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Results of FITT Oxidation Study

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Nuclear Fuel Development Section

Oak Ridge National Laboratory

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Outline

- Objectives/Background
- Experiment design
- Particle failure fraction analysis
  - Increase in irradiated particle failure response compared to that of unirradiated
  - External factors most likely caused more failures than anticipated
- Oxide formation kinetics
  - Similar oxide growth rate between irradiated and unirradiated particles
- Microstructure examination
  - Crystalline oxide structures observed in all samples
- FITT Update

Objectives

- Measure TRISO particle failure fraction as a function of oxidizing conditions
  - Provide data to support Air/Moisture-Ingress Experiment (AMIX) test plan development
- Compare oxidation behavior of the SiC layer in unirradiated and irradiated TRISO particles
  - Analyze differences in oxidation kinetics between unirradiated and irradiated SiC
  - Observe oxidation microstructure in individual TRISO particles

FITT: Furnace for Irradiated TRISO Testing

- Flexible, intentionally-simple, cost-effective capability to heat small batches of irradiated TRISO particles up to 1700°C over times >1500 h outside a hot cell
  - Closed-bottom ceramic tube in box furnace containing 10–30 particles under flowing inert gas or oxidizing environments (up to 21% O_2)
  - Installed in the Irradiated Fuels Examination Laboratory (IFEL) radiological facility at ORNL where AGR hot cell work is performed
  - Intended to support integral release/oxidation tests in the Core Conduction Cooldown Test Facility (CCCTF), Fuel Accident Condition Simulator (FACS), and AMIX systems

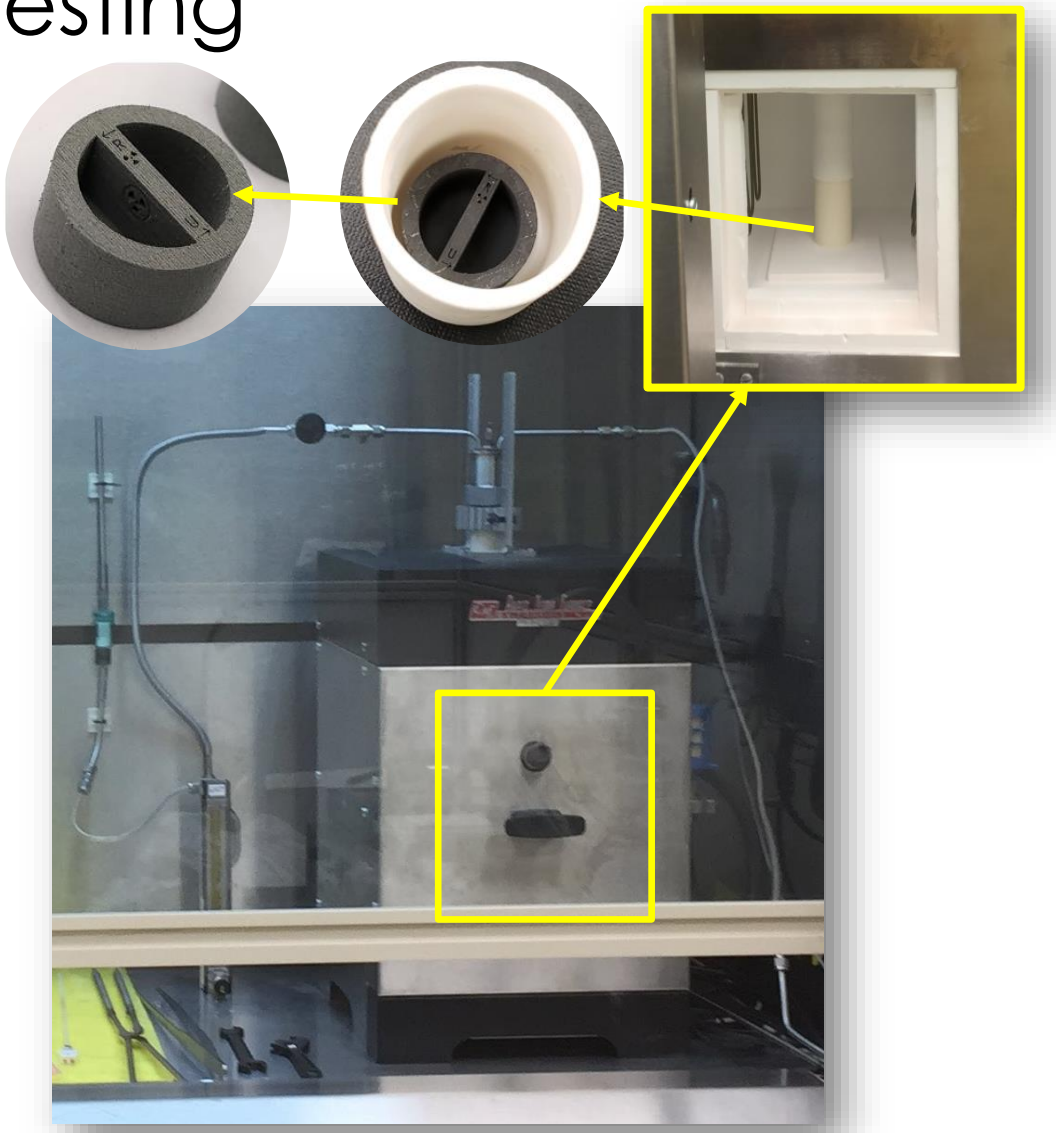
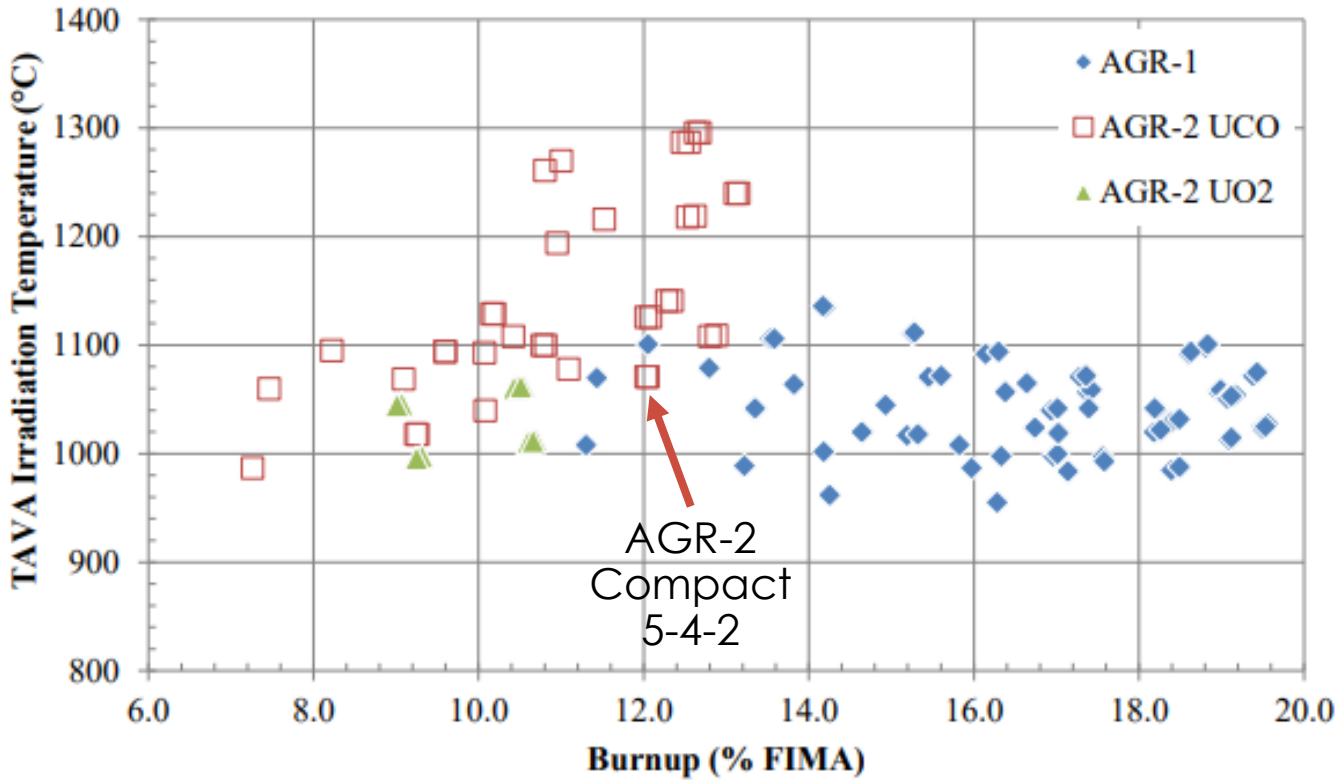


