INL/MIS-22-67925-Revision-0

Graphite Material Behavior: NRC Graphite Behavior Model

August 2022

Changing the World's Energy Future

William E Windes

Idaho National Laboratory

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

INL/MIS-22-67925-Revision-0

Graphite Material Behavior: NRC Graphite Behavior Model

William E Windes

August 2022

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Graphite Material Behavior

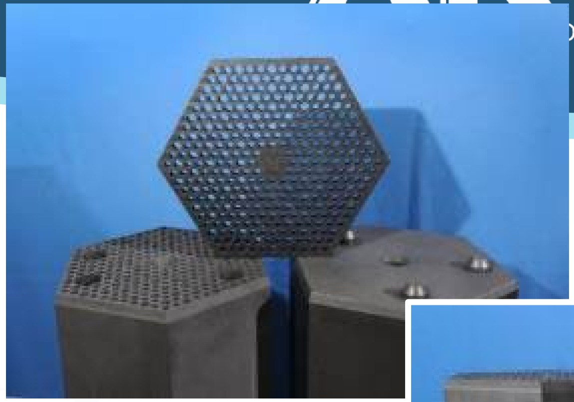
NRC Graphite Behavior Model

NRC Graphite Behavior Model Presentation
NRC Headquarters, Gaithersburg
1-2 August 2022

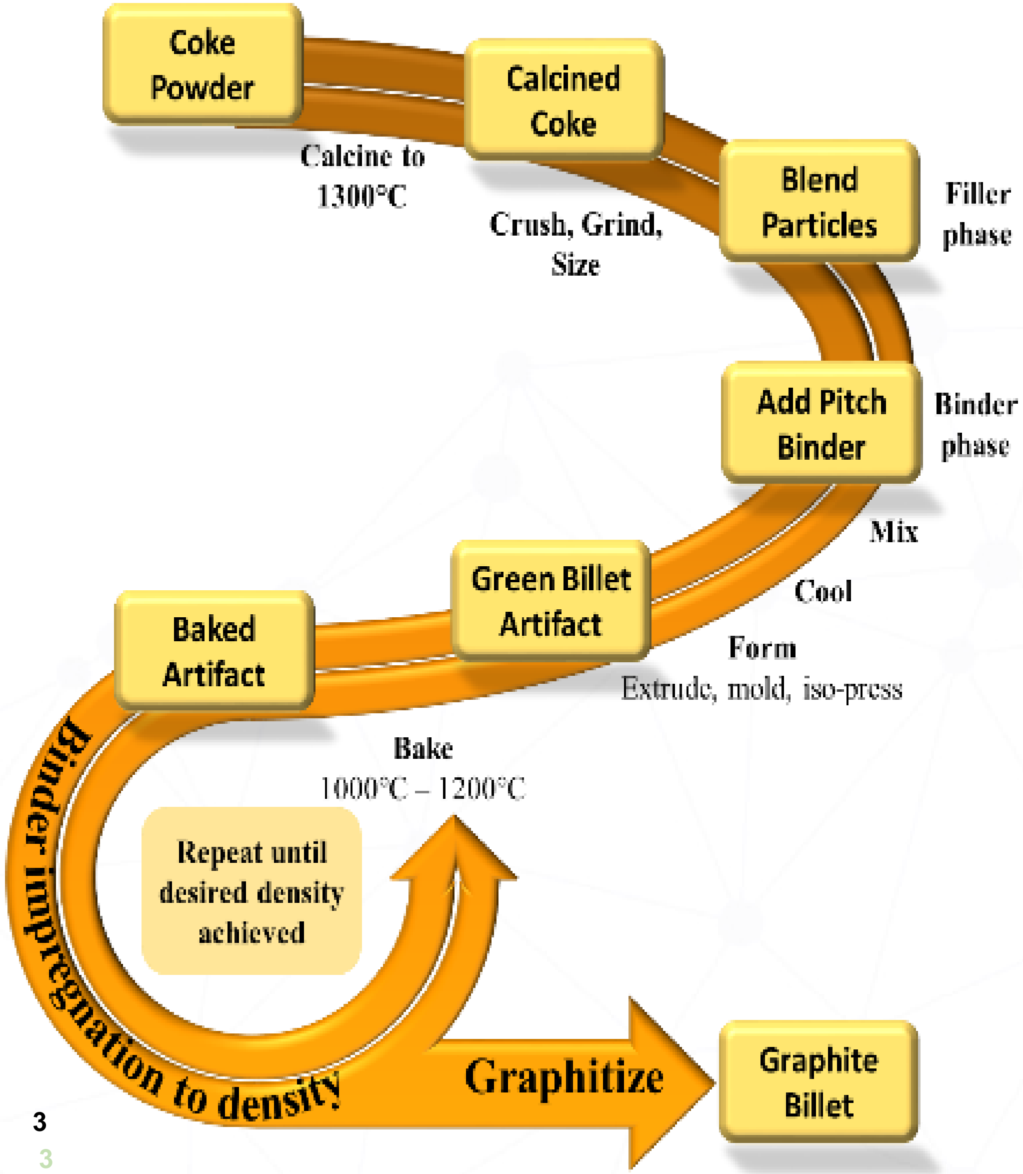
ADVANCED REACTOR TECHNOLOGIES

General graphite material properties: Topics

- Introduction to graphite
  - Fabrication of graphite
  - Unique features of nuclear grade graphite
    - *Providing the properties*
  - As-fabricated material properties of interest
    - *Thermal diff, thermal stability, mechanical strength, etc.*
- General graphite behavior and degradation
  - Microstructure: key to behavior
    - *Crystallographic structure*
      - *Basal plane (covalent) bonding*
    - *Porosity and pore microstructure*
  - Degradation
    - *Irradiation behavior*
    - *Oxidation behavior*
    - *Molten salt issues*



Graphite Manufacture and some unique properties

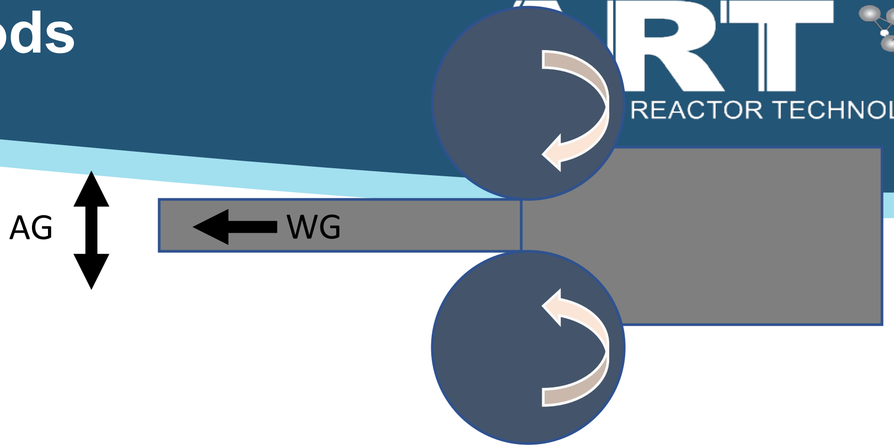


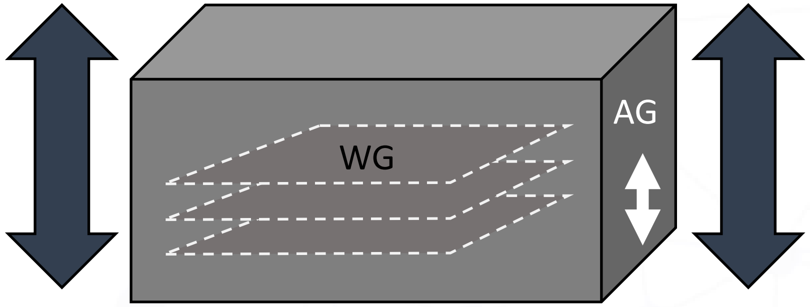
- To understand graphite behavior need to know the unique manufacturing process
  - Filler particles: petroleum coke/pitch coke
  - Binder phase: pitch-based liquid binder
    - *Impregnation process and density achieved*
  - Filler-binder ratio: range of particle sizes
  - Fabrication methods: extruded, vibrationally molded, isostatically molded
- Graphite is manufactured from calcined coke and a pitch binder.
  - Multiple pitch impregnations to increase density
- Graphite is anisotropic naturally.
  - How do we make isotropic material?
    - Grind filler particles to desired size
    - Mix randomly in liquid binder
    - Form into large billet (three different methods)
    - Baked green billet is heterogenous mix of filler particles bound by carbonaceous binder phase

