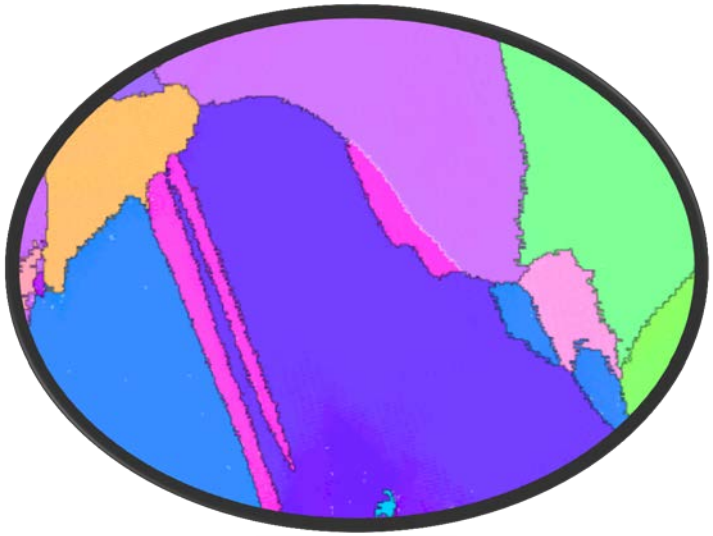
Identification of Nano Crystallographic Parameters of Irradiated SiC to understand Fission product Transport

Isabella van Rooyen, Tom Lillo, Yaqiao Wu

June 24, 2015



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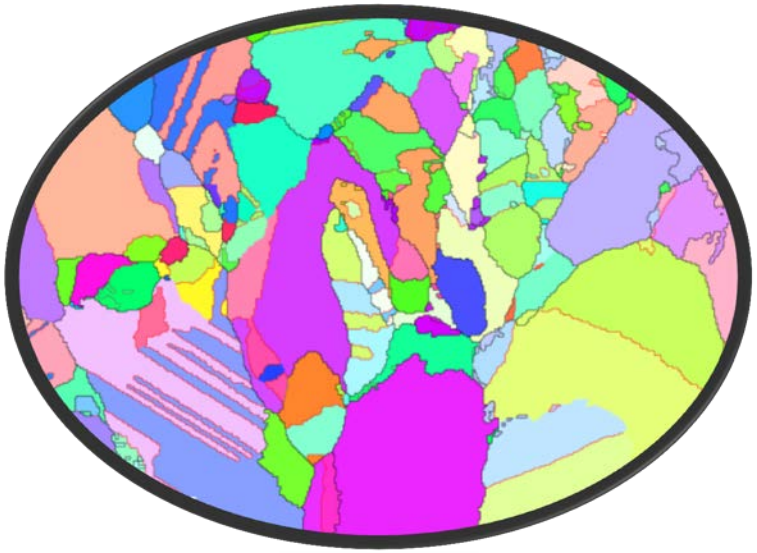
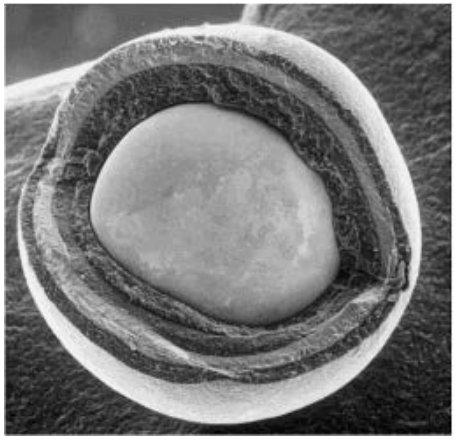
Outline

- Background
- Project Description & Research Approach
- Overview of Crystallographic Techniques Considered
- Preliminary results
- Conclusions
- Activities in progress and collaborations
- Publications and conference papers
- Acknowledgements



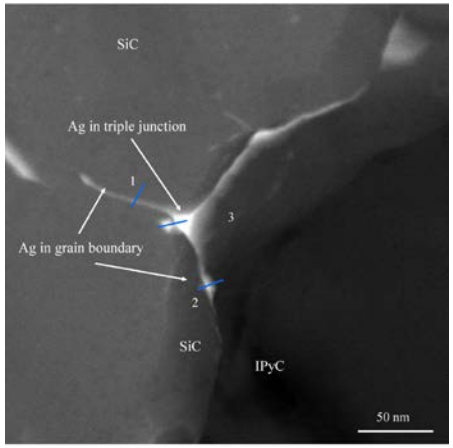
Background: Importance of Silver and Palladium

- TRISO coating is part of high temperature gas reactor (HTGR) functional containment
- Evidence of metallic fission product release through intact TRISO particles found in German studies (1970/1980's) and recent AGR-1 experiment at INL
- ^{110m}Ag release is a potential worker safety concern due to plate-out on cooler turbine metallic parts which can pose a risk for maintenance personnel
- Pd corrosion on SiC layer potentially a problem and was identified as a main constituent of fission product precipitates in initial AGR studies
- Mechanism of ^{110m}Ag transport in intact SiC layer of TRISO coated particles (CP) studied for ~ 40 years without satisfactory result
  - Various Ag transport mechanisms studied:
    - Grain boundary diffusion
    - Vapor transport
    - Radiation –Induced Point Defects/Voids



Background

- ***First*** microscopic evidence of silver in ***irradiated*** SiC structures
  - ✓ Discovered March 2013 on INL AGR-1 TRISO particle (Published 2014)
  - ✓ Idaho National Laboratory & Boise State University Research Team



[*I.J. van Rooyen et al. / Journal of Nuclear Materials 446 (2014) 178–186*]

- Knowledge gaps still exists:
  - ✓ Accurate quantification of elemental composition
  - ✓ Accurate distributions of elements in a specific precipitate
  - ✓ Phases of precipitates
  - ✓ Fission product transport mechanisms through “intact” layers---specifically Ag and Pd
  - ✓ Crystallographic properties
- Leads to exploration of more advanced electron microscopy and micro-analysis techniques

Previous AGR-1 Electron Microscopy Results

- Can use STEM with HAADF in conjunction with EDS to identify fission product precipitates (Pd, Ag, and U)
- Precipitates are very small with relatively low concentrations
  - Intragranular Pd precipitates, ~10 nm
  - Intergranular Pd, Ag and/or U, generally less than 10 at%
- Pd found alone, in conjunction with Ag or in conjunction with U
- Ag and U never found together
- Extent of fission product migration differs for the different elements
- Not all grain boundaries contained fission product precipitates

Results suggest grain boundary character may play a role in fission product migration

- *TM Lillo, IJ van Rooyen, "Associations of Pd, U and Ag in the SiC Layer of Neutron-Irradiated TRISO Fuel,"* Journal of Nuclear Materials (2015), pp. 97-106, DOI information: 10.1016/j.jnucmat.2015.02.010.
- Bin Leng, Isabella van Rooyen, Yaqiao Wu, Izabela Szlufarska, Kumar Sridharan, *STEM/EDS Analysis of Fission Products in Irradiated TRISO Coated Particles of the AGR-1 Experiment*, peer review comment resolution in process, to be submitted to Journal of Nuclear Materials
- Haiming Wen, Isabella J van Rooyen, Connie Hill, Tammy Trowbridge, Ben Coryell, *Fission product distribution in TRISO coated particles neutron irradiated to 3.22 X 10^{25} n/m2 fast fluence at 1092°C*, ASME Power and Energy 2015, June 28 – July 2, 2015, San Diego, California
- IJ van Rooyen, EJ Olivier, JH Neethling, *Investigation of the Fission products silver, palladium and cadmium in neutron irradiated SiC using a Cs-corrected HRTEM*, Paper HTR2014-31255, Proceedings of the HTR2014, Weihai, China, October 27-31 (2014)

