High Temperature Testing of Representative Fuel Materials in Air and Moisture

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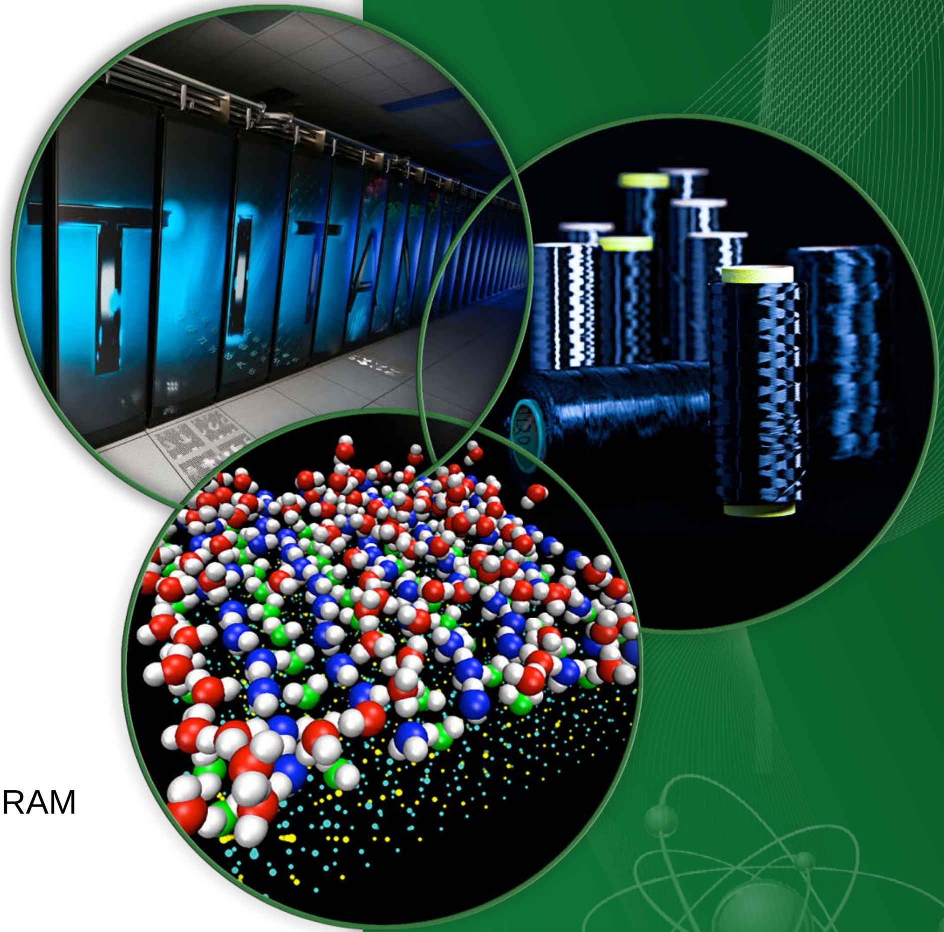

ADVANCED GAS REACTOR TRISO FUELS PROGRAM REVIEW

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CENTER FOR ADVANCED ENERGY STUDIES (CAES)

Idaho Falls, ID

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Testing the fuel component's response to air and moisture ingress events

- Gas reactor fuel is composed of multiple components; *tristructural-isotropic (TRISO) fuel surrounded by a graphitic matrix*
- Accident scenarios include air and moisture ingress events at elevated temperature
- To understand fuel performance in such events the response of each component must be understood
- Testing each component separately allows for the oxidation behavior of each component to be isolated and measured

Air or Moisture Ingress Events

- Air-ingress[1]:
  - Break of primary coolant pipe
  - Reactor coolant system depressurization
  - Air entrance and natural circulation within system
- Moisture-ingress[1]:
  - Initiated by moderate-sized break of steam generator tube
  - Steam leaks into primary system
  - Primary system depressurizes

1. Preliminary Safety Information Document for the Standard MHTGR, Vol. 1, HTGR-86-024 (1986).

Range of Air/Moisture Ingress Conditions

- Air ingress:

Maximum Fuel Temperature (°C)	1600 +
Total air pressure (kPa)	101.3
O_2 partial pressure (kPa)	~ 0 to 21
Total Duration (hours)	100 +

- Moisture ingress:

Range of Fuel Temperatures (°C)	1000 to 1630
H_2O partial pressure (kPa)	≤ 2 (for tens of hours) ≤ 400 (for up to several hours)
Total Duration (hours)	100 +

