NE 795-014: Advanced Reactor Materials

Fall 2023

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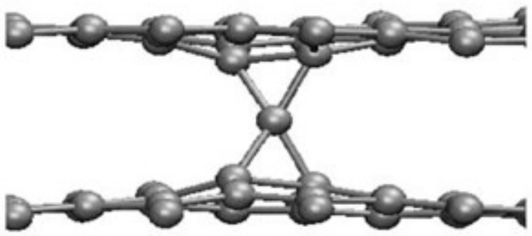
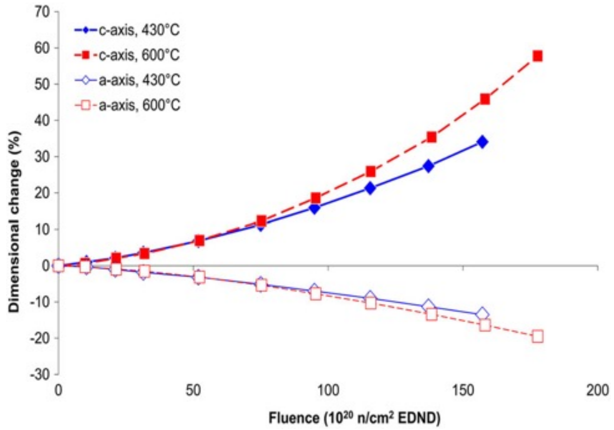
Last Time

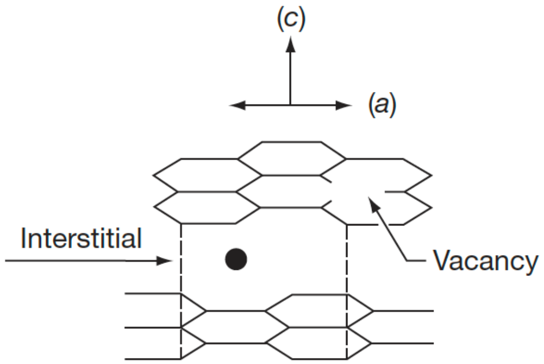
- Medium to high temperature irradiation effects in SiC
- Point defect swelling regime, saturates with dose and is negatively correlated with temperature
- Void swelling regime above 1000C, does not saturate
- Thermal conductivity degrades more to point defects and interstitial clusters than voids
- Fission product attack on SiC can be life limiting
- Graphite has a lot of texture and porosity, dependent upon fabrication
- Graphite shrinks, then undergoes turnaround