Approach and Electron Microscopic Techniques

Decontamination in glove box

Electron probe micro-analyzer (EPMA)

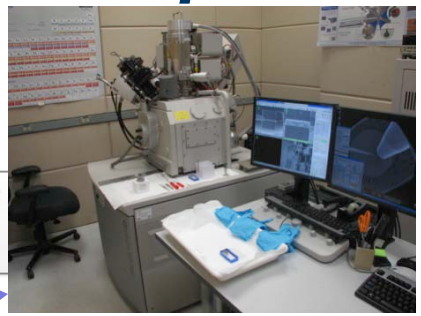
Scanning Electron Microscopy (SEM)

- 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



FEI Quanta 3D FEG Dualbeam FIB at EML at MFC

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

ASTAR ★

- Crystallographic information

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

Overview of Crystallographic Techniques

Conventional EBSD

Mounted sample
Micro examination
SEM

Transmission Kikuchi Diffraction

TEM lamella
Micro & Nano Examination
SEM

Transmission Precession Diffraction

TEM lamella
Micro & Nano Examination
TEM

Polished mounted TRISO particles
- Tested successfully on unirradiated SiC (various references)
- Not achieved yet on irradiated TRISO

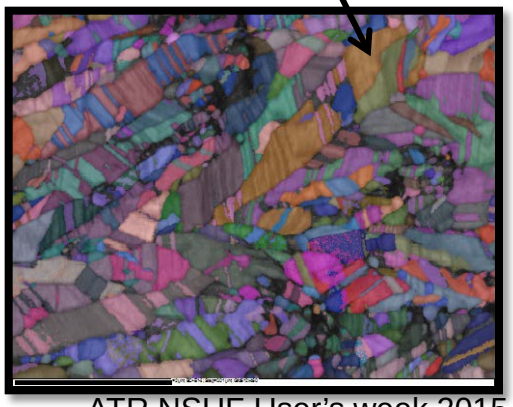
FIB polished surface
- Tested successfully on unirradiated AGR SiC
- Not feasible on irradiated TRISO mounts (no cutting allowed, size limitation)

FIB prepared Thick Lamella
- Modified method tested on unirradiated SiC (NSUF project)
- Partially successful on irradiated AGR1 SiC (equipment limitations/ damage)

- Time delays between modification of surface prep
- Detectors out of operation
- Equipment Scheduling conflicts

FIB-TEM lamella
- Tested successfully on unirradiated SiC from AGR-1 TRISO(May 2013)
- Tested successfully on unirradiated & irradiated research SiC (June 2013)
- Tested successfully irradiated SiC from AGR-1 TRISO (**Sept 2013**)

- Collaboration (Bruker nano & NMMU)
- Can be used as micro- and nano measurement
- **Resolution ~ 10 nm**



FIB-TEM lamella
- Boise State University research SiC (Sept 2013)
- 2014 NSUF funding proposal with BSU

- Very advantageous
- **Resolution ~ 1 to 2 nm (TEM mode)**

★ ★ ★

Project Description

Research Question

The proposed study aims to gain insight into a possible link between crystallographic information and fission products location and compositional analysis in the silicon carbide (SiC) layer of the TRISO fuel. By having this information, more knowledge is gained to identify a transport mechanism for these fission products, especially for Ag through the SiC layer.

FIB sample preparation

Experimental

Equipment time and support funded by ATR-NSUF

- **Effect of lamella thickness on PED results (EELS)**
- **Crystallographic characteristics (PED)**

Interpretation & correlation with AGR -STEM examination

Funded by INL-AGR

Collaborators:

- Isabella van Rooyen (Idaho National Laboratory): PI
- Yaqiao Wu (Boise State University, CAES): Co-PI
- Tom Lillo (Idaho National Laboratory): Co-PI
- Dr John Youngsman (Boise State University, CAES): Team Member
- James Madden (Idaho National Laboratory): Team Member
- Haiming Wen (Idaho National Laboratory: Post-Doctoral Researcher): Team Member

Expected Outcomes for Precession Electron Diffraction (PED) measurements

- Implement emerging technique to map crystallographic orientation in the TEM for irradiated materials
- Determine the influence on sample thickness on the quality of crystallographic orientation data
- Crystallographic orientation data from PED will be used to determine grain boundary misorientation of grain boundaries with and without fission products.
  - Determine whether fission products are associated with “special” grain boundary misorientation (CSL boundaries, high angle or low angle)
  - Determine which grain boundary types will not support fission product migration
- Provide information on the fission product transport mechanism for subsequent modeling of fuel behavior during irradiation

Preliminary Results: Crystallographic Information (PED) ASTAR

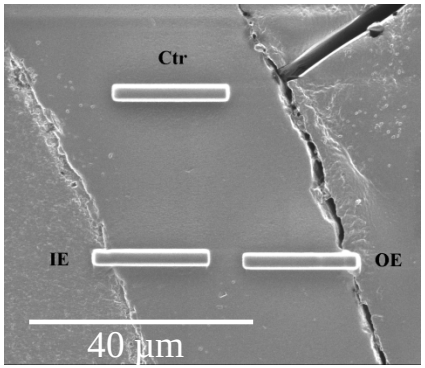
NSUF RTE13-460

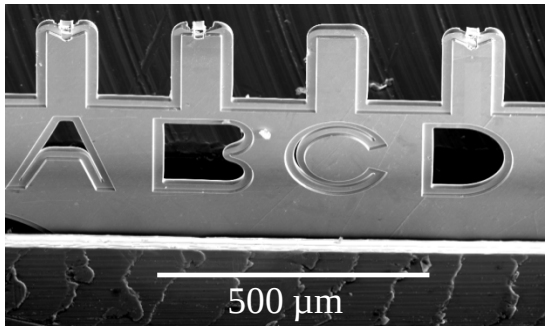
Experimental

- Grind and polish to approximately mid-plane of TRISO particle
- Extract and thin lamellae, oriented radially, using FIB
- Identify fission product precipitates using STEM HAADF - Tecnai TF30-FEG STwin, 300 kV, Center for Advanced Energy Studies
- Identify fission product elements using EDS
- Collect grain orientation data using ASTAR, 5 nm beam diameter, 10 nm step size
- Analyze grain orientation and grain boundary information using EDAX, OIM software (Orientation Imaging Microscopy, Version 7.1)

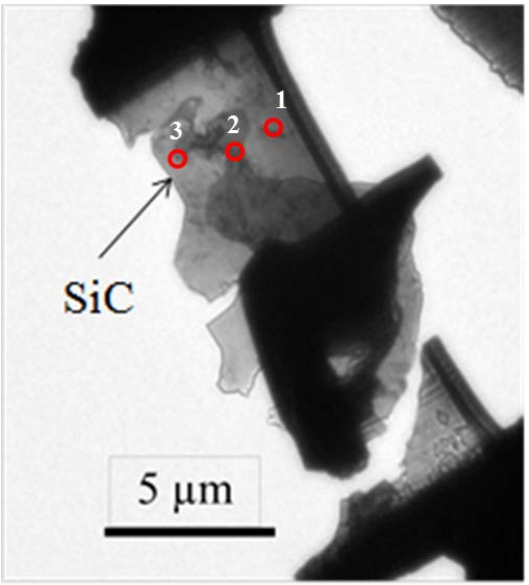
Table 1. Irradiation Parameters for TRISO Particle