Previous Oxidation Tests

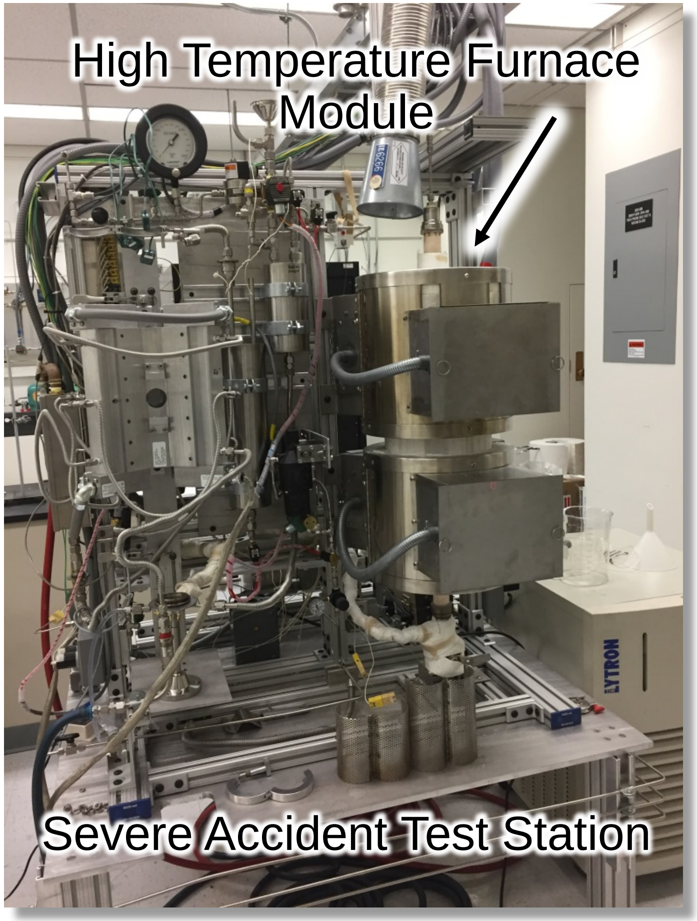
- Graphitic matrix has not been tested in moisture, but it has been tested in air at temperatures ranging from about 500 to 1600°C.[1,2]
- Steam oxidation testing of nuclear graphite has largely been limited to the kinetic regime (T < 1100°C and P_{H2O} generally 0.01 to 3 kPa).[3-5] Accidents could exceed these conditions.
- Limited TRISO SiC oxidation testing in air and moisture has been performed on AGR fuel with representative SiC microstructure.[6,7] Active-to-passive oxidation regime has not been explored with TRISO SiC layers.

1. Contescu, C.I., et. al., “Practical aspects for characterizing air oxidation of graphite,” Journal of Nuclear Materials, **381**, 15-24 (2008).
2. Lee, J.J., Ghosh, T.K., and Loyalka, S.K., “Oxidation rate of graphitic matrix material in the kinetic regime for VHTR air ingress accident scenarios,” Journal of Nuclear Materials, **451**, 48-54, (2014).
3. Velasquez, C., Hightower, G., and Burnette, R., “The Oxidation of H-451 Graphite by Steam,” GA-A14951 (1978).
4. Overholser, L.G. and Blakely, J. P., “Oxidation of graphite by low concentrations of water vapor and carbon dioxide in helium.” Carbon, **2**, 385-394 (1965).
5. Contescu, C. I., Mee, R. W., et al., “Oxidation of PCEA nuclear graphite by low water concentrations in helium,” Journal of Nuclear Materials, **453**, 225-232 (2014).
6. Terrani, K. A. and Silva, C. M., “High temperature steam oxidation of SiC coating layer of TRISO fuel particles,” Journal of Nuclear Material, **460**, 160-165 (2015).
7. Tang, C. and Liu, Bing, et al., “SiC performance of coated fuel particles under high-temperature atmosphere of air,” Nuclear Engineering and Design, **27,** 64-67 (2015).