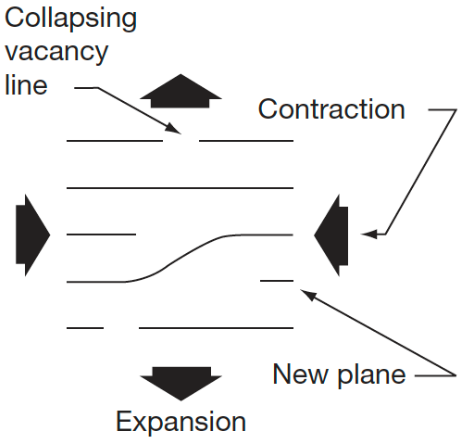
Interstitials in Graphite

- 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



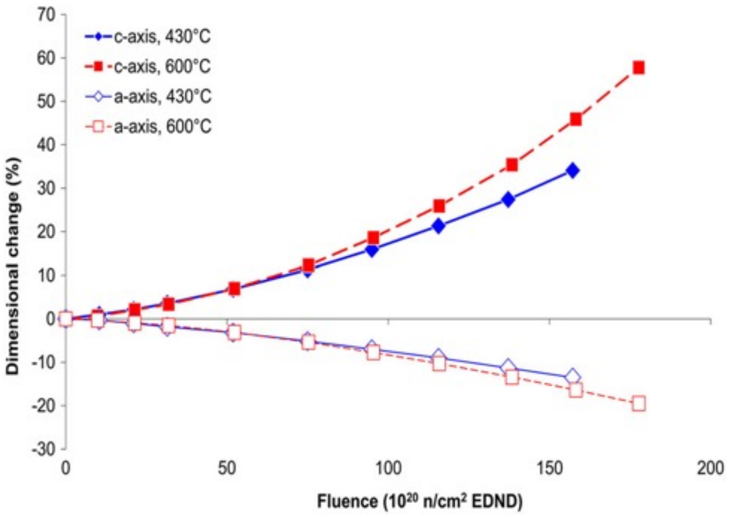


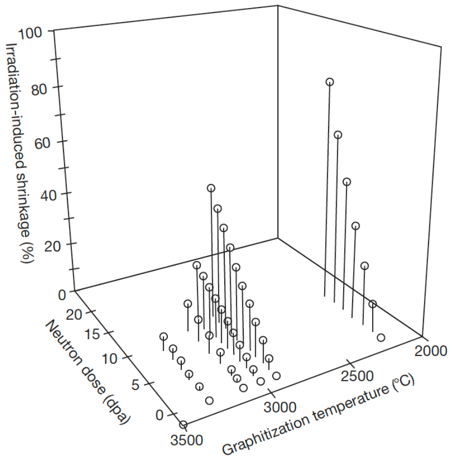




Graphite Shrinkage

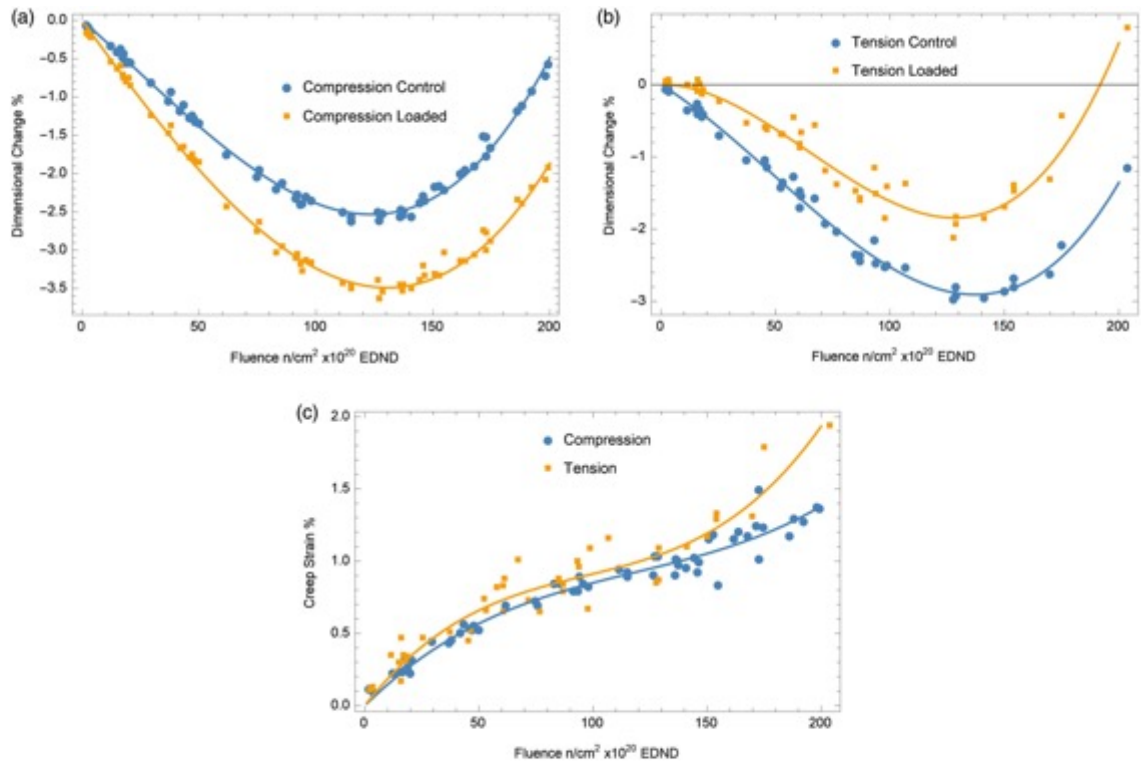
- Nuclear graphite possess a polycrystalline structure, usually with significant texture resulting from the method of forming during manufacture
- Thermal shrinkage cracks that occur during manufacture and that are preferentially aligned in the crystallographic a-direction will initially accommodate the c-direction expansion
- So, *a* direction contraction will be observed, and graphite thus undergoes net volume shrinkage
- With increasing dose, the 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