Graphite fabrication : 3 primary forming methods

Extrusion

- Quick and cheap method
- Maximum texturing
  - *With grain = parallel to extrusion direction*
  - *Against grain = perpendicular to extrusion*



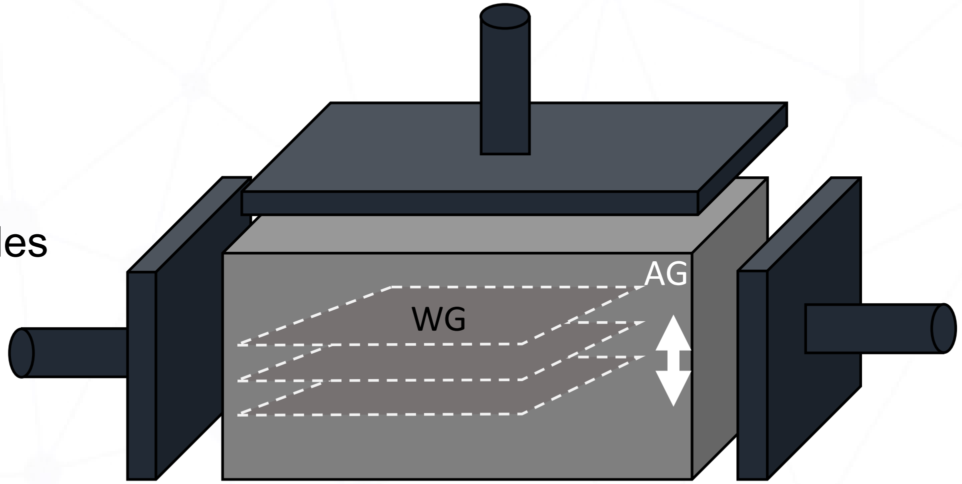


Vibration molding

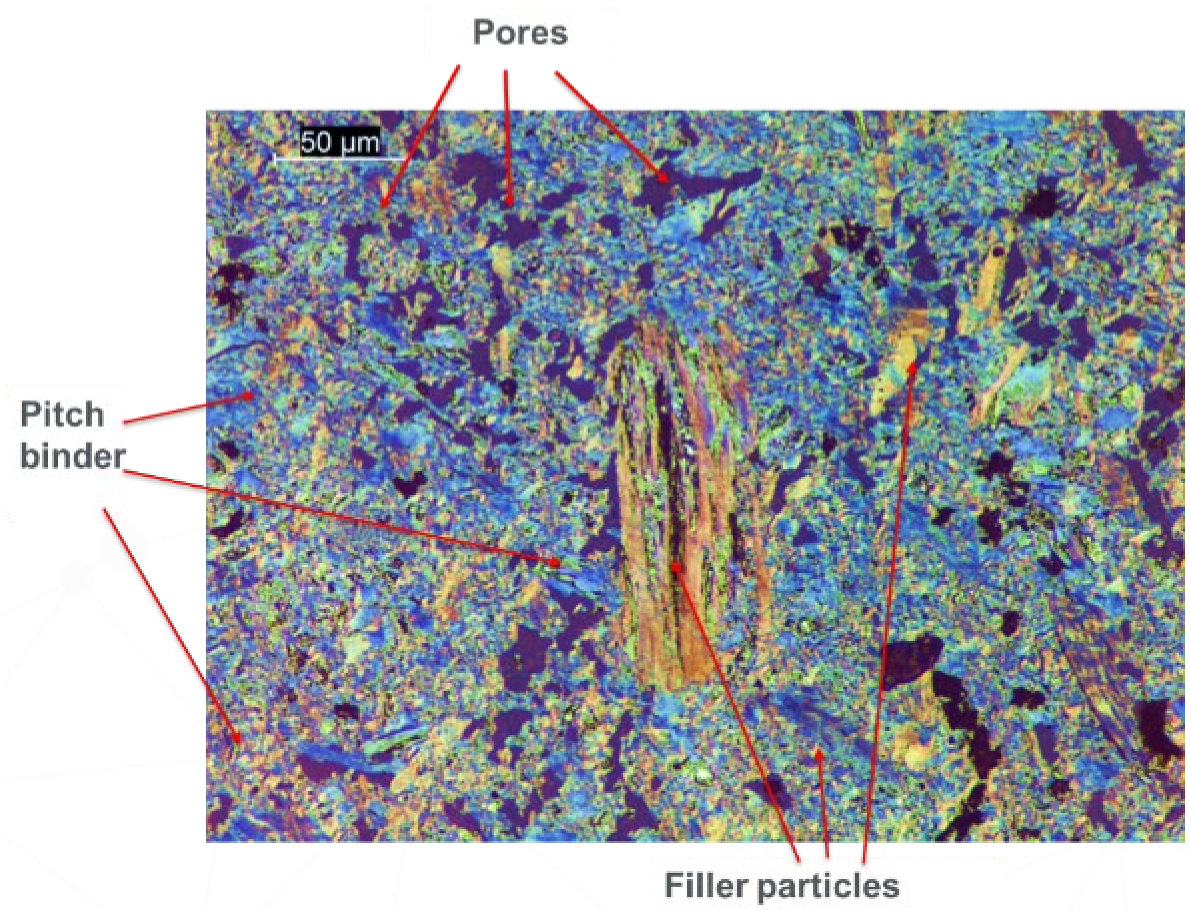
- Pour grain and binder mixture into a box and shake it
- Moderate texturing
  - *With grain = planes perpendicular to gravity direction*
  - *Against grain = parallel to gravity direction*

Isostatic molding

- Grain and binder mixture pressed from all six sides
- Small texturing
  - *With grain = planes perpendicular to gravity*
  - *Against grain = parallel to gravity direction*



Graphite Manufacture and some unique properties



- Three phases in graphite microstructure
  - Filler particles, binder phase, and pores (~20%)
- Pores and pore structure define graphite behavior
  - Pore size range : nm to mm
  - Large flaws (cracks/pores) result from fabrication
    - *Filler particles bound together with carbonaceous binder*
    - *Interstitial gaps between filler provide pores and cracks*
  - **But** small (nm) pore structure gives irradiation stability also comes from
    - *Mrozowski cracks (accommodating porosity) within crystallites*
    - *Basal planes are separated during graphitization step during fabrication.*
- **Must have pores**
  - More accurate : must have accommodating porosity

Graphite Manufacture and some unique properties

ADVANCED REACTOR TECHNOLOGIES

Material Properties

- Near-isotropic material response
- High thermal stability > 3000°C
  - *Well above any accident temperatures*
- High heat capacity (thermal sink)
- High thermal conductivity (better than metal)
- Density: 15% - 20% porosity
- Purified graphite: Low activation (Medium waste)
- Chemically inert (Molten salt)
- Neutron moderator (thermal designs)
- Easy machinability / cheap material
- High compressive / Low tensile strength
  - *Ceramic composites for tensile*
- Ceramic like material response
  - *Low fracture toughness (~ 1-2 MPa √m)*
  - *Quasi-brittle cracking*

Component Behavior

Decent irradiation response

- Smooth dimensional change
  - *Life-limiting mechanism*
  - *Multiple decades of safe operation*
  - *And **even longer** at lower temperatures*
- Generally gets stronger with irradiation
- Isotropy stays relatively constant
- Thermal stability and capacity are unaffected

Oxidation and molten salt intrusion

- Graphite does oxidize at all temperatures

  But it does not burn!
- Oxidation behavior depends on pore structure
  - *Irradiation increases oxidation rate*
- Molten salt can penetrate pore structure
  - *Potential for erosion/abrasion*