Image of FITT system in IFEL hood

TRISO Particle Sample Selection

- Irradiated particles from AGR-2 Compact 5-4-2 had outer pyrolytic carbon (OPyC) layer "burned back" to expose SiC
  - Exposed SiC layer to initiate oxidation growth at t = 0
  - Not expected to influence failure fraction based on previous post-burn failure fraction measurements [1]
  - Resulting oxide thickness extrapolated to be <0.01 μm [2]
- Unirradiated particles from Compact LEU09-OP2-Z002
  - Subjected to a similar burn back process as Compact 5-4-2



Time-averaged, volume-averaged (TAVA) temperature versus burnup for AGR-1 and AGR-2 UCO Compacts [3]

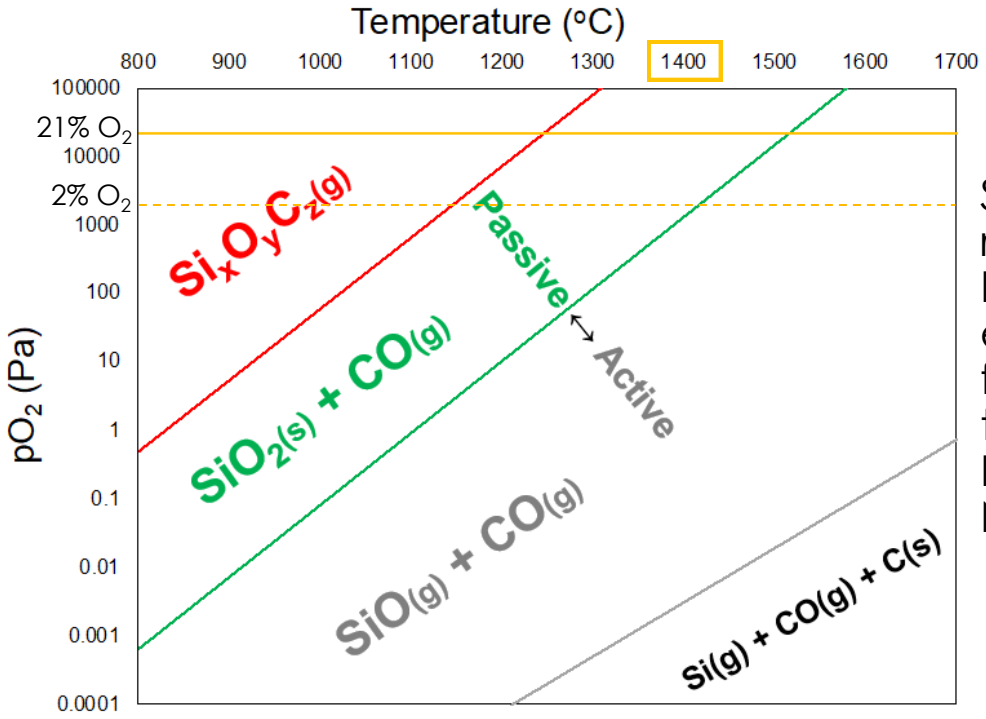
[1] Hunn, J.D., F.C. Montgomery, and P.J. Pappano. 2010. *Data Compilation for AGR-2 UCO Variant Compact Lot LEU09-OP2-Z*, ORNL/TM-2010/017, Revision 1. Oak Ridge: Oak Ridge National Laboratory.
[2] Cao, Fangcheng, D, Zhang, Q. Chen, H. Li, and H. Wang. 2020. "Evaluation of Oxidation Performance of TRISO Fuel Particles for Postulated Air-Ingress Accident of HTGR." *Journal of Chemistry* 2020, Article ID 6568987: 8 pages. doi: 10.1155/2020/6568987.
[3] Stempien, John D, J.D. Hunn, R.N. Morris, T.J. Gerczak, and P.A. Demkowicz. 2021. "AGR-2 TRISO Fuel Post-Irradiation Examination Final Report," INL/EXT-21-64279-Rev000. Idaho Falls: Idaho National Laboratory

Experimental Approach

- Ten irradiated particles and ten unirradiated particles loaded into a SiC cup separated by a partition
- Once at temperature, the flow gas was switched from Argon to oxidant.
  - Dispersed ~1" above the SiC cup at 50 mL/min (internal volume of system was ~321 mL)
    - Refreshes system atmosphere every ~6 min
- Sample location temperature confirmed with separate thermal profiling test
- Hach Orbisphere K-M1100 Oxygen Sensor
  - Measured oxygen concentration from system exhaust
  - Confirmed no oxygen starvation during 2% O_2 exposure

Conditions of six oxidation tests performed

Temperature (°C)	Atmosphere	Exposure Times (h)
1200	21% O_2 (balance N_2)	400
1400	21% O_2 (balance N_2)	50, 100, 200, 400
1400	2% O_2 (balance He)	400



SiC oxidation response. Figure extrapolated from data taken from Presser and Nickel [1]