Parameter	Value
% FIMA average burnup	11.3
Time-average, volume average temperature, °C	1070
Time-average, maximum temperature, °C	1144
Approximate time-at-temperature, days	620.2
Approximate fast fluence, n/cm^2	2.38 x10^{23}
Fuel type	Baseline

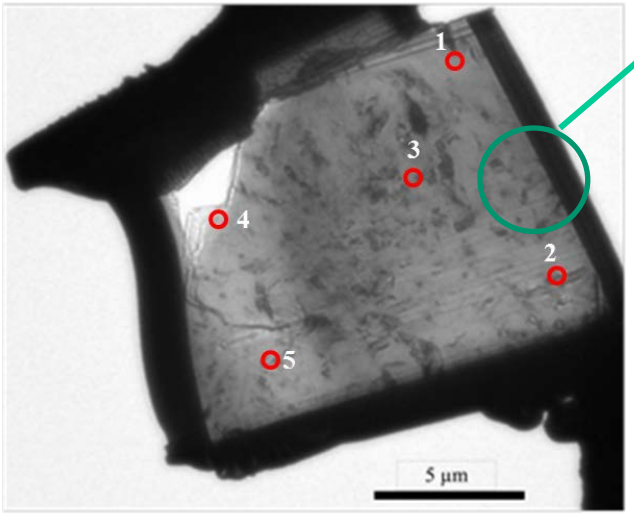




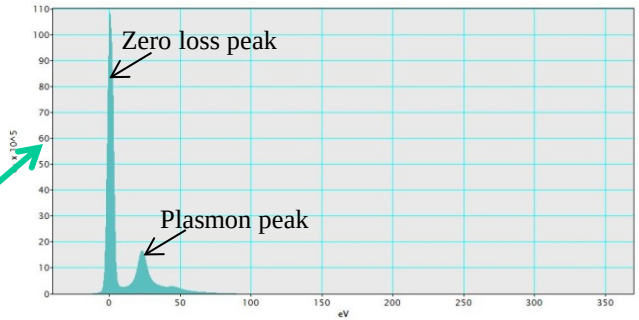
Thickness Measurement Results



Post A



Post D



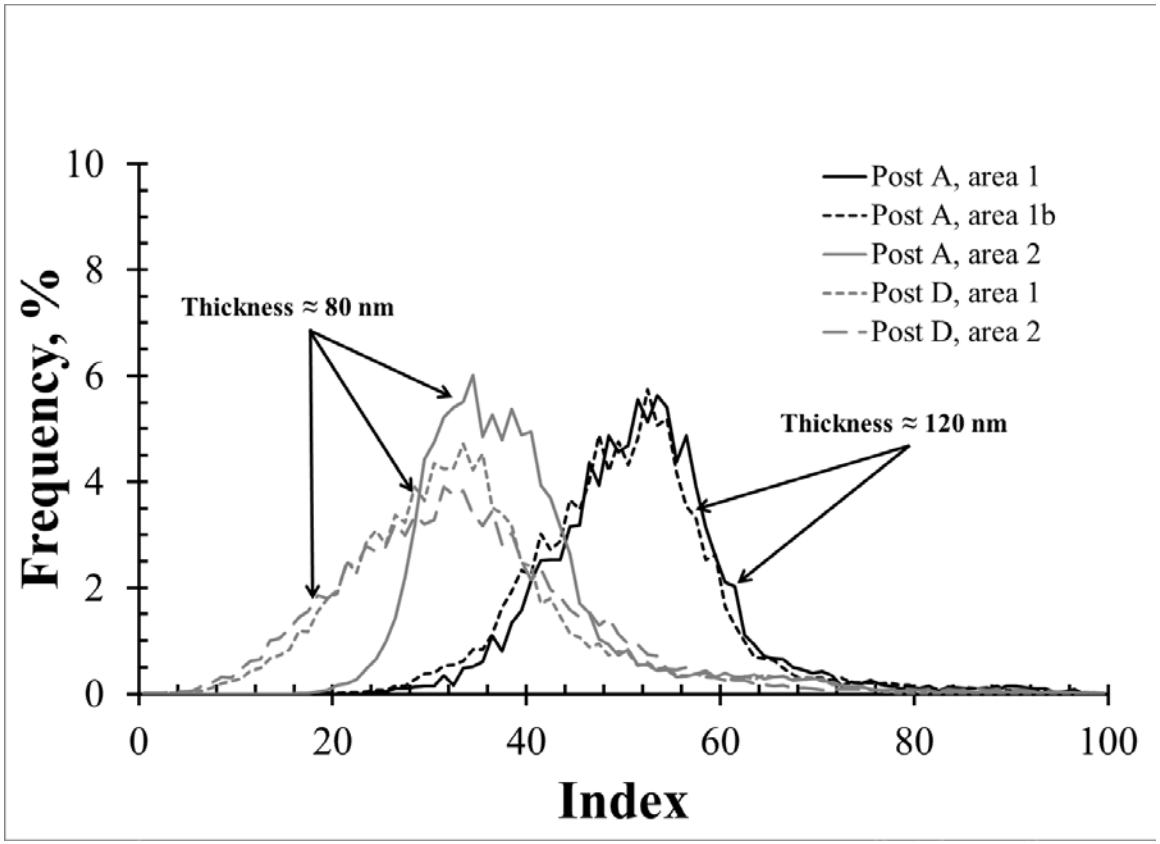
An EELS spectrum for thickness measurement, which was obtained from location #2 of the TRISO lamella sample Post D.

Point #	EELS Thickness, nm
1	117
2	76
3	82

Point #	EELS Thickness, nm
1	65
2	82
3	103
4	60
5	71

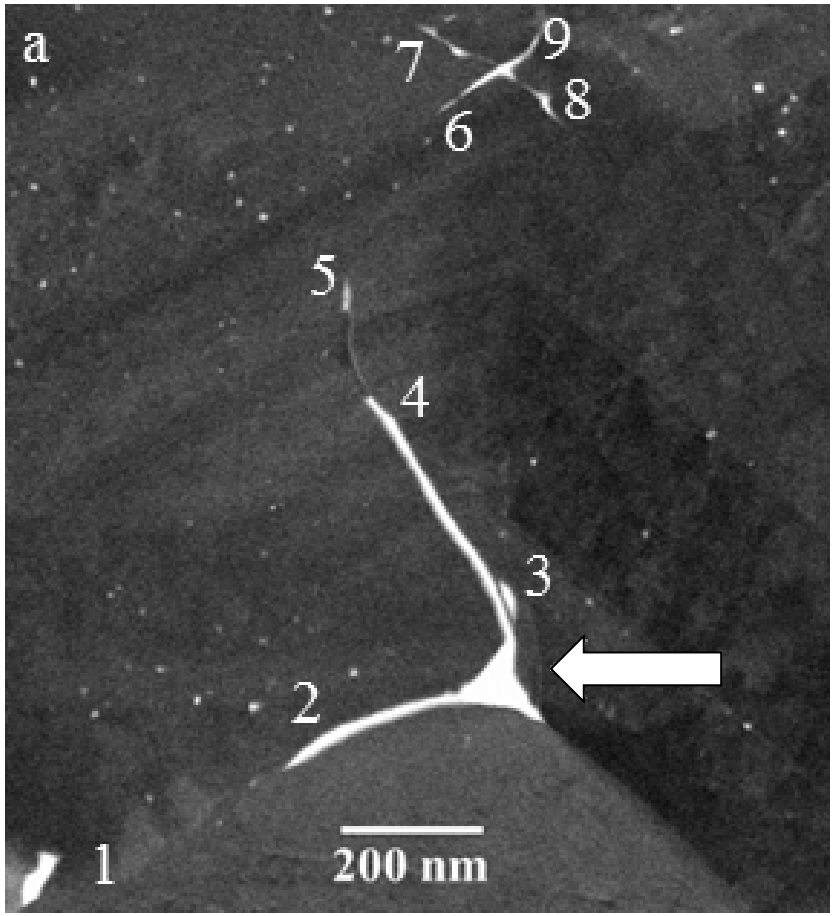
Effect of FIB-lamella thickness: PED measurements (Unirradiated SiC)