Qualifying graphite: As-fabricated properties

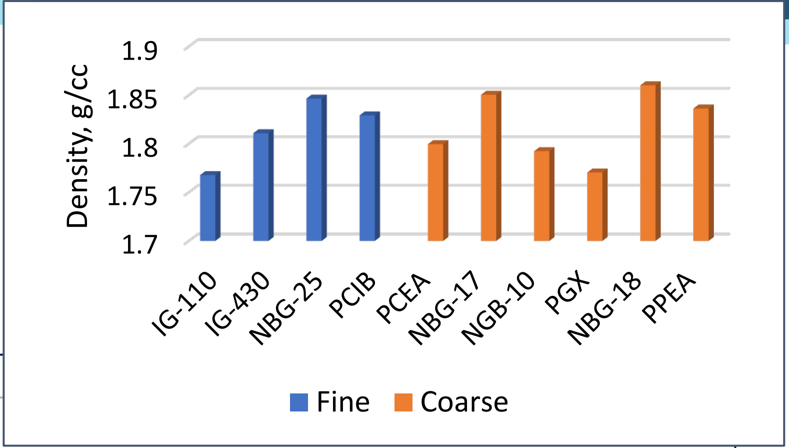
From ASTM D7219 : *Standard Specification for Isotropic and Near-isotropic Graphites*

Property	Nominal Range	Performance Attributes
Density	1.7 - 1.9 g/cm^3	Neutron efficiency, Structural integrity, Thermal efficiency
Thermal Conductivity (at Room Temperature)	> 90 W/m/K	Heat transport
Purity (Total Ash Content)	< 300 ppm	Reduced component activity levels during replacement and/or disposal Reduced graphite oxidation under normal and accident conditions.
Tensile Strength	> 15 MPa	Structural integrity
Compressive Strength	> 45 MPa	Structural integrity
Flexural Strength	> 20 MPa	Structural integrity
CTE (20°C to 500°C)	3.5 to 5.5 x 10^{-6} K^{-1}	High value is indication of isotropy = dimensional stability under irradiation Lower value potentially beneficial in terms of thermal stress
CTE Isotropy Ratio	< 1.10	Irradiation dimensional stability Structural integrity
Dynamic Elastic Modulus	8 – 15 GPa	Structural integrity Irradiation creep
Dimensional Changes with Irradiation	Minimal shrinkage Minimal differences in with-grain and against-grain directions	Structural integrity (lower internal stresses)

Graphite unirradiated vs. irradiated properties

ADVANCED REACTOR TECHNOLOGIES

- Now you **can** make a graphite with better properties
  - Increase the **density** and you increase unirradiated material properties
  - Improved unirr. strength, modulus, CTE, etc.
- But the irradiated properties can be reduced
  - PCIB is a good example
    - *Fine-grain graphite*
    - *Dense, strong, good thermal properties*
    - ***But** it has the lowest turnaround & crossover doses*
  - Bulk density isn't only parameter for irradiated performance
    - *NBG-18 and NBG-25 have higher densities*
    - *The key is accommodating porosity levels*
  - More **accommodating porosity** = higher dose lifetime
- Graphite specialists are still trying to figure out underlying mechanisms
  - Accommodating porosity is probably the entire range of pore sizes (nm – mm).



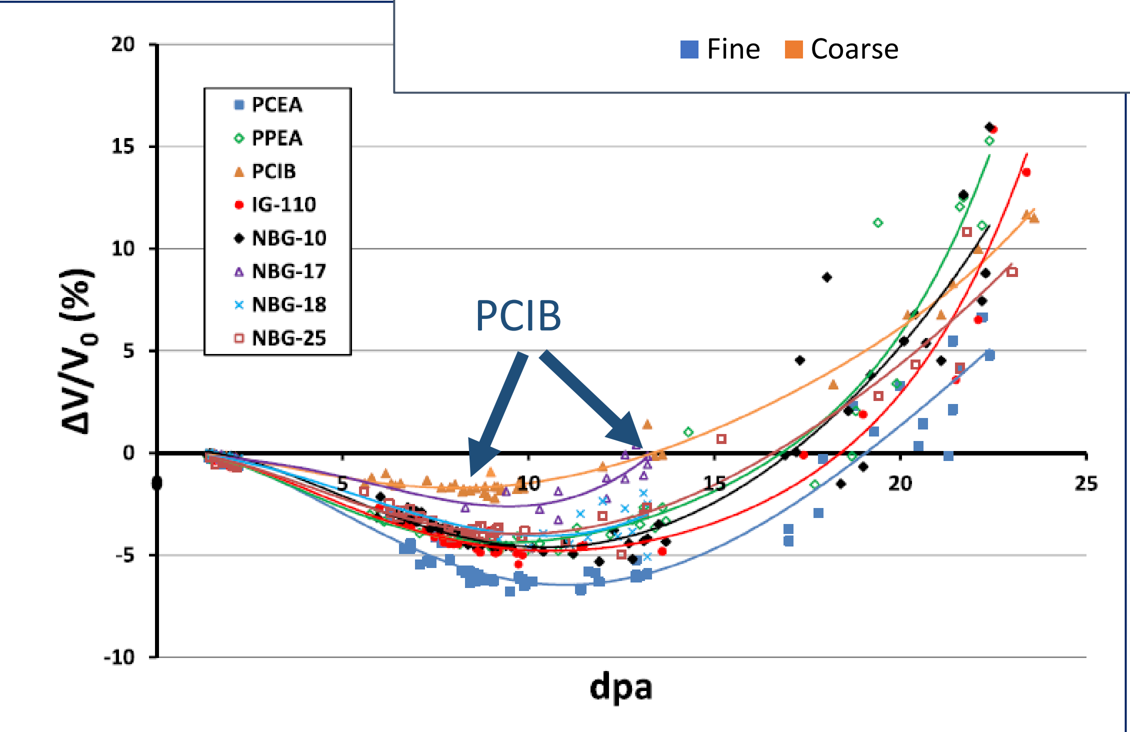
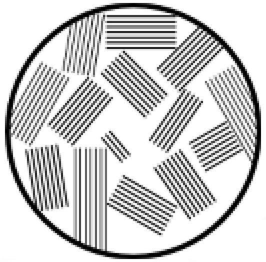


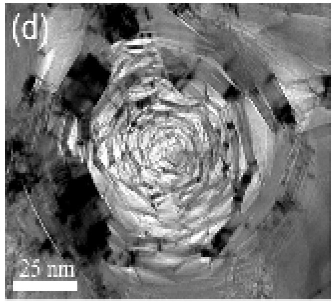
Fig. 2. Dimensional change as function of dpa at 750 °C.