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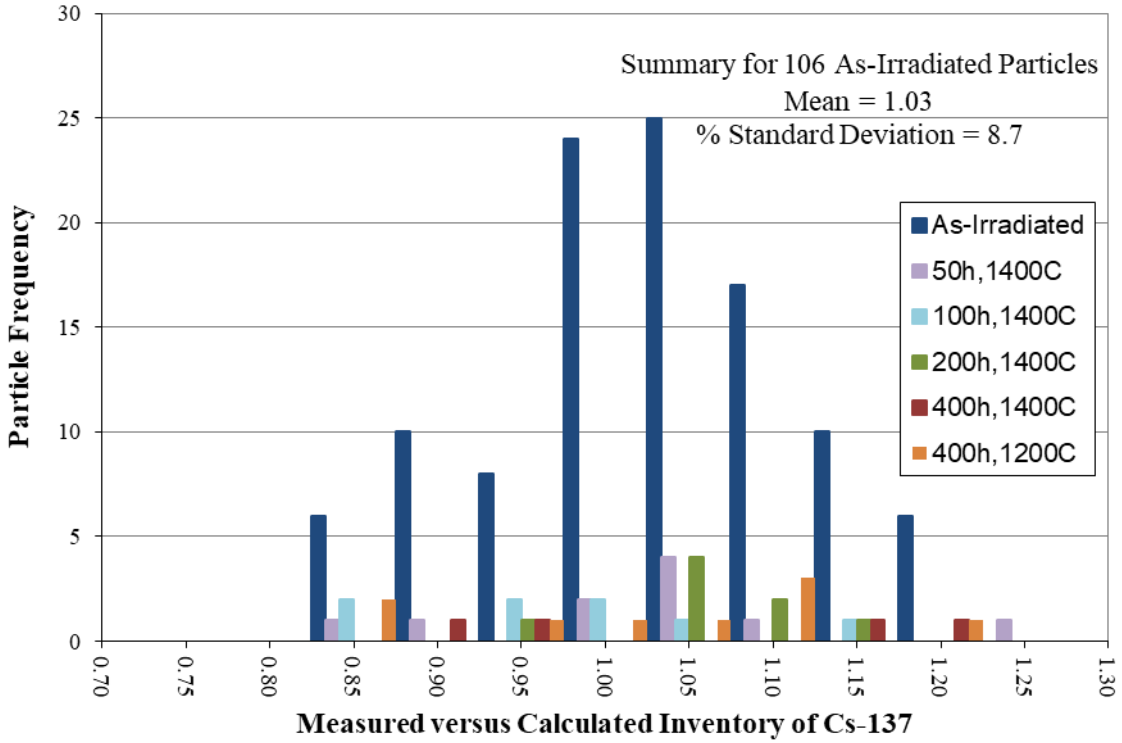
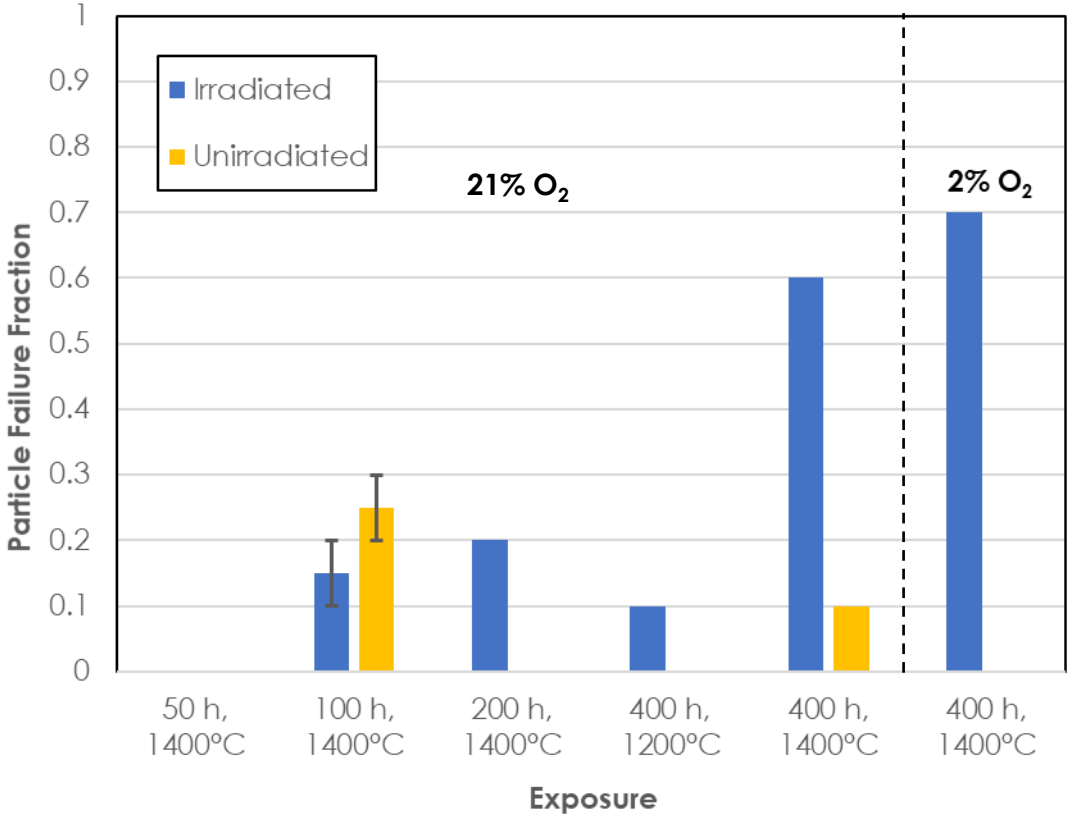
[1] Presser and Nickel, "Silica on Silicon Carbide", Critical Reviews in Solid State and Materials Sciences, 33:1, 2008, 1–99.

Irradiated TRISO particle failure fraction increased with exposure time and temperature



Particle failure during various oxidation tests



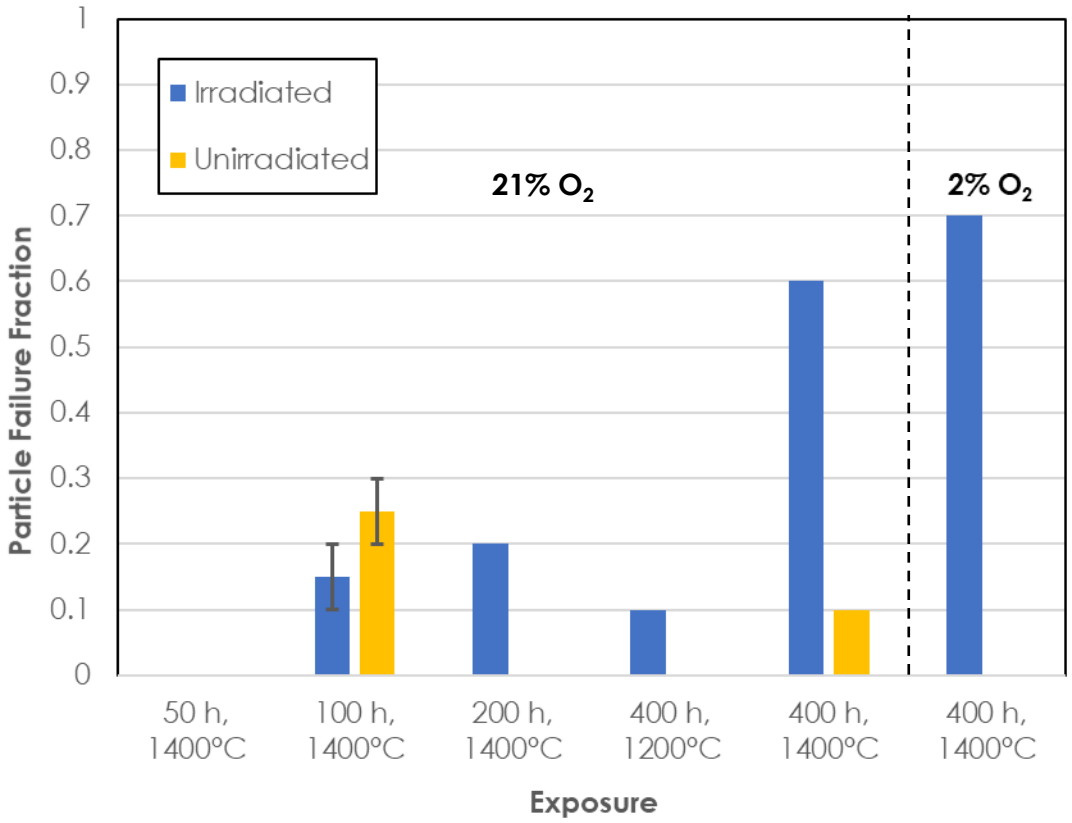
- Failed SiC layer would be indicated by ^{137}Cs release
- No low ^{137}Cs particles detected by IMGA

- Complete failure resulted in particle consumption by system and lack of recovery
- Evidence of particle fragments/debris at bottom of SiC cup

External factors from experimental approach influencing particle failure fraction

- No trend observed in failure rate of unirradiated particles
  - Suggested variables besides oxidizing conditions promoted particle failure
  - Previously observed in inert heating tests of burned back Compact 5-4-2 particles [1]
- Possible factors biasing particle failure
  - Nitric acid exposure during burn back process
  - SiC cup interaction with particles
  - SiC shell damage from handling
  - Variations in oxygen flow rate
  - Temperature gradients

Particle failure during various oxidation tests



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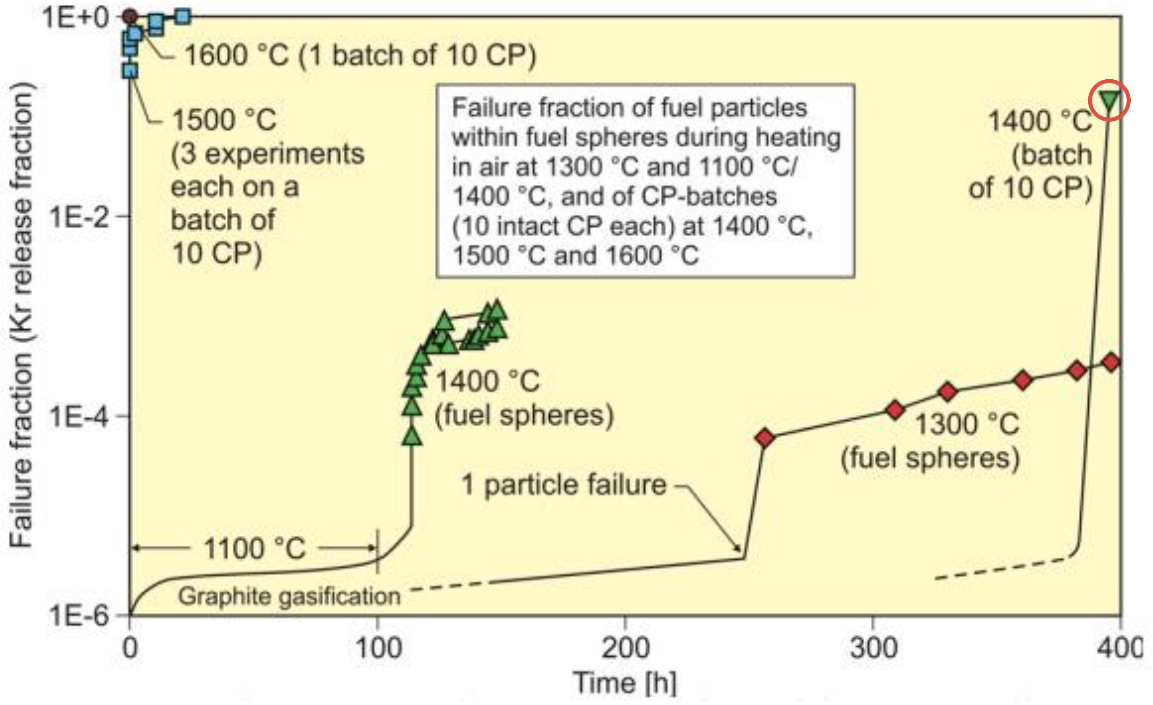
[1] Gerczak, T.J., Z.M. Burns, D.J. Skitt, R.N. Morris, and J.D. Hunn, 2020. *AGR 2 loose particle heating tests in the furnace for irradiated TRISO testing*, ORNL/TM-2020/1715-R0. Revision 0. Oak Ridge: Oak Ridge National Laboratory.