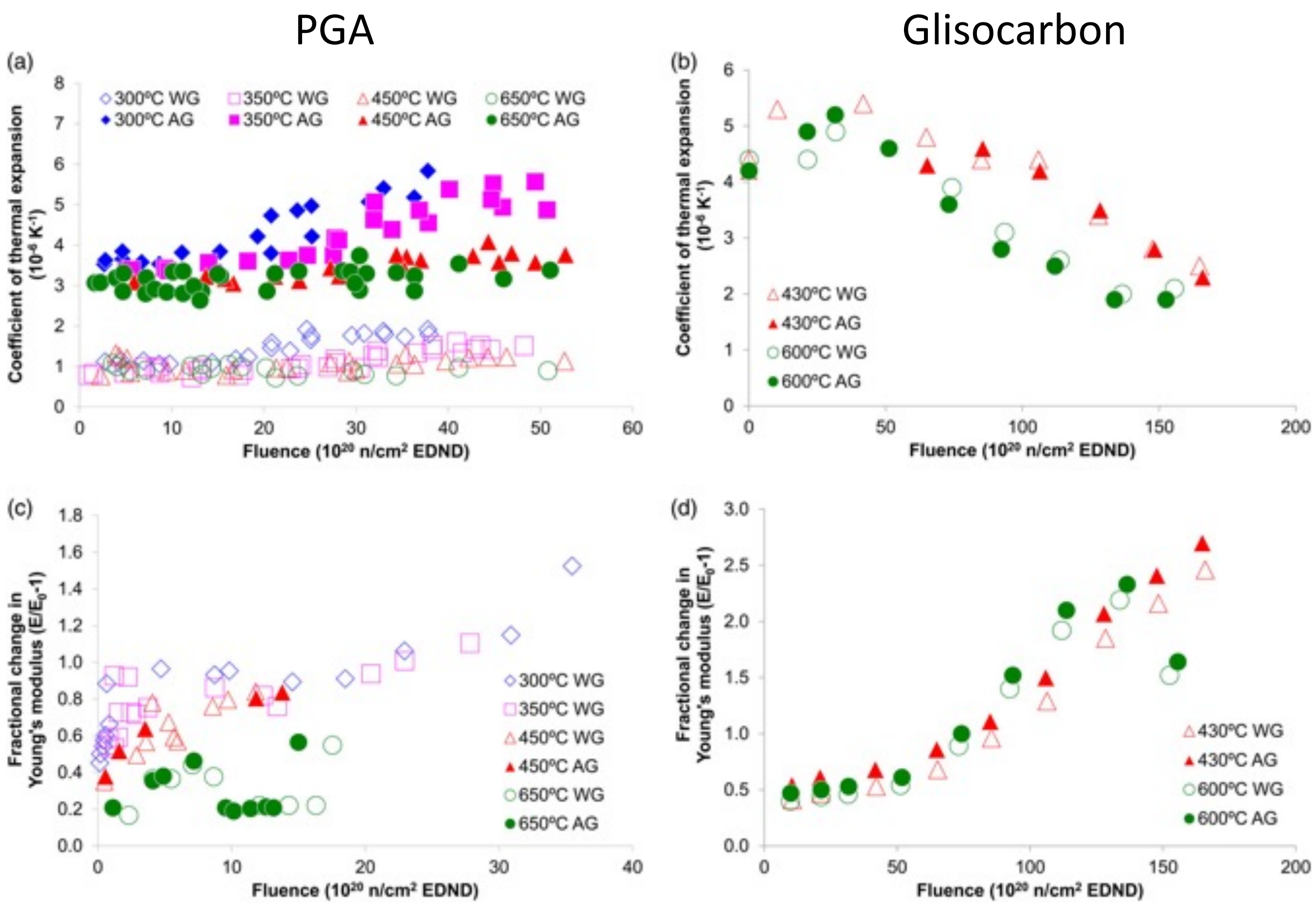
Graphite Irradiation Under Loading

- 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



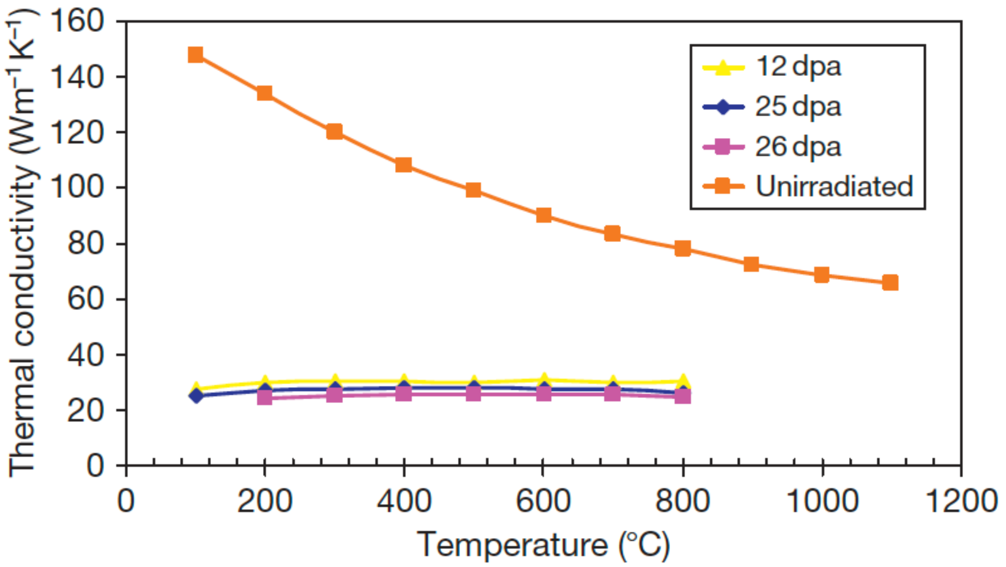
CTE and Young's Modulus

- 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

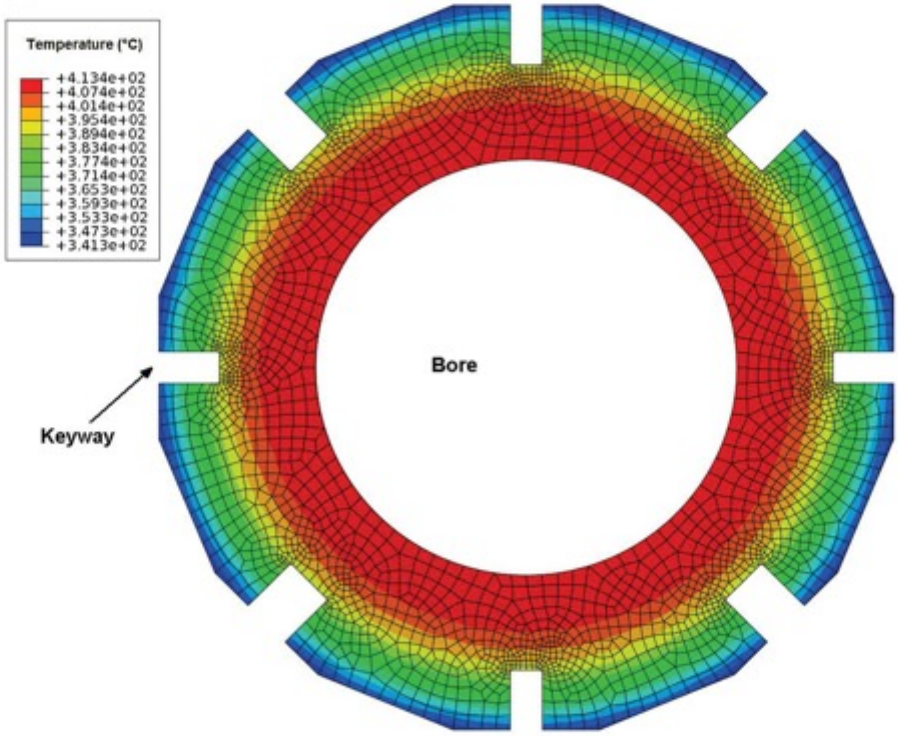
- Graphite is a phonon conductor of heat
- Similar to SiC, larger grain size, theoretical densities, low defect content, improve k
- The increase of thermal resistance due to irradiation damage has been ascribed to the formation of (1) small interstitial clusters, (2) vacancies, (3) vacancy loops
- At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