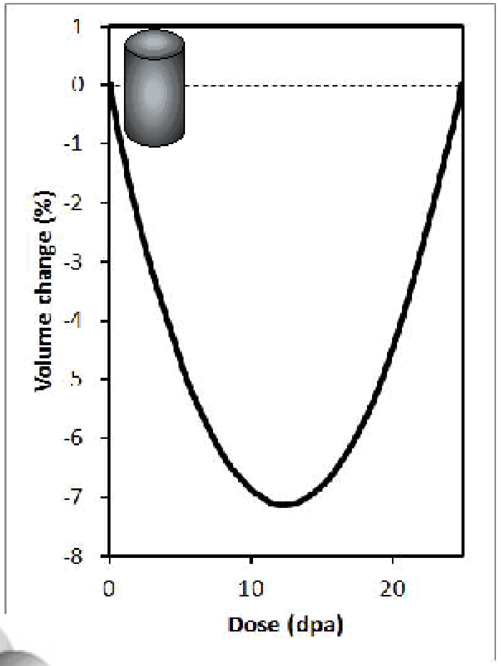
Graphite irradiation behavior ☢

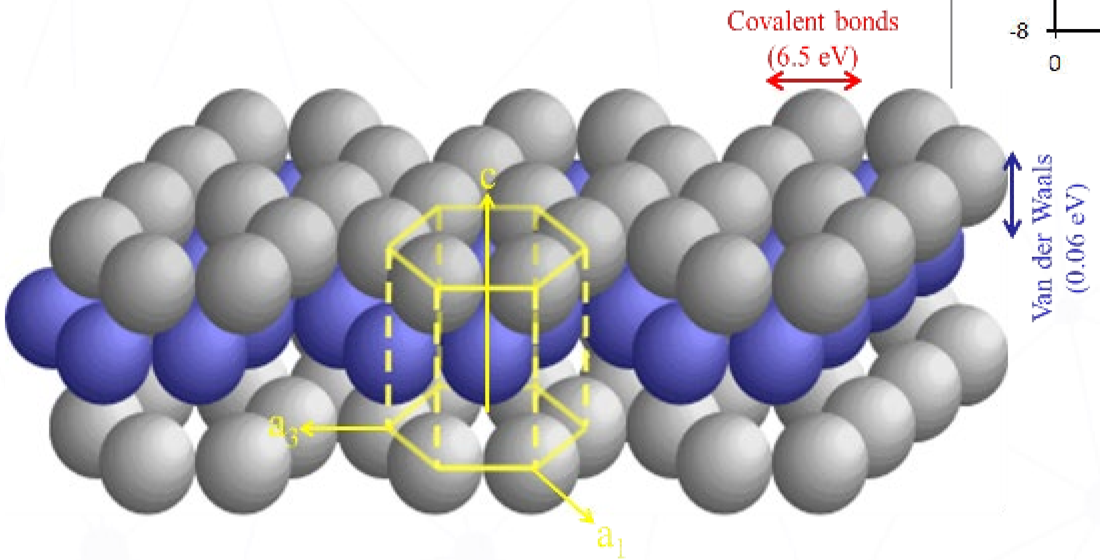
Key irradiation parameters

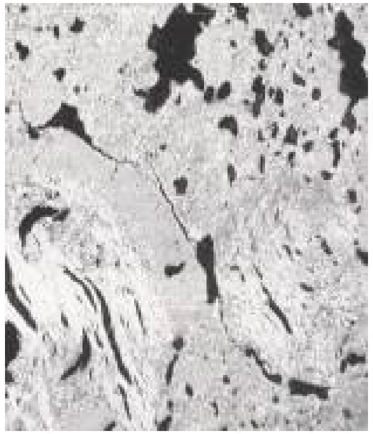
1. Irradiation dimensional change is life-limiting mechanism
   I. All designs **must determine** selected graphite turnaround dose
   II. Build-up of internal stresses ➔ cracks
2. Irradiation creep is good
   I. Creep relieves internal stresses
3. A basic understanding of graphite microstructure is needed
   I. To understand changes in irradiation behavior
   II. To assess whether design conclusions are accurate
4. Temperature is critical in nearly all irradiation induced property changes





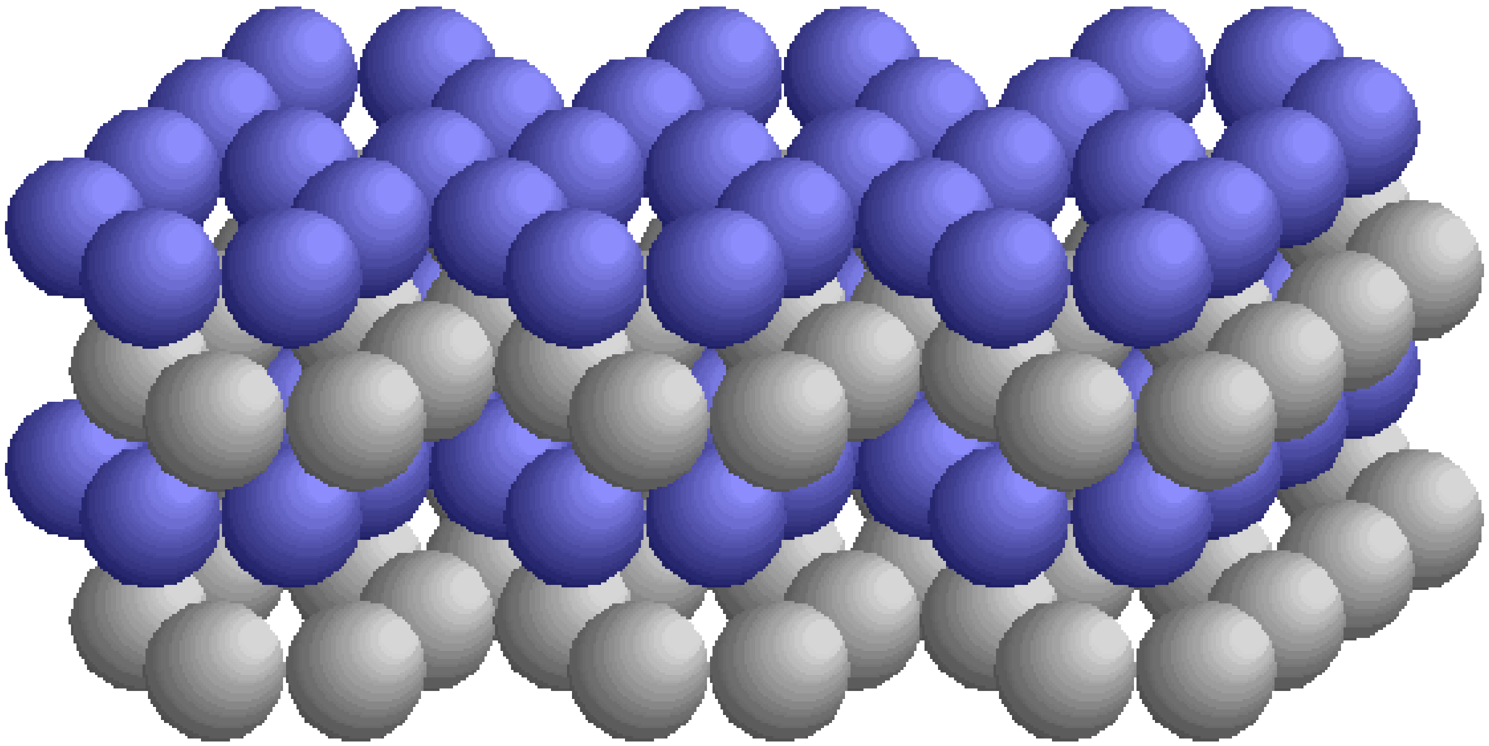






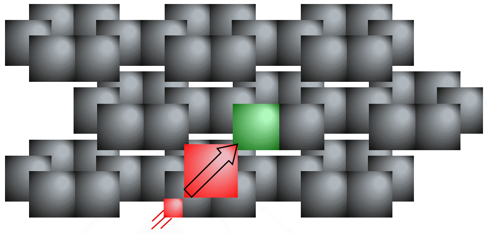
Mechanisms underlying irradiation damage

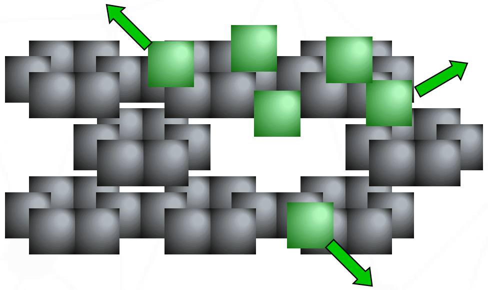
- Ballistic event physically displaces atoms for lattice position
- Sub-plane formation, vacancy clusters



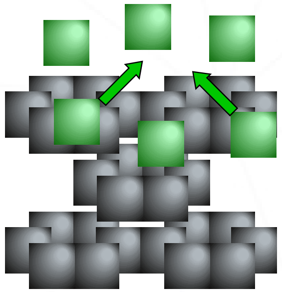
Model describing irradiation damage

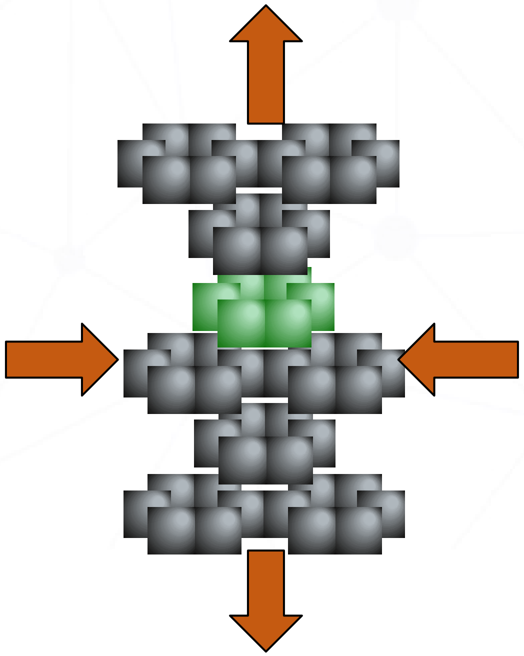
- Ballistic event physically displaces atoms for lattice position
- Sub-plane formation, vacancy clusters



