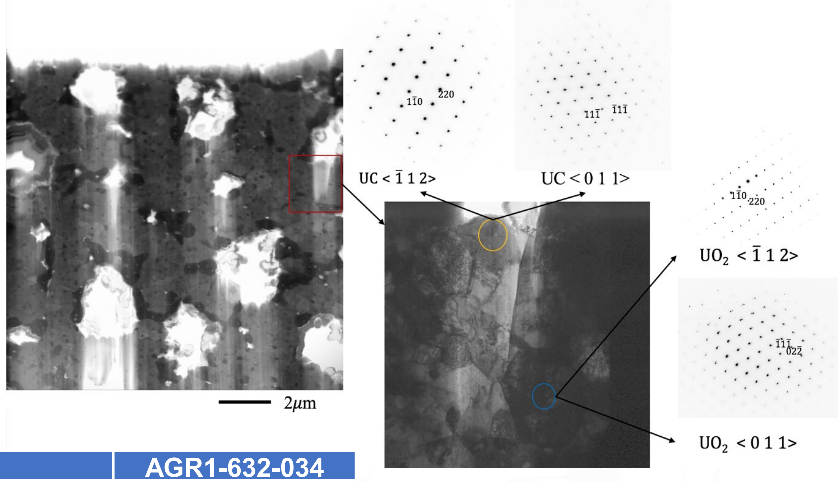


Position A:
UC_2 crystal structure; BCT;
Space group $I4/mmm$;
a = b = 3.509 Å; C = 5.98 Å

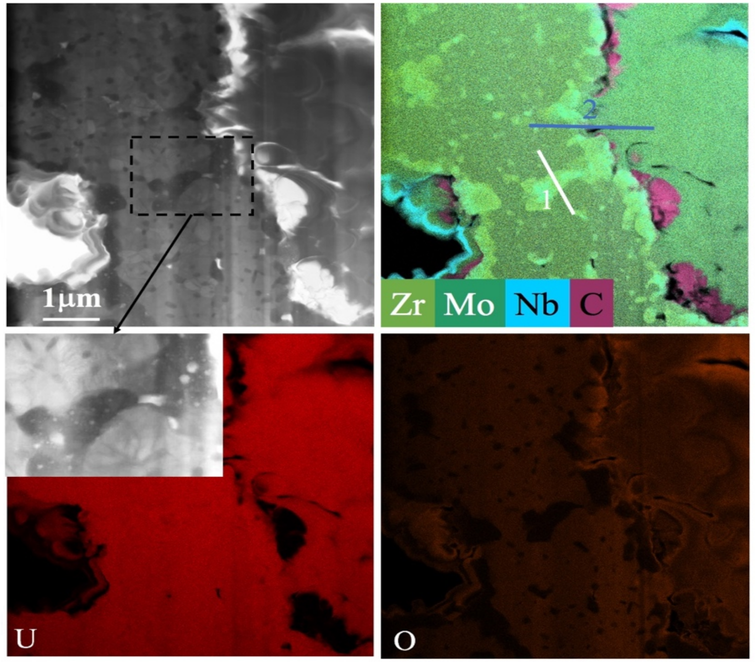
Position B:
UO_2 crystal structure; FCC;
Space group $Fm\bar{3}m$;
a = 5.4203 Å)

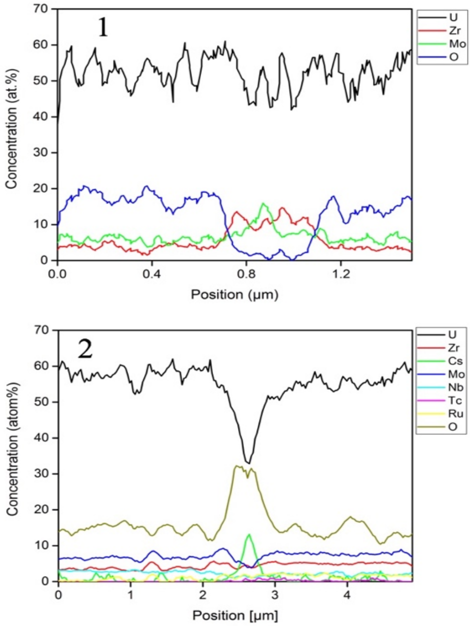
Irradiated Microstructure of AGR-1 Fuel Kernel





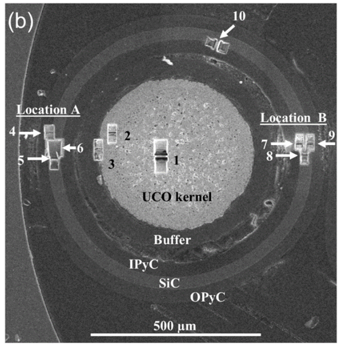
Compact	AGR1-632-034
Burnup (%FIMA)	11.4
Fast neutron fluence (x 10^{25} n/m^2), E>0.18 MeV	2.55
Time-average volume-average temperature (°C)	1070
Time-average peak temperature (°C)	1144



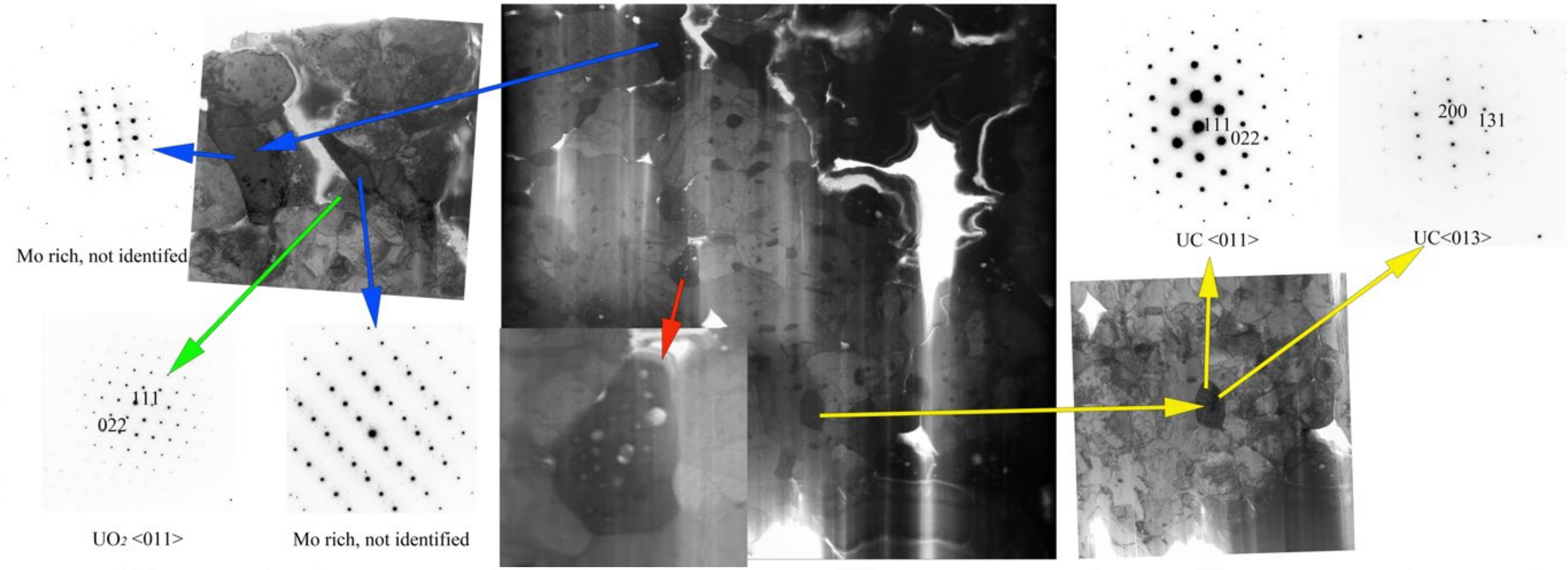


- Fuel matrix consists of UC and UO_2, and UO_2 presents as the dominating phase.
- Zr forms carbide in the solid solution of UC.
- Mo, Ru and Tc also enrich in UC phase, and Nb tends to enrich at pore surface.
- Ultra-fine Fission gas bubbles located in UC phase, while UO_2 is free of fission gas bubbles.