Irradiated particle failure fraction increased with longer oxidation exposure times

- Failure fraction increased from 200 h to 400 h of exposure, as well as from 1200°C to 1400°C

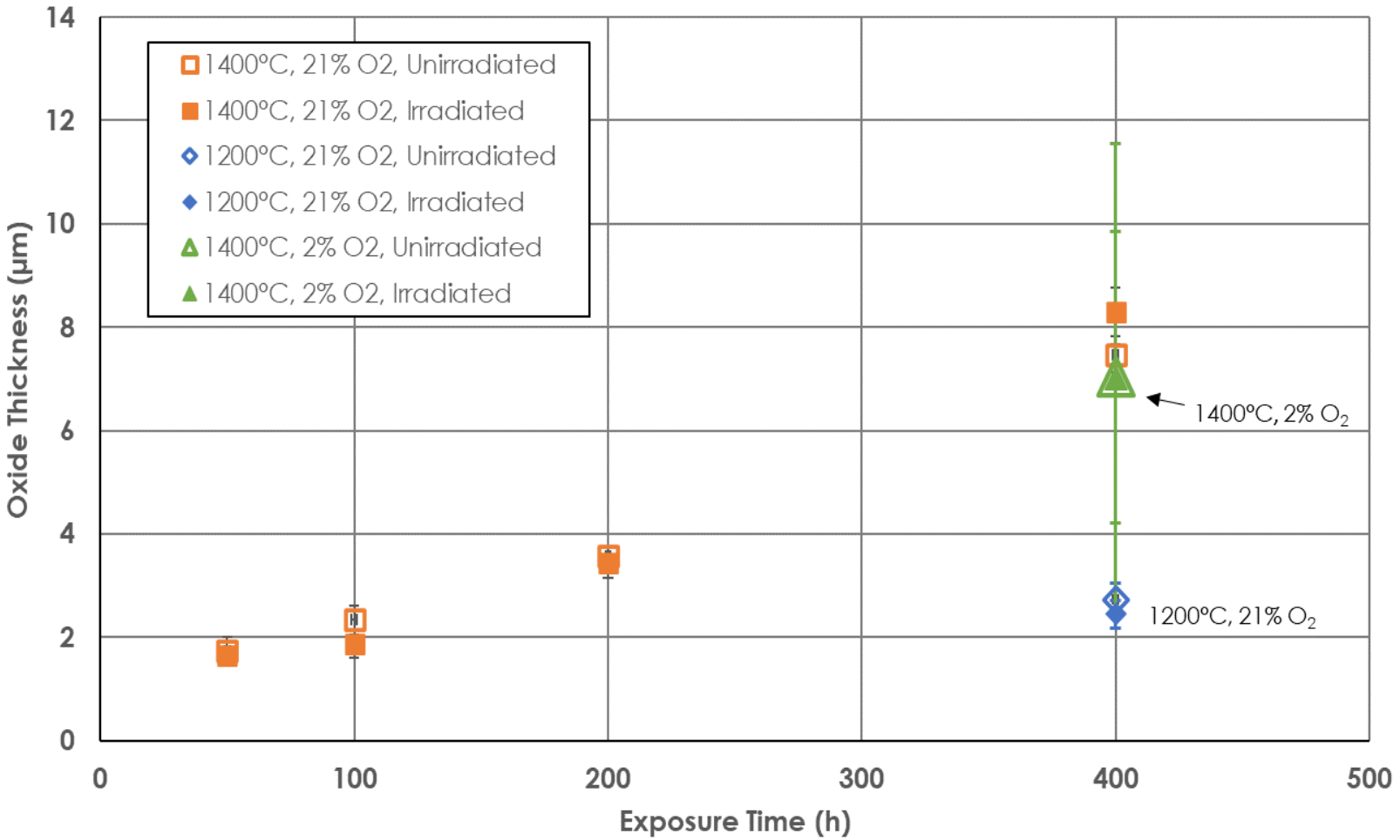
- Higher failure rate observed in FITT than historic KORA tests at 1400 °C [1]
  - KORA experienced first TRISO failure (10% of particles) after 397 h of exposure to air



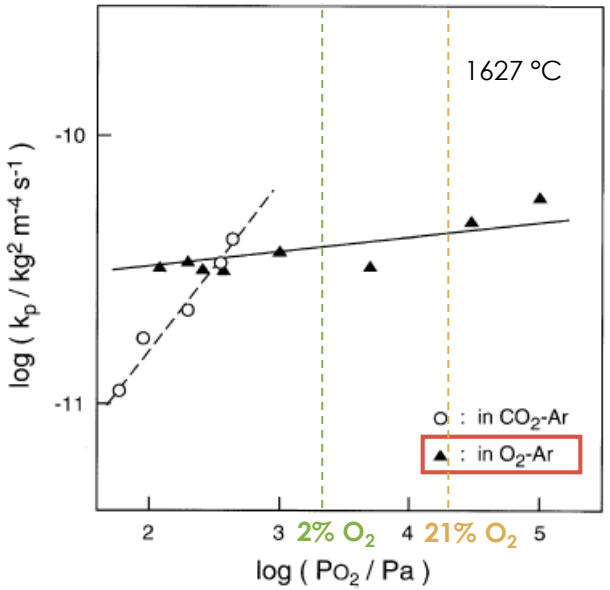
KORA results of heating LEU UO_2 TRISO in air [1]

[1] International Atomic Energy Agency. 1997. *Fuel performance and fission product behaviour in gas cooled reactors*. IAEA-TECDOC-978. Vienna: International Atomic Energy Agency.