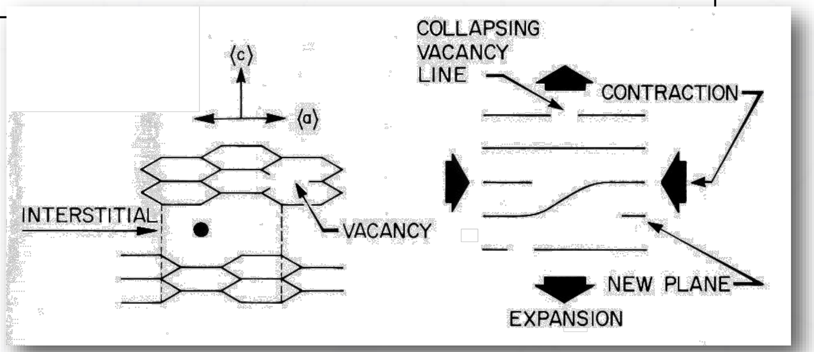


- Sub-plane formation between basal planes
- Vacancy cluster/loop collapse

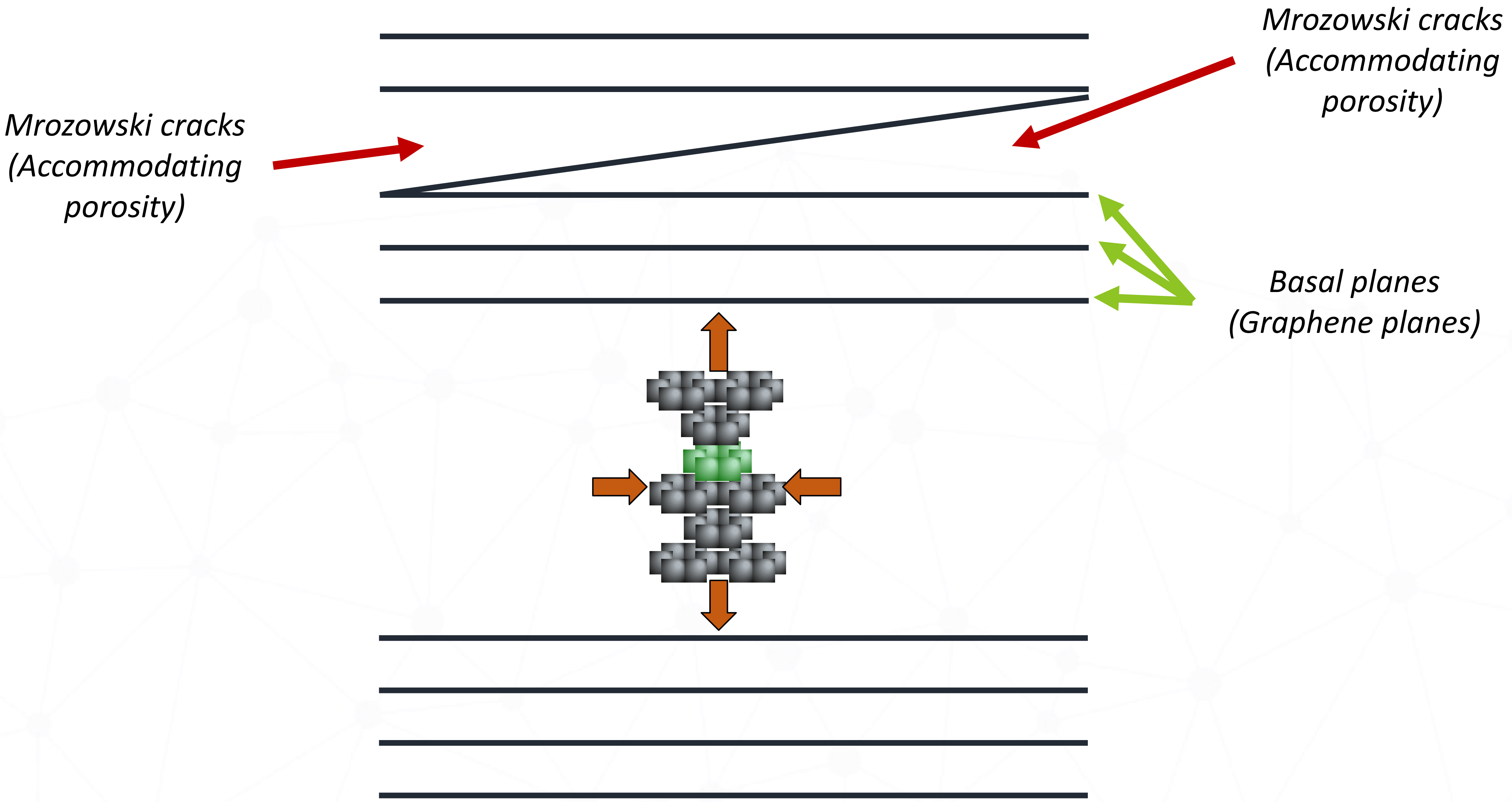




- **Crystallites shrink parallel to basal planes**
- **They grow perpendicular to planes**

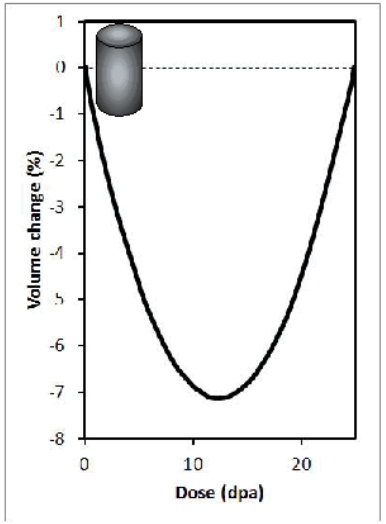


Model describing irradiation damage

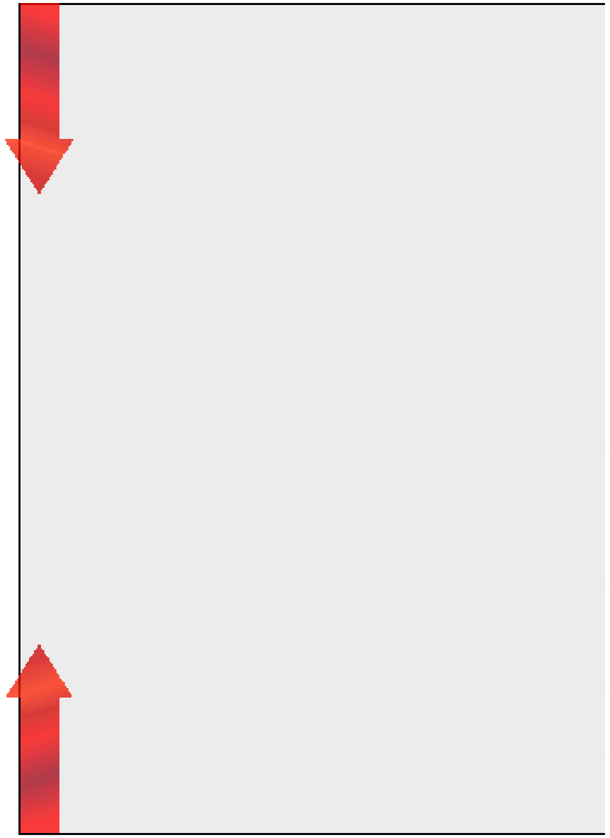


What makes irradiation so detrimental?