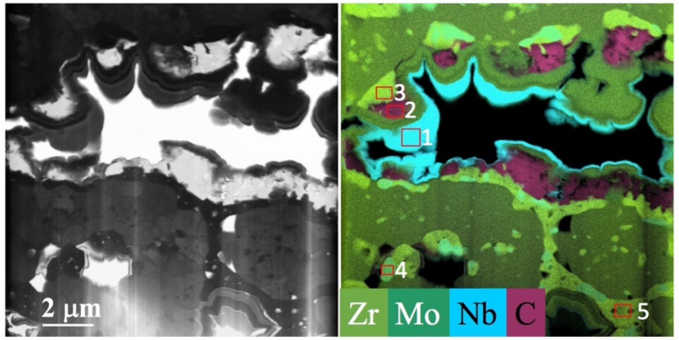
Irradiated Microstructure of AGR-2 Fuel Kernel

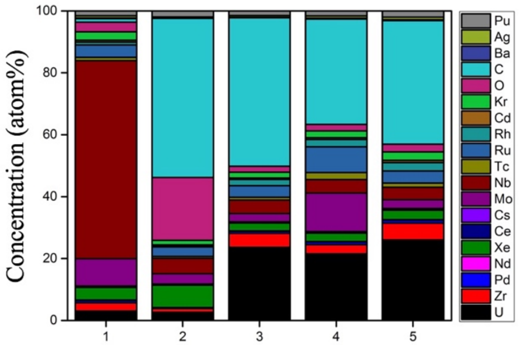


Compact	AGR2-223-RS06
Burnup (%FIMA)	10.8
Fast neutron fluence (x 10^{25} n/m^2), E>0.18 MeV	2.99
Time-average volume-average temperature (°C)	1161
Time-average peak temperature (°C)	1335



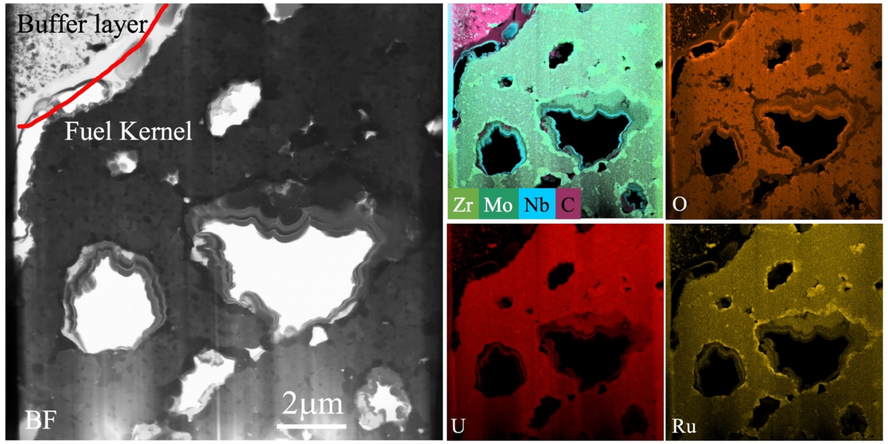
- The irradiated microstructure consists large pores and their interfaces show a multiple layer shell structure.
- Fuel matrix consists of UC and UO_2, and UO_2 presents as the dominating phase.
- Zr forms carbide in the solid solution of UC.
- Mo, Ru and Tc enrich in UC phase.



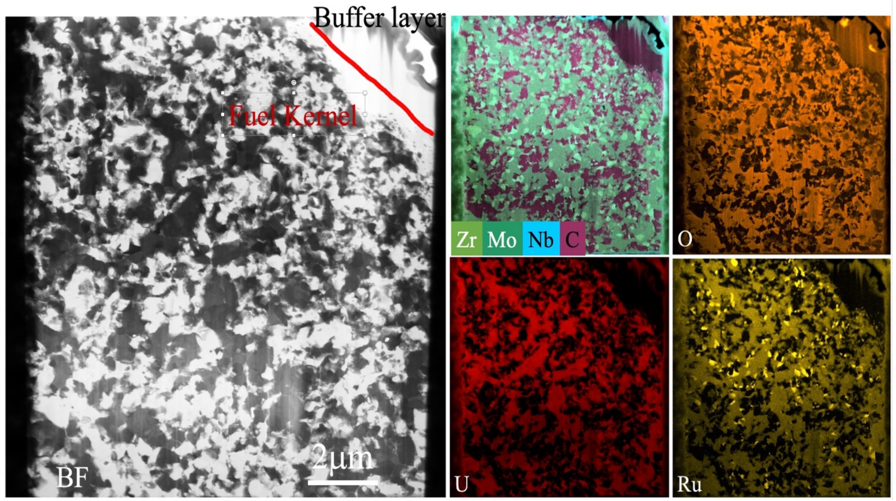


Comparison between Irradiated AGR-1 and AGR-2 Fuel Kernels

Interface between buffer layer and fuel kernel



AGR1-632-034

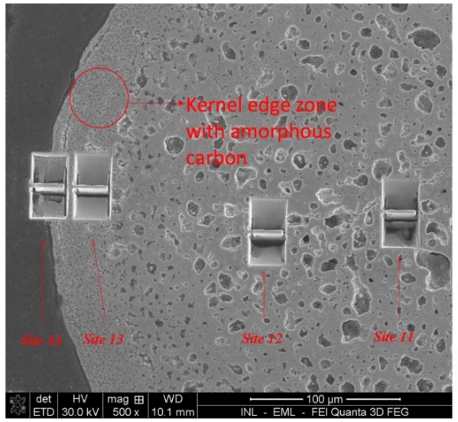


AGR2-223-RS06

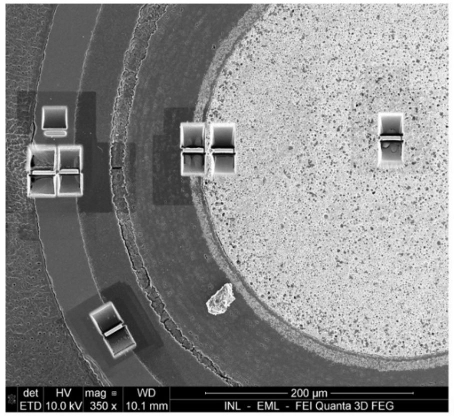
UCO fuel kernel		AGR-1	AGR-2
Diameter (μm)		348.4 ± 8.3	426.7 ± 8.8
Density (g/cm^3)		10.7 ± 0.026	11.0 ± 0.030
^{235}U enrichment (at.%)		19.74	14.03
Chemistry (mole%)	UO_2	67.9	71.4
	$UC_{1.86}$	0.4	12.3
	UC	31.7	16.4

- No Pd was positively identified in the fuel kernel for either AGR-1 or AGR-2 fuel particles.
- Overall, the identified fission products in AGR-1 and AGR-2 kernels display the same chemical states.
  - Zr, Mo, Ru and Tc tend to concentrate in the UC phase.
  - Mo, Tc, and Ru starts to precipitate to form $UMoC_2$ or $URu(Tc)C_2$ phases as they exceed the solubility limit in UC phase.
- Nb is prone to forming Nb oxide at the free surface of pores or cracks.
- Prominent difference between AGR-1 and AGR-2:
  - AGR-1 fuel preserve as two-main-phases structure with large pores and small gas bubblies residing in the UC phase.
  - AGR-2 fuel shows structure resulted possibly from a strong inter-diffusion between the fuel kernel and buffer layer.