Oxide Thickness Analysis



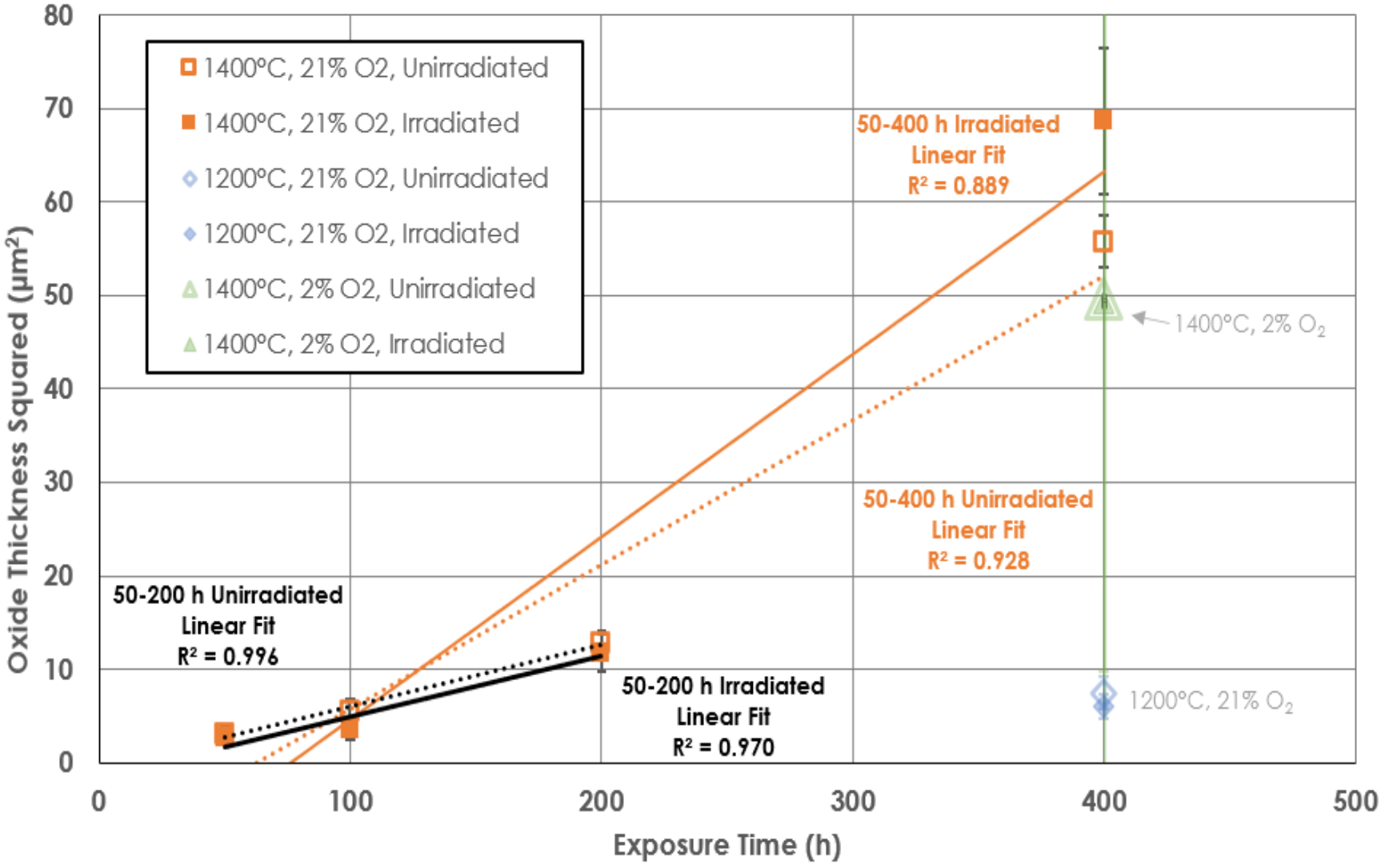
- Increased oxidation response for prolonged exposures at 1400°C, 21% O_2
- Decreasing pO_2 only reduced average oxidation rate at 1400°C by 5–15%
  - Supported by prior studies for low pO_2 oxidation of SiC at similar exposures [1,2]



Effect of pO_2 on SiC oxidation rate [2]

[1] Narushima, T., T. Goto, T. Hirai, and Y. Iguchi. 1997. "High-Temperature Oxidation of Silicon Carbide and Silicon Nitride." *Materials Transactions*, JIM 38 (10): 821–835.
[2] Goto, T., Homma, H. 2002. "High-temperature active/passive oxidation and bubble formation of CVS SiC in O_2 and CO_2 atmospheres." *J. of European Ceramics Society*, 22 (2002) 2749-2756.

1400°C Oxidation Kinetics



- Deal-Grove model gives non-physical fit for long exposure times *($x = B(t/x) - A$)*
- Parabolic oxidation rate used instead *($x^2 = Bt$)*
  - Previous parabolic rate studies typically observed at < 48h timescale [1,2]
- Longer (400 h) exposures resulted in deviation from parabolic oxide growth

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[1] Cao, Fangcheng, D, Zhang, Q. Chen, H. Li, and H. Wang. 2020. "Evaluation of Oxidation Performance of TRISO Fuel Particles for Postulated Air-Ingress Accident of HTGR." *Journal of Chemistry* 2020, Article ID 6568987: 8 pages. doi: 10.1155/2020/6568987.
[2] Liu, Rongzheng, B. Liu, K. Zhang, M. Liu, Y. Shao, C. Tang, 2014. "High temperature oxidation behavior of SiC coating in TRISO coated particles." Journal of Nuclear Materials 453, 107-114.

Parabolic rate constant, B, for various exposure ranges

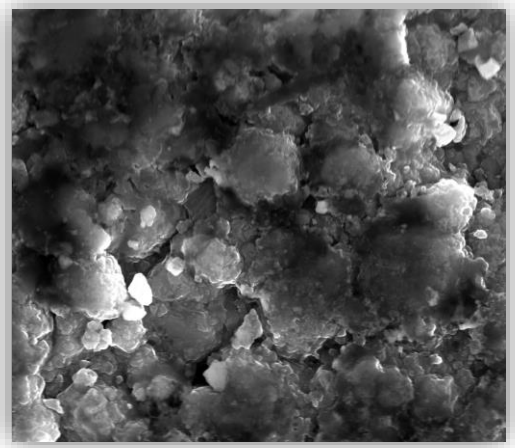
	Unirradiated		Irradiated	
Exposure	**B ($\mu m^2/h$)**	**R^2**	**B ($\mu m^2/h$)**	**R^2**
50–100 h, 1400°C	0.055	0.998	0.039	0.963
50–200 h, 1400°C	0.062	0.996	0.055	0.970
50–400 h, 1400°C	0.120	0.928	0.143	0.889
0–48 h, 1300°C (Literature) [1,2]	0.042–0.058			
0–48 h, 1400°C (Literature) [1,2]	0.121–0.126			
400 h, 1200°C	0.018		0.015	
0-48 h, 1200°C (Literature) [1,2]	0.017–0.036			

- Deviation from parabolic growth observed at 1400°C, 400 h
  - Attributed decomposition and complexity of oxide structures at longer exposure times [3]
- Rate constant for 1400°C, 50-200 h range similar to literature on unirradiated TRISO oxidation at 1300°C
- Single observation for rate constant at 1200°C in agreement with literature

