NE 591: Advanced Reactor Materials

Fall 2021

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Last Time

- Talked through SiC
- SiC is the primary fission product barrier/pressure vessel for TRISO particles
- Low T radiation damage is primarily BSDs, Frank interstitial loops and voids start to form at medium to high temperatures
- Swelling saturates with dose if in the low T regime (point defect swelling regime); Void swelling dominates at high T, with no saturation
- Extensive thermal conducitivty degradation exists under irradiation; more prevalent at low T, as point defects are more efficient phonon scatterers
- SiC is susceptible to fission product corrosion, namely Pd

GRAPHITE

Graphite Usage

- Graphite was the moderator in the first reactor to sustain a chain reaction and has been used as a moderator in over 100 nuclear reactors, many of which are still operating
- Graphite has a high neutron scattering cross-section and a very low neutron absorption cross-section, making it an ideal moderator

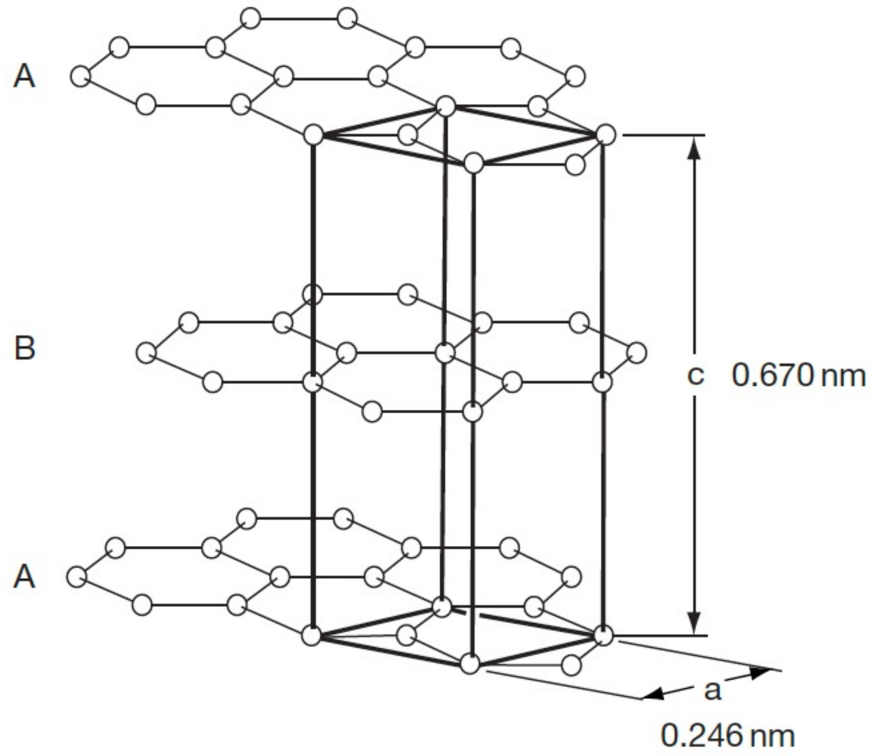
Delineate Types of Graphite

- TRISO Graphite
  - CVD deposition
  - treated to ensure ultra dense and high purity
- Prismatic Blocks and Pebbles
  - large scale
  - different fabrication process from TRISO
  - different microstructure

- We will generally be talking about graphite, which most directly applies to prismatic block type graphite
- Similar radiation effects are assumed to occur in PyC layers

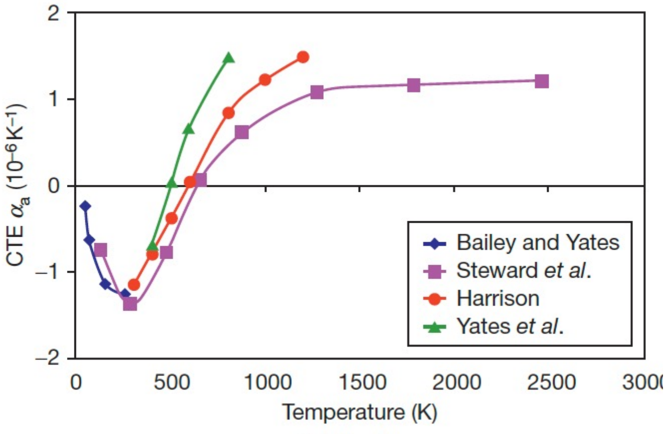
Graphite Structure

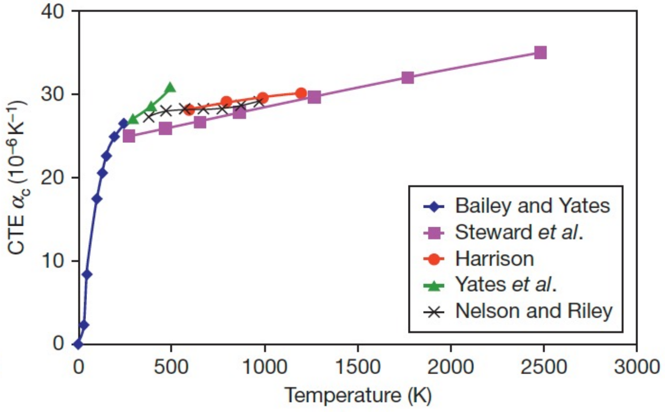
- The electronic hybridization of carbon atoms (1s2, 2s2, 2p2) allows several types of covalent-bonded structures
- In graphite, we have sp2 hybridization where the carbon atom is bound to three equidistant nearest neighbors in a given plane to form the hexagonal graphene structure
- The sheets are weakly bound with van der Waals type bonds in an ABAB stacking sequence with a separation of 0.335 nm



Fundamental Properties

- The CTE for graphite displays anisotropic behavior, and strongly varies as a function of temperature
- Due to the structure the strength along the basal planes is higher than the strength perpendicular to the planes, and the shear strength between the basal panes is relatively weak
- The thermal conductivity along the basal planes is much greater than perpendicular to the planes