- Quality of orientation assignment by PED (ASTAR) indicated by "Index" parameter – larger value indicates high quality
- Thicker samples produce higher average values of the index parameter – thicker samples produce higher quality orientation data
- At some point, overlapping grains will degrade data – grain size dependent

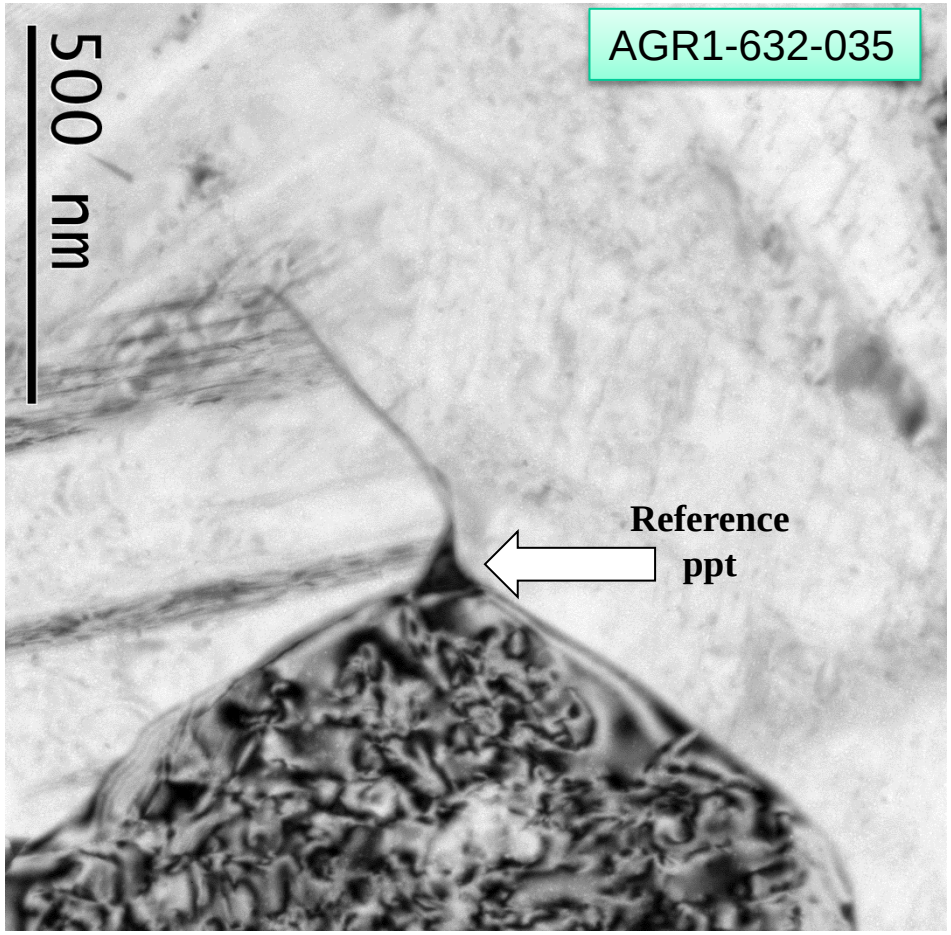


- I. J. van Rooyen, J. Youngsman, T. M. Lillo, Y. Q. Wu, D. Goran, M. E. Lee, W. E. Goosen5, J. H. Neethling, T. L. Trowbridge and J. W. Madden, Methods for identification of crystallographic parameters of irradiated SiC to understand fission product transport, The 3rd Workshop on HTGR SiC Material Properties, Sept. 30-Oct 1, Jeju Island, South Korea
- T. Lillo, I.J. van Rooyen, "Precession Electron Diffraction for SiC Grain Boundary Characterization in unirradiated TRISO Fuel", to be submitted to Nuclear Engineering and Design or the Journal of Nuclear Materials, June/July 2015
- Isabella J van Rooyen, Yaqiao Wu, Tom Lillo, John Youngsman and Jan H Neethling, Approach and Micro-analysis techniques applied to study fission product transport mechanisms in neutron irradiated SiC layers, IMRC XXIII, Cancun, Mexico, August 17-21, 201