Impacts of Changes Under Irradiation

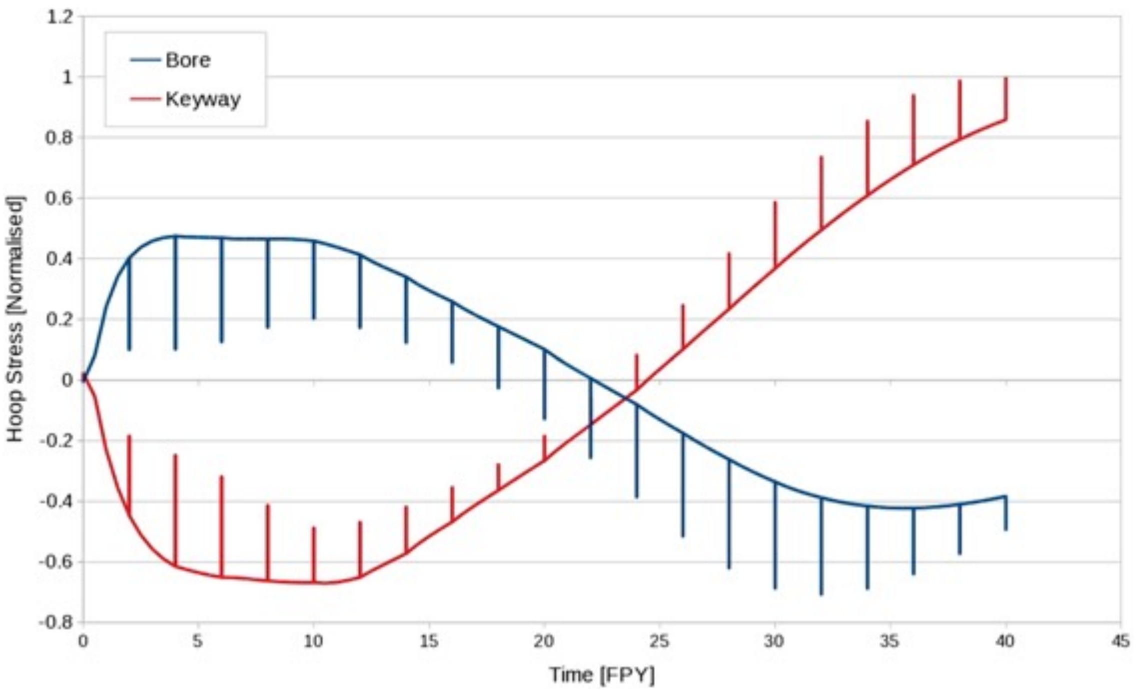
- In graphite moderated reactors, the graphite structure provides channels for fuel, fuel-cooling, and control rod entry, the structural integrity of the graphite components is important from safety and lifetime considerations
- Components develop stresses which need to be accounted for
- Temperature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

(b)



