NEUP Integrated Research Project -2, Workshop 2: FHR Code Benchmarking

MATT Session 2: Tritium in Graphite

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Session 2 Goals

Goals

- Graphite Characterization
  - Standardized graphite characterization procedures
  - Sample Prep for different techniques
  - Irradiation affect on graphite microstructure
- Salt-Graphite Interaction
  - Variables should consider (sample size, time, temperature, etc) ?
  - Salt-graphite interface characterization
  - Relate graphite microstructure to salt graphite interaction both at the surface and in the bulk
- Tritium in Carbon
  - Variables should be considered in the experiment (hydrogen partial pressure, temperature, Sample size)
  - Understand what graphite microstructures can affect tritium retention/transport
  - Method to identify trapping sites in graphite
- Collaboration between universities for benchmarking, data comparison and validation

Motivation

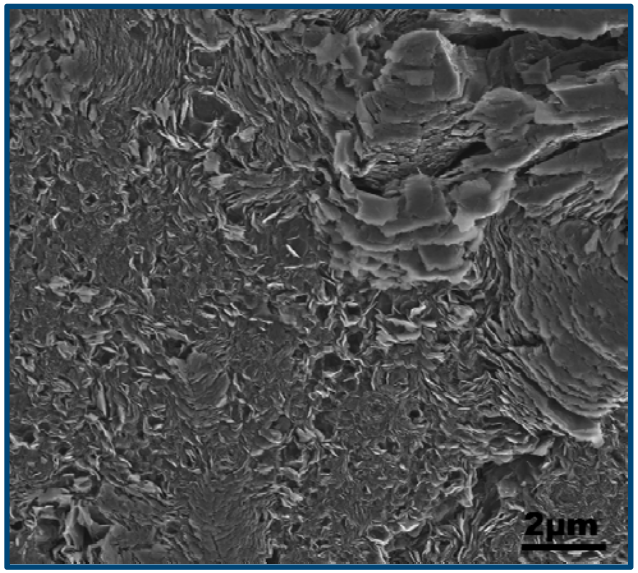
- To understand and analyze microstructure of nuclear grade graphite and graphite matrix
- To understand
- To understand how graphite microstructure will affect salt-graphite interaction and tritium transport
- To understand the important of graphite surface condition for salt-graphite interaction and tritium transport

Summary of Discussion Topics

1. Graphite Characterization
2. Salt-Graphite Interaction
3. Hydrogen Isotope in Graphite
4. Other Species in Carbon: corrosion products, activation products(EDS results)

Graphite Sample Preparation

- Sample preparation causes:
  - Exfoliation
  - Smearing
  - Microstructural defects
  - And……
- These inevitable effects increase the uncertainty of microstructural characterization (BET, Raman, XRD, SEM), especially for comparison of multiple types of graphite.
- What are standard/recommended procedures?
- If not, how to standardize a widely accepted procedure?



SEM image of gently polished IG-110 showing graphite flakes on surface

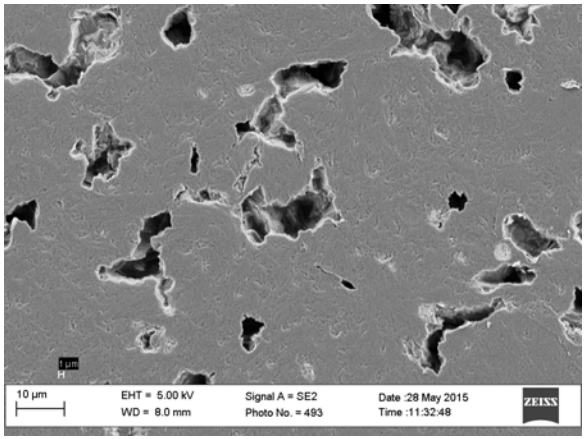
Characterization of Nuclear Graphite

- In addition to the physical properties, what are the necessary or required microstructural characterizations to evaluate nuclear graphite?
- Physical properties:
  - Density
  - Porosity
  - ash content
  - strength
- Microstructure:
  - Grain size
  - Crystallization
  - Graphitization
  - d(002) spacing
  - Nano-size cracks
  - And ……