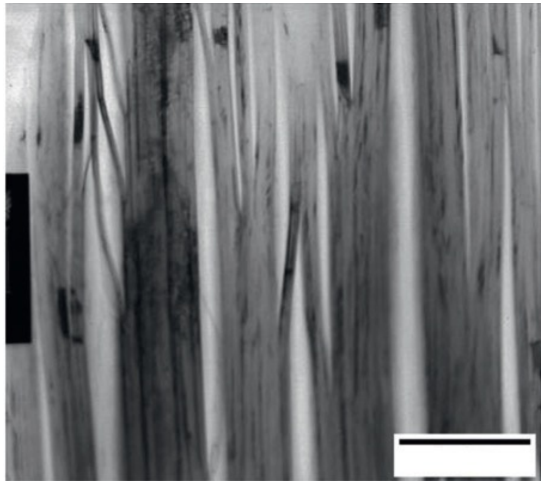




‘a’ direction

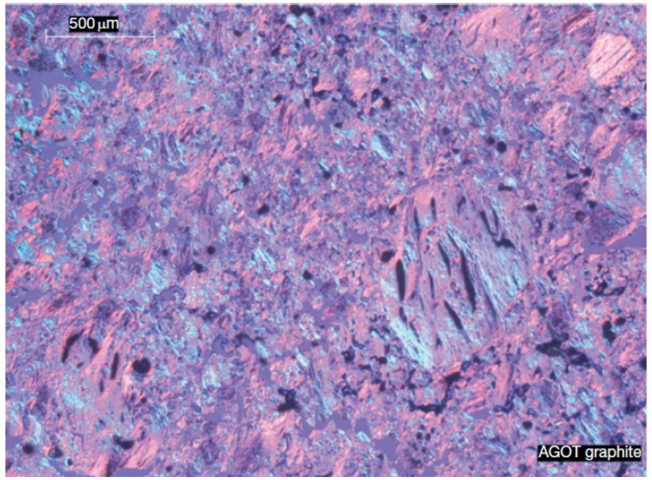
Mrozowski Cracks

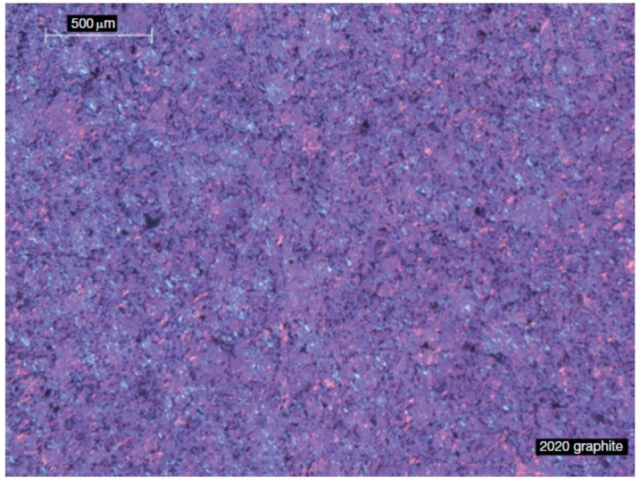
- During the manufacture of artificial graphite, very high temperatures (2800–3000 C) are required
- Upon cooling, the anisotropy in thermal expansion coefficients leads to the formation of long, thin microcracks parallel to the basal planes, often referred to as ‘Mrozowski’ cracks
- The presence of these microcracks is very important in understanding the properties of nuclear graphite
- These cracks for in both TRISO PyC, sometimes called highly orientated pyrolytic graphite (HOPG), and standard nuclear graphite



Graphite Texture

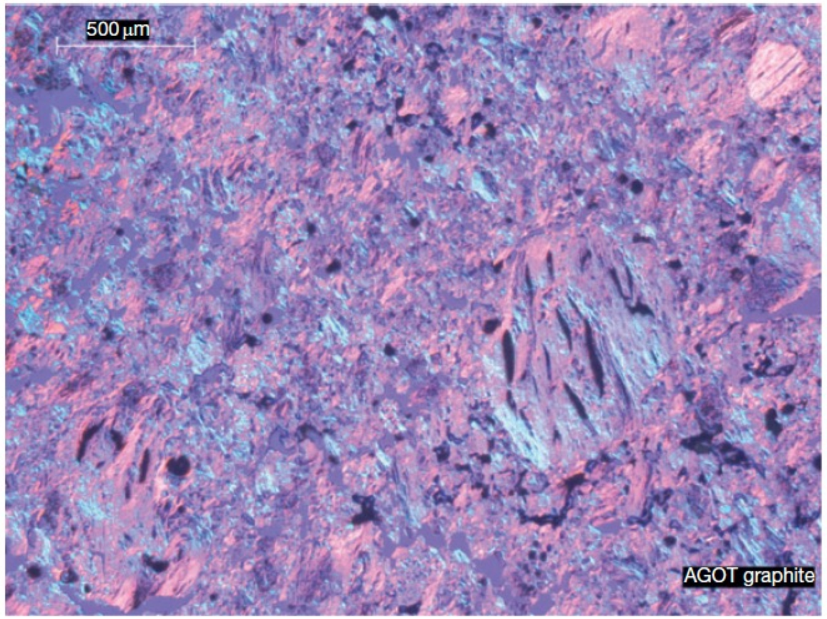
- Graphite structure is largely dependent upon the manufacturing process
- Graphites are classified according to their grain size from coarse-grained (containing grains in the starting mix that are generally >4mm) to microfine-grained (containing grains in the starting mix that are generally <2 mm)
- Grade AGOT was used as the moderator in the earliest nuclear reactors in the United States
- 2020 graphite was a candidate for the core support structure of the modular high temperature gas-cooled reactor in the United States





Initial Porosity

- A dominant feature of graphite texture is the amount of porosity
- About half the total porosity is open to the surface
- The formation of pores and cracks in the graphite during manufacture adds to the texture arising from grain orientation and causes anisotropy in the graphite physical properties
- Three origins of porosity:
  - Those formed by incomplete filling of voids
  - Gas entrapment during pyrolysis
  - Thermal cracks