- Irradiation = internal stress build-up inside graphite
  - Due to the anisotropic material response of graphite crystal structure, internal stresses build up
    - *Stresses are dose dependent and temperature sensitive*
      - ***As dose increases the accumulated dimensional change increases***
      - ***At high dose levels volumetric shrinkage becomes expansion***
    - *Seen as macroscopic dimensional change*



G. Haag," ***Properties of ATR-2E Graphite and Property Changes due to Fast Neutron Irradiation", Juel-4183, 2005***

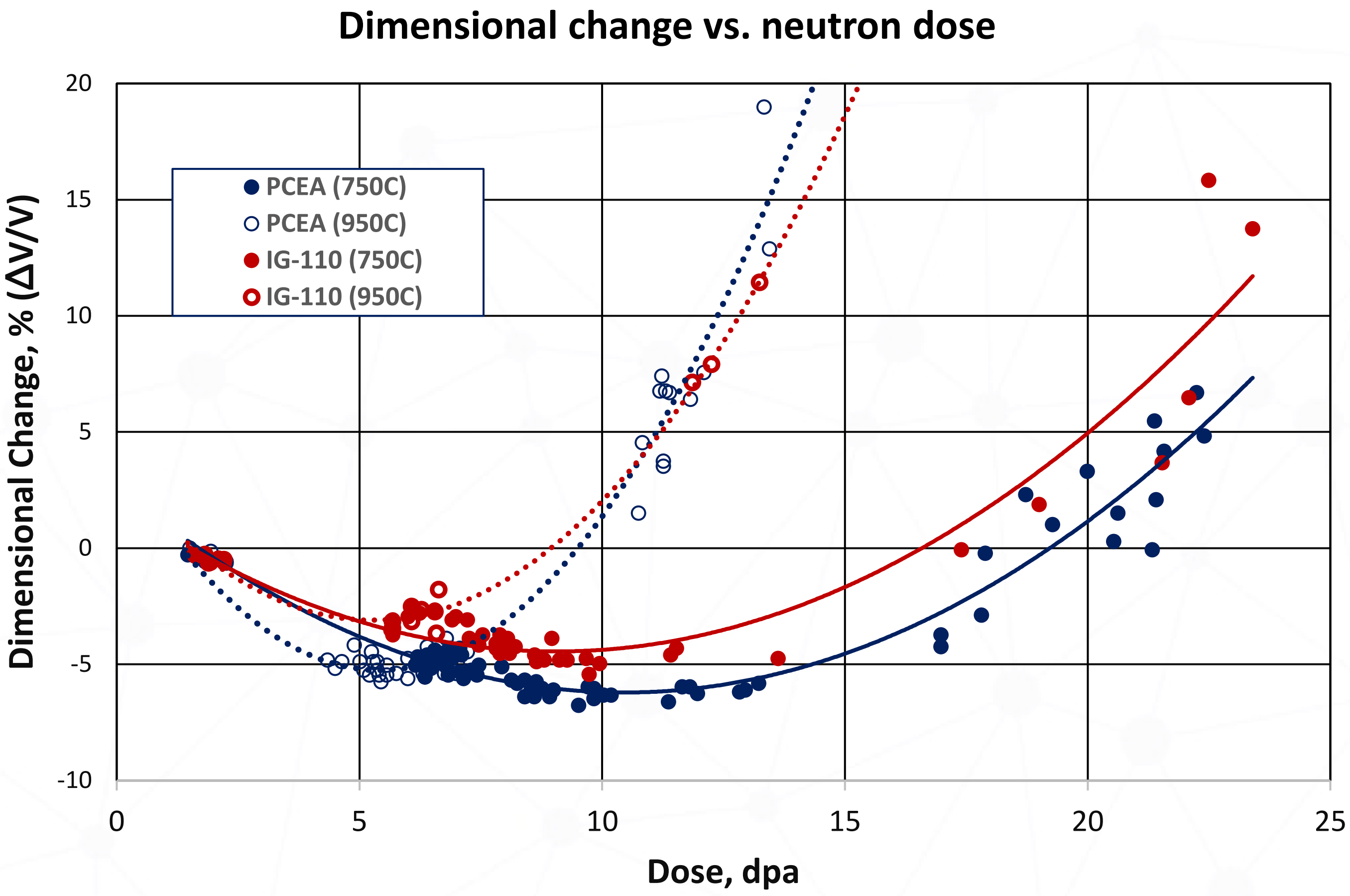


  - Due to the anisotropic material response of graphite crystal structure
    - *New cracks formed after Turnaround*
    - *Internal stresses from dimensional change. Need creep response, too*
    - *Changes to density, strength, CTE, thermal conductivity, modulus, etc.*

Turnaround dose – critical parameter

ADVANCED REACTOR TECHNOLOGIES

All vendors must establish turnaround dose for their graphite grade



- Why do we care?
  - Point where irradiation induced material property changes begin to reverse.
  - Point where microstructural **densification** stops. Microcracking begins.
- Think of "before" and "after" turnaround
  - Behavior is much more predictable for all graphite grades ***before*** turnaround
    - *Much less predictable (more data scatter)* ***after*** *turnaround*
  - Crack propagation retarded in compressive stress fields.
  - Crack propagation accelerated in tensile
- Turnaround dose changes significantly with temperature
  - IG-110 (50μm) ➔ 10 dpa to 5 dpa
  - PCEA (1800μm) ➔ 11 dpa to 6 dpa

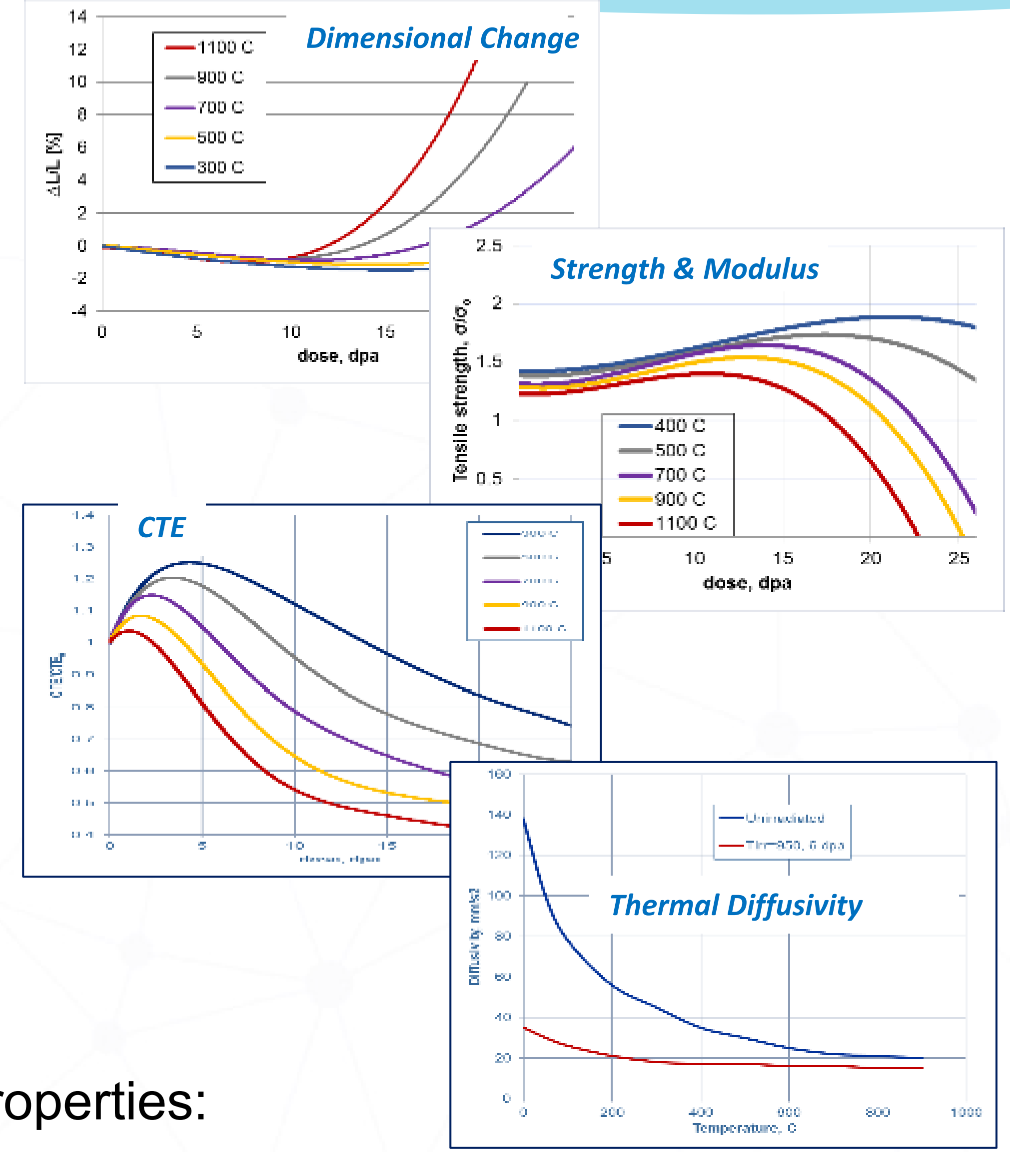
From: M.C.R. Heijna, S. de Groot, J.A. Vreeling, "Comparison of irradiation behaviour of HTR graphite grades", Journal of Nuclear Materials 492 (2017) 148e156