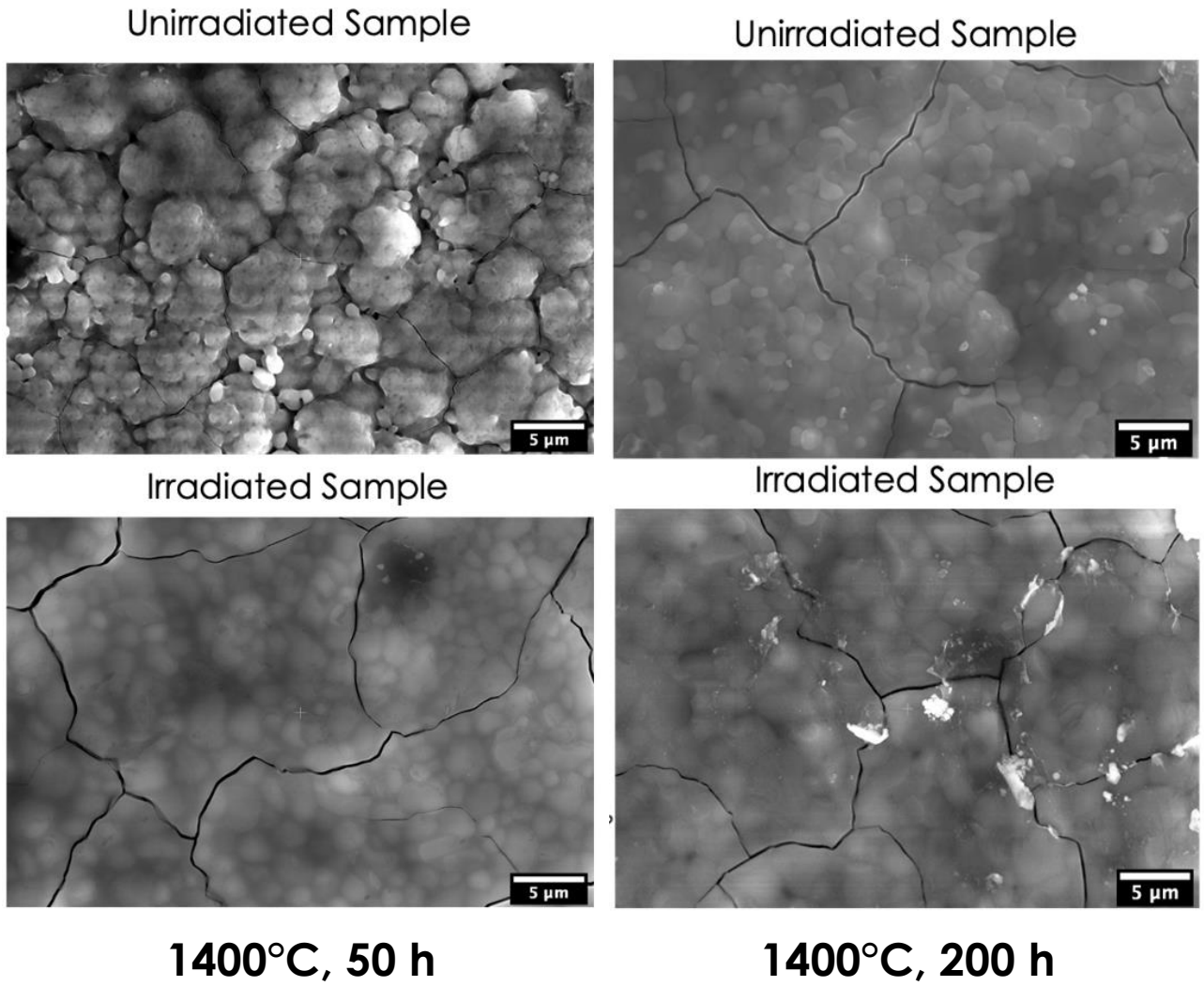
[1] Cao, Fangcheng, D, Zhang, Q. Chen, H. Li, and H. Wang. 2020. "Evaluation of Oxidation Performance of TRISO Fuel Particles for Postulated Air-Ingress Accident of HTGR." *Journal of Chemistry* 2020, Article ID 6568987: 8 pages. doi: 10.1155/2020/6568987.
[2] Liu, Rongzheng, B. Liu, K. Zhang, M. Liu, Y. Shao, C. Tang, 2014. "High temperature oxidation behavior of SiC coating in TRISO coated particles." Journal of Nuclear Materials 453, 107-114.
[3] Costello, J.A., and R.E. Tressler. 1986. "Oxidation Kinetics of Silicon Carbide Crystals and Ceramics in Dry Oxygen." *Journal of the American Ceramics Society* 69 [9]: 674–681.

Surface Oxide Structural Differences at 1400°C

- 50–100 h
  - Unirradiated oxide surfaces showed coarser microstructures than that of the irradiated particles
- 200–400 h
  - Similar topography between irradiated and unirradiated samples



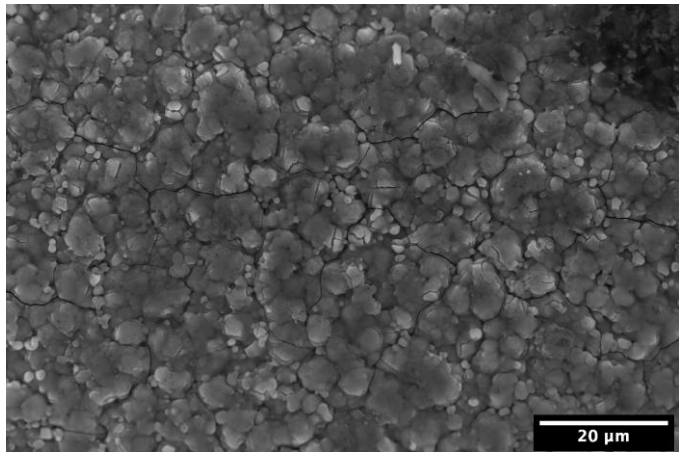
Unexposed Compact 5-4-2 particle SiC layer

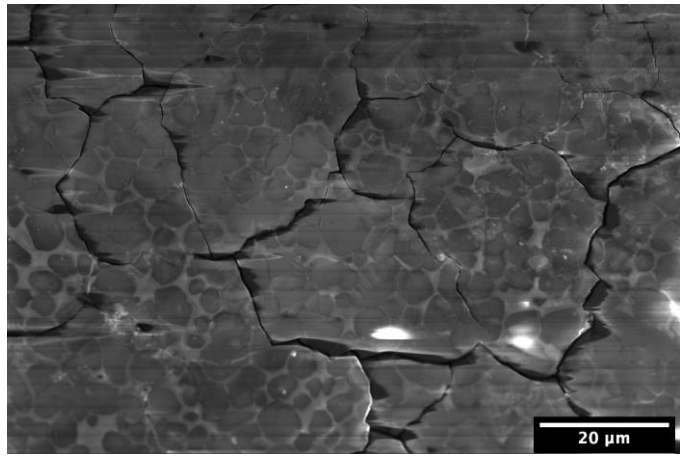


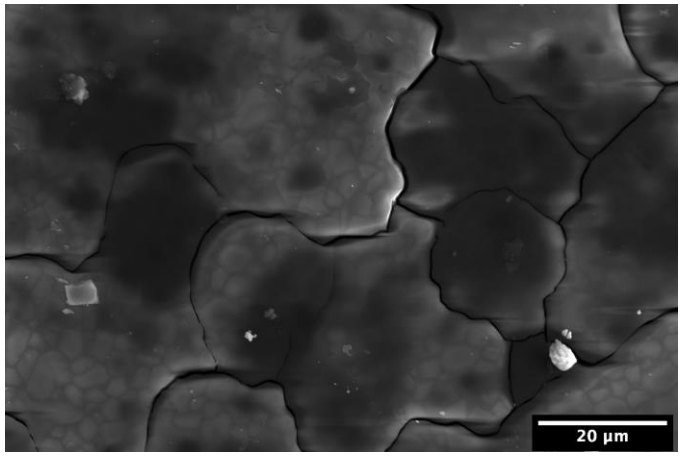
400 h surface layer observations varying temperature and O_2 concentration