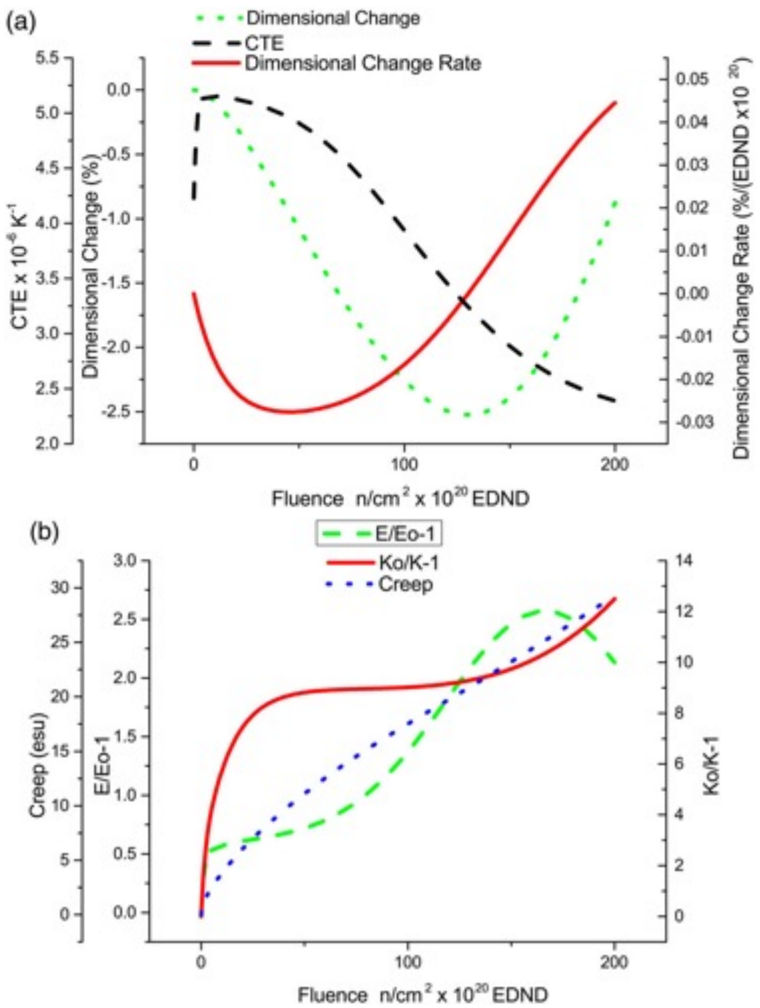


RADIATION EFFECTS IN GRAPHITE

Graphite Shrinkage

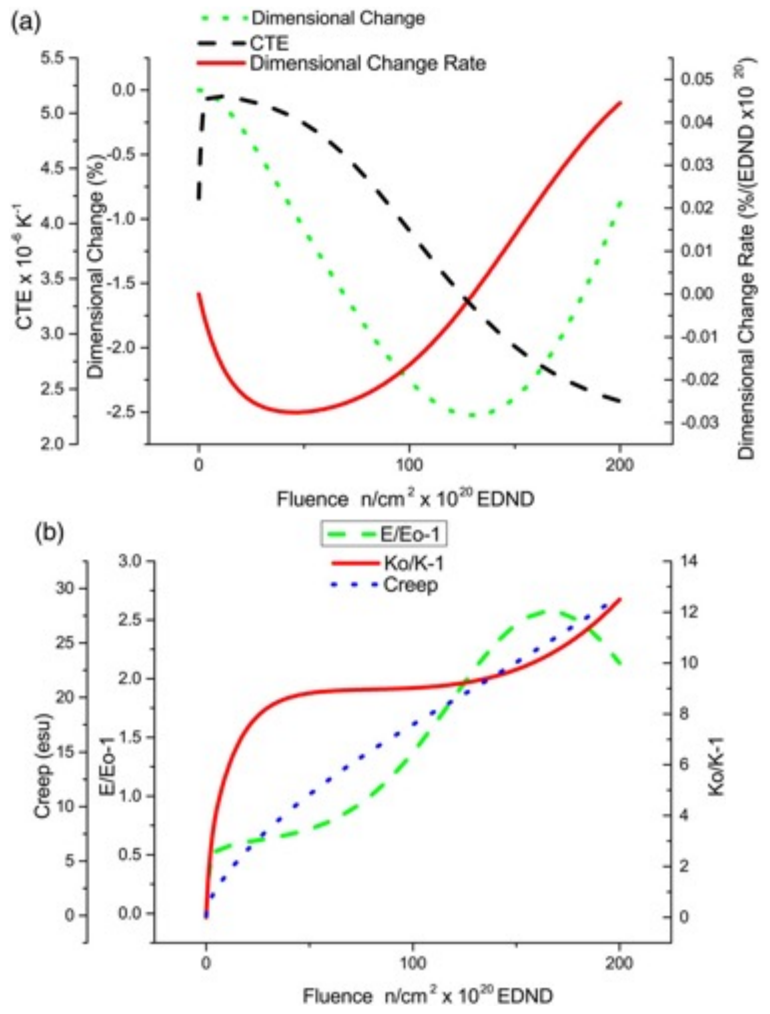
- When graphite components are irradiated in a reactor, significant changes to their dimensions and properties occur
- The unit of irradiation exposure EDND used in the figures is particular to nuclear graphite technology
- EDND = Equivalent DIDO Nickel Dose
- EDNF = Equivalent DIDO Nickel Flux
- They are based upon the equivalent nickel activation in the DIDO reactor

$$^{58}\mathrm{Ni(n,p)}^{58}\mathrm{Co} \qquad \varphi_{\mathrm{Ni}} = \frac{\varphi_{\mathrm{Ni}(s)}\varphi_d}{\varphi_{ds}}\ n/\mathrm{cm}^2/\mathrm{s}$$



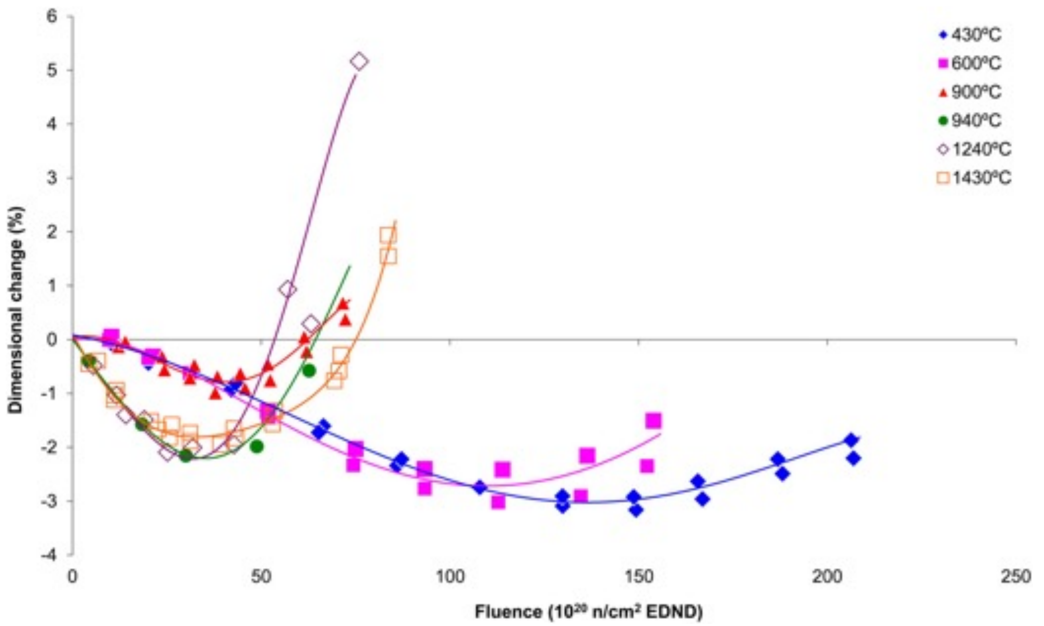
Graphite Shrinkage

- Graphite typically shrinks with age until a point is reached where the shrinkage stops, and the graphite starts to swell
- This change from shrinkage to swelling is known as "turnaround”
- Due to the manufacturing process of nuclear graphite, the graphite component has a much lower density than may be expected (1.7-1.9 g/cm3) compared with 2.2.6 g/cm3 for pure graphite crystals
- The original state of the graphite, and the particular radiation defects in graphite, govern this fluence-dependent behavior



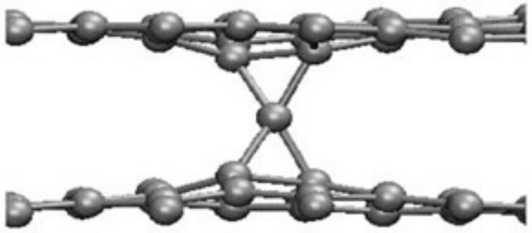
Graphite Dimensional Change

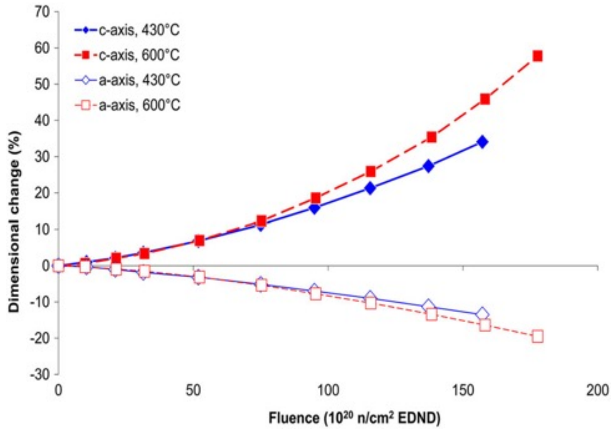
- Dimensional change data obtained on AGR graphite samples are shown in figure
- The higher the temperature the sooner ‘turnaround’ from shrinkage to swelling occurs
- This behavior is typical for most semi-isotropic, medium and fine-grained graphite grades, although the magnitude of the changes varies from grade to grade
- Nuclear graphite, such as Glisocarbon, is semi-isotropic
- Anisotropic graphite can display significantly different irradiation behavior

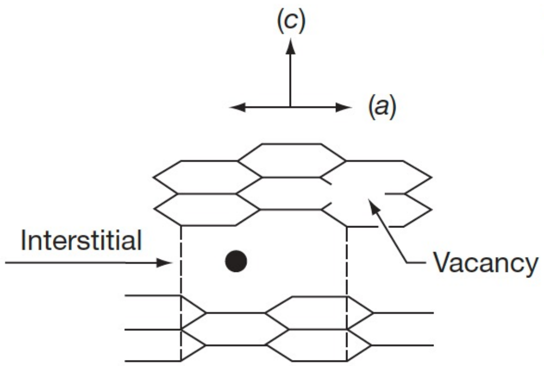


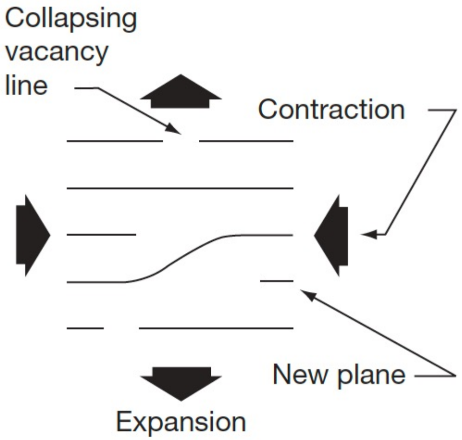
Interstitials in Graphite

- The interstitial atom prefers to form a bridge-like structure on the graphene surface
- Repelling the two graphene sheets increases *c*, yielding a corresponding contraction in *a*
- Vacancies shrink the basal plane, further reducing *a*
- Turnaround occurs when the matrix can no longer accommodate the defect-induced dimensional change