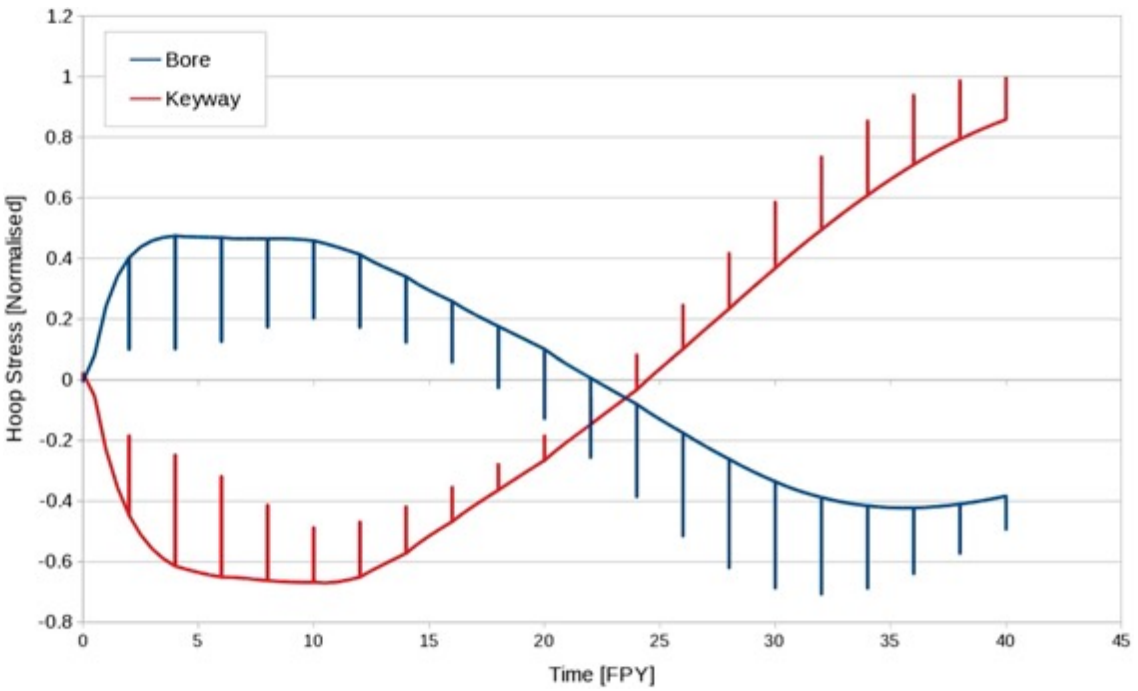
Impacts of Changes Under Irradiation

- 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

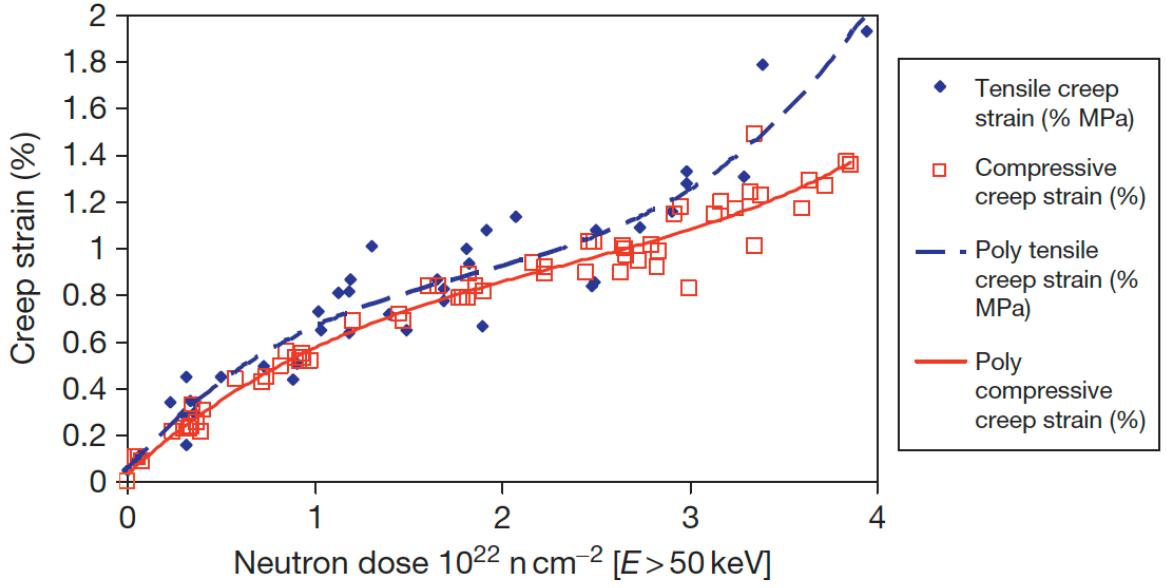
- Graphite will undergo creep (inelastic strain) during neutron irradiation and under stress at temperatures where thermal creep is generally negligible
- Creep is so fundamentally important to graphite that if irradiation-induced stresses in graphite moderators could not relax via radiation creep, rapid 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

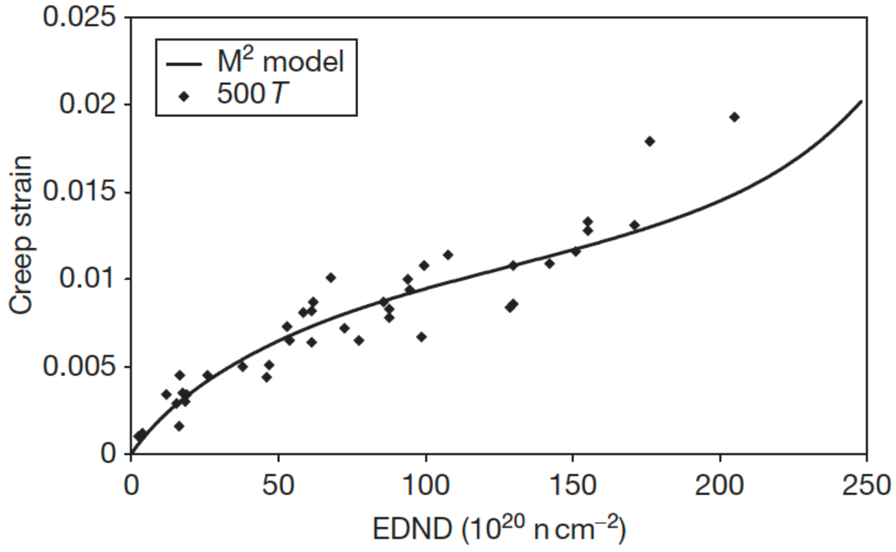


Irradiation Creep

- 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



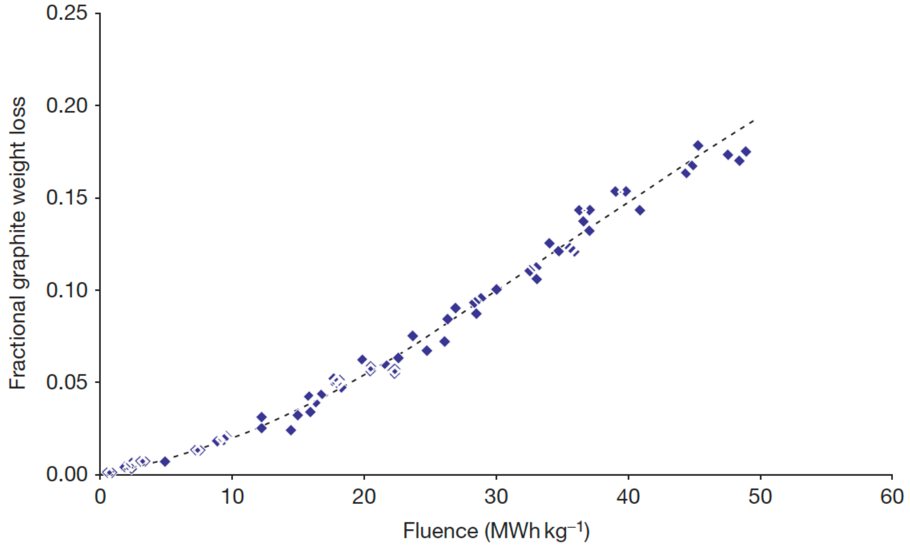
Radiolytic Oxidation

- 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

Fuel Kernel Fabrication

- The sol–gel technique for kernel microsphere preparation is based on the following two chemical reactions starting from U3O8 powder

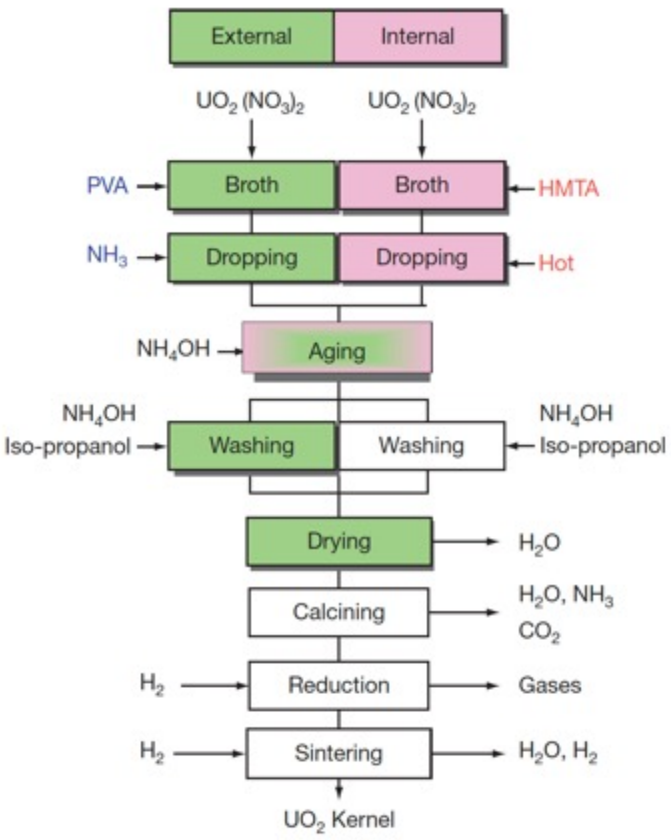
$$3U_3O_8 + 20HNO_3(aq) \rightarrow 9UO_2(NO_3)_2(aq) + 10H_2O + 2NO(g)$$