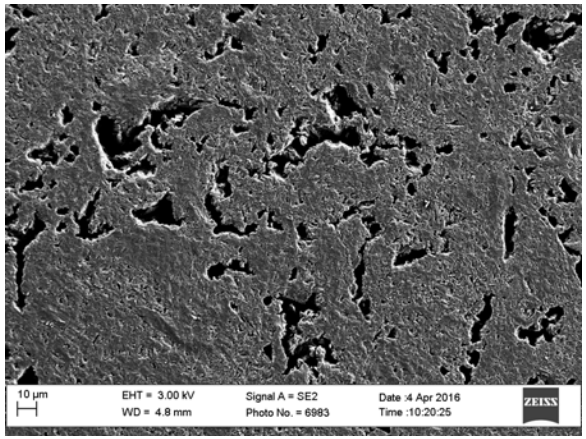
Photo courtesy of Japan Atomic Energy Agency

Graphite Characterization (UW-Madison)

- Ongoing Work:
  - Density Measurement
  - X-ray Diffraction
  - Raman
  - SEM
  - Optical Spectroscopy



A3 Matrix graphite 2500x Magnification

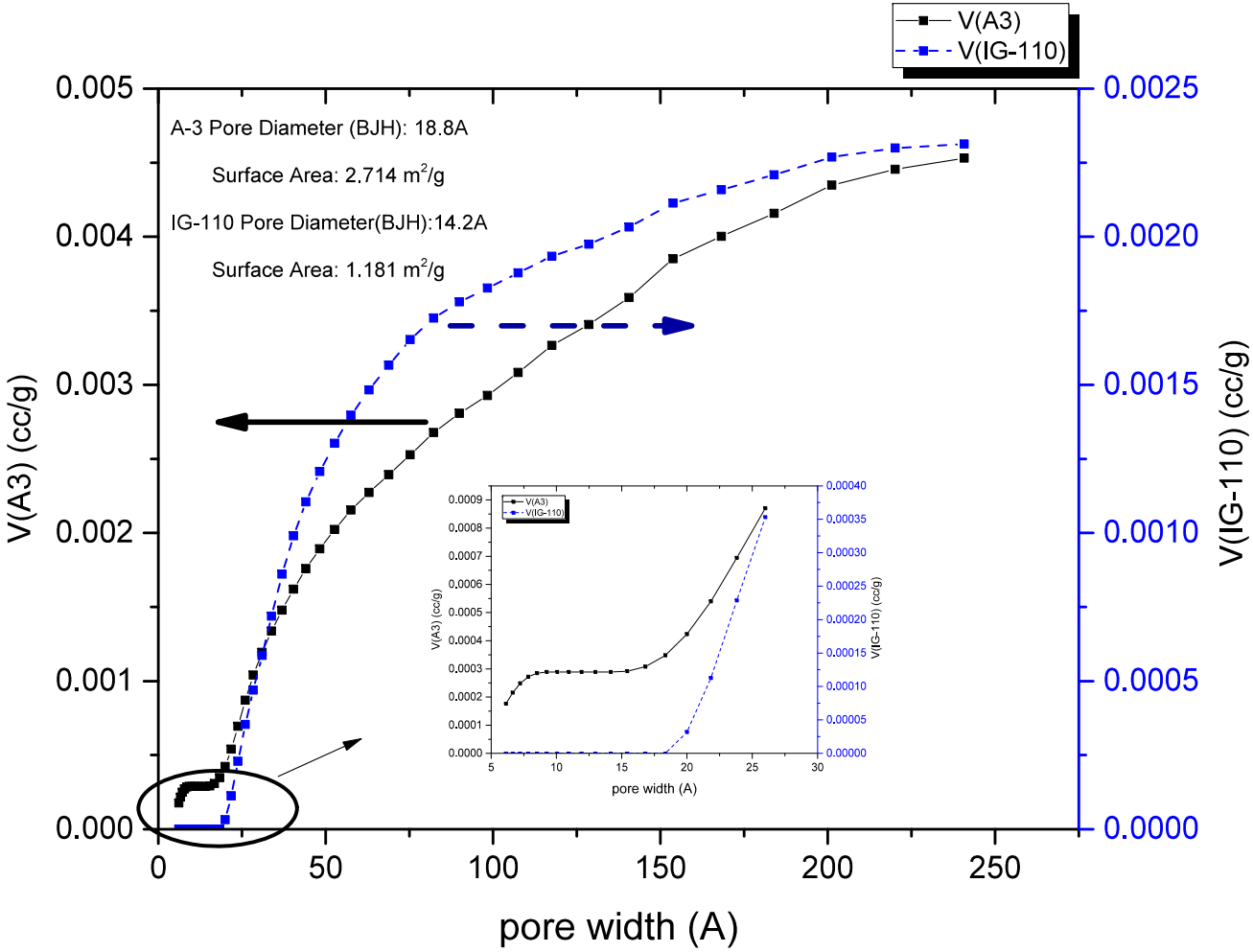


IG-110 1000x magnification

- Summary

Graphite	Porosity (%)	Average Pore size [µm]	Surface area [m2/g]	Crystallite size		Lattice Parameters		G (%)
				Lc[nm]	La[nm]	a[nm]	c[nm]	
A3	33.82	2.720	2.564	4.25	9.04	.24657	.6729	87.98
IG-110	24.42	.8104	1.018	8.04	17.1	.24626	.6748	76.74