Safety test irradiated AGR-1 and AGR-2 Comparison.



AGR2-222-RS36



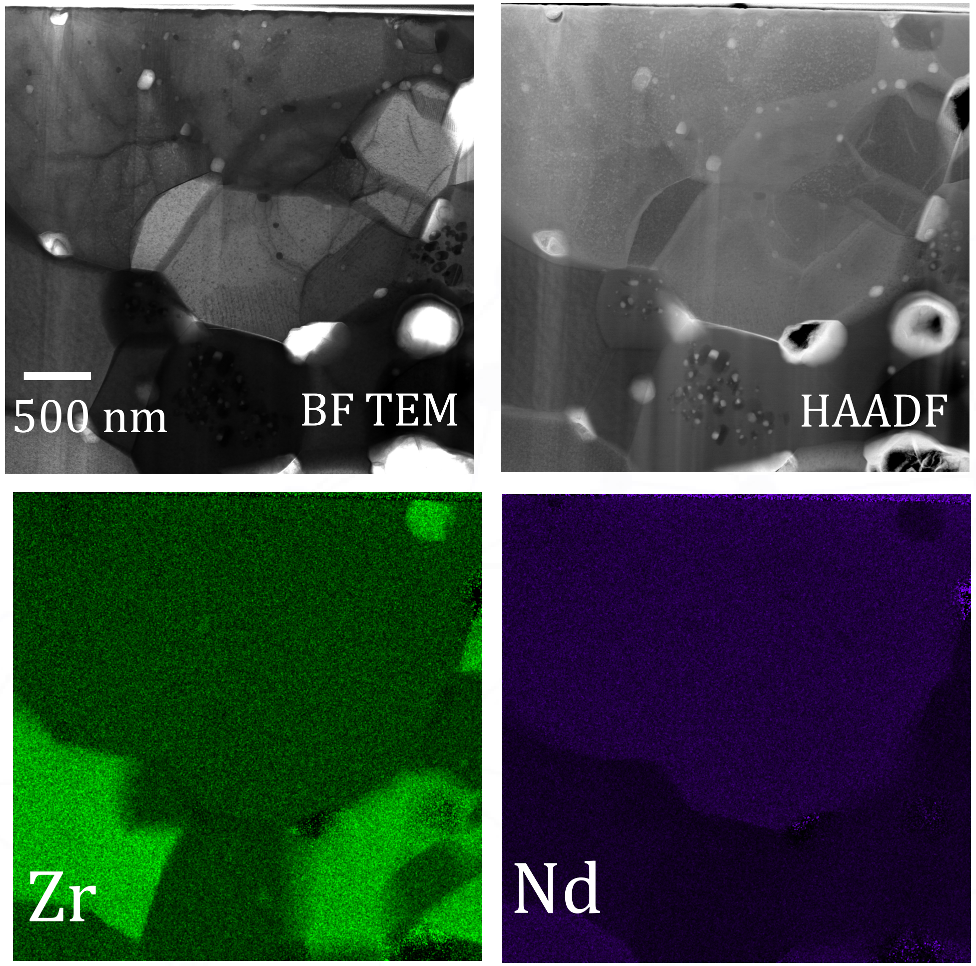
AGR1-433-004

Compact	AGR2-222-RS36	AGR1-433-004
Burnup (%FIMA)	12.55	18.63
Fast neutron fluence (x 10^{25} n/m^2), E>0.18 MeV	3.39	4.16
Time-average volume-average temperature (°C)	1287	1094
Time-average peak temperature (°C)	1354	1179
Safety tested	300 hrs at 1600(°C)	300 hrs at 1600(°C)

- AGR-2 fuel kernel mainly consists of UC, UO_2, $UMoC_2$, $U_2Ru(Tc)C_2$. Safety testing clearly promotes the precipitation of $UMoC_2$ and $U_2Ru(Tc)C_2$ phases.
- Few UC_2 grains were identified at the fuel kernel half center.
- No U_2RuC_2 or $UMoC_2$ precipitates positively identified in AGR-1 fuel kernels (possible correlation between presence of U_2RuC_2/$UMoC_2$ and initial fuel chemistry (significant high content of $UC_{1.86}$ in the AGR-2)).
- Various rod-shaped precipitates observed in fuel center and edge zone of the AGR-1 fuel kernel. EDS maps show that the precipitates are enriched with Rh, Ru, Tc, Pd, w./wo. Mo.

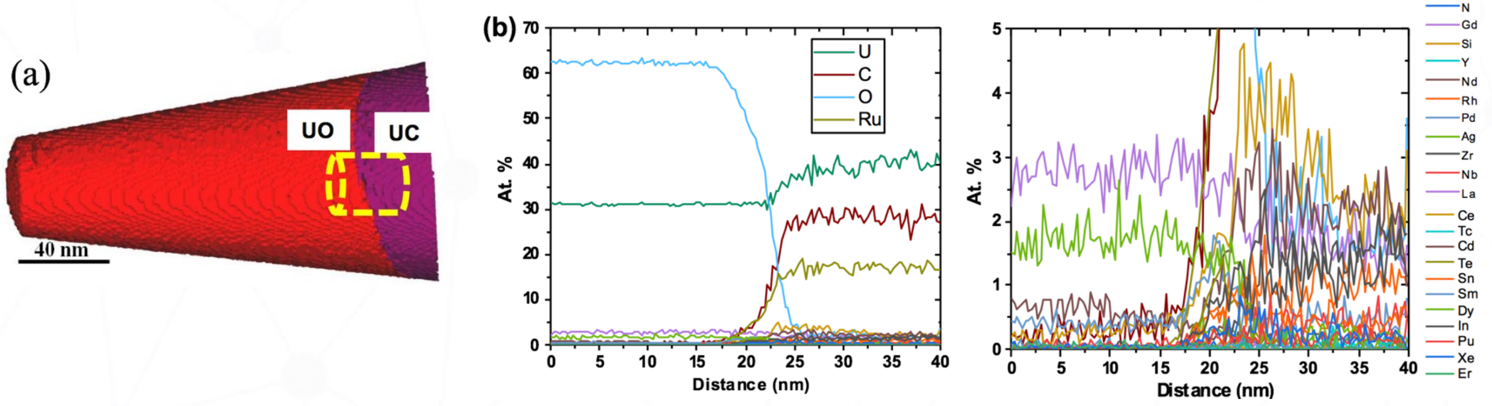
UCO fuel kernel		AGR-1	AGR-2
Diameter (µm)		348.4 ± 8.3	426.7 ± 8.8
Density (g/cm^3)		10.7 ± 0.026	11.0 ± 0.030
^{235}U enrichment (at.%)		19.74	14.03
Chemistry (mole%)	UO_2	67.9	71.4
	$UC_{1.86}$	0.4	12.3
	UC	31.7	16.4