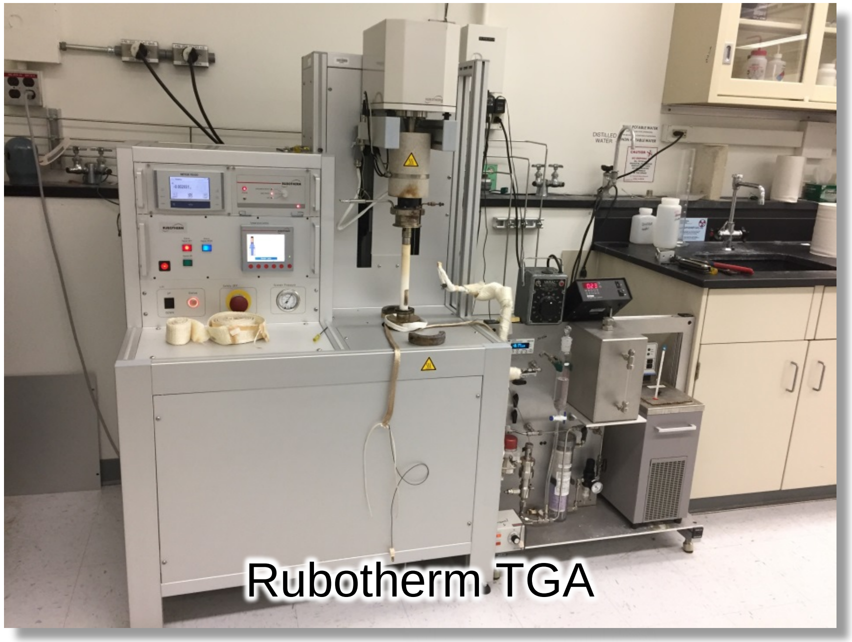
Scope of planned testing: Three test systems to be explored

- TRISO-SiC oxidation in steam and air at high temperatures (1200 to 1600ºC)
  - Understand oxidation behavior under different accident conditions for surrogate TRISO particles with representative AGR-5/6/7 SiC microstructure
- Graphitic matrix oxidation kinetics (800 to 1000ºC)
  - Obtain Langmuir-Hinshelwood kinetic parameters
    - Use parameters to predict high temperature oxidation performance
- Graphitic matrix oxidation in steam at high temperatures (1200 to 1600ºC)
  - Steam oxidation of graphite is well understood, however…
    - Matrix material is different than standard nuclear grade graphite and its performance is not well studied
    - Gas reactor conditions are different than those that have been traditionally explored

Identified thermal exposure systems



High temperature (>1600ºC), variable atmosphere control



Mass change for kinetics study, lower maximum temperature, variable atmosphere control

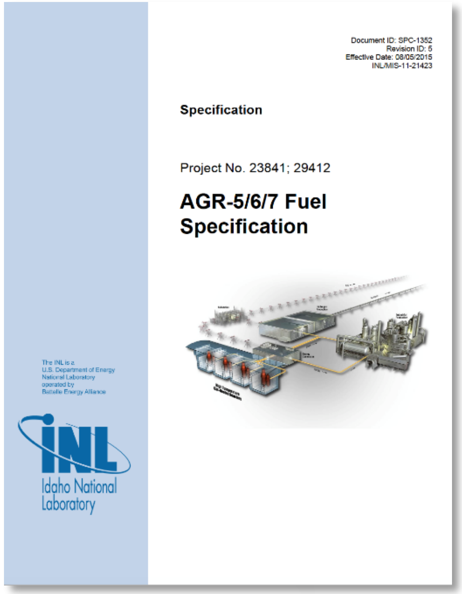
- Two different systems to achieve scope of test conditions and measurements

Outline of remainder of presentation

- **Discuss the ongoing graphitic matrix oxidation in steam at high temperatures test**
  - Sample preparation
  - Test Conditions
  - Furnace modifications
  - Current testing
- **Introduce plan for:**
  - **TRISO-SiC oxidation** in steam and air at high temperatures (1200 to 1600ºC)
  - **Graphitic matrix oxidation kinetics** (800 to 1000ºC)

Representative fuel materials: Graphitic matrix sample preparation

- No ideal samples were available for oxidation testing
- Samples for separate effects testing were fabricated to meet specifications of AGR-5/6/7 graphitic matrix following compact pressing procedures defined by AGR program
- Need >150 total samples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Specification

Project No. 23841; 29412

AGR-5/6/7 Fuel Specification

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

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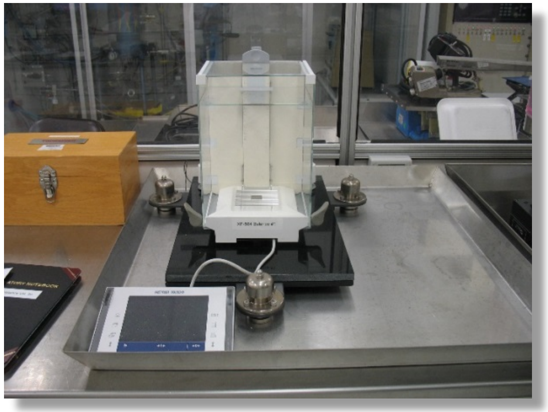
  - Targeted surface area to volume ratio of 1:1.1 to minimize volume effects
  - Disk geometry (~2.58-mm-thick with 12.1-mm-dia.) used to minimize density variations across the sample thickness
  - Graphitic resin blends from AGR-5/6/7 used to fabricate matrix samples
    - Materials supplied by BWXT, same raw materials/ratios as AGR-5/6/7 specification