Graphite Characterization (UW-Madison)



Porosity Distribution from BET
(BET is done in ORNL by Cristian Contescu)

Graphite Characterization (MIT)

- Ongoing Work:
  - In-Situ X-ray Diffraction (PANalytical X-pert Pro)
  - Pore Size Distribution (QuantaChrome IQC)
  - BET surface Area (Micromeritics ASAP2020, QuantaChrome IQC)
  - SEM (Zeiss Martin HR)

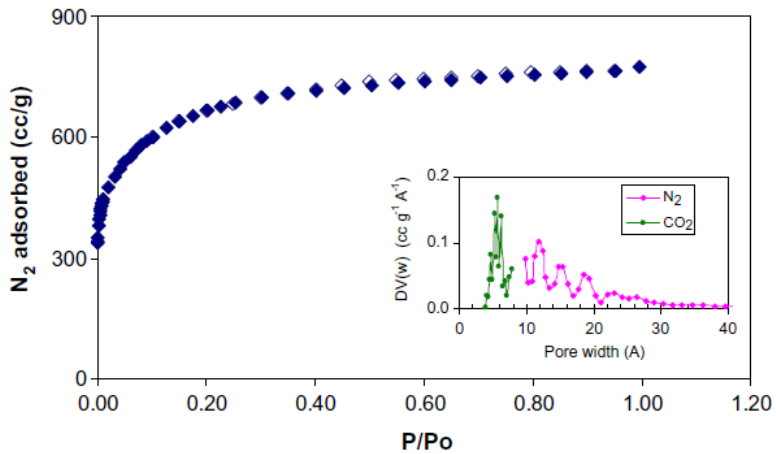
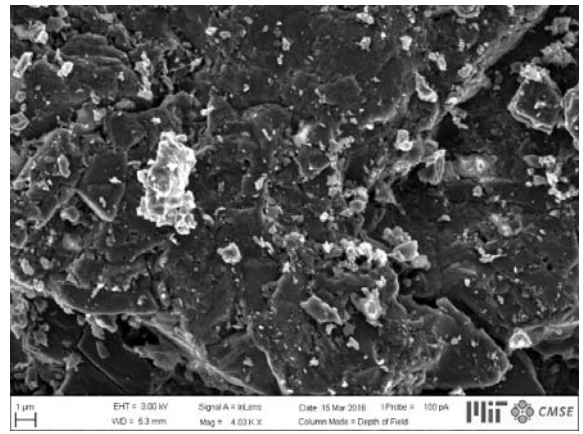
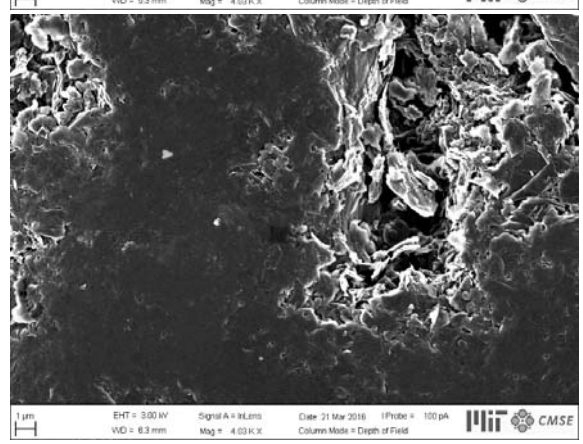


Fig. 1 – Nitrogen adsorption isotherm (77 K) on UMC (adsorption – solid symbols; desorption – open symbols). The inset shows the differential pore size distribution calculated from CO_2 and N_2 adsorption data (NLDFT method, slit-shaped pore model).