AGR2-222-RS19 Other Fission Products: Ce, Nd, Pr, Sr and Eu



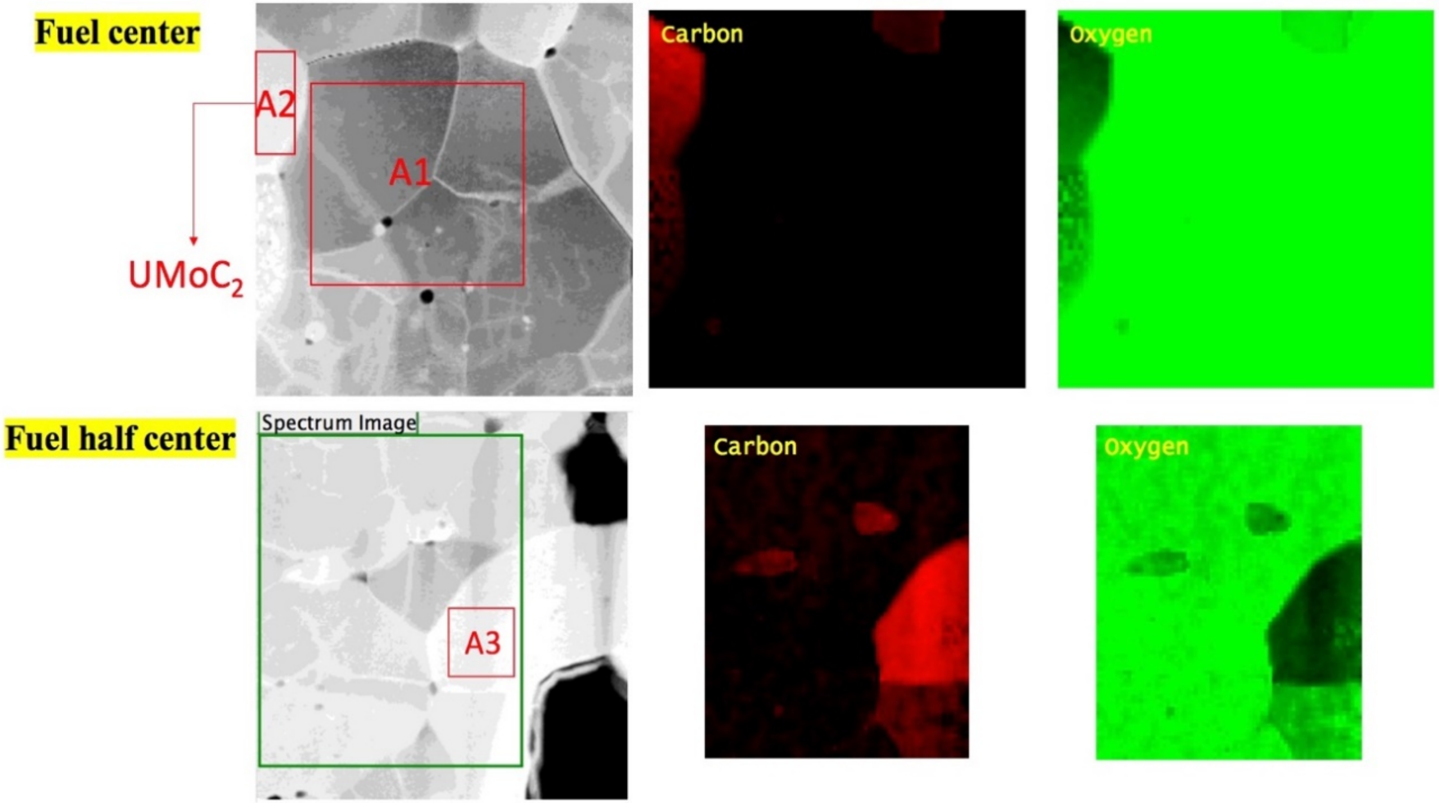
EDS maps from the fuel kernel center for AGR2-222-RS19 particle

- From EDS analysis, only Nd shows enrichment in UO_2 phase, while the other elements were not positively detected (under the detection limit).
- Limited APT work shows enrichment of Nd, Pd in UO_2.
- More APT and TEM work is needed to locate Sr, Eu and other interested fission products. (APT should be calibrated for laser energy as Dy below might be mis-identified).



Preliminary EELS study on AGR2-222-RS36

Area	Element	Relative concentration (at.%)
A1	C	$0 \pm 6 \times 10^{-6}$
	O	100.0 ± 5.0
A2	C	83.0 ± 4.0
	O	16.5 ± 0.7
A3	C	83.0 ± 4.0
	O	16.5 ± 0.7

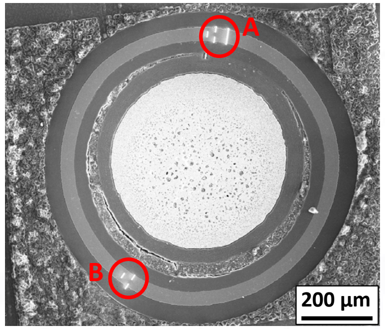


- Additional data collections needed using optimized energy windows and exposure times.
- In both the fuel center and half-center, the UO_2 phase consistently showed almost no carbon, whereas the UC/$UMoC_2$ phase contained a small fraction of oxygen.

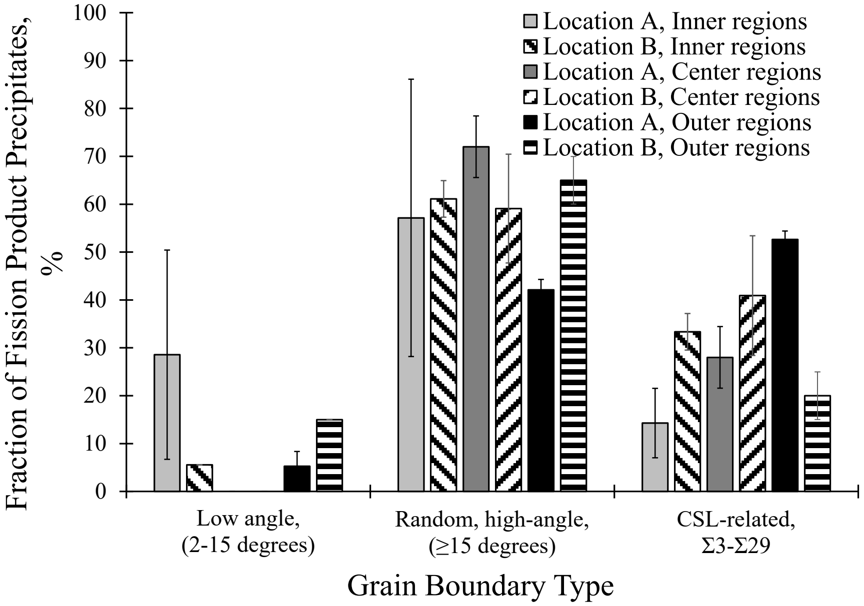
Advanced Microscopy Examination of SiC layer

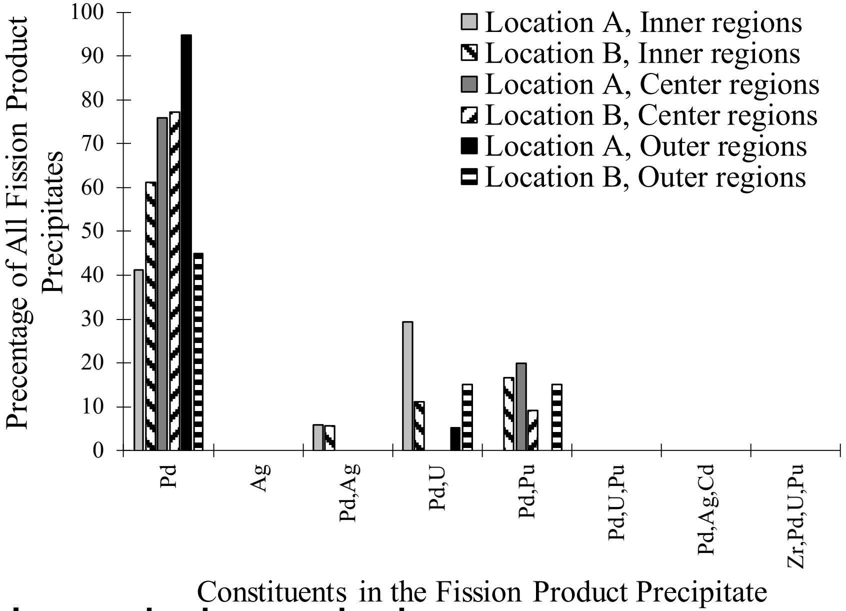
SiC layer examination: Fission Product Transport Mechanisms Safety Tested AGR2-222-RS027