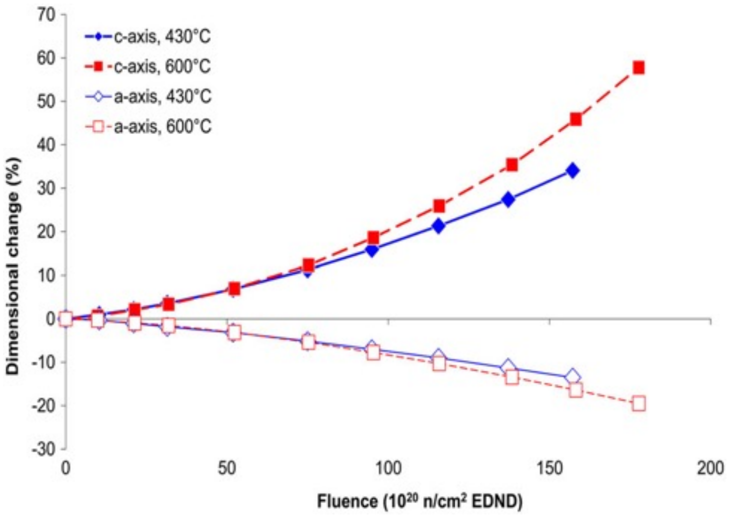


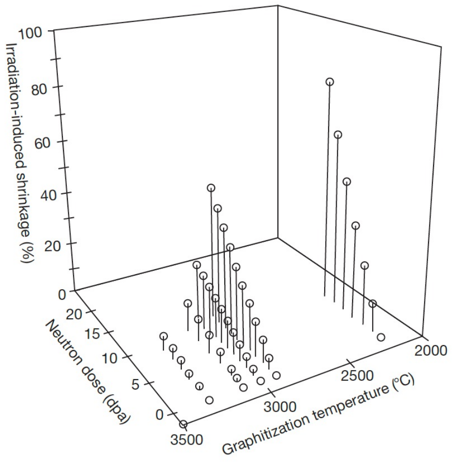




Graphite Shrinkage

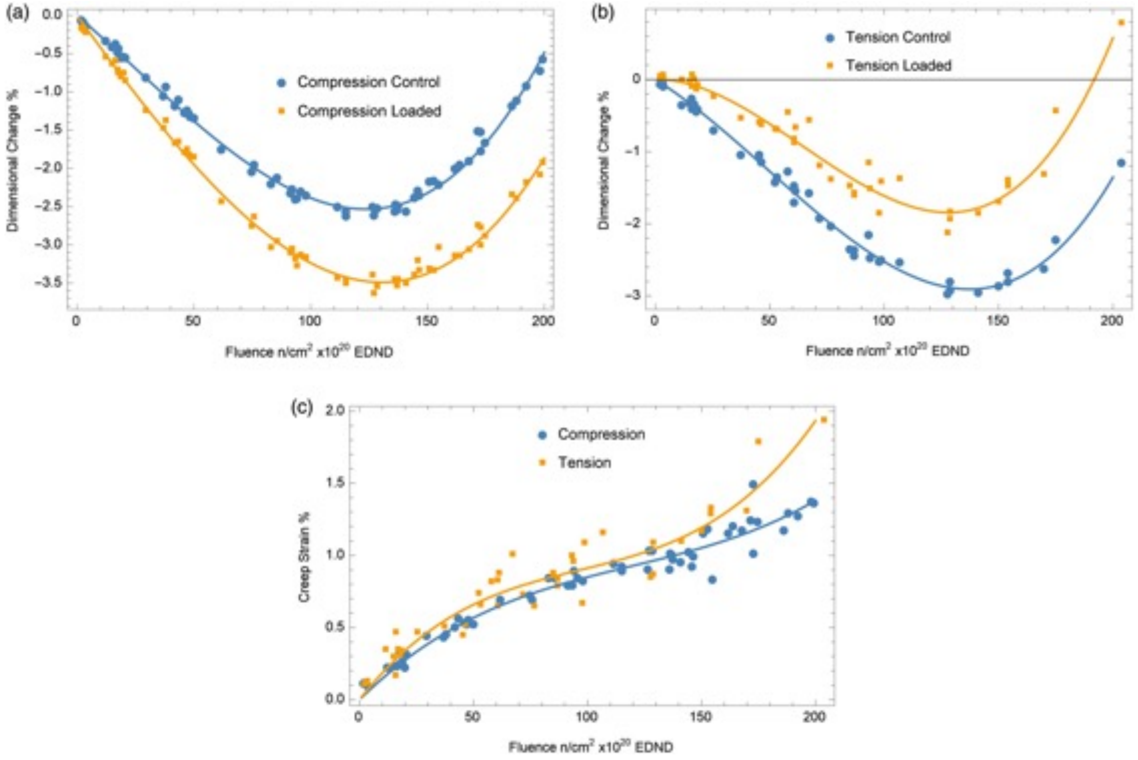
- Nuclear graphite possess a polycrystalline structure, usually with significant texture resulting from the method of forming during manufacture
- Thermal shrinkage cracks that occur during manufacture and that are preferentially aligned in the crystallographic a-direction will initially accommodate the c-direction expansion
- So *a* direction contraction will be observed, and graphite thus undergoes net volume shrinkage
- With increasing neutron dose (displacements), the incompatibility of crystallite dimensional changes leads to the generation of new porosity, and the volume shrinkage rate falls, eventually reaching zero
- The graphite now begins to swell at an increasing rate with increasing neutron dose