a) Calgon Carbon CAL TR12x40



b) IG-110U

Graphite - Discussion Questions

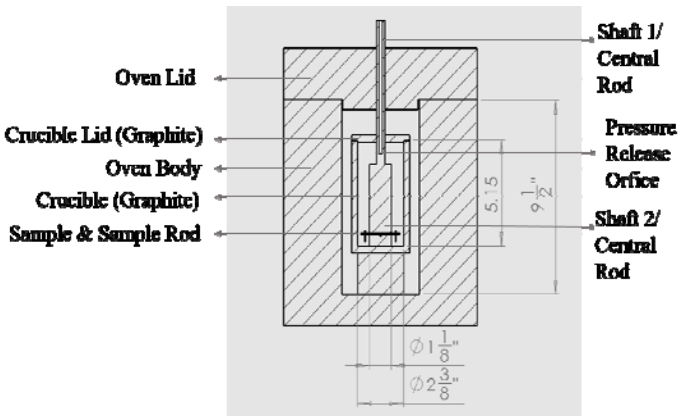
- Identification of graphitization, what will affect graphite graphitization, how to calculate graphitization?
- What should we use as a reference graphite? How can we have a similar images for graphite samples?
- What should we agree on as a sample preparation procedure?
- What graphite parameters will be of the most importance to tritium retention?
- What will be the effects of irradiation on graphite characteristics, especially with respect to tritium absorption?
- How can we optimize tritium absorption in the graphite?

Salt-Graphite Interaction

- **Samples Summary (post-baking): (surface area)**

Sample #	Material	Weight (g)	Surface Area (mm^2)	Dimension(mm)
1(1200)	IG-110	0.46640 ±0.00003	311.788	10.6*10.69*2
2(CUT)	IG-110	0.61898 ±0.00003	333.0302	9.78*9.37*3.91
3(S,CUT)	A-3	0.52002 ±0.00008	384.869	10.97*11.01*3.26
4(L,CUT)	A-3	1.06414 ±0.00002	544.8504	10.95*10.98*6.94

- **Experiment Apparatus:**



SolidWorks Drawing of FIE Setup

Actual FIE Setup

- **Experiment Condition:**
  - Temperature: 700±10 ° C
  - Pressure: GB pressure, 1atm+0.00888atm
  - Salt Type: Flibe ~ 67.4984 g
  - Experiment Time: 12hr

- Note: Crucible, Midrod and lid are all made from IG-110 (provided by INL). The whole weight is 244.4315g

Salt-Graphite Interaction - Priliminary Result

Salt before the Experiment

Salt After the Experiment

Salt in Crucible after the Experiment

Preliminary Result Analysis

- Didn't see graphite particles inside solid Flibe
- No significant weight change observed
    - 12 hr exposure time is not enough
    - GB pressure (~atmospheric pressure is not enough)
- Path Forward:
    - Spectroscopy
    - Elemental Analysis
    - Longer exposure time
    - Higher pressure

Salt-Graphite Interaction -Discussion Questions

- Is there a threshold pressure for salt(Flibe) intrusion into graphite ? Will atmospheric pressure be above or below the threshold pressure?
- How to identify salt-graphite interaction mechanism under high temperature? How to define interface between salt and graphite ? Will new phases be created or just impregnation of salt into pores?
- After static salt-graphite experiment, black particles will appear in solid salt, what spectroscopy or elemental analysis can be applied to identify the black particles (considering light element-Li,F,Be, etc.)
- How to relate data from salt-graphite interaction to tritium in carbon ? How tritium behavior in this interface will be different from else where?
- Will we see big difference between Flibe and Flinak, A-3 and IG-110 ? Will redox potential of salt will affect salt graphite interaction
- Is it useful to model salt-graphite interaction? How?

Hydrogen Isotope in Carbon (UW-Madison)