-Ag retention: 11%
-12.55 % FIMA
-1287°C TAVA,
-1354 °C peak T



Location A: Buffer layer intact
Location B: Slightly broken Buffer layer

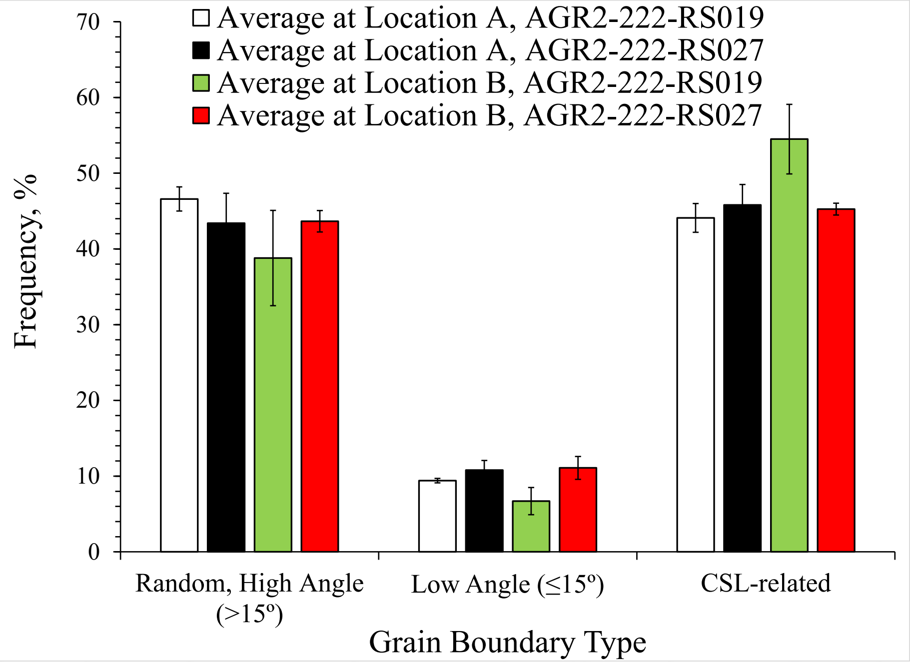


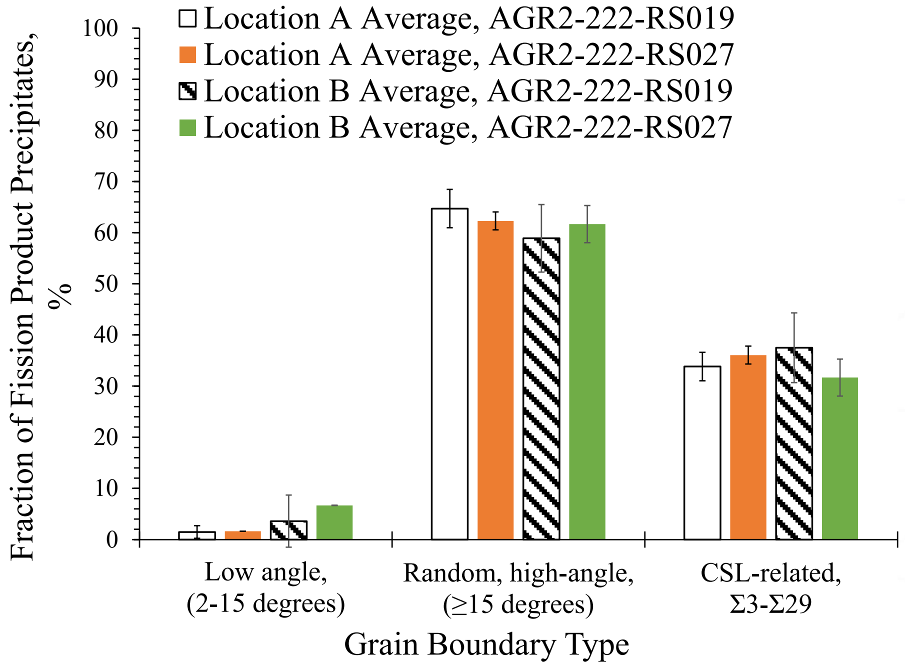


- Most precipitates are associated with random, high-angle grain boundaries
- Small amount of precipitates are associated with low angle grain boundaries
- Ag is observed near IPyC/SiC interfaces and central part of SiC layer
- The compositional complexity of fission product precipitates decreases towards the outer layer

SiC layer examination: Fission Product Transport Mechanisms Comparison of two Safety-Tested AGR2 Particles