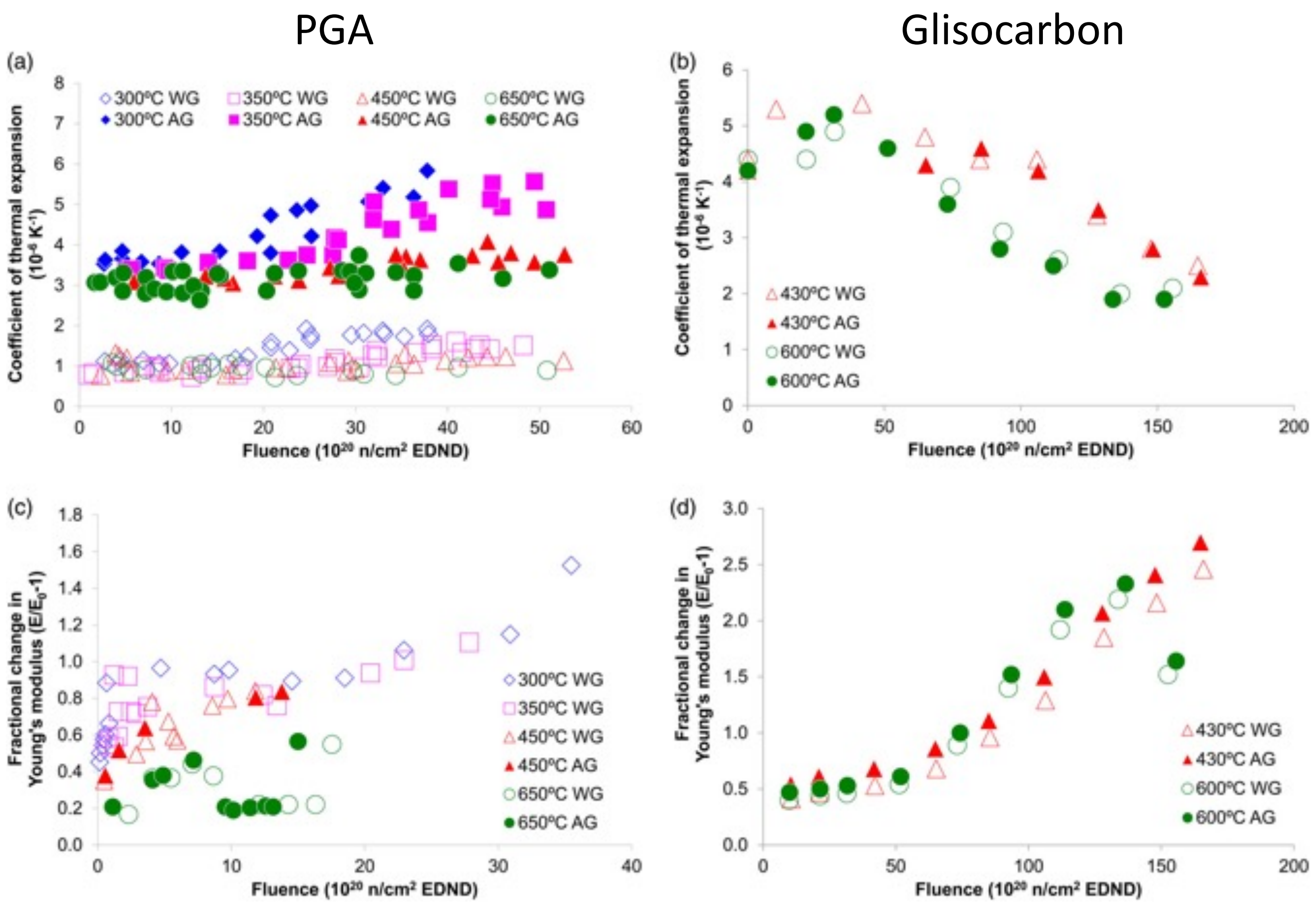
Graphite Irradiation Under Loading

- If graphite is irradiated under load the dimensional change data are modified
- The difference between loaded and unloaded dimensional change is referred to as creep
- The shrinkage is increased under compression and reduced under tension
- With increasing fluence the creep strain increases fairly linearly at first, and then the rate reduces before finally increasing



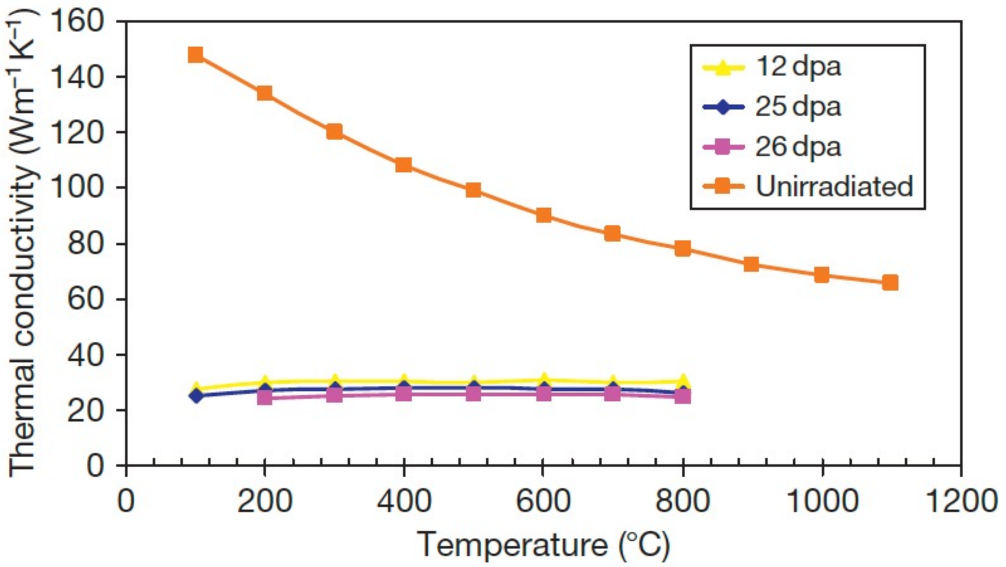
CTE and Young's Modulus

- The behavior of the CTE and E is complex and differs between anisotropic and semi-isotropic grades
- The CTE of Gilsocarbon first increases then reduces
- For E there an increase with increasing fluence for Glisocarbon
- If irradiated past turnaround, significant degradation occurs and the modulus starts to reduce
- PGA = Pile Grade A, course, anisotropic graphite



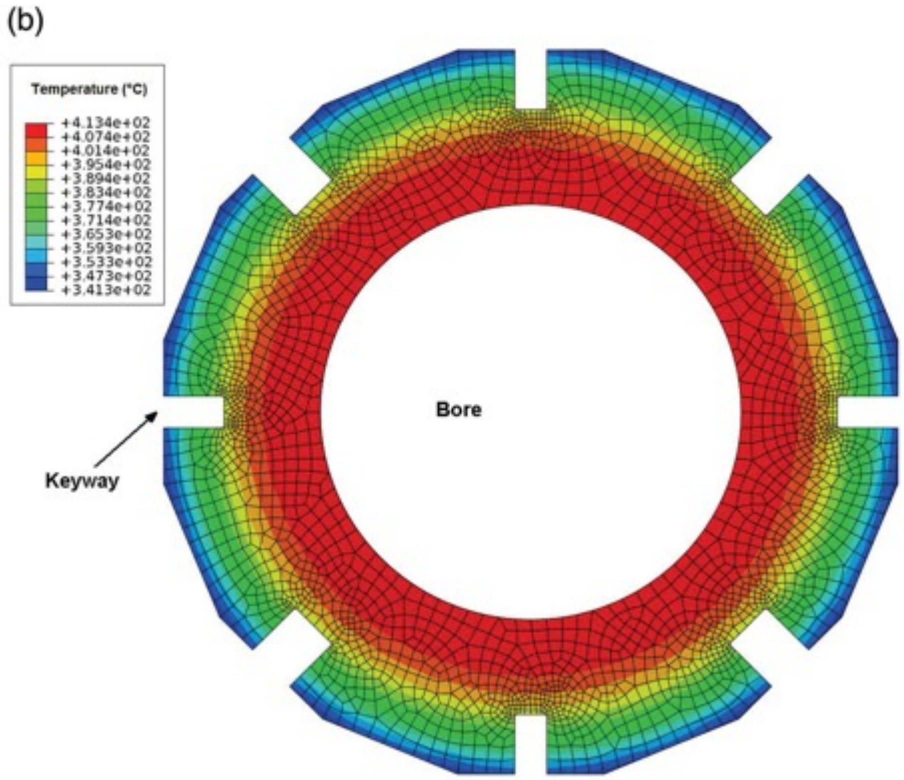
Thermal Conductivity

- Graphite is a phonon conductor of heat
- Similar to SiC, larger grain size, theoretical densities, low defect content, improve k
- The increase of thermal resistance due to irradiation damage has been ascribed to the formation of (1) small interstitial clusters, (2) vacancies, (3) vacancy loops
- At any irradiation temperature, the decreasing thermal conductivity will reach a ‘saturation limit’