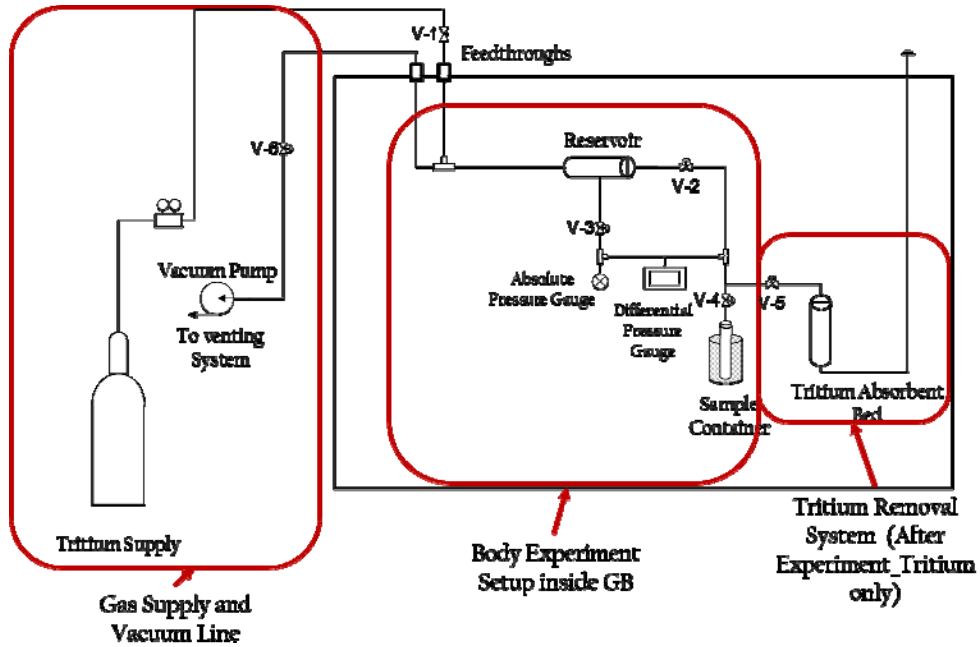
- Experiment Apparatus

Sample Container:

- Size: 5.6 in
- Volume: ~0.81 in^3

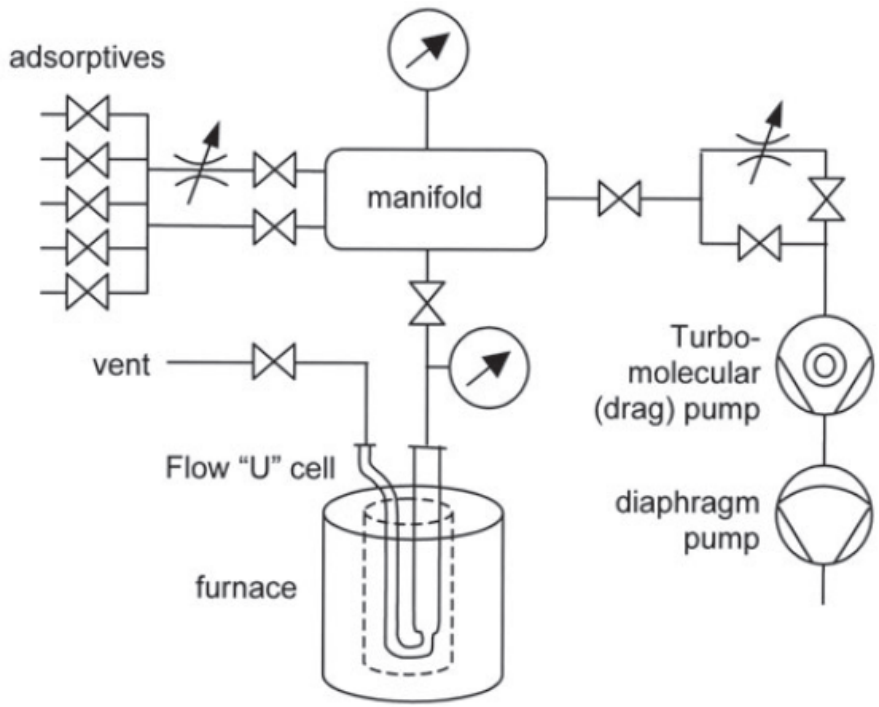
Reservoir:

- Size: 5.5 in
- Volume: ~4.18 in^3



- Experiment Condition:
  - Temperature: ~650 ° C
  - Pressure: 1 Pa – 20 Pa (hydrogen is supplied from 5% H_2+Ar gas cylinder)
  - Sample: Un-irradiated and Irradiated IG-110 & A3
- Future Work:
  - Sample Prep: hydrogen baked under 1000 C for hours & high T baked under Ar Gas environment
  - Leakage calculation
  - Leak test
  - Base Run
    - » 1st run under room temperature for the whole system
    - » 2nd run with heated sample container

H_2/D_2 Adsorption Apparatus (MIT)



Instrument Schematic

Samples

- Activated Carbon (Maxsorb, etc.)
- C/C Composites
- Nuclear Graphite (A3, IG-110U)
- Graphene

Instruments

- QuantaChrome IQ-C
- Pfieffer Prisma Plus

Standards

- Palladium Sponge

Analyses

- Static Adsorption
- Dynamic Temperature Programmed Desorption
- Mass spectrometry

S. LOWELL et. Al. "Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density". Norwell, MA, USA: Kluwer Academic Publishers.

Static Adsorption Experiment (MIT)

Experimental Conditions

- Sample weight: 1 – 5 grams
- Sample Prep: Ultrasonication in acetone, drying in air at 150°C, de-gas at 1100°C for 2 hr
- Pressure: 0 – 10,000 Pa
- Temperature: 700°C

Data Analysis

- Fit to adsorption isotherms
  - Freunlich
  - Langmuir
  - Etc.