- Grain boundary nature & grain boundary precipitation

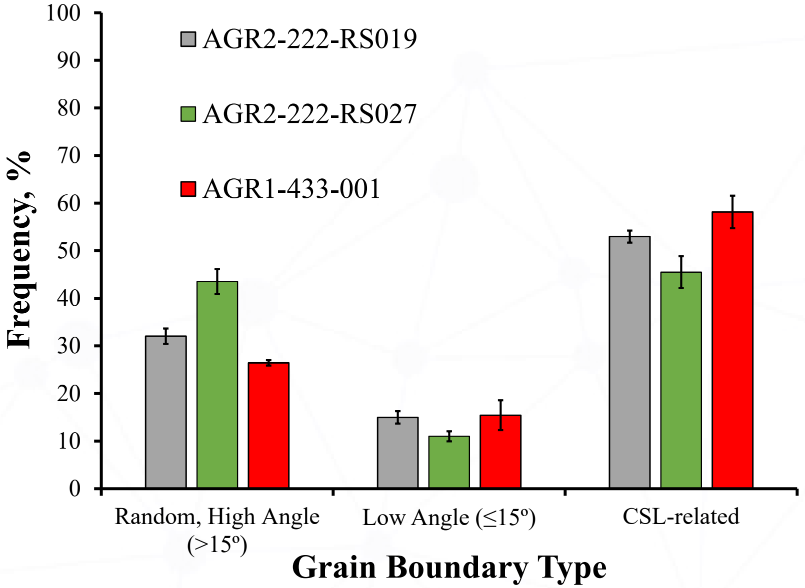


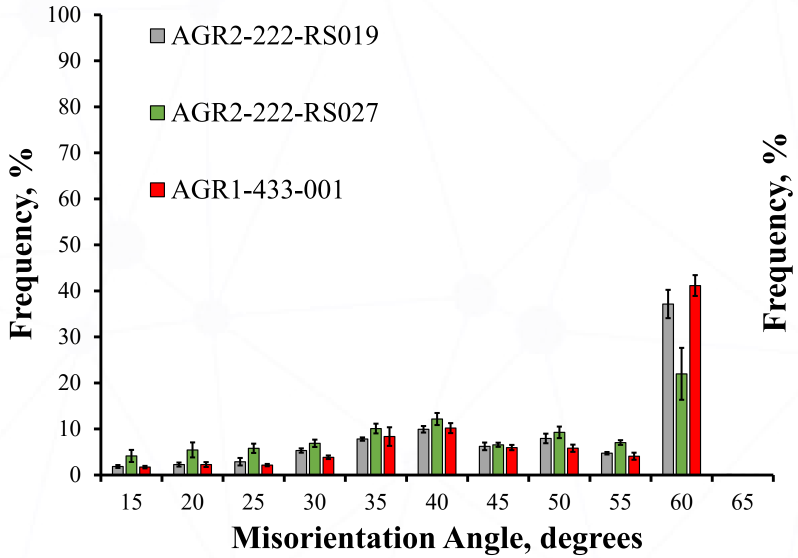


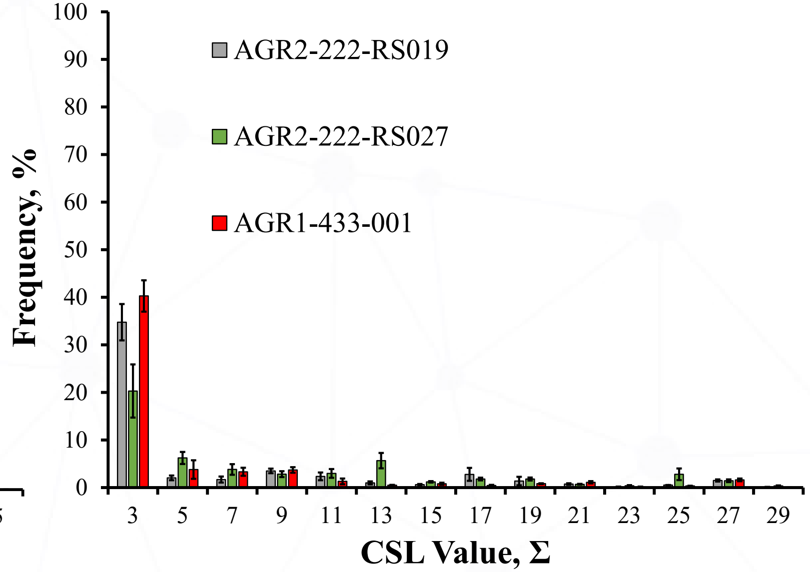
- The grain boundary distribution nature in both AGR-2 particles are very similar
- As expected, most of the fission product precipitates are observed at **high angle grain boundaries**

SiC layer examination: Fission Product Transport Mechanisms Comparison of Safety-Tested AGR-1 and AGR-2 Particles

Differences: Fabrication methods, Ag retention







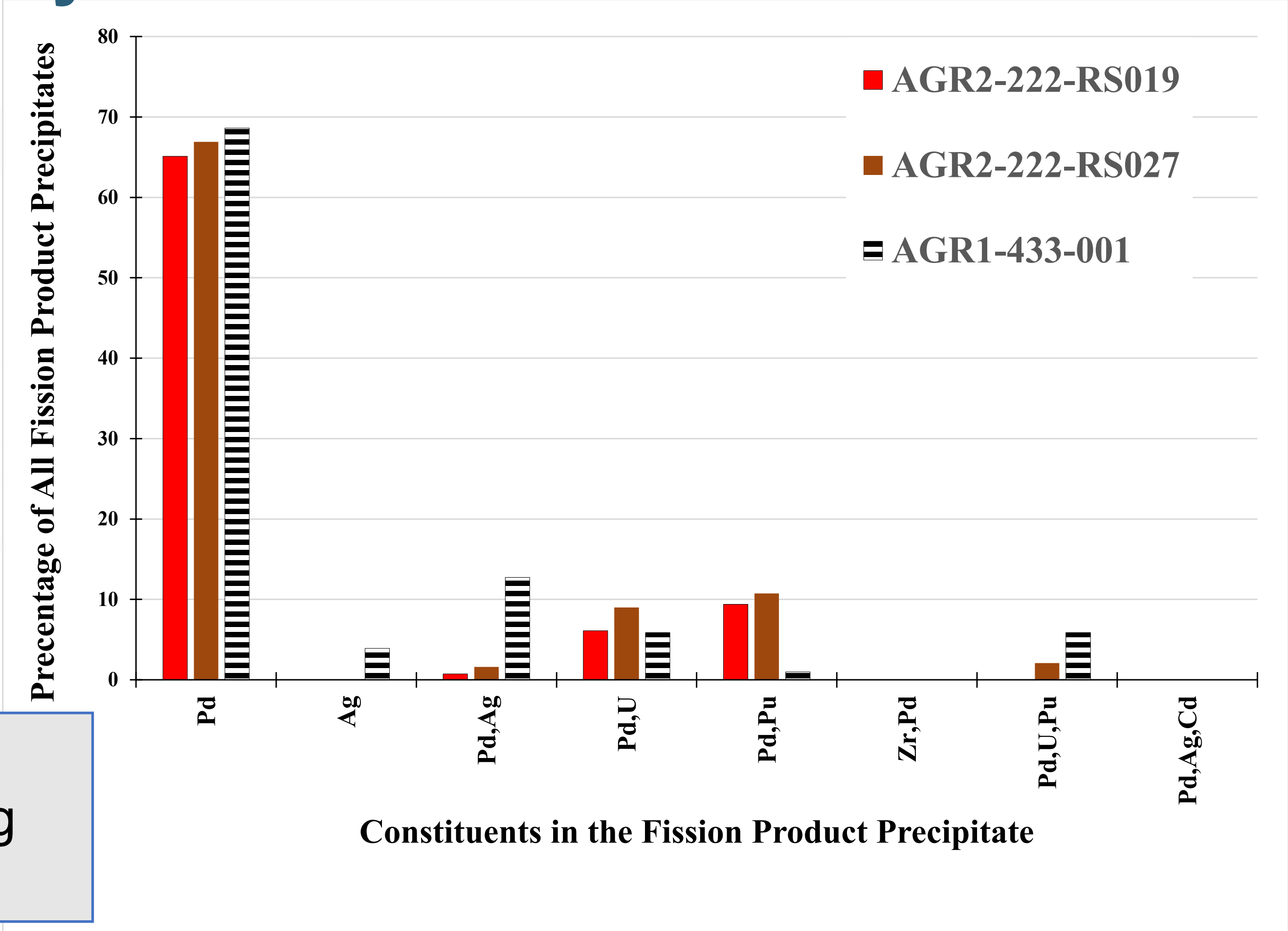
- Both AGR-2 particles have significantly higher percentage of high angle grain boundary = AGR-2 particles may contain larger amount fission products at grain boundary as compared to that in AGR-1 particles.
- Among the AGR-2 particles, the misorientation Angle of 60° in AGR2-222-RS019 particles are very high, possibly due to inherent variations during the fabrication method.