Iradiated SiC PED Experimental Results



STEM - HAADF

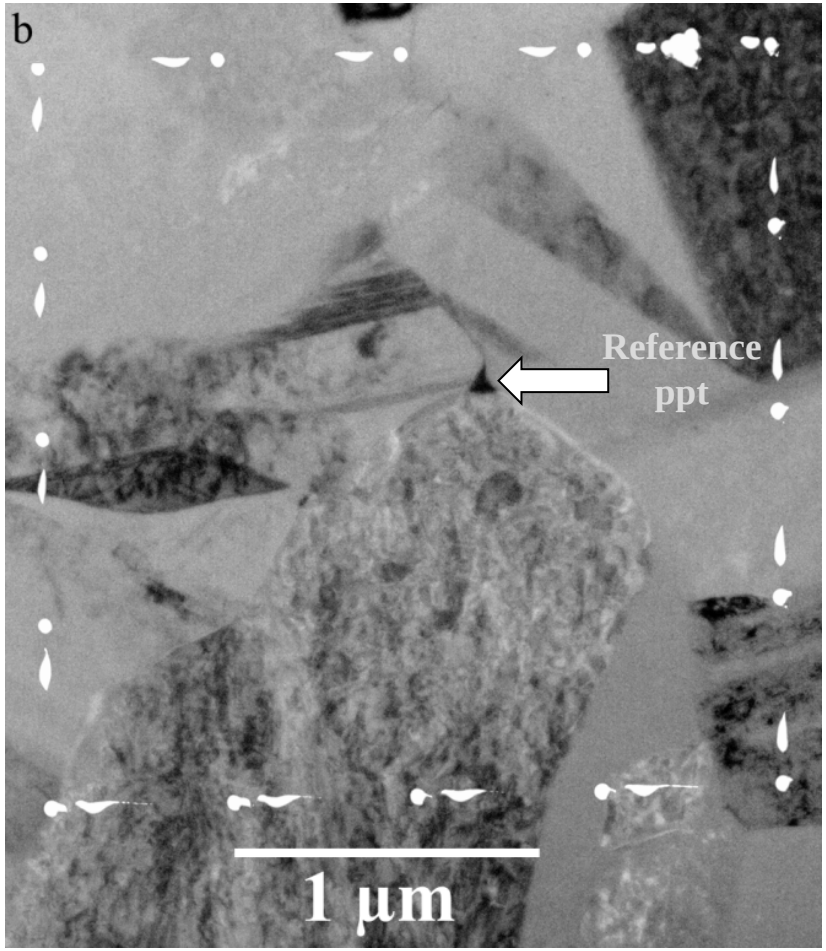


Bright Field TEM

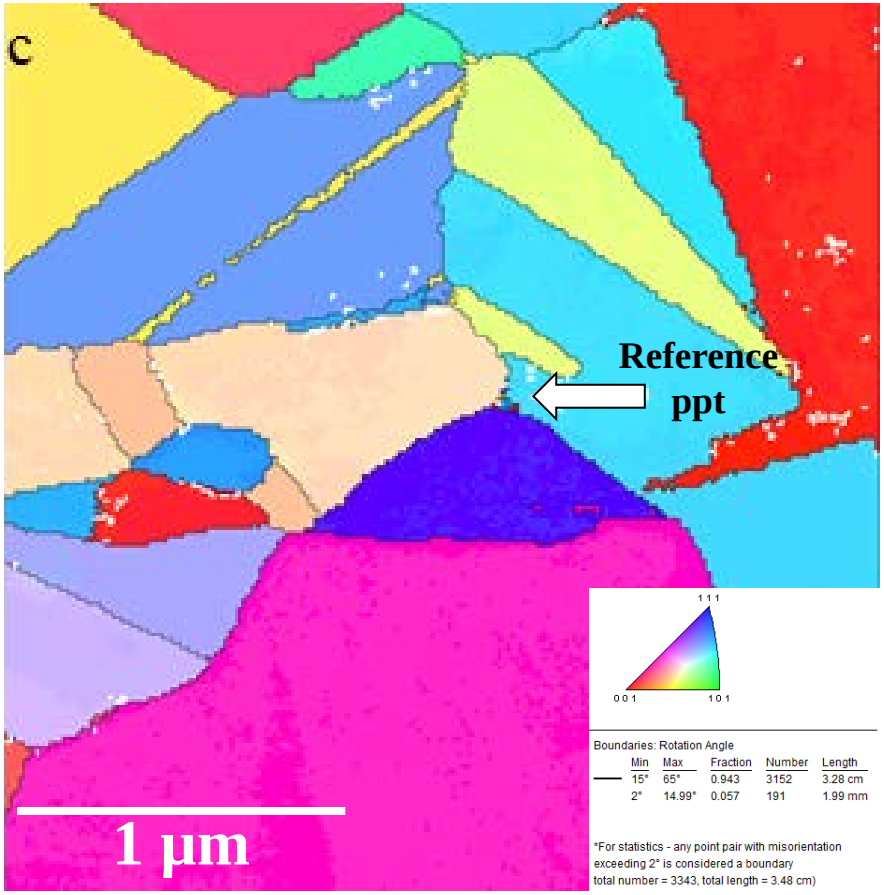
T. Lillo, I.J. van Rooyen, "Influence of SiC Grain Boundary Character on Fission Product Transport in TRISO Fuel" Draft in progress, to be submitted to the Journal of Nuclear Materials, July 2015

Grain Orientation Map from PED data

AGR1-632-035



TEM with scan area



Orientation image:

High angle grain boundaries – black
Low angle grain boundaries - white

T. Lillo, I.J. van Rooyen, "Influence of SiC Grain Boundary Character on Fission Product Transport in TRISO Fuel" Draft in progress, to be submitted to the Journal of Nuclear Materials, July 2015

Summary PED measurements: Grain boundary Misorientation Angle

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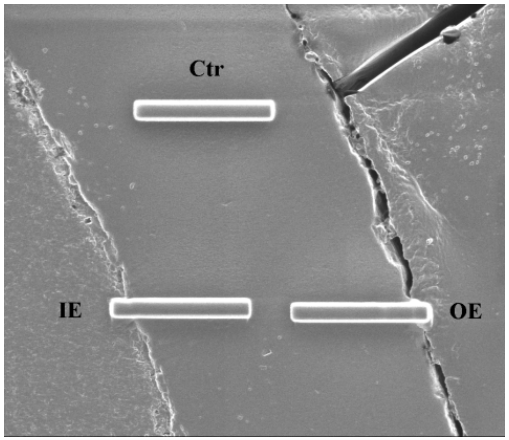
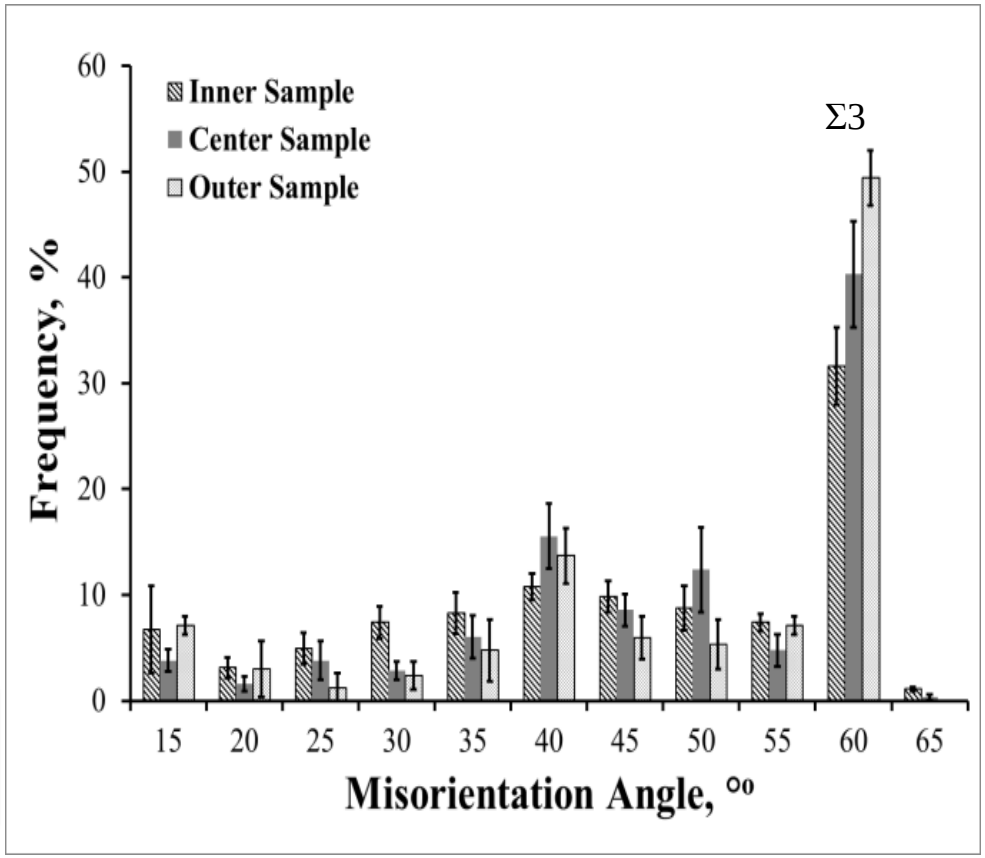


- Total number of grain boundaries analyzed > 900
- Only 11.1% of boundaries analyzed contain fission products



- Majority of grain boundaries: Twin boundaries, with a 60° misorientation angle; smaller peak in distribution occurs around 40°.
- The only difference among Ctr, IE, OE: frequency of twin boundaries.
  - significantly fewer twins in the IE sample where growth the SiC layer began, compared to the OE sample

T. Lillo, I.J. van Rooyen, "Influence of SiC Grain Boundary Character on Fission Product Transport in TRISO Fuel" Draft in progress, to be submitted to the Journal of Nuclear Materials, July 2015