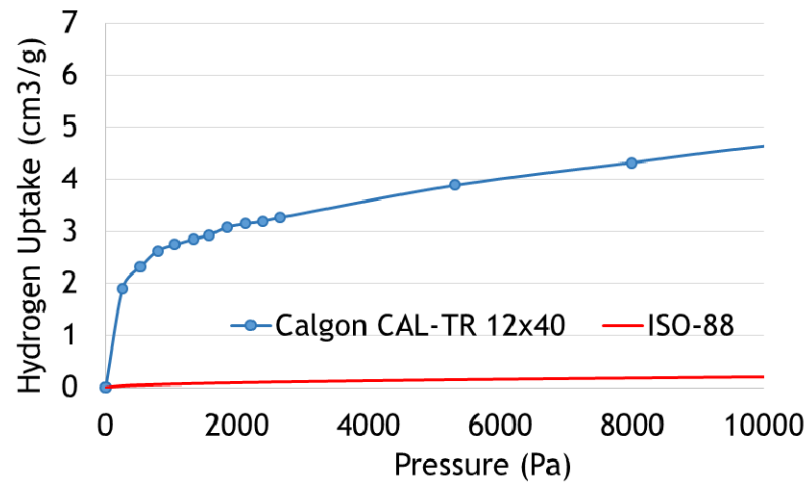
Preliminary Data

- Activated Carbon: 1.9 to 6.6 cm^3/g
- ISO-88[1]: 0.03 – 0.36 cm^3/g (Base Case)
- Molecular Freundlich (R^2=0.9927)

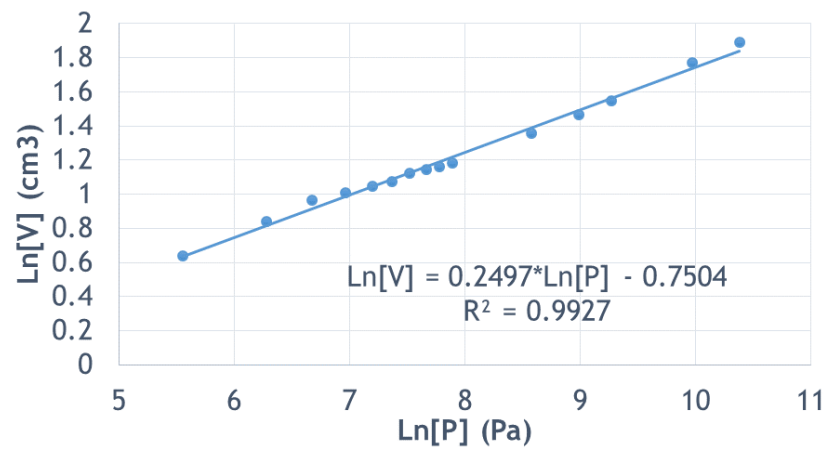
Future Work

- H2/D2 Adsorption: Solubility and diffusion over FHR operating conditions. 600-800degrees C, 0 – 20 Pascal
- Characterization: Characterization of Carbon: SEM, XRD, BET, Pore Size, etc.

Preliminary Measurement



H_2 Uptake vs. Pressure (700°C)



Ln[V] vs. Ln[P]

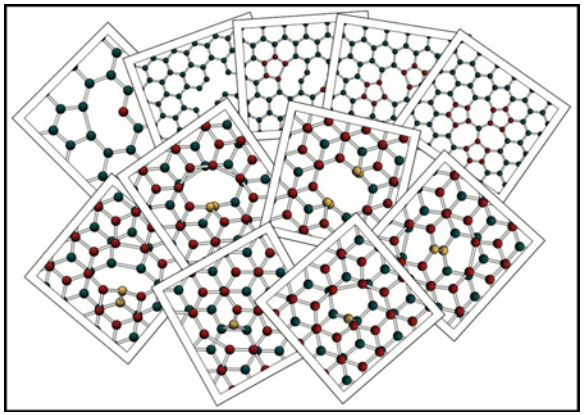
Hydrogen Isotope in Carbon - Discussion Questions