Representative fuel materials: Graphitic matrix sample preparation



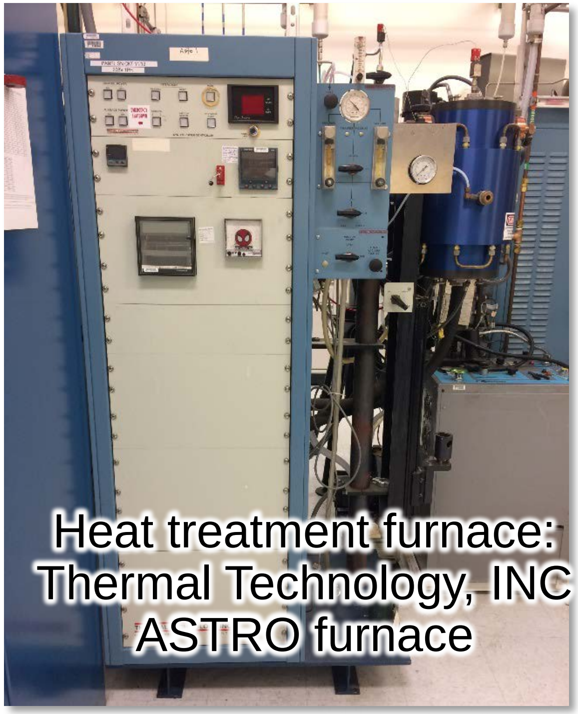
Balance for measuring matrix material

Die for pressing sample

Promess servo press

- Press ~0.6200 g matrix material by hand to produce a “charge” then sand to achieve a constant mass of ~0.5800 g
- Press “charge” in an Promess automated servo press
  - Die is heated to 155^{o}C then “charge” is placed in die and subjected to 300 lbs of force for 60 sec using an automated routine to fabricate green compact

Representative test materials: Graphitic matrix sample preparation

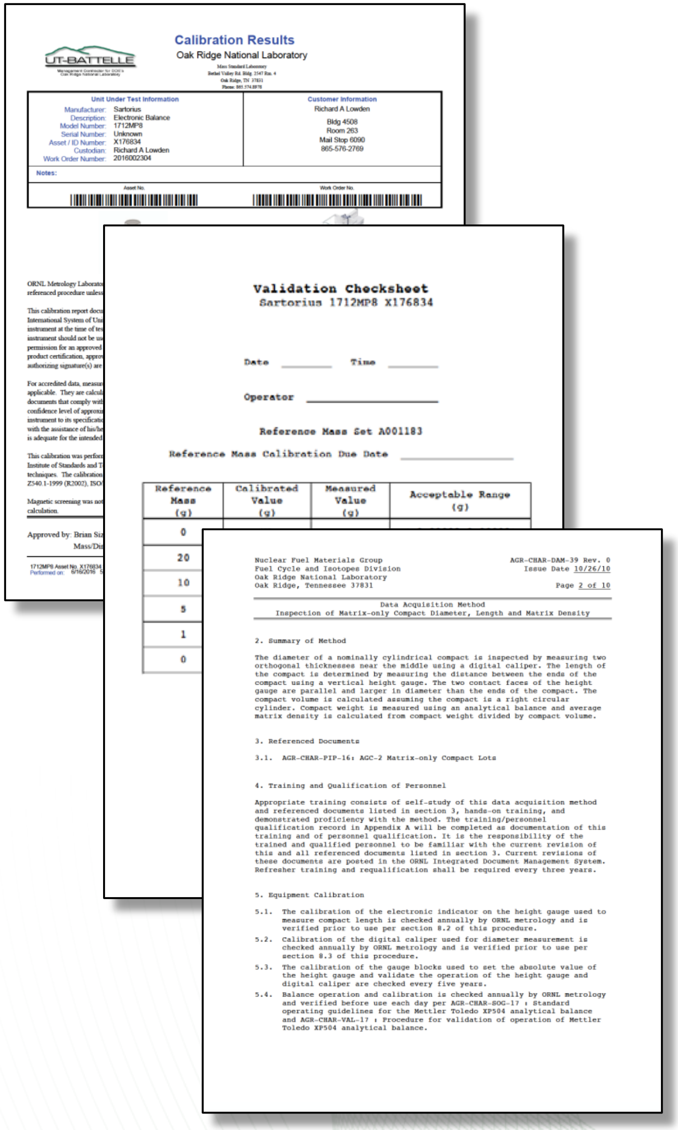


- Carbonize green compact by exposing the samples to 900 °C for 0.5 hours under inert atmosphere
- Heat treatment at 1800°C for 1 hour under vacuum to completely densify the matrix material
- Sample ID is tracked throughout pressing and thermal processing