SiC layer examination: Fission Product Transport Mechanisms Comparison of Safety-Tested AGR-1 and AGR-2 Particles

Safety Tested AGR1-433-001
-Ag retention: 11%
-12.55 % FIMA
-1287°C TAVA,
-1354 °C peak T

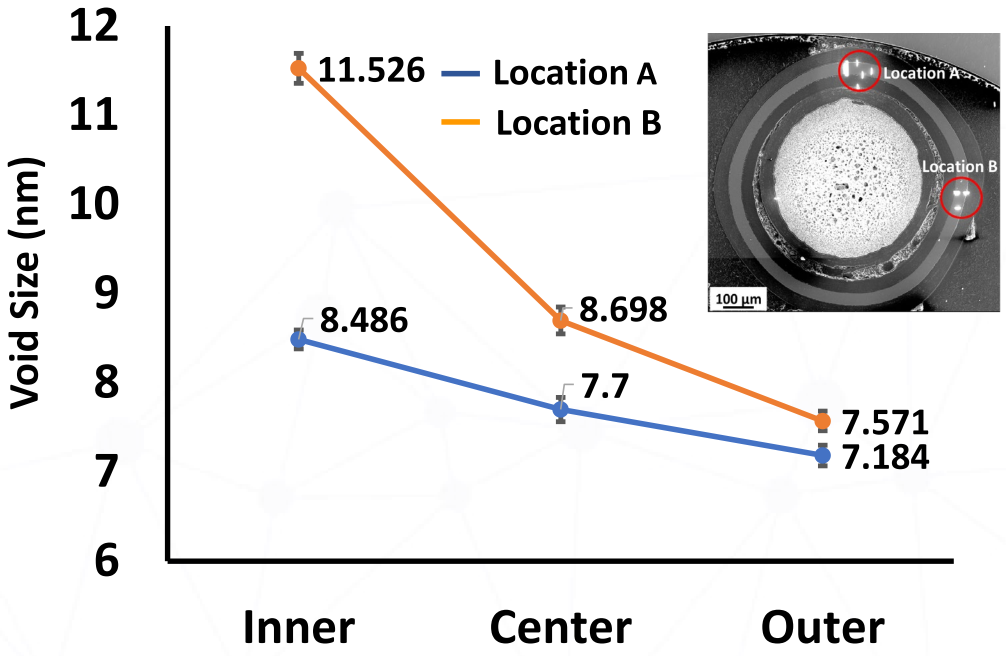
Safety Tested AGR2-222-RS019
-Ag retention: 20%
-12.55 % FIMA
-1287°C TAVA,
-1354 °C peak T

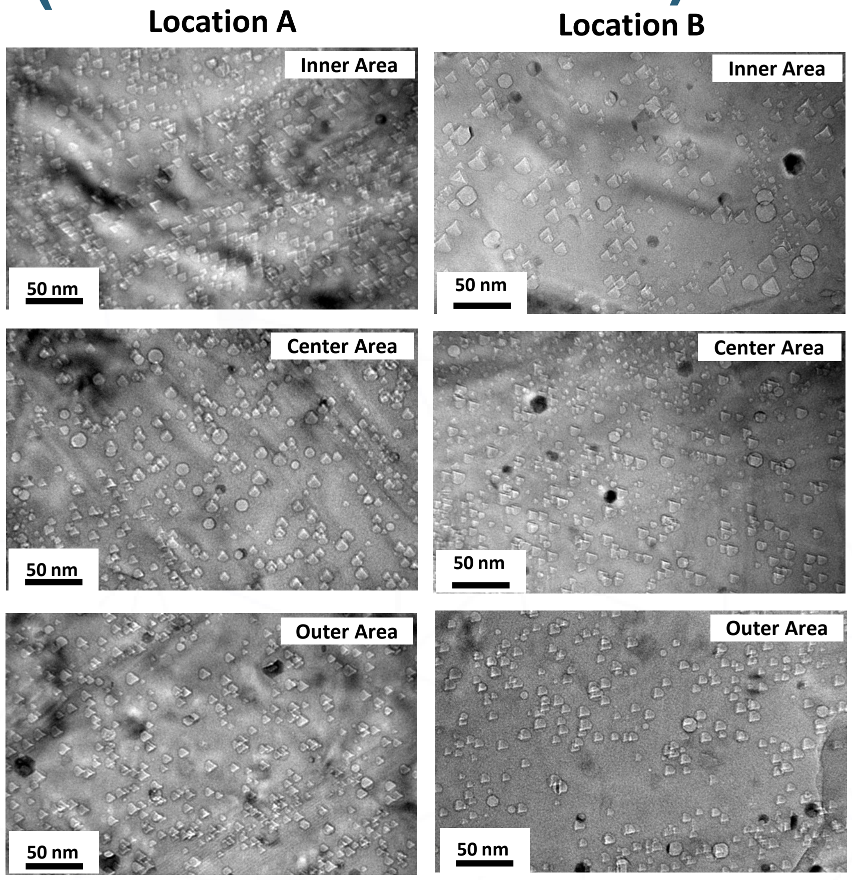
Safety Tested AGR2-222-RS027
-Ag retention: 11%
-12.55 % FIMA
-1287°C TAVA,
-1354 °C peak T



- Exclusively in the AGR-1 particle, some GB precipitates have only Ag as fission product.

Effects of Irradiation on TRISO- SiC layer (AGR2-222-RS019)





- The void sizes are larger in SiC layer adjacent to the region where buffer layer is broken.
- The observed void size variation with integrity of buffer layer can potentially affect the fission product retention.
- Comparison with AGR-1 and other AGR-2 particles are to be completed next.

Preliminary Conclusions

- **SiC layer:**
  - No statistically significant differences in GBC between irradiated AGR-1 and AGR-2 particles, although indications that safety tested AGR-2 particles have more high angle grain boundaries compared to AGR-1 safety tested particle (fabrication?).
  - Compositional complexity of FP precipitates decreases towards the outer layer of SiC.
  - Neutron irradiation damage in AGR-2 particles are larger in SiC layer adjacent to region where buffer layer is broken. This may potentially affect the fission product retention.
- **Irradiated Fuel Kernel:**
  - No palladium was positively identified in the fuel kernel for either AGR-1 or AGR-2 fuel particles.
  - Overall, the identified fission products in the AGR-1 and AGR-2 display the same chemical states.
    - Zr, Mo, Ru and Tc tend to concentrate in the UC phase.
    - Mo, Tc, and Ru starts to precipitate to form $UMoC_2$ or $URu(Tc)C_2$ phases as they exceed the solubility limit in UC phase.
  - Forming Nb oxide at the free surface of pores or cracks.
  - Prominent difference between AGR-1 and AGR-2 (caution: small sample set):
    - AGR-1 fuel preserve as two-main-phases structure with large pores; small gas bubblies in UC phase.
    - AGR-2 fuel shows structure possibly from a strong inter-diffusion between the fuel kernel and buffer layer.
- **Safety Tested Fuel Kernel:**
  - AGR-2 fuel kernel mainly consists of UC, UO_2, $UMoC_2$, $U_2Ru(Tc)C_2$.
  - Few UC_2 grains were identified at the fuel kernel half center.
  - No U_2RuC_2 or $UMoC_2$ precipitates in AGR-1 fuel kernels. (possible correlation between presence of U_2RuC_2/$UMoC_2$ and initial fuel chemistry (significant high content of $UC_{1.86}$ in the AGR-2)).
  - Various rod-shaped precipitates (enriched with Rh, Ru, Tc, Pd, w./wo. Mo) observed in AGR-1 fuel kernel.