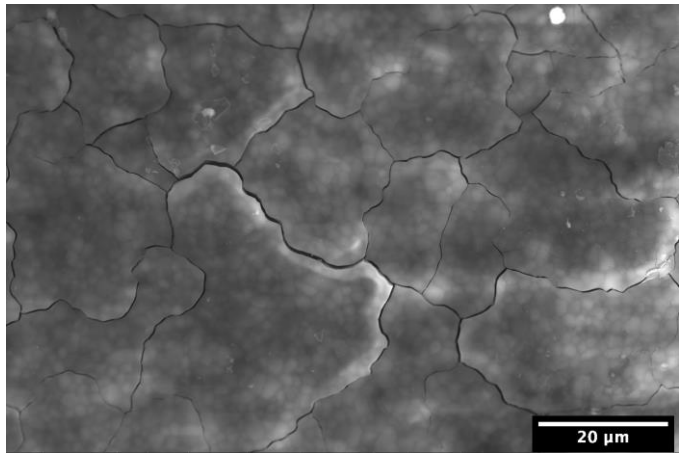
Unirradiated Sample

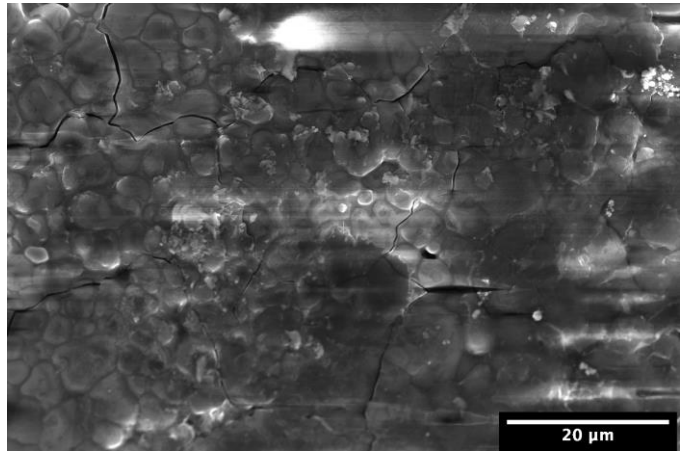
Irradiated Sample

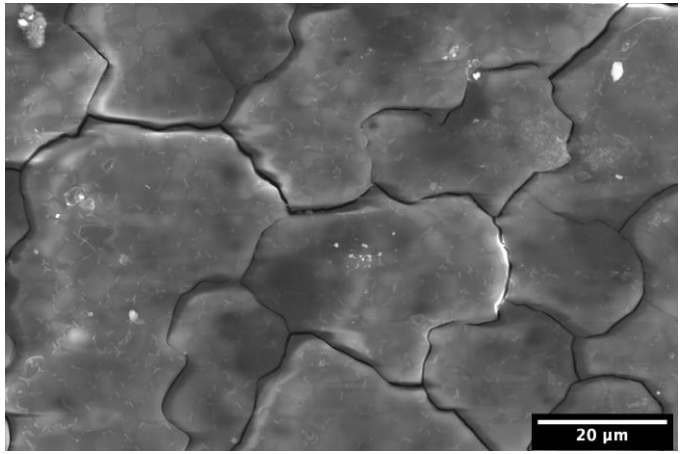










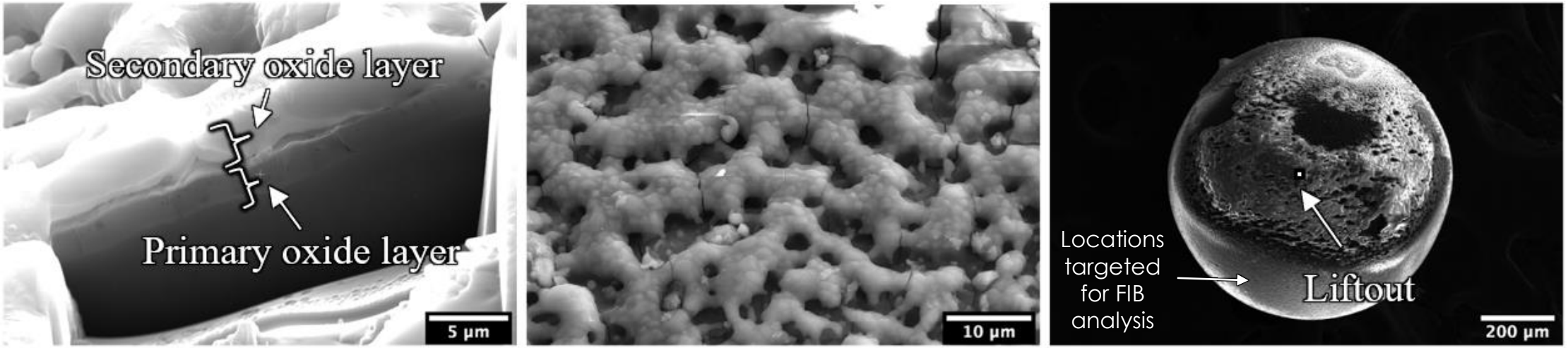


1200°C, 21% O_2 **1400°C, 21% O_2** **1400°C, 2% O_2**

- 1200°C, 400 h oxide topography differences between particle types align with observations from 50 h and 100 h exposures at 1400°C

Non-uniform secondary oxide

- Certain particles had a secondary oxide deposited on top of the primary oxide layer
  - Non-uniform and localized, compared to uniform primary oxide
  - Theorized to be the result of oxide buildup at the contact points between the particles and SiC cup
- Focused liftouts on regions away from contact points during primary oxide thickness analysis



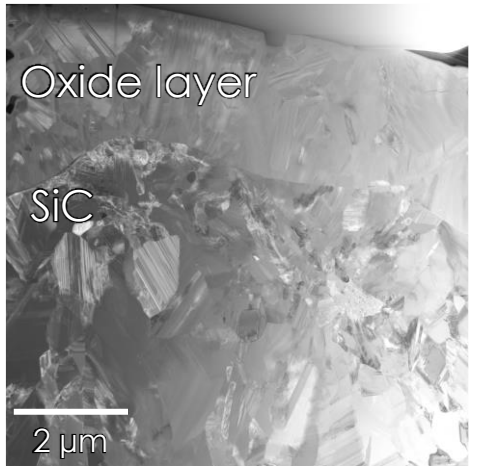
Example of secondary oxide formed on a 1400°C, 100 h particle

Oxide Microstructure Characterization

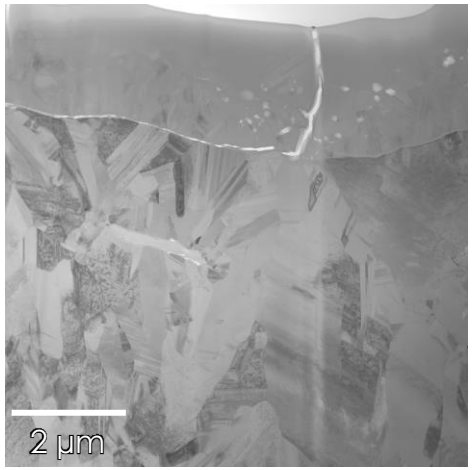
- SiC/oxide lamellas prepared with FIB/SEM
- S/TEM analysis
  - General characterization to confirm microstructure
- EDS performed to examine fission product presence

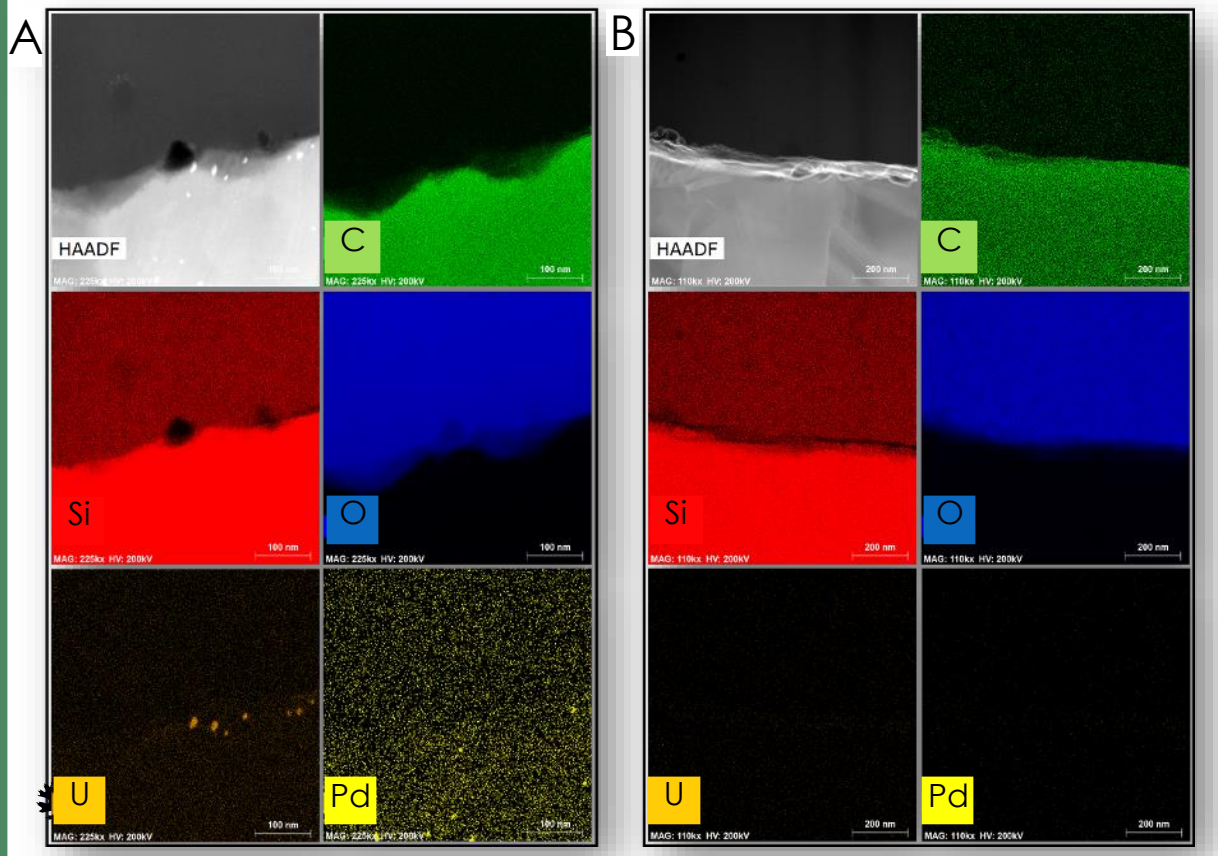
1400°C, 100 h

Unirradiated



Irradiated





EDS mapping of the (A) 50 h irradiated sample and (B) an unirradiated sample, which show element locations within the chosen interface areas [1].