Representative test materials: Graphitic matrix sample preparation

- Density specification for AGR-5/6/7 targeted: ≥ 1.65 g/cm^3
- Density measurements are made after each subsequent processing step to track progress
  - Follow modified* standard operating procedures for compact density measurements *(AGR-CHAR-DAM-39)*

    **Sample height does not allow for multiple diameter measurements*
  - All measurement equipment and instrumentation has been calibrated and validated prior to measurement



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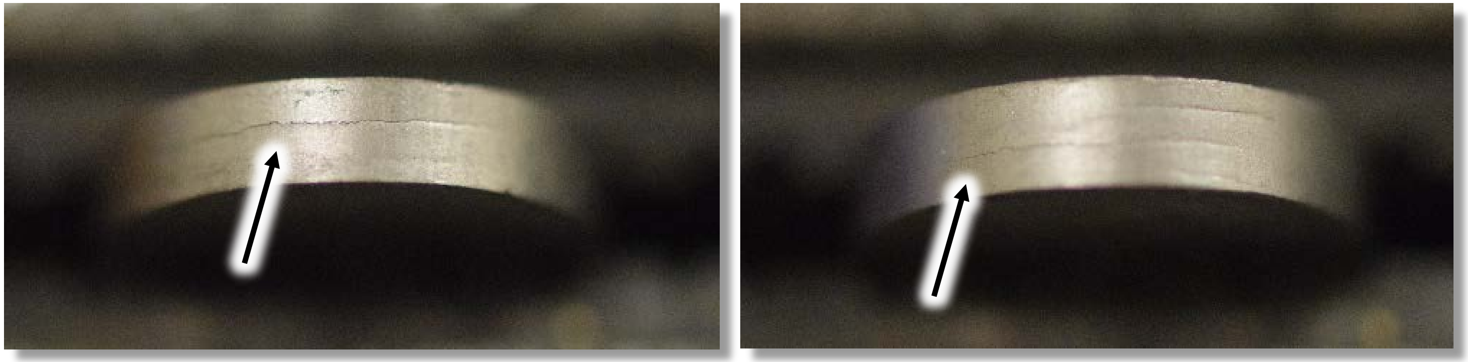
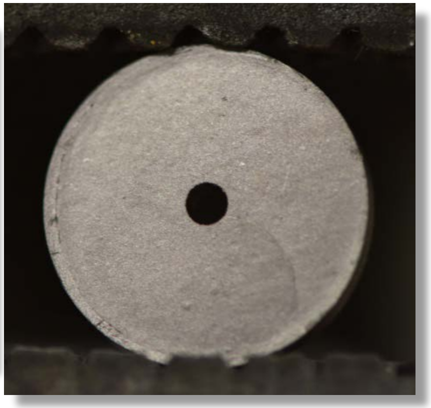
Final sample preparation and acceptance