Irradiation Effects on Graphite Properties

ADVANCED REACTOR TECHNOLOGIES

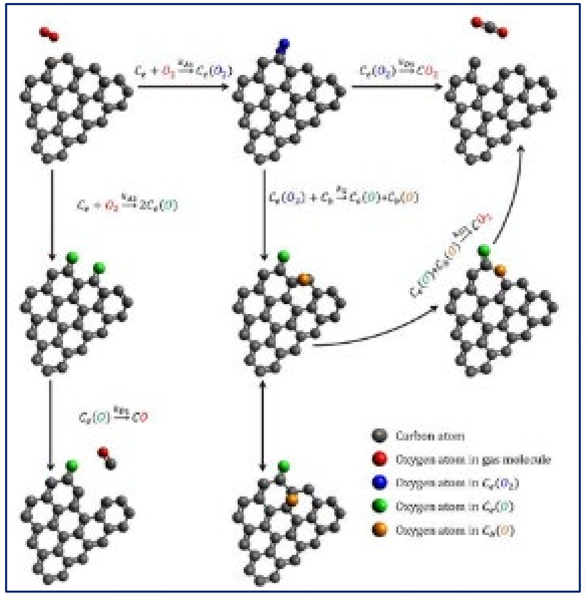
General graphite irradiation behavior

- Significant changes occur during normal operation:
  - Dimensional change
    - ***Turnaround*** *dose is key parameter*
    - *Highly temperature dependent*
  - Density
    - *Graphite gets denser with irradiation until* ***Turnaround*** *dose*
    - *After* ***Turnaround*** *density decreases (volumetric expansion)*
    - *Formation of microcracks (molten salt consideration)*
  - Strength and modulus
    - *Graphite gets stronger with irradiation …*
    - *Until* ***Turnaround*** *dose is achieved. It then decreases*
  - Coefficient of thermal expansion
    - *Initial increase but then reduces before* ***Turnaround***
    - *CTE is why properties are so temperature dependent*
  - Thermal conductivity
    - *Decreases almost immediately to ~30% of unirradiated values*
    - *At temperatures it is same as unirradiated conductivity*
  - Oxidation rate
    - Increases approximately 2-3 times over unirradiated rates

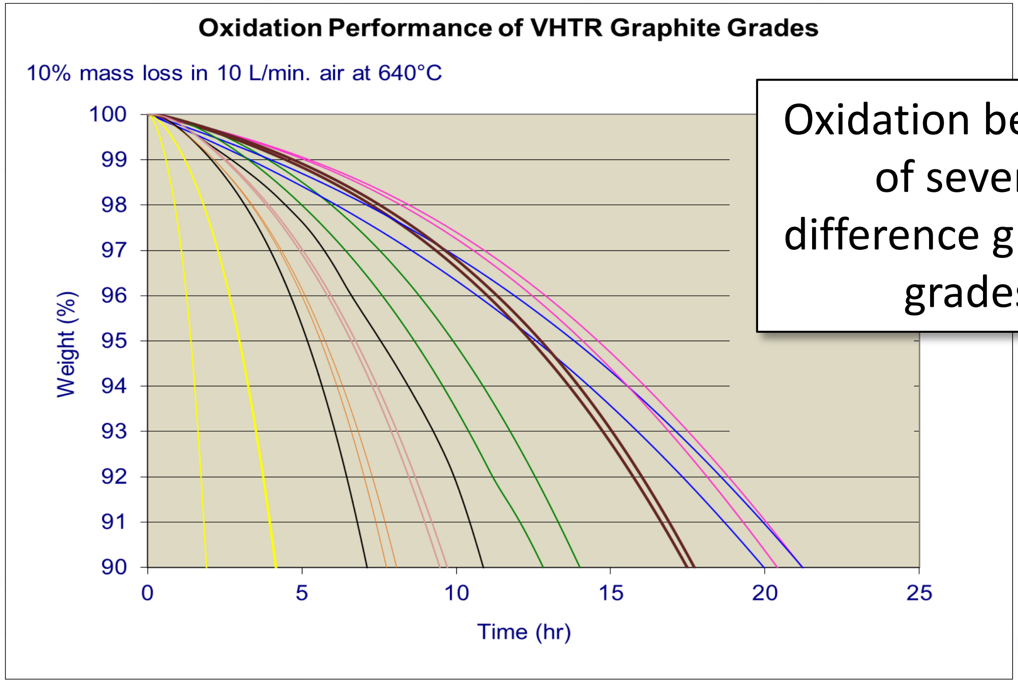


- Significant changes **do not** typically occur in the following properties:
  - Neutron moderation, specific heat capacity, or emissivity

Graphite Oxidation



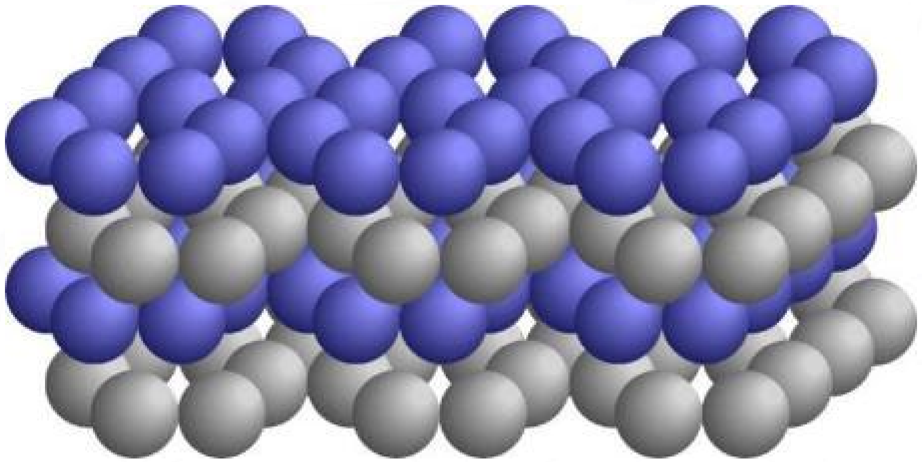
- Graphite **can** and **does** oxidize – rapidly at high temperatures
- Needs continuous oxygen and temperatures above ~ 200°C.
  - *Temperatures > 400°C is rapid acute oxidation (accidents)*
  - *Temperatures < 400°C slow chronic oxidation (normal op)*
- **How** oxidation occurs is more important than strict mass loss
  - *Low temperature kinetic-controlled oxidation*
  - *High temperature diffusion-controlled oxidation*