Publications and Presentations: FY2020

1. Olivier, E.J., J.H. Neethling and I.J. van Rooyen, Investigation of the structure and chemical nature of Pd fission product agglomerations in irradiated TRISO particle SiC, in press Journal of Nuclear Materials, https://doi.org/10.1016/j.jnucmat.2020.152043, Volume 532, 15 April 2020, 152043
2. Chao Jiang, Isabella J. van Rooyen, and Subhashish Meher, “Ab initio study and thermodynamic modeling of the Pd-Si-C system”, https://doi.org/10.1016/j.commatsci.2019.109238, Computational Materials Science, Volume 171, January 2020, 109238
3. S. Meher, I.J. van Rooyen, C. Jiang, “Understanding of fission products transport in SiC layer of TRISO fuels by nanoscale characterization and modeling”, https://doi.org/10.1016/j.jnucmat.2019.151793, Journal of Nuclear materials, Volume 527, 15 December 2019, 151793
4. Zhenyu Fu, Isabella J. van Rooyen, Mukesh Bachhav, Yong Yang*, “Microstructure and fission products in the UCO kernel of a AGR-1 TRISO fuel particle after post irradiation safety annealing”, https://doi.org/10.1016/j.jnucmat.2019.151884 Journal of Nuclear Materials, Volume 528, January 2020, 151884 (*corresponding author)
5. Zhenyu Fu, Lingfeng He, Isabella van Rooyen, and Yong Yang, Microstructural and micro-chemical characterization of safety tested TRISO UCO Fuel Kernels Irradiated in the Advanced Test Reactor, TMS2020, San Diego, 24-28 February 2020
6. Isabella van Rooyen, Subhashish Meher, Thomas M. Lillo, Neutron irradiation induced intergranular fission product precipitation in SiC layer of TRISO fuel, TMS2020, San Diego, 24-28 February 2020
7. Zhenyu Fu, Isabella J. van Rooyen, Yong Yang* “Comparison of microstructural and micro-chemical evolutions between ATR irradiated AGR-1 and AGR-2 fuel particles”, (*corresponding author), in preparation. To be submitted to Journal of Nuclear Materials
8. Karen E. Wright, John Stempien, Isabella J. van Rooyen, Fission Product Distribution in Irradiated Safety-Tested and Non-Safety-Tested AGR-2 TRISO Particles, (currently in draft form, intended to submit to Journal of Nuclear Materials)
9. Isabella J. van Rooyen, S. Meher, Karen Wright, Thomas Lillo “Overview of Neutron Irradiated SiC Layer Behavior using Micro-and Nano-Characterization Techniques". HTR2020 conference, Indonesia
10. Zhenyu Fu, Yong Yang, Isabella J. van Rooyen, Subhashish Meher, Boopathy Kombaiah, “Microstructural and Micro-Chemical Evolutions in Irradiated UCO Fuel Kernels of AGR-1 and AGR-2 TRISO Fuel Particles”. HTR2020 conference, Indonesia

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- Transmission electron microscopy work was carried out at the Center for Advanced Energy Studies (CAES) Microscopy and Characterization Suite (MACS); IMCL(MFC) and University of Florida

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INL

Idaho National Laboratory

Advanced Microscopy and Micro-analysis Techniques

Fission Product Identification & Location

Microstructure
(Neutron Irradiation Damage (Voids, loops…))

Decontamination in glove box

Electron probe micro-analyzer (EPMA)

Scanning Electron Microscopy (SEM)
- Main elements of precipitates
- Precipitate distribution
- Identify areas for TEM

Electron back scatter diffraction (EBSD)

Focused Ion Beam (FIB)
- Preparation for TEM, STEM, APT, HRTEM
- EBSD, TKD; ASTAR collection

Transmission Electron Microscopy (TEM)
- Micro-Nano sized imaging
- Analytical tools (EDS)
- 2 D imaging

Scanning Transmission Electron Microscopy (STEM)

Energy Dispersive Spectroscopy (EDS)
Energy Filtered TEM (EFTEM)
Electron Energy Loss Spectroscopy (EELS)
- Nano sized imaging
- Analytical tools
- 2 D imaging

Atom Probe (APT)
- 3D analytical tool

High Resolution Transmission Electron Microscopy (HRTEM)
- Atomic structure and imaging
- EELS higher resolution

Transmission Kikuchi Diffraction (TKD)
- Crystallographic information

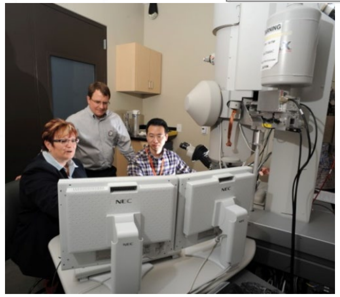
Precession Electron Diffraction (PED)
- Crystallographic information

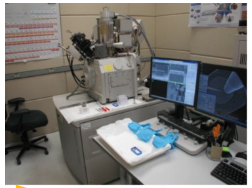
Microstructure

Fission Product Transport

Grain boundary Characteristics

FEI Tecnai G[2] F30 STEM at the Center for Advanced Energy Studies (CAES)

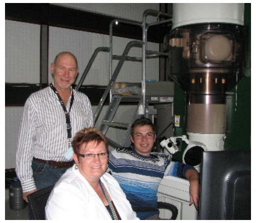




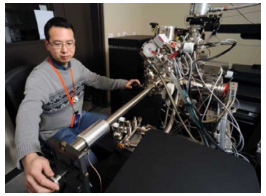
FEI Quanta 3D FEG Dualbeam FIB at EML at MFC

Preferred Methods after AGR-1 Shakedown

Specialized Applications

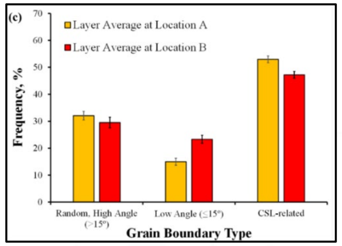


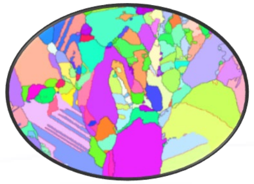
JEOL ARM 200F TEM two CEOS spherical aberration correctors



Cameca LEAP 4000XHR at CAES

Current Focus

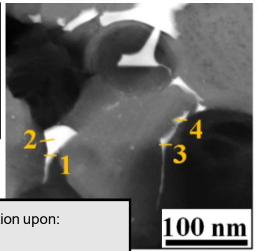




AGR-2 particle examination

Predominantly SiC, IPyC

INL: Subhashish Meher
Karen Wright
Tom Lillo
Isabella van Rooyen
BSU: Yaqiao Wu



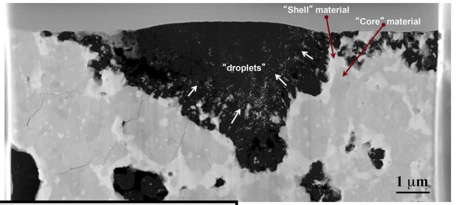
- Characterize effects of Radiation upon:
  - ❖kernel porosity
  - ❖layer degradation or corrosion,
  - ❖layer debonding,
  - ❖fission product precipitation,
  - ❖Microstructure; grain characteristics.
- Determine microstructural differences between particles exhibited high and low releases of Ag-110m

1

Kernel Examination

2

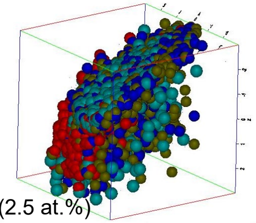
UF: Yong Yang, Zhenyu Fu
INL: Subhashish Meher
Mukesh Bachhaf
Karen Wright
Isabella van Rooyen
LANL: Terry Holesinger



Characterize effects of Radiation upon:
❖kernel porosity
❖layer debonding,
❖fission product precipitation,
❖microstructure

4

Fission Product Transport Mechanism(s)

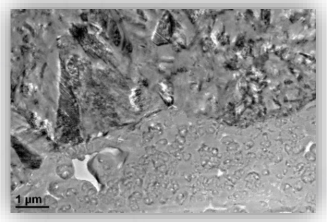


Pd (9 at.%) U (2.5 at.%)
Ag (2.7 at.%) Ru (0.4 at.%)

INL: Isabella van Rooyen
Paul Demkowicz
Paul Humrickhouse
William Skerjanc
Subhashish Meher
and others
Sandia, UF, UM

3

Neutron Irradiation Damage



INL:
Subhashish Meher
Tom Lillo
Jhonathan Rosales
Isabella van Rooyen