$$2UO_2(NO_3)_2(aq) + 3NH_4OH \rightarrow (NH_4)_2U_2O_7(s) + 2NH_4NO_3(aq) + H_2O$$

- The (NH4)2U2O7 (ammonium di-uranate – ADU) is converted to UO2 by sintering in hydrogen gas
- For the production of UCO kernels, carbon black is added to the broth and the sintering is performed in CO gas to ensure adequate C/O stoichiometry

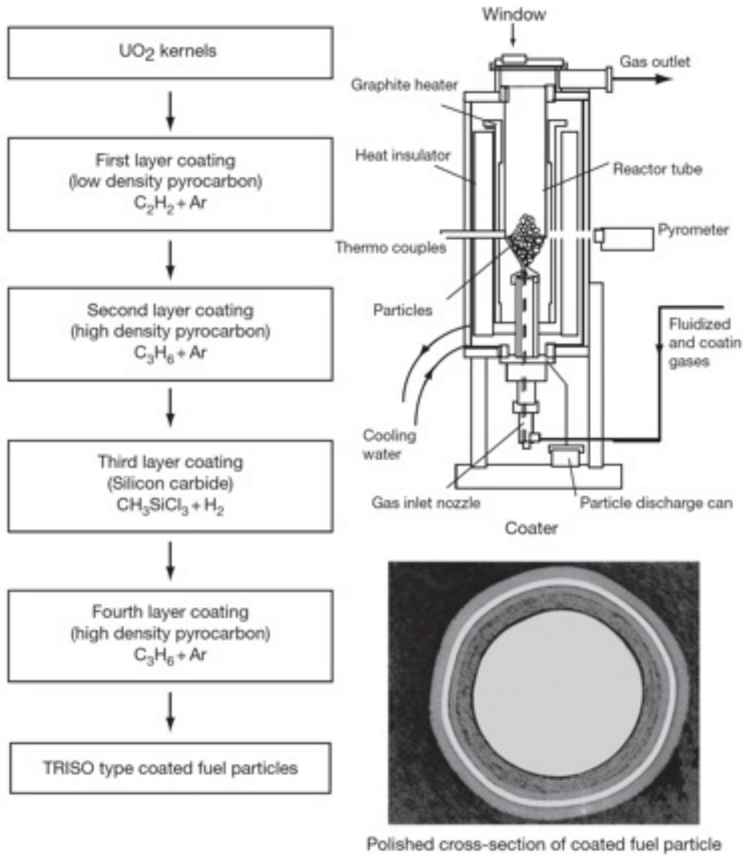
Fuel Kernel Fabrication

- The mechanical strength of the coated layers depends on their thickness and sphericity, and thus strongly depend on the diameter and sphericity of the kernels
- Vibrating nozzles from which droplets are emitted with high speed were developed for uniform and spherical kernel fabrication
- A process is applied to prevent the deformation of droplets while they are landing on the ammonia water, where droplets are solidified while falling in ammonia gas blown against them