Examples of surface fissures prompting rejection

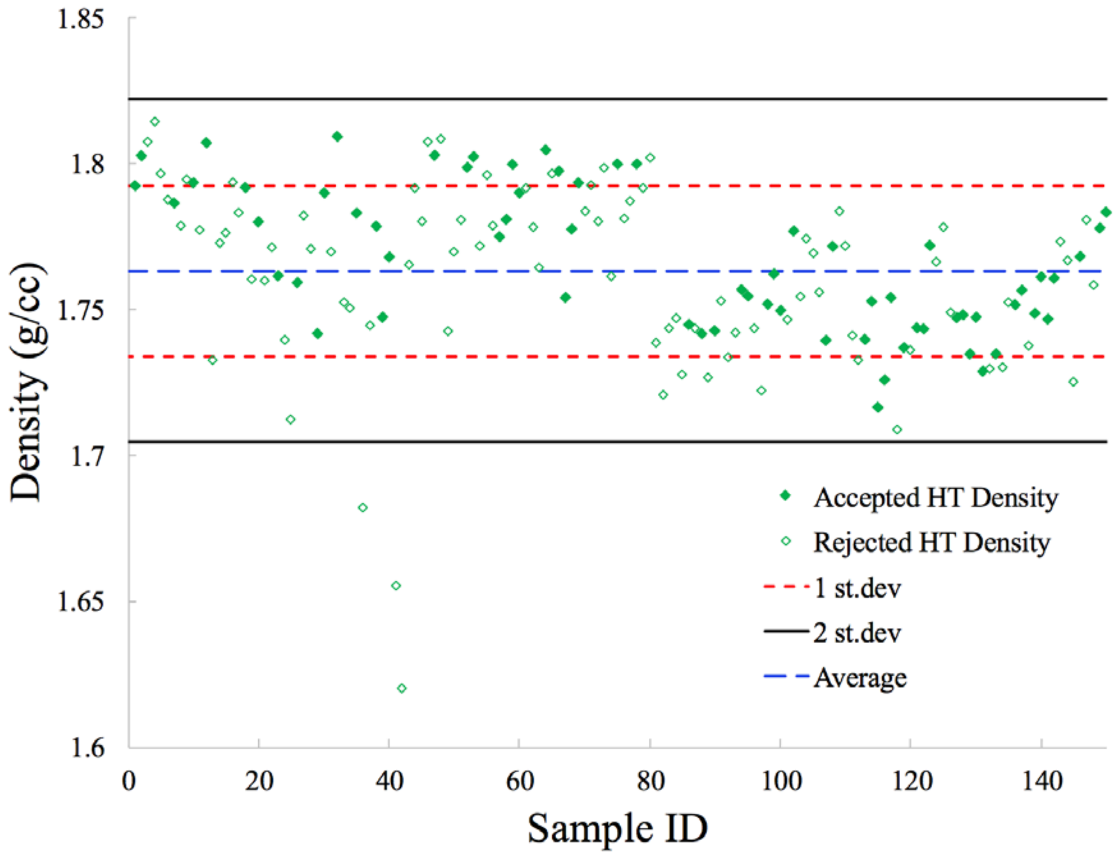


Final sample

- A central hole (1/16” dia.) is drilled to hang the sample in the furnace center
- Samples then are visually inspected for surface irregularities, samples with surface fissures were rejected
  - Similar fissures were readily overserved in full size blank compacts produced using similar materials and methods[1]
- Samples are conditioned according to ASTM standard D7542-09[2]
  - 130°C, 3 hours in air with samples stored in a desiccator after conditioning

1. Trammell, M.P. and Jolly, B.C., “AGC-4 Compact Fabrication Study,” Oak Ridge National Laboratory (2014).
2. D7542-09 Standard Test Method for Air Oxidation of Carbon and Graphite in the Kinetic Regime

Variation in sample density



- Accepted samples within 2-σ, most samples are rejected due to visual cracks
  - Sample yield is ~30%, low yield expected from previous experience[1]
- Samples are assigned a number corresponding to fabrication chronology but randomly assigned to each test condition

1. Trammell, M.P. and Jolly, B.C., "AGC-4 Compact Fabrication Study," Oak Ridge National Laboratory (2014).

Graphitic matrix oxidation in steam at high temperatures

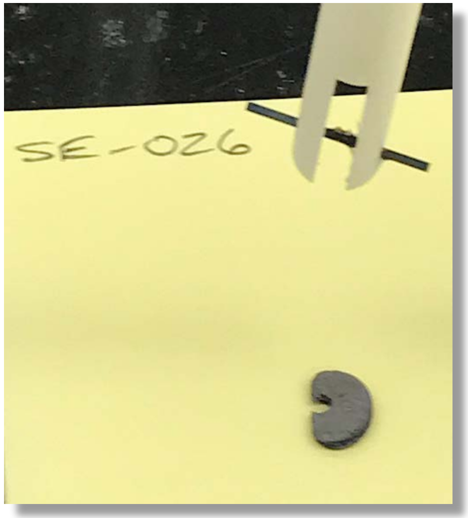
	Atmosphere				
Temperature	He	He-10% Steam	He-20% Steam	He-30% Steam	He-50% Steam
1200 ^{o}C	0.5,1,4,6 hrs	0.5,1,4,6 hrs	X	X	X
1400 ^{o}C	X	X	X	X	X
1600 ^{o}C	X	X	X	X	X