Summary of All PED measurements: Grain boundary type

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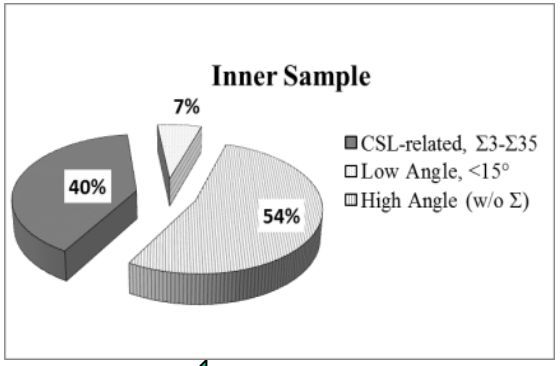
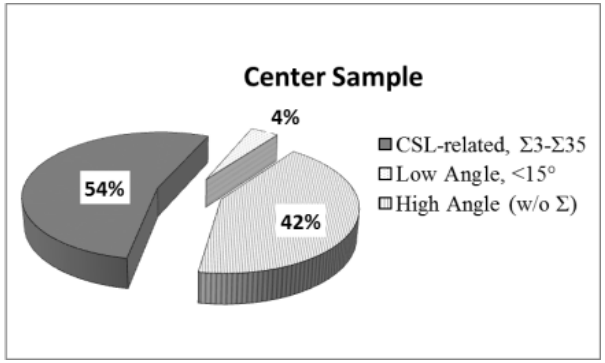
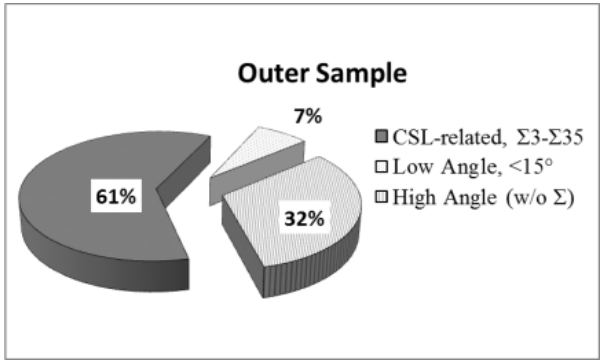
CSL-related grain boundary fraction







Fraction of random, high angle grain boundaries

Fraction of low angle grain boundaries is relatively constant across the thickness (< 10% of grain boundaries)

T. Lillo, I.J. van Rooyen, "Influence of SiC Grain Boundary Character on Fission Product Transport in TRISO Fuel" Draft in progress, to be submitted to the Journal of Nuclear Materials, July 2015

Summary of All PED measurements: Fission product precipitates on the various boundary types

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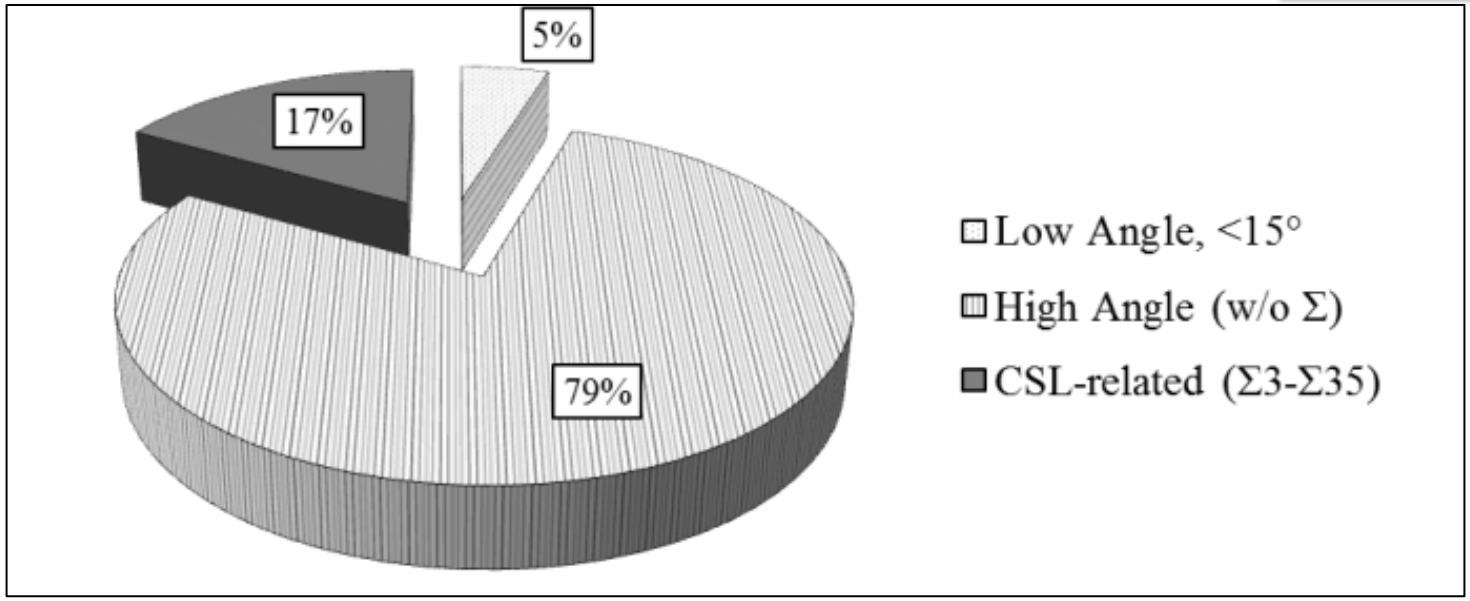

Fission products favor precipitation on random, high angle grain boundaries but can precipitate out on low angle and CSL-related grain boundaries to a limited degree.

T. Lillo, I.J. van Rooyen, "Influence of SiC Grain Boundary Character on Fission Product Transport in TRISO Fuel" Draft in progress, to be submitted to the Journal of Nuclear Materials, July 2015

Distributions of Fission Products by Grain Boundary Type.

T. Lillo, I.J. van Rooyen, "Influence of SiC Grain Boundary Character on Fission Product Transport in TRISO Fuel" Draft in progress, to be submitted to the Journal of Nuclear Materials, July 2015

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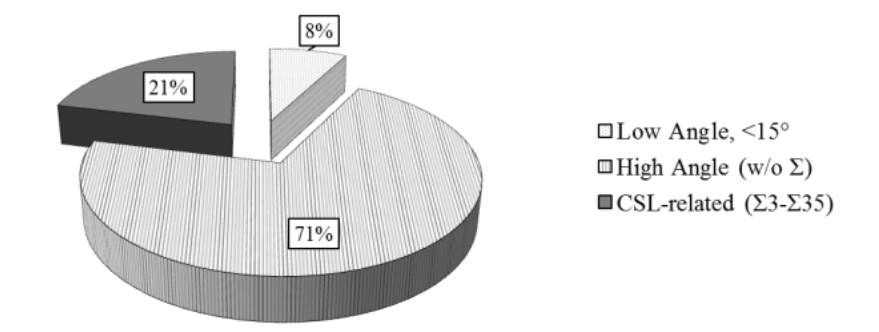
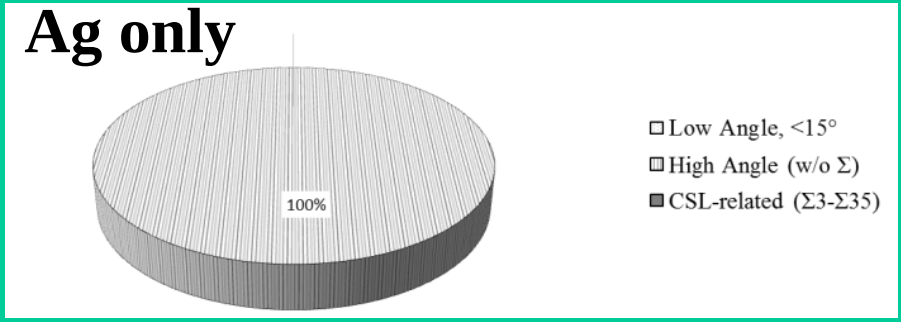
All three grain boundaries types