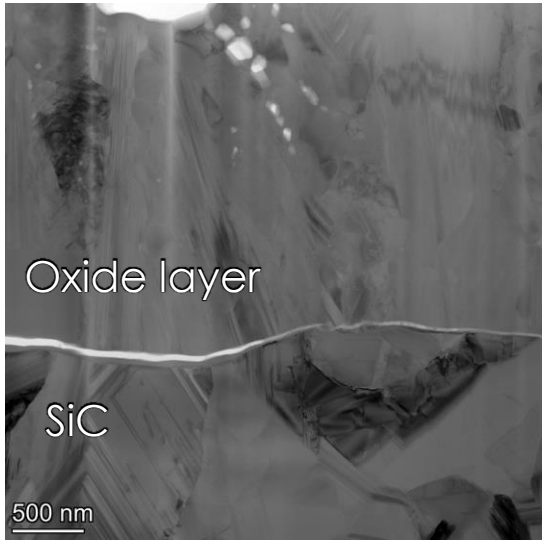
- Previous studies suggest an increased oxidation rate due to appreciable impurities present at the SiC/oxide interface [2].
- Note: Pd signal intensity was increased to observe Pd features in the SiC layer. Noise in the oxide layer does not suggest Pd presence.

[1] Skitt, D.J., R.L. Seibert, T.J. Gerczak, J.D. Hunn, Z.M. Burns, G.W. Helmreich. 2021. *Oxidation Testing and Examination of AGR-2 TRISO Particles,* ORNL/TM-2021/2092, Revision 0. Oak Ridge: Oak Ridge National Laboratory

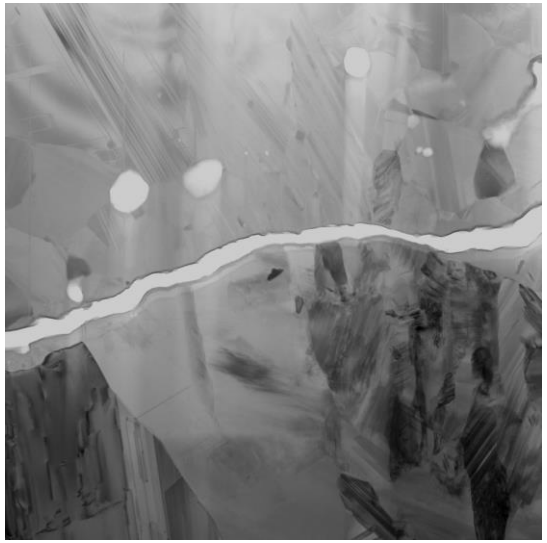
[2] Singhal, S.C., and F.F. Lange. 1975. "Effect of Alumina Content on the Oxidation of Hot-Pressed Silicon Carbide." *Journal of the American Ceramic Society* 58 (9-10): 433–435.

All oxide microstructures examined were crystalline

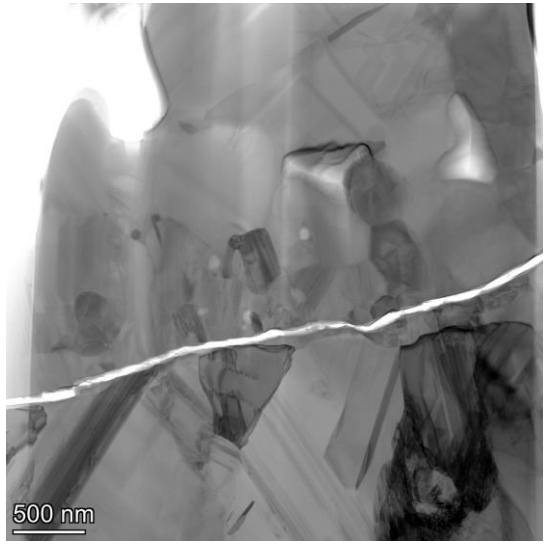
- Irradiated and unirradiated samples revealed similar crystalline microstructures
  - Could not analyze differences due to amorphization from 200 kV electron beam
- 1400°C, >200 h irradiated particles exhibited larger grain size than that of unirradiated samples



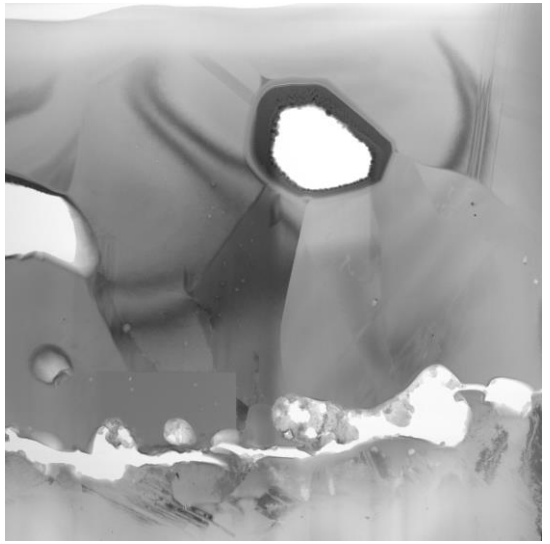
1200°C, 400 h
Unirradiated



1400°C, 400 h
Unirradiated



1400°C, 200 h
Unirradiated



1400°C, 200 h
Irradiated

1400°C, 50–200 h oxidation rate was slightly slower in irradiated particles, but faster after 400 h

	Unirradiated		Irradiated	
Exposure	**B (μm^2/h)**	**R^2**	**B (μm^2/h)**	**R^2**
50–100 h, 1400°C	**0.055**	0.998	0.039	0.963
50–200 h, 1400°C	**0.062**	0.996	0.055	0.970
50–400 h, 1400°C	0.120	0.928	**0.143**	0.889
0–48 h, 1300°C (Literature) [1,2]	0.042–0.058			
0–48 h, 1400°C (Literature) [1,2]	0.121–0.126			
400 h, 1200°C	0.018		0.015	
0-48 h, 1200°C (Literature) [1,2]	0.017–0.036			

- Irradiated and unirradiated oxidation kinetics overall were similar
- Increase in irradiated oxidation rate at 400 h was theorized to be the result of larger grain sizes
  - Possible contribution from presence of excess impurities (e.g., fission products) [1]
  - Oxidant diffusion previously noted to be faster in amorphous, quartz, and cristobalite structures [2]

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[1] Opila, E. 1995. "Influence of Alumina Reaction Tube Impurities on the Oxidation of Chemically-Vapor-Deposited Silicon Carbide." Journal of the American Ceramic Society 78 (4): 1107–1110.
[2] Costello, J.A., and R.E. Tressler. 1986. "Oxidation Kinetics of Silicon Carbide Crystals and Ceramics in Dry Oxygen." *Journal of the American Ceramics Society* 69 [9]: 674–681.

Summary

- Irradiated TRISO particles failure fraction increased with prolonged exposures at 1400°C.
  - Similar trend observed in KORA → temperature and duration affects failure fraction
  - External factors contributed to uncorrelated particle failures
    - E.g., burnback particles, handling methods
- Irradiated oxidation rate was slower for 50—200 h but faster after 400 h at 1400°C, 21% O_2
  - Difference between irradiated and unirradiated not substantial
- Minor variations observed suggest oxidation rates in unirradiated TRISO studies can be used to estimate irradiated TRISO oxidation kinetics.

Current and Future FITT Efforts

- AGR-5/6/7 inert gas thermal exposures in FITT
  - Examine ^{110m}Ag and ^{154}Eu release
  - Compact 2-2-1 particles (non-burnback)
  - Six 100 h tests, 1100–1600°C

- AGR-5/6/7 oxidation testing in 21% O_2 atmosphere
  - Compact 2-2-1 particles (non-burnback)
  - Two 1400°C exposures, 100 & 200 h
  - ZrO_2 cup to replace SiC cup to reduce interaction with particles

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Questions?

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