- What pressure range for hydrogen-graphite absorption experiment?
- What kind of uncertainty of the experiment (non-uniform heating, leakage, pressure gauge, etc.) should we focus on? how this uncertainty will affect the result? How to characterize these uncertainty?
- $H_2/D_2/T_2$
- For the purpose of standardization, what are good practices for sample preparation? Ie. Cutting, grinding, polishing?
- Does the hydrogen diffusion behavior change at low pressure?
- What output can be expected from TDS and what analysis can be done (hydrogen diffusion path, trapping sites, etc.)
- How to introduce hydrogen into salt-graphite system? How will this affect salt chemistry?
- De-couple hydrogen diffusion in bulk salt, salt-graphite interface, and bulk graphite

Other Species Diffusing into Graphite

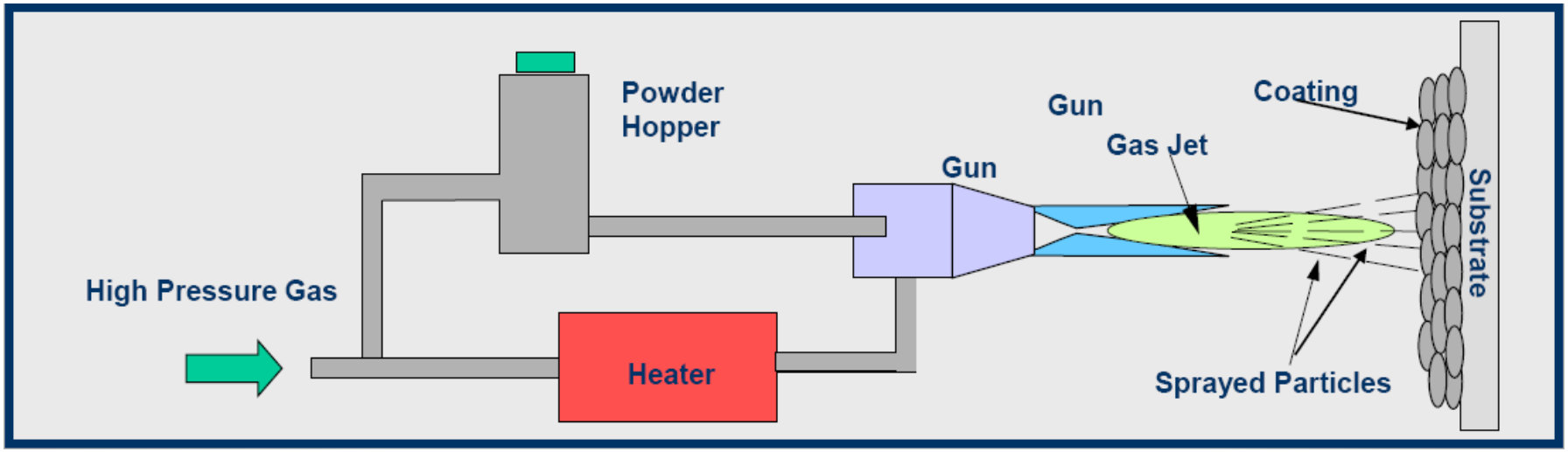
- In high-temperature molten salt system including fluorides, graphite and alloys, what are the other species diffusing into graphite?
  - Initial impurities from salt: metal ions, oxides, sulfurs
  - Corrosion products: mainly Cr
  - Fission products: Ag and Cs, for instance
  - Any others should be considered?

- How do these diffusions impact the performance of graphite in molten salt?
  - Irradiation resistance
  - Thermal conductivity
  - Tritium absorption
  - And…….



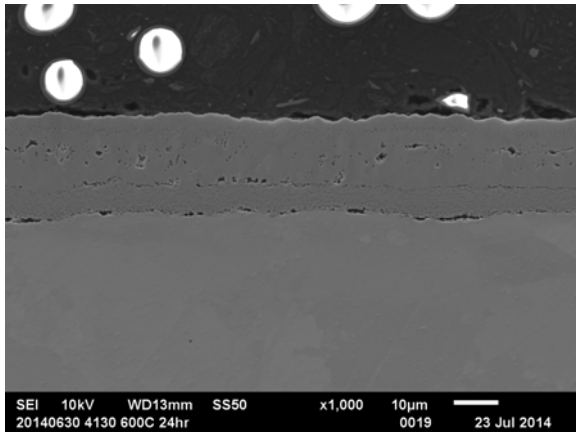
Vacancies and Frenkel defects in graphite