Pd only



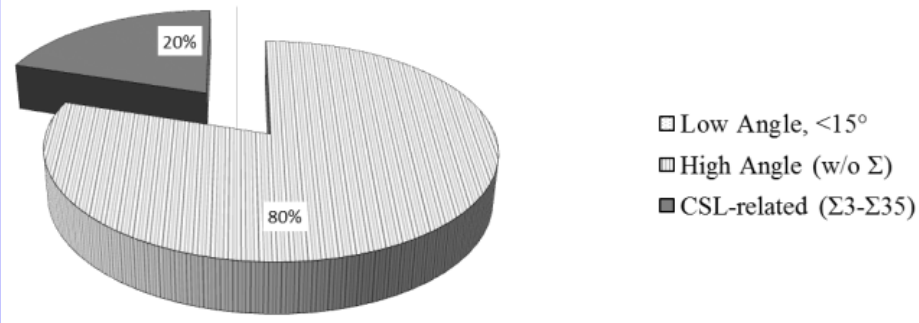
Random, high angle boundaries, never low angle or CSL related boundaries

Ag only

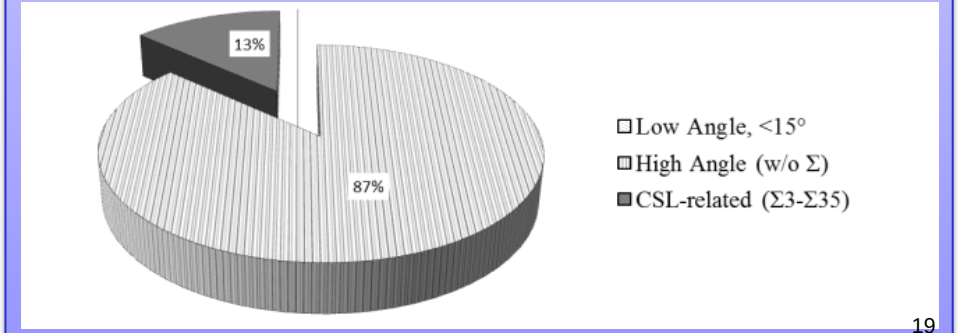


No low angle boundaries

Pd+Ag



Pd+U



Continuing work under AGR

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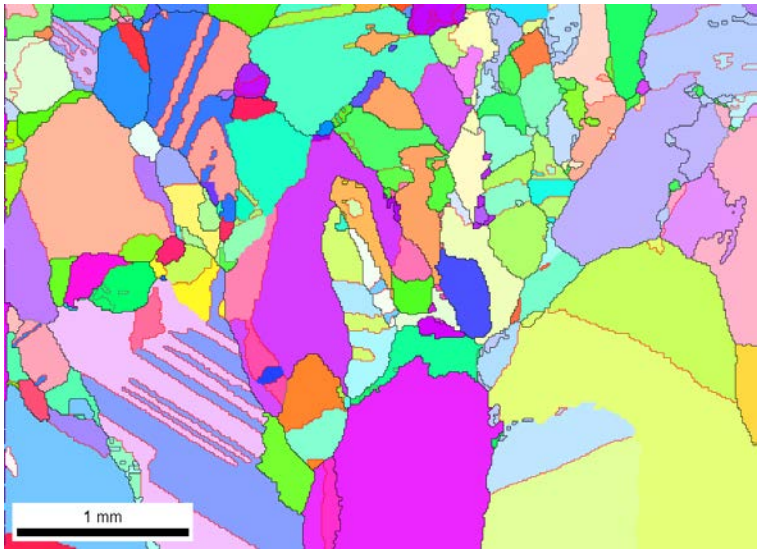
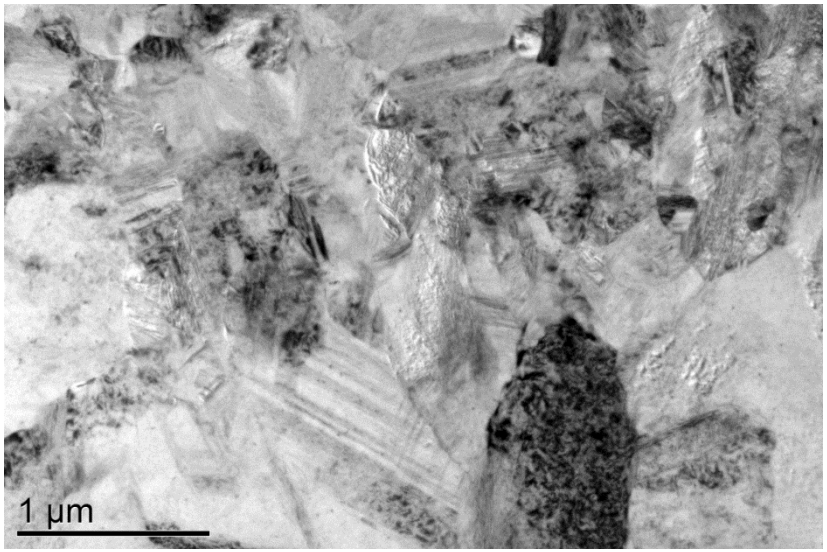




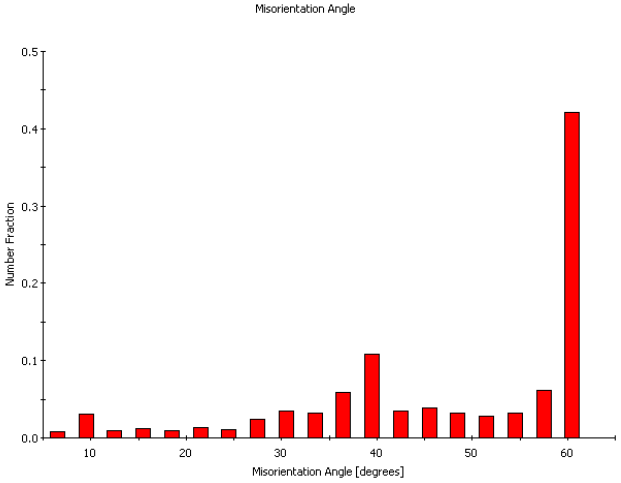
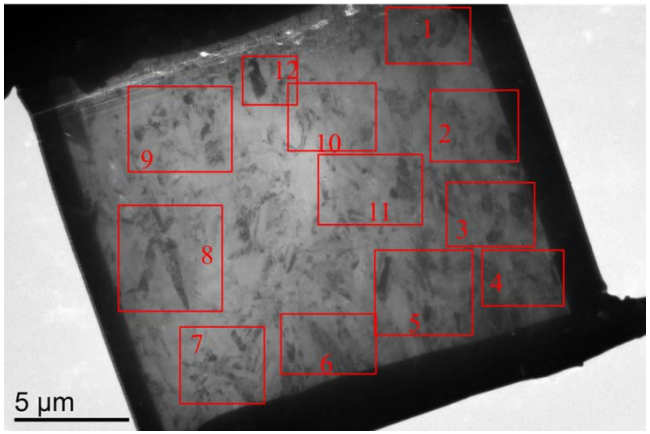


Chart: Misorientation Angle

Angle [degrees]	Number Fraction
6.5	0.00847126
9.5	0.0303613
12.5	0.00886279
15.5	0.011817
18.5	0.00872041
21.5	0.0132764
24.5	0.0107136
27.5	0.0240612
30.5	0.0353088
33.5	0.0321054
36.5	0.0589429
39.5	0.10792
42.5	0.03538
45.5	0.0391173
48.5	0.0316782
51.5	0.0276206
54.5	0.0324969
57.5	0.0613632
60.5	0.421783
63.5	0
Average Number	47.272