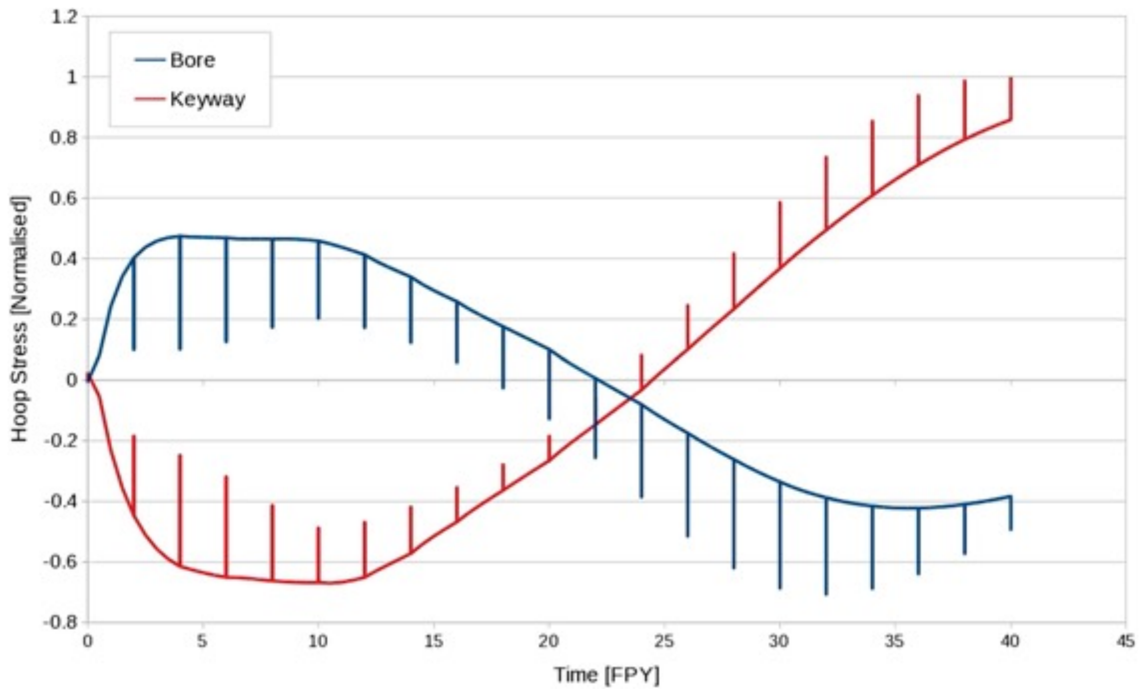
Impacts of Changes Under Irradiation

- In graphite moderated reactors, the graphite structure provides channels for fuel, fuel-cooling and control rod entry, the structural integrity of the graphite components is important from safety and lifetime considerations
- Components develop stresses which need to be accounted for
- Temperature distribution across a graphite channel is shown at the right
- Fluence also changes radially
- Fuel is in the center (bore)



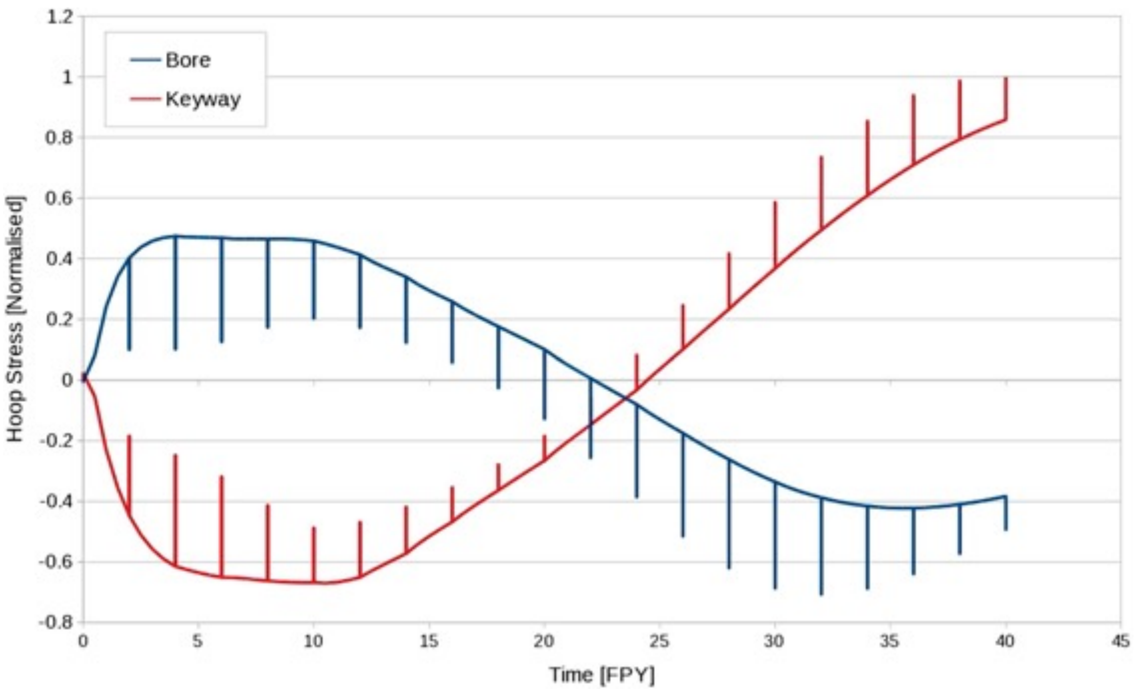
Impacts of Changes Under Irradiation

- Properties and dimensions change as a function of both temperature and fluence
- First, the graphite brick will shrink faster at the bore than at the outside, and properties will vary radially
- Graphite brick internal shrinkage and thermal stresses are generated; first tensile at the bore and compressive at the outside, and then reversing in sign towards the end of reactor life
- Fortunately much of this stress is reduced by irradiation creep



Impacts of Changes Under Irradiation

- Discontinuities in the figure are due to shutdowns every 2 years
- The difference in CTE between the inside and the outside of the brick, along with irradiation creep, causes the stresses to significantly change when the reactor is shutdown and the graphite cools
- The change in stress at shutdown is mainly due to the temperature difference across the brick, which creep out during reactor operation
- Towards the EOL, this leads to significantly different stress states for the inside/outside of the graphite brick



Irradiation Creep

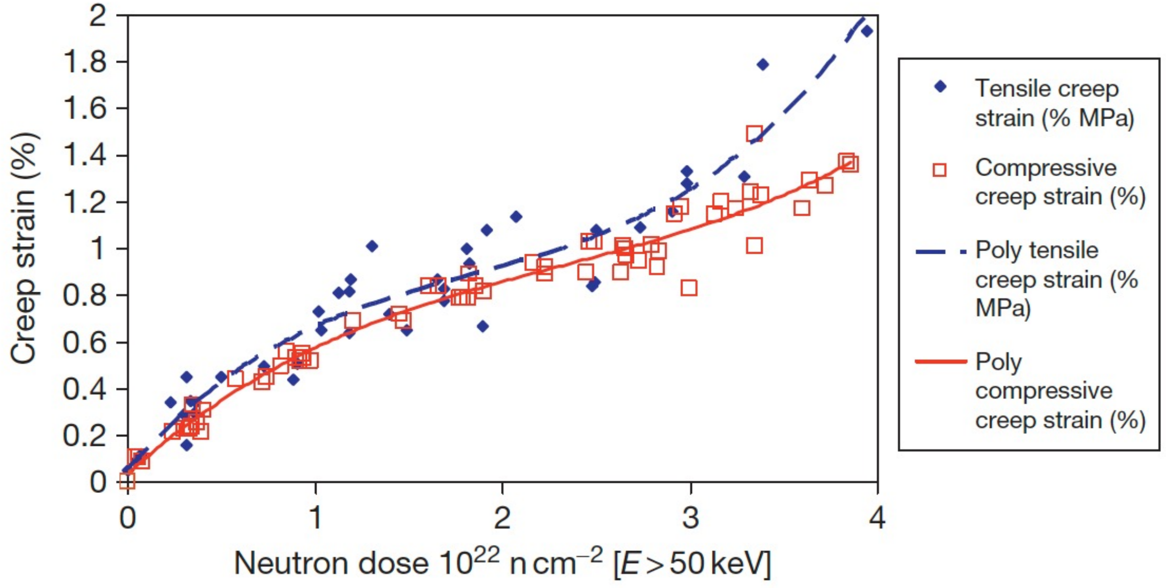
- Graphite will undergo creep (inelastic strain) during neutron irradiation and under stress at temperatures where thermal creep is generally negligible
- Creep is so fundamentally important to graphite that if irradiation-induced stresses in graphite moderators could not relax via radiation creep, rapid core disintegration would result
- One study showed that a 50% decrease in the assumed creep strain resulted in a 50% increase in the predicted hoop stress in a hollow cylindrical core brick
- The total strain, in a graphite component under irradiation in a reactor core is given by:

$$\varepsilon_{\mathrm{Total}} = \varepsilon_{\mathrm{e}} + \varepsilon_{\mathrm{t}} + \varepsilon_{\mathrm{d}} + \varepsilon_{\mathrm{c}}$$

- where ε_e is the elastic strain; ε_t, the thermal strain; ε_d, the dimensional change strain; and ε_c is the creep strain

Irradiation Creep

- Because of the significance of irradiation-induced creep to the stress levels in graphite core components, accurate models of creep have long been sought, but current models tend to break down at high temperature and fluence
- Stress state (compressive/tensile) has an impact on the creep rate
- The creep rate increases more rapidly in the tensile loading case compared to the compressive case at high dose

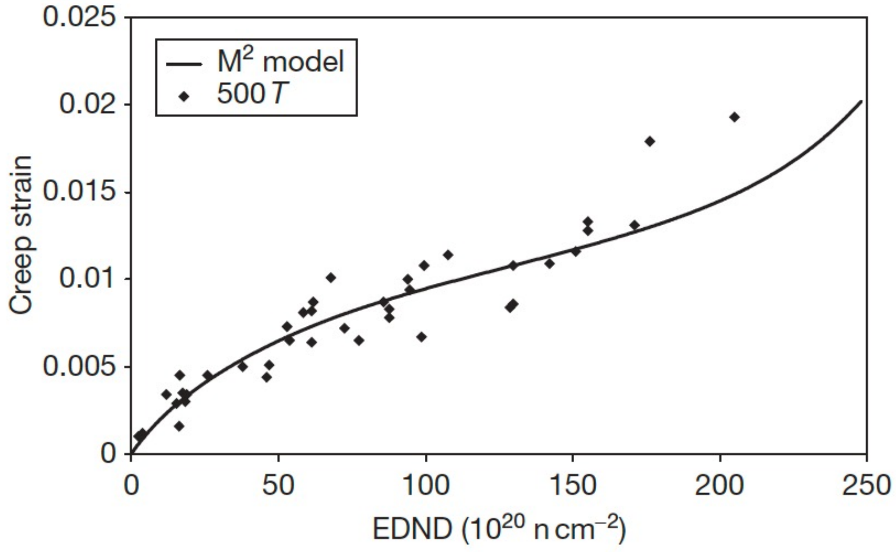


Irradiation Creep

- Irradiation-induced basal plane dislocation pinning/unpinning in the graphite crystal is the expected mechanism for the irradiation-induced creep
- The pinning points are speculated to be interstitial atom clusters
- The interstitial clusters are temporary barriers as they are destroyed by further irradiation
- The concentration of pinning sites increases under irradiation from the initial value to a steady-state concentration
- The initial creep rate is high and decreases to a near steady-state value as the pinning concentration saturates at a level controlled by the neutron flux and temperature
- At high dose, the creep rate can again increase because of (1) high internal stress enhancing the creep rate, and (2) the destruction of interstitial pins by thermal diffusion of vacancies

Irradiation Creep Models

- Since creep is so important to graphite, a number of creep prediction models have been developed:
  - Linear viscoelastic creep, UK creep, Kennedy, Kelly and Burchell, etc.
- These models can take into account evolving pore structure, thermal expansion, recoverable strain, etc.
- The M^2 model potentially performs the most accurately as a function of dose at relatively low temperatures
- However, no model is sufficiently accurate at both high dose and high temperature



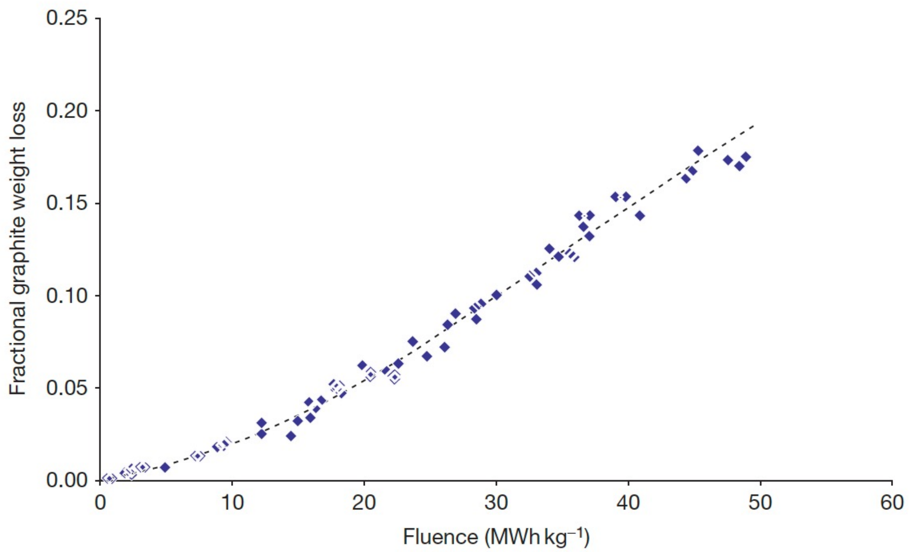
Radiolytic Oxidation

- In carbon dioxide (CO2)-cooled reactors, two types of oxidation can occur: thermal and radiolytic
- Radiolytic oxidation occurs when CO2 is decomposed by ionizing radiation (radiolysis) to form CO and an active oxidizing species (something like CO3), which attacks the graphite