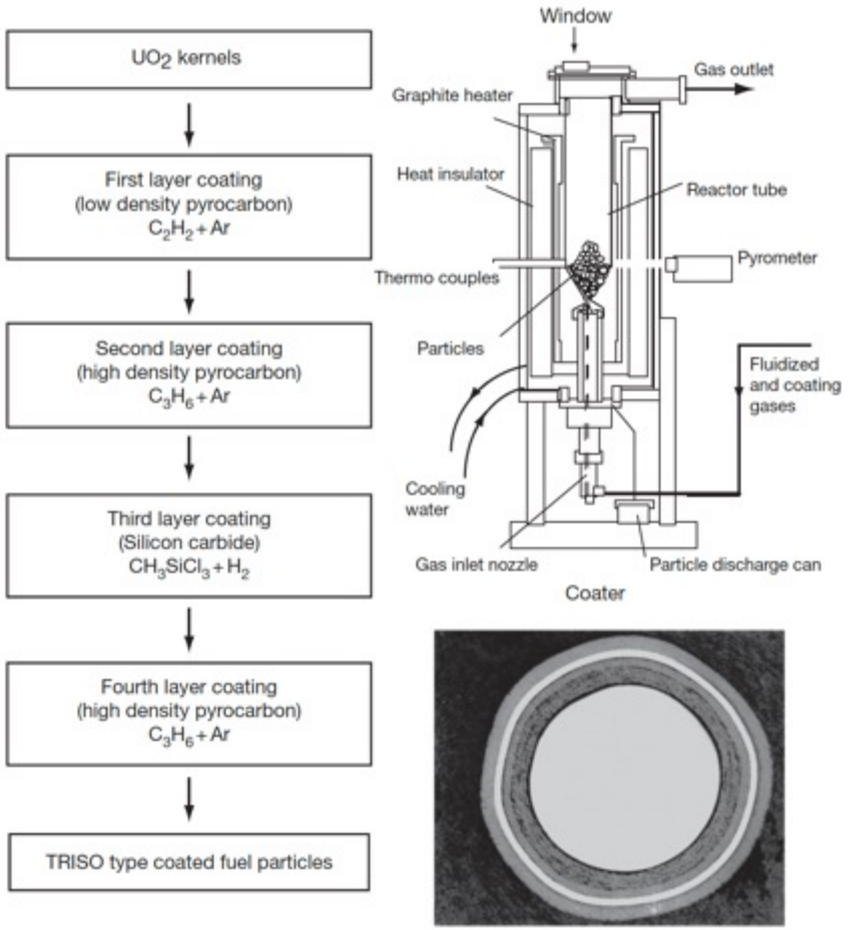
SiC (and PyC) Fabrication

- The coating technology of both the SiC and PyC layers involves a fluidization of the kernel microsphere bed and chemical vapor deposition (CVD) coating
- TRISO coating process is divided into four coating processes for the porous PyC, IPyC, SiC, and final OPyC layers
- A specific mixture of gases is used for the deposition of each layer
  - buffer: C2H2+Ar; IPyC/OPyC: C3H6+Ar; SiC: CH3SiCl3+H2



TRISO Fabrication

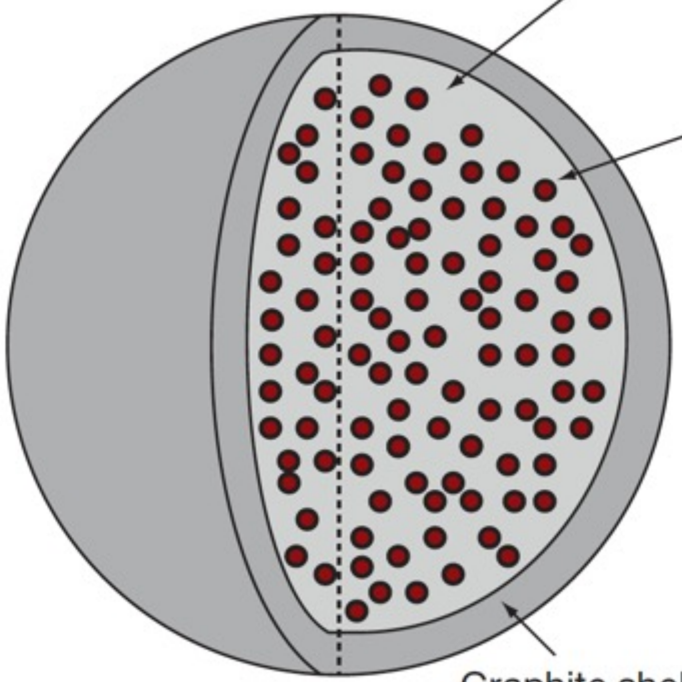
- Rigorous control is applied at every step of the fabrication process to produce high-quality, very low-defect fuel
- Defect levels are typically on the order of one defect per 100,000 particles
- Specifications are placed on the diameters, thicknesses, and densities of the kernel and layers; the sphericity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