X = exposure time may be modified to allow measurement of mass loss

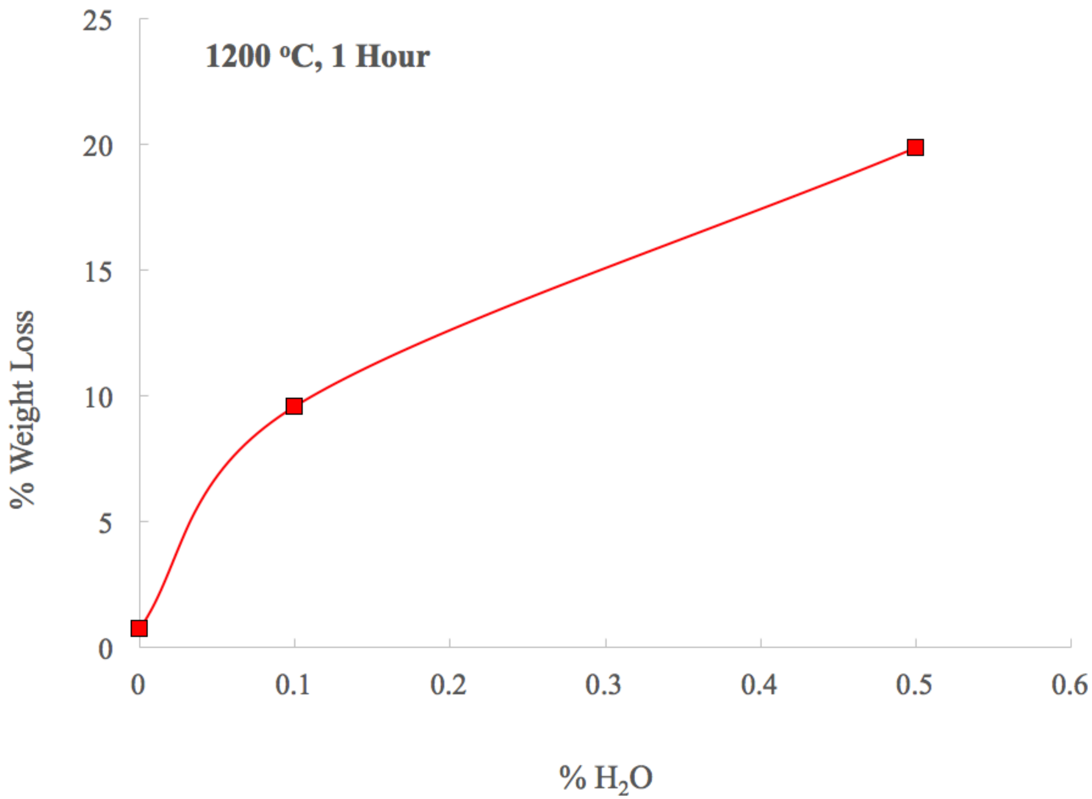
- Testing in High Temperature Oxidation Furnace; 60 individual conditions
  - Measure mass change before and after – find empirical rate law
  - Four test durations for each temperature and atmosphere
  - Research Grade He flow rate ~ 500 cc/min
- He-only condition is studied to provide a baseline measurement from oxidation resultant from residual oxygen in system (300-600 ppm O_2)

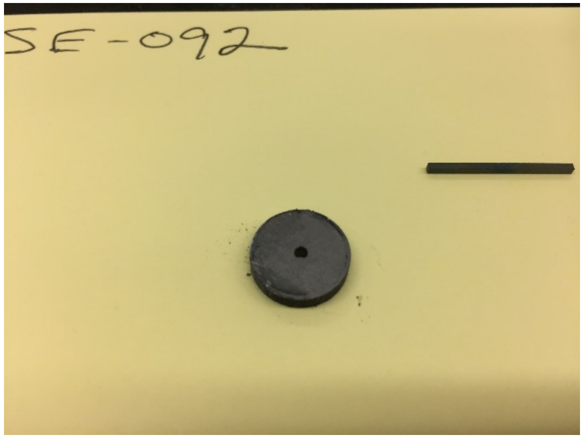
Modifications to high temperature furnace system

- Oxygen ingress was observed from initial test runs
  - Noted by directional oxidation of graphitic matrix sample
  - A modified end cap and sample holder was developed that mitigated back flow of O_2
- Implemented measurement of baseline oxygen in system
  - Positioned inlet of Centorr Oxygen Monitor Model 2D to analyze oxygen concentrations at furnace exhaust
  - Measured 300-400 ppm oxygen at temperature using 500 cc/min research purity He (<10 ppb O_2) with modified end cap
  - Up to 600 ppm O_2 was measured (~47% steam)