$$CO_2 \xrightarrow{\text{ionizing radiation}} CO + O^*$$

$$CO + O^* \rightarrow CO_2$$

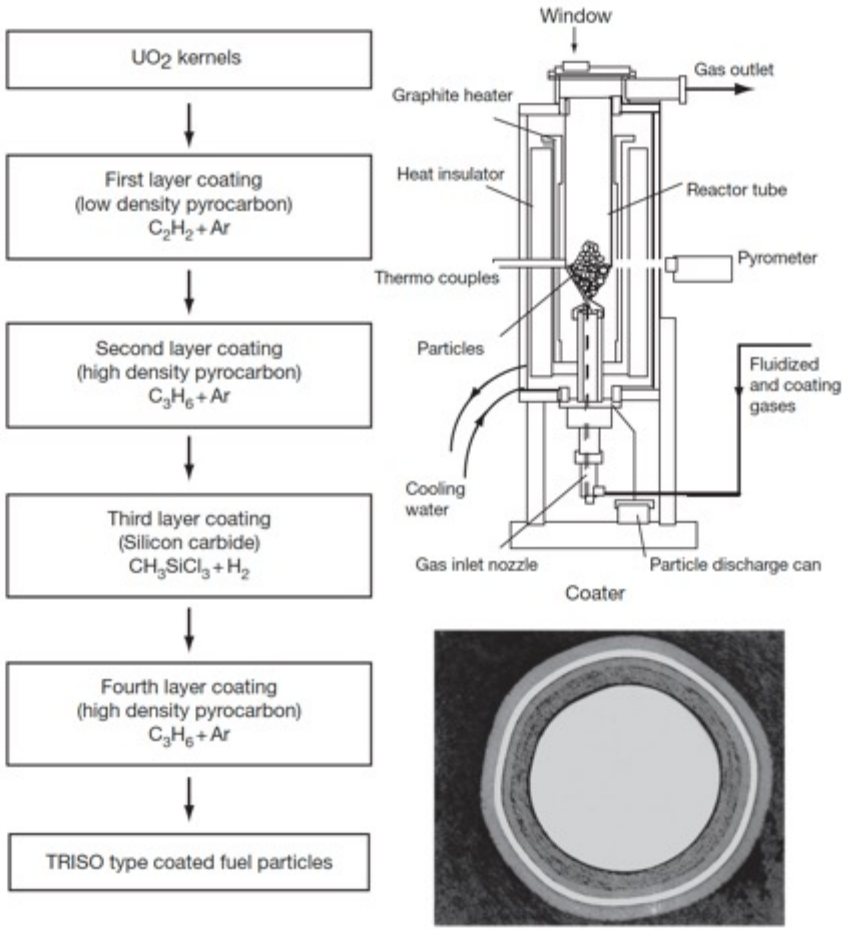
- Radiolytic oxidation occurs predominantly within the graphite open porosity
- Can result in weight loss and wastage from graphite



FABRICATION

TRISO Fabrication

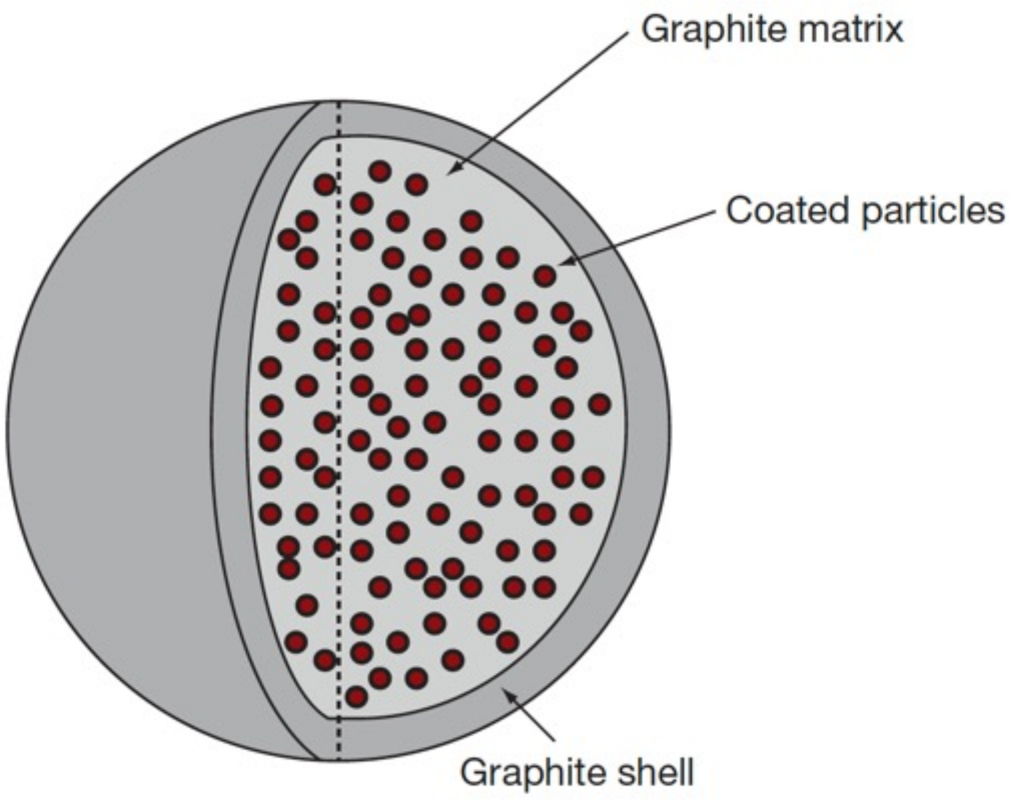
- Rigorous control is applied at every step of the fabrication process to produce high-quality, very low-defect fuel
- Defect levels are typically on the order of one defect per 100,000 particles
- Specifications are placed on the diameters, thicknesses, and densities of the kernel and layers; the sphericity of the particle; the stoichiometry of the kernel; the isotropy of the carbon; and the acceptable defect levels for each layer



Polished cross-section of coated fuel particle

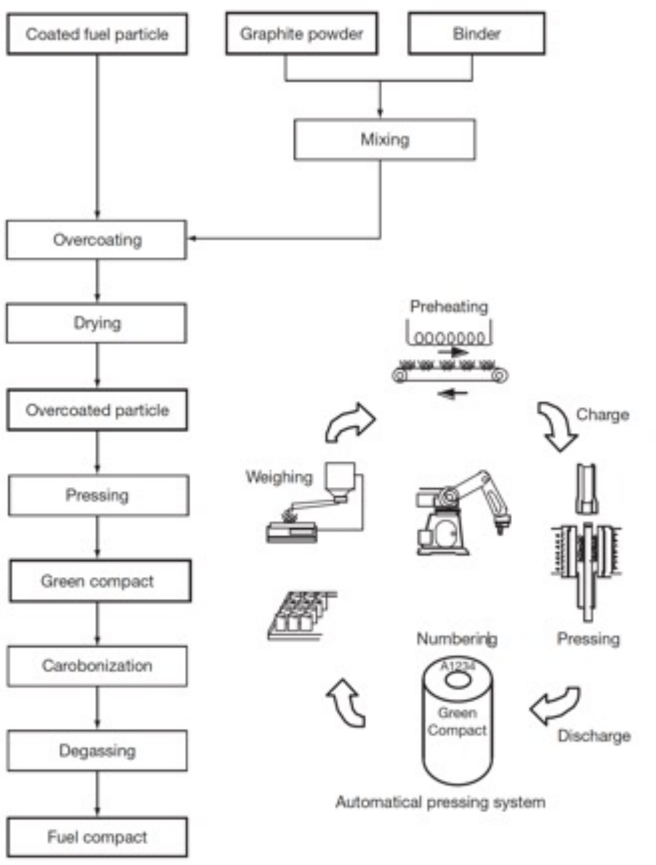
Pebble and Compact Fabrication

- The fuel element of the pebble bed type HTGR is a spherical fuel element
- The coated particles are overcoated with a layer of matrix graphite powder (MGP) and pressed to the core of a fuel sphere
- Then, an additional 5-mm layer of matrix graphite material is added to form a 'nonfuel' zone
- The resulting fuel sphere gets its final diameter by a machining process and is then carbonized and annealed at 2000C



Pebble and Compact Fabrication

- HTGR fuel elements are graphite compacts stacked into a graphite core
- To form compacts, coated fuel particles are overcoated with the MGP and warm-pressed to make the annular cylinder of green compacts
- Green compacts are heat treated for carbonization at 800C and then sintered at 1800C to make fuel compacts
- In order to decrease the failure fraction of coating layers, it is necessary to disperse coated fuel particles in a green compact as uniformly as possible



Summary

- Graphite day
- Graphite has a lot of texture and porosity, dependent upon fabrication
- Graphite shrinks, then undergoes turnaround
- This behavior is governed by point defects and Mrozowski cracks
- Turnaround happens quicker at higher temperatures, and it dependent upon applied stress
- Irradiation creep is critically important in graphite
- Fabrication of pebbles/compacts