Cold Spray Materials Deposition Process

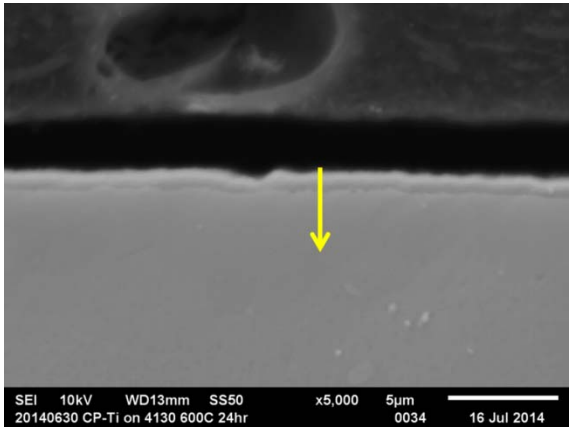


- High velocity powder particles propelled by a gas onto the surface of a substrate/part to form a coating
- Particle temperature is low – particles are <u>not melted and deposition occurs in solid state</u>
- High deposition efficiency

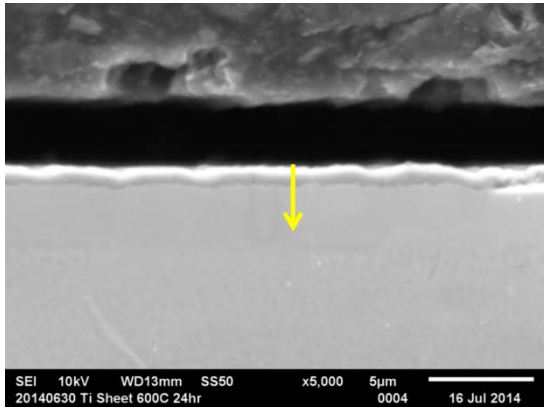
Samples after Ambient Air Oxidation Tests at 600°C for 24 hours



4130 Steel

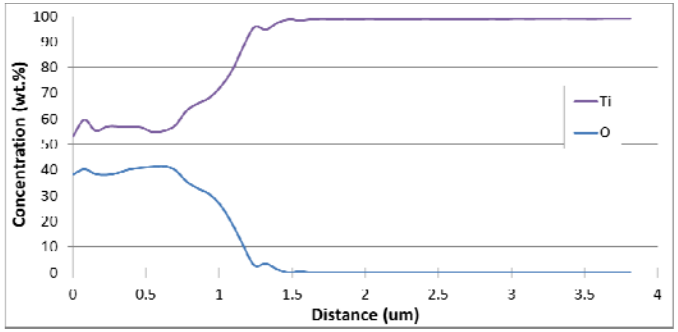


CS Titanium Coating on 4130 Steel

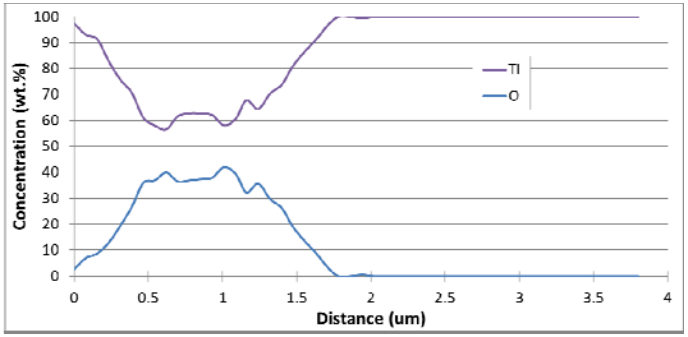


Titanium Sheet

Oxide layer thickness ~ 20µm



~ 1µm



~ 1µm

Wrap-Up Discussion

- Future Work
  - Graphite Chracterization (both UW and MIT)
    - ✓ UW focuses on A3 and IG-110
    - ✓ MIT will investigate various of materials, including nuclear grade graphite, C-C, graphene and activated carbon
  - Benchmarking and data comparison between UW (HGE_Constant Volume Method) and MIT (Static Adsorption Experiment)
    - ✓ Material: IG-110 & A-3 (UW); Activated Carbon, C/C Composites, Nuclear Graphite and Graphene (MIT)
    - ✓ Sample Prep
    - ✓ Experiment condition: pressure, temperature, time, etc …
    - ✓ Post-Experiment Measurement: TDS, CNPGAA, etc …
  - Salt-Graphite Interface
    - ✓ Different sample prep to relate graphite microstructure to salt intrusion
    - ✓ Different Exposure time to investigate dynamic process of salt intrusion through depth profiling from elemental analysis
    - ✓ Salt intrusion for both A3 and IG-110 with same surface condition to relate back to crystallite size, porosity, specific surface area, etc… which are determined by raw material and manufacturing process

Recap of Questions

1. Summary of questions asked and brief summary of main take-aways from the discussion, to be given by the facilitators.