- Grain orientation mapping performed in TEM using ASTAR based on precession electron diffraction
- Grain boundary character (GB misorienta - tion, GB type, GB plane) obtained

- ~95% high-angle GBs; ~40% $\sum 3$ twin boundaries
- Results on 12 areas similar to each other

Haiming Wen: INL Post-Doctoral Graduate Researcher

Conclusions

- Successful achievement of grain boundary characteristics using ASTAR provides next scientific milestone for transport studies
- The influence of sample thickness on the quality of crystallographic orientation data obtained by PED was determined (120 nm best results).
  - However, at some point, grains will significantly overlap, resulting in the degradation of the orientation data and more diffuse zones between grains. The critical thickness of significant overlap will likely be grain size dependent with the critical thickness decreasing with decreasing grain size.
- Standard FIB-prepared samples from the SiC layer of TRISO coated fuel appear to be of sufficient thickness to produce high quality orientation data.
- PED measurements completed on unirradiated SIC and on three irradiated sample sets (11.4% , 15.3% and 16.7% FIMA)
- Results (11.4% FIMA) consistent with a strong influence of grain boundary character on fission product migration behavior
- Dataset still relatively small – additional areas required for statistical significance
- The effect of irradiation damage on the orientation data may be of concern and is not determined in this study. This may be considered for future research work.
- Future research work need to consider the effect of grain boundary plane

Activities in Progress and Collaborators

SiC Crystallographic Studies:

- Continue TKD measurements on unirradiated and irradiated SiC layers in collaboration with:
  - Nano Bruker Germany: t-EBSD or also called TKD
  - Nelson Mandela Metropolitan University, South Africa (NMMU)
- Complete EBSD studies on unirradiated SiC to determine the effect of temperature on grain boundary characteristics
  - National Scientific User Facility (NSUF) funding with Idaho State University (Two Awards: Sept 2012 and May 2013)
- Crystallographic examination of irradiated SiC using PED: Complete interpretation and journal publications
  - NSUF funding with Boise State University (One Award: January 2014)
- Complete Crystallographic (PED) measurement interpretations under the AGR program on other compacts with different irradiation histories to determine irradiation effects.

Publications and Presentations Resulting directly from NSUF funded work

- **[1] Invited presentation**: Isabella J van Rooyen, Yaqiao Wu, Tom Lillo, John Youngsman and Jan H Neethling, Approach and Micro-analysis techniques applied to study fission product transport mechanisms in neutron irradiated SiC layers, IMRC XXIII, Cancun, Mexico, August 17-21, 201
- **[2] Presentation**: I. J. van Rooyen, J. Youngsman, T. M. Lillo, Y. Q. Wu, D. Goran, M. E. Lee, W. E. Goosen, J. H. Neethling, T. L. Trowbridge and J. W. Madden, Methods for identification of crystallographic parameters of irradiated SiC to understand fission product transport, The 3rd Workshop on HTGR SiC Material Properties, Sept. 30–Oct. 1, 2014, Jeju Island, South Korea
- **[3] Conference Paper**: Thomas M. Lillo, Isabella J. van Rooyen, Yaqiao Wu, Grain Boundary Character and Fission Product Precipitation in SiC, 2015 ANS Annual Meeting, San Antonio, TX, 7-11, 2015
- **[4] Journal Paper:** T. Lillo, I.J. van Rooyen, “Precession Electron Diffraction for SiC Grain Boundary Characterization in unirradiated TRISO Fuel”, to be submitted to Nuclear Engineering and Design or the Journal of Nuclear Materials, June/July 2015
- **[5] Journal Paper:** T. Lillo, I.J. van Rooyen, "Influence of SiC Grain Boundary Character on Fission Product Transport in TRISO Fuel" Draft in progress, to be submitted to the Journal of Nuclear Materials, July 2015

Technique Acronyms

Acronyms	Description
APT	Atom Probe Tomography
EDS	Energy Dispersive Spectroscopy
EBSD	Electron Back Scattered Diffraction
EELS	Electron Energy Loss Spectroscopy
EFTEM	Energy Filtered TEM
FIB	Focused Ion Beam
HAADF	High Angle Annular Dark Field
HRTEM	High Resolution Transmission Electron Microscopy
PED	Precession Electron Diffraction
SAD	Selected Area Diffraction
SEM	Scanning Electron Microscope
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscope
t-EBSD	Transmission-EBSD
TKD	Transmission Kikuchi Diffraction
WDS	Wavelength Dispersive Spectroscopy

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Questions?

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Irradiation Parameters

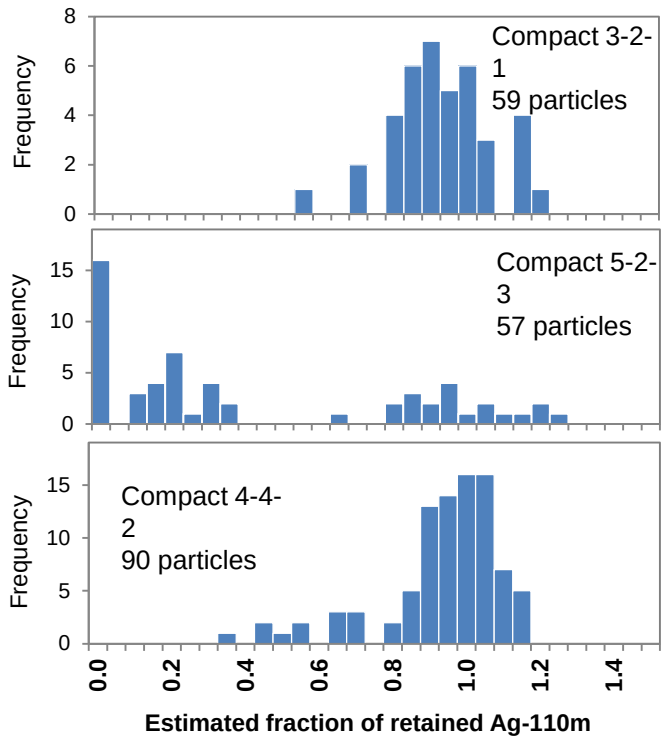
Compact	Fuel Type[a]	TAVA[b] Temp. (°C)	TA Max[c] Temp. (°C)	Burnup (% FIMA)	Fast fluence (10^{25} n/m^2)
6-3-2	B	1070	1144	11.4	2.55
6-1-1	B	1111	1197	15.3	2.43
3-2-1	B	1051	1143	19.1	4.21
5-2-1	V1	1057	1140	17.4	3.71
5-2-3	V1	1059	1141	17.4	3.77
5-3-1	V1	1040	1122	16.7	3.60
4-4-2	V3	1024	1139	16.6	3.59
4-1-1	V3	1072	1182	19.4	4.13
1-3-1	V3	1092	1166	15.3	3.22

[a] B=Baseline; V1=Variant 1, V2= Variant 2, V3=Variant 3

[b] Time average, volume average temperature

[c] Time average maximum temperature

Silver Retention of Individual Particles



Average retained fraction of release ^{110m}Ag in the particle sample

Compact	Retained ^{110m}Ag fraction
6-3-2	0.36 – 0.51
6-1-1	0.39 – 0.45
3-2-1	0.92
5-2-3	0.43 – 0.45
5-2-1	0.30 – 0.45
5-3-1	0.48 – 0.57
4-4-2	0.93
4-1-1	1.02
1-3-1	0.12 – 0.28

- Particles within a single compact could often exhibit a large range of silver retention, from complete release to complete retention

- Possible causes:
  - Temperature variations
  - SiC microstructure variations
  - Kernel and coating morphology
- Detailed microanalysis of particles exhibiting high and low silver release is in progress to compare microstructure