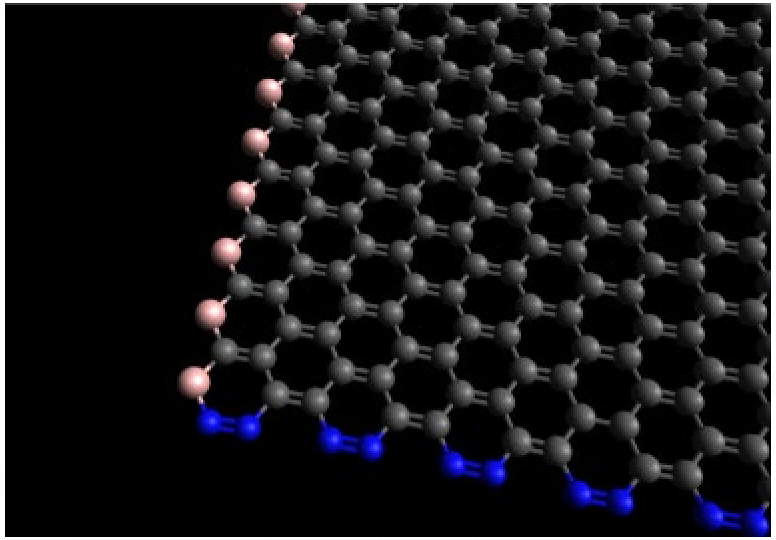


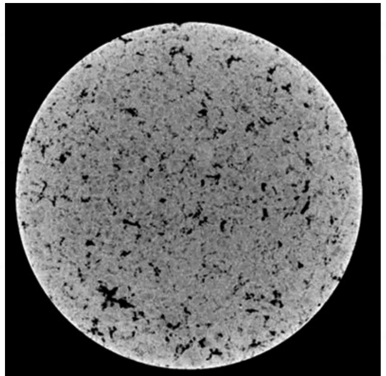
- Oxidation behavior of different grades can be compared using ASTM D7542 standard
  - Small grain grades >> than large grain size
  - Microstructure influences more kinetic- or diffusion-controlled oxidation behavior
- D7542 can (should) be used to determine when diffusion-controlled oxidation occurs in specific grade

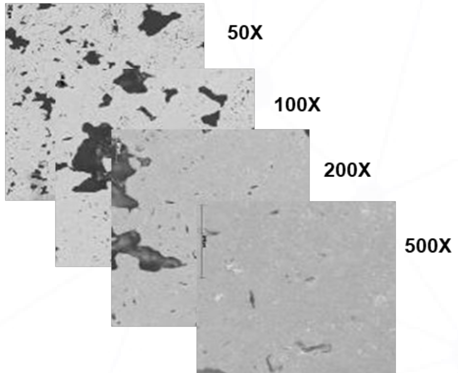
How does graphite oxidize?

- Due to bonding structure of graphite, oxidation only occurs along the outer edges of the basal planes
  - Arm-chair and zig-zag structures are the Reactive Surface Area (RSA) sites
  - Oxygen-graphite chemical reaction does not occur in the center of a basal plane
    - Too energy intensive





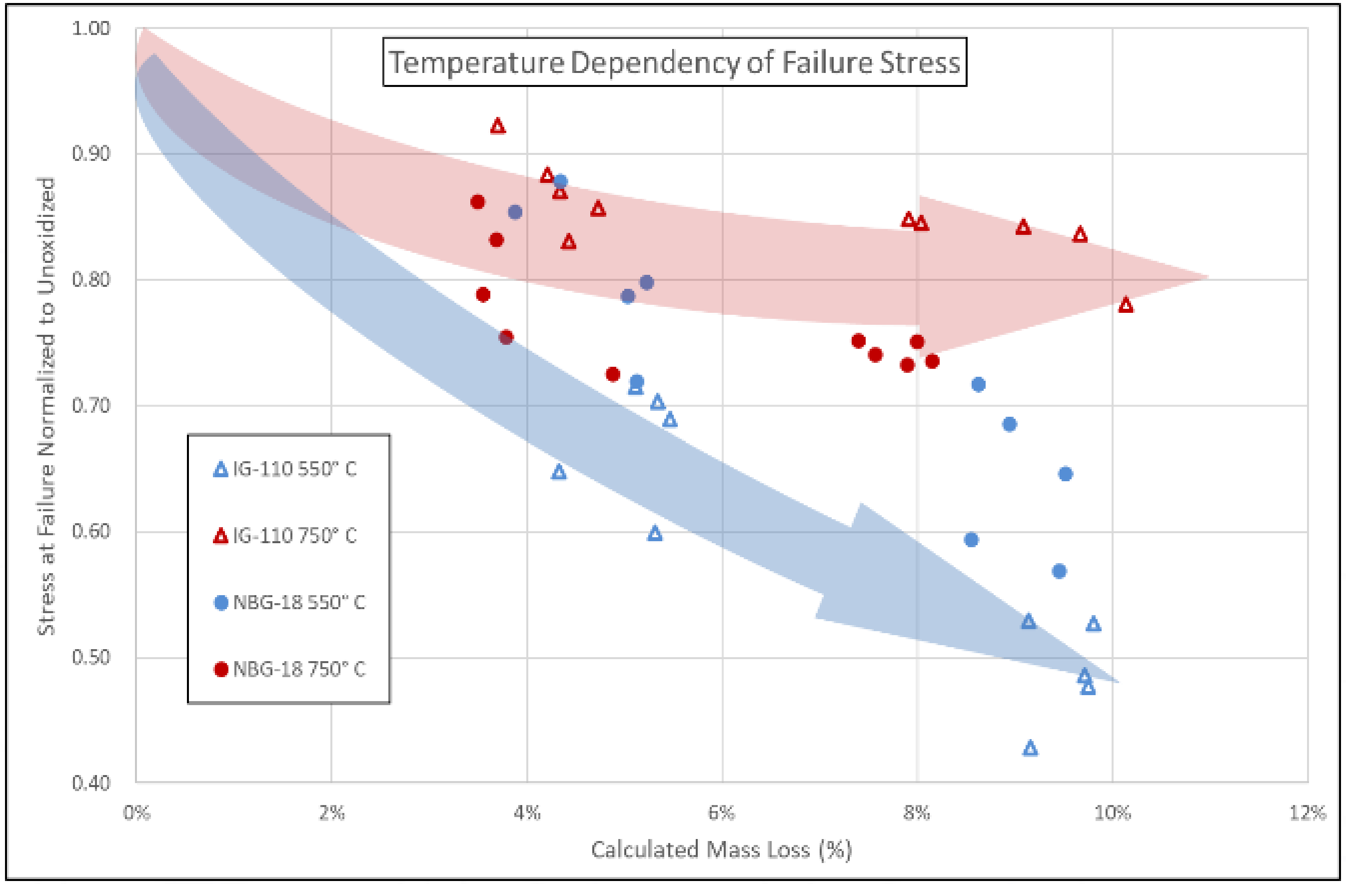




- Oxygen can penetrate into interior of graphite pore microstructure
  - **Must** be low temperature = low reactivity
  - Penetration depth due to temperature and pore interconnectivity
    - *If temperature is very high the oxygen will react on the 1st C atom*

Residual strength after oxidation

- What's important are the effects from oxidation:
  - Strength remaining after oxidation
- Depends upon **how** graphite oxidizes
  - Diffusion-controlled (HT) oxidation = less interior oxidation
  - Kinetic-controlled (LT) oxidation = more interior oxidation



Need to understand how the graphite oxidizes before you can determine the effects

Molten Salt Issues

(Potential) Molten Salt Issues

- Salt impregnation into graphite pores
  - Physical damage/cracks
  - “Hot spots” from fueled molten salt
- Wear/abrasion/erosion
  - Molten salt has higher density than graphite
  - Liquid flow over soft graphite has potential
- Chemical coupling with metallic systems
  - Graphite – MS is inert
  - There are questions when a metallic component is added

Before immersion in FLiNaK

Salt residue

After immersion in FLiNaK

Conclusions

- Microstructure is key to understanding irradiated and unirradiated graphite behavior
  - Pore structure phase is considered most important phase of microstructure
  - Irradiation response related to ***accommodating*** porosity within crystallites
- Macroscopic response = formed microstructure (intrinsic), temperature (extrinsic), and degradation environment (extrinsic)
  - As-fabricated macroscopic properties dependent upon crystallites and formed microstructure
  - Irradiation macro response dependent upon crystallites, microstructure, and dose. Sensitive to temperature
    - *All properties initially increase with neutron irradiation (except thermal diffusivity)*
    - *All properties decrease at or before turnaround dose (CTE changes before turnaround)*
  - Oxidation macro response dependent upon crystallites, microstructure, and oxygen level. Sensitive to temperature
    - *All properties decrease with increasing oxidation mass loss*
    - *Oxidation **must occur** at lowest temperatures possible for full penetration and effect*
  - Molten salt (*potential*) interactions dependent upon molten salt environment (density, abrasion, salt chemistry). Purely extrinsic factors.
    - *There is some question about fluoride bearing salts reacting with graphite. The extent is yet to be proven*

INL

Idaho National Laboratory