Initial data





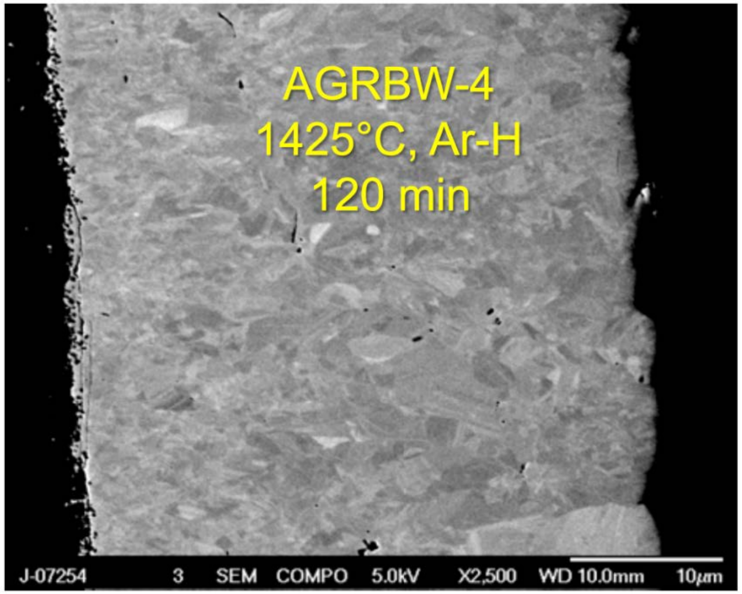
- Observe expected increase in oxidation rate with increased steam concentration
- To date: successfully fabricated samples for graphitic matrix oxidation testing and started oxidation testing
  - More involved analysis will follow as testing continues

Representative test materials: Surrogate TRISO

Comparison of Coating Conditions with AGR-5/6/7

Lot	Temp. (°C)	Run Time (min)	H_2 (sccm)	Ar (sccm)	MTS (sccm)	SiC Thickness (µm)	SiC ρ (g/cm^3)
AGR-5/6/7	1565		70:30 (Ar:H)		0.030±0.005 (CGF)	35±3	
AGRBW-4	1425	120	5200	5200	160	N/A	3.2026±0.0011
ZRX05-26T	1425	247	2870	3250	91	34.5±0.9	3.2062

- Identified particle lots ZRX05-26T and AGRBW-4
  - Sufficient particle inventory
  - ZrO_2 kernels, similar coating conditions to AGR-5/6/7 – target SiC density (ρ) and fine grain SiC
  - Requires a burnback to remove OPyC, <700°C in air to limit oxidation of SiC layer



Example of SiC microstructure

Test conditions for surrogate TRISO particles

	Atmosphere					
Temperature	He	He-10% Steam	He-25% Steam	He-50% Steam	He-100% Steam	Air
1200 °C			4,12,24 hrs			4,12,16,32 hrs
1400 °C						
1600 °C						

- Testing is conducted in the high temperature oxidation furnace
  - Particles will be hung in furnace in a SiC perforated basket[1]
- Measure weight change to determine the oxidation rate of particle lot
- Cross-section select particles to measure oxide thickness and microstructure of oxide layer via scanning electron microscopy (SEM)
  - Approach will provide insight on reactions governing oxidation at varying exposure environments

1. Terrani, K. A. and Silva, C. M., "High temperature steam oxidation of SiC coating layer of TRISO fuel particles," Journal of Nuclear Material, **460**, 160-165 (2015).

Graphitic matrix oxidation kinetics in steam

P_{H2} = 0 kPa								
H2O Partial Pressures (Pa)	Temperatures, °C							
2	800	850	900	925	950	975	1000	1100
15	800	850	900	925	950	975	1000	1100
30	800	850	900	925	950	975	1000	1100
45	800	850	900	925	950	975	1000	1100
65	800	850	900	925	950	975	1000	1100
100	800	850	900	925	950	975	1000	1100
150	800	850	900	925	950	975	1000	1100
250	800	850	900	925	950	975	1000	1100
500	800	850	900	925	950	975	1000	1100
750	800	850	900	925	950	975	1000	1100
1000	800	850	900	925	950	975	1000	1100

- Repeat above matrix (T = 900–1100°C) with P_{H2} = 50 and 150 kPa
- Conducted on Rubotherm TGA system
- Obtain L-H kinetic parameters to predict oxidation behavior and rates at the conditions studied
  - Extrapolate to more aggressive conditions (SATS)

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Timeline for testing

- TRISO-SiC oxidation in steam and air at high temperatures
  - **Initiate testing in FY18**
  - Samples available with minimal pretest development (burnback)
- Graphitic matrix oxidation kinetics
  - **Initiate testing in FY18**
  - Samples preparation in progress to achieve required sample
- Graphitic matrix oxidation in steam at high temperatures
  - **Goal to complete testing by end of FY17**
  - All samples have been fabricated and furnace has been modified to run samples: data collection has been started

Summary

- Significant effort has been undertaken to fabricate appropriate graphitic matrix samples for oxidation testing
- Modifications to high temperature oxidation furnace system have been completed to facilitate high temperature oxidation testing
- Initial planning for TRISO-SiC oxidation and L-H kinetics study of graphitic matrix materials have been completed

Acknowledgments

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Thank you for your attention

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