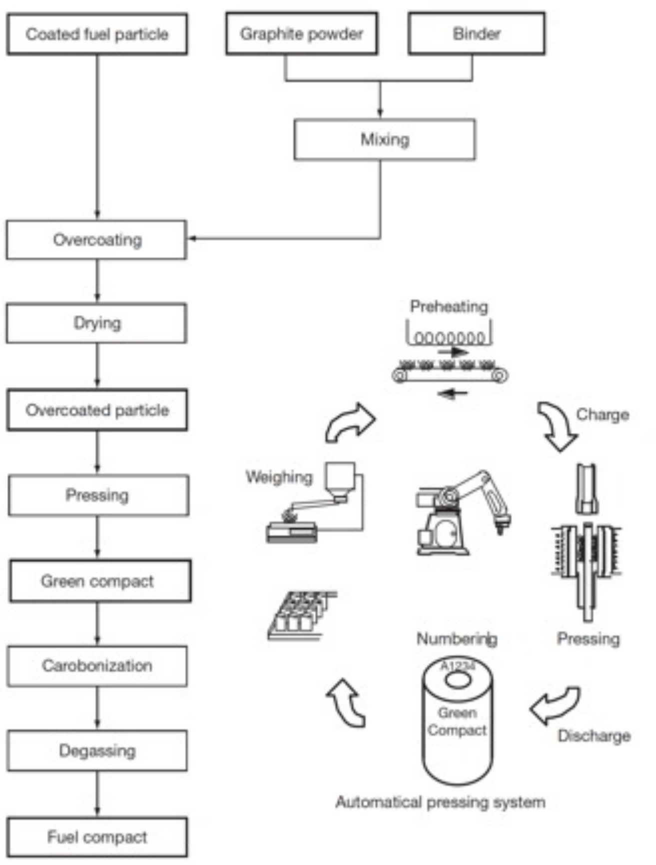
Pebble and Compact Fabrication

- 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



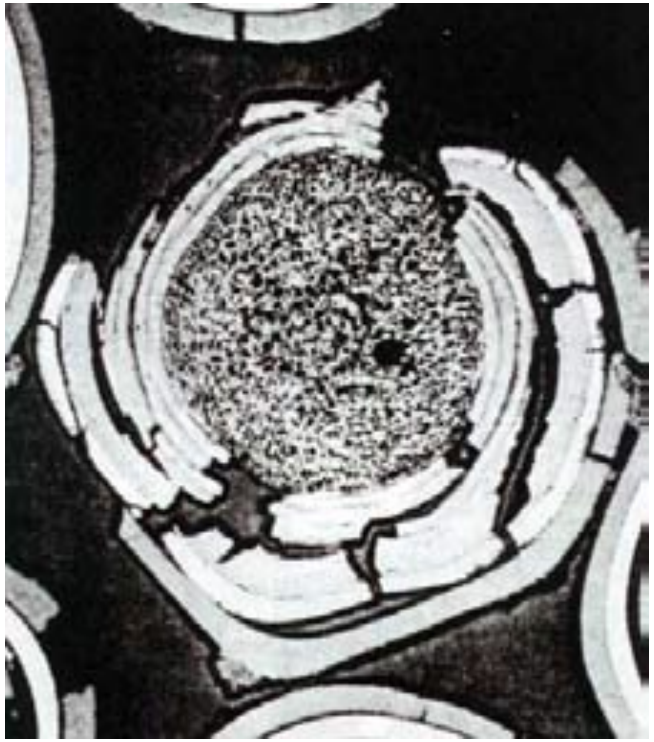
Summary

- 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

TRISO FUEL FAILURES

Fuel Failure Mechanisms

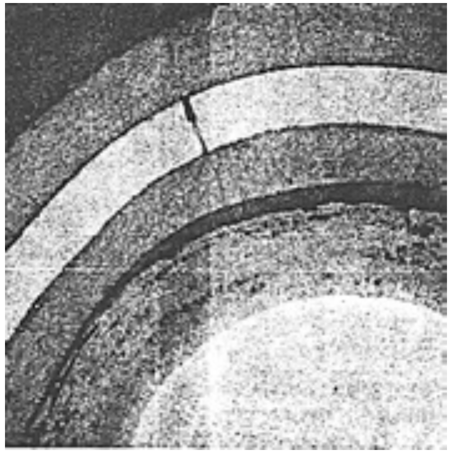
- Overpressure
- During irradiation, fission gases are released from the kernel into the porous buffer layer. The pressure that is generated exerts tensile forces on the SiC layer of the particle
- For UO2 kernels, there is also excess oxygen released during fission which will react with carbon from the buffer to form CO and CO2 gas
- Particles are generally sized with a large enough buffer void volume to ensure that they do not fail by overpressure during irradiation
- Particle failure is postulated to occur as a result of an insufficient or missing buffer layer that occurs during the coating process

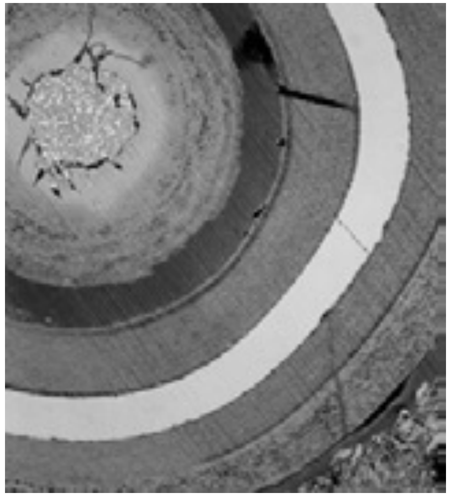


Fuel Failure Mechanisms

- Irradiation-induced IPyC cracking

- Under irradiation, pyrocarbon (PyC) shrinks in both the radial and tangential directions
- At modest fluences it begins to swell in the radial direction
- This behavior puts the PyC layers into tension in the tangential direction
- However, irradiation-induced creep works to relieve the tensile stress in the PyC layer
- If the PyC is strongly attached to the SiC layer, the PyC shrinkage provides a strong compressive stress that offsets the tensile stresses generated by gas production in the kernel





Fuel Failure Mechanisms

- Debonding between IPyC and SiC
- The debonding is related to the strength of the IPyC/SiC interface
- Weakly bonded coating layers can partially detach because of the tensile stresses generated by the IPyC shrinkage under irradiation
- A particle for which partial debonding of the IPyC from the SiC has occurred can develop relatively large tensile stresses in the SiC
- Irradiation induced creep relieves the stress at longer times

Fuel Failure Mechanisms

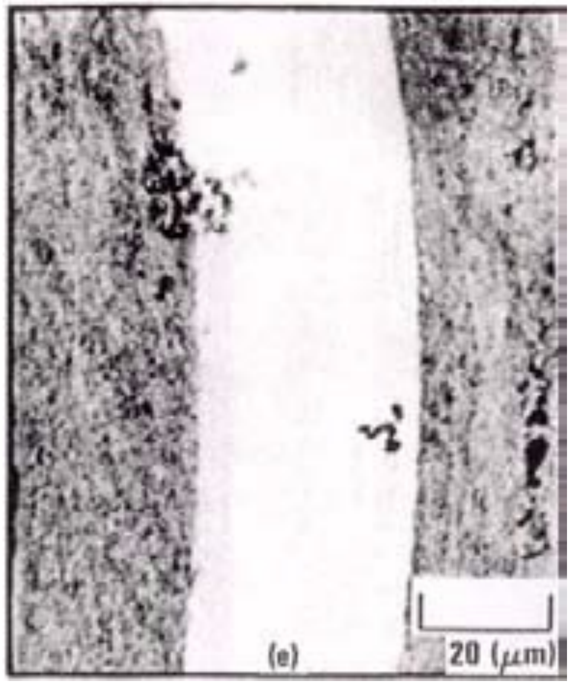
- Kernel migration

- Kernel migration is defined simply as movement of the kernel toward the TRISO-coating, which can lead to the kernel penetrating the TRISO-coating
- Kernel migration is associated with carbon transport in the particle in the presence of a temperature gradient
- A thermal gradient generates different equilibrium conditions for C, UO2, CO and CO2 at either side of the particle
- Carbon diffuses up the temperature gradient, the kernel diffuses down

Fuel Failure Mechanisms

- Fission product attack

- Fission products can be transported from the kernel to the inner surface of the SiC where they interact and can damage and potentially fail the SiC layer
- This is more of an issue in UC kernels
- In UCO kernels, the oxycarbide form of the kernel generally ties up all but the noble fission products (e.g., Pd) as either carbides or oxides, which tend to limit their mobility in the UCO system
- However, Pd and Ag transport have still been observed in UCO coated particle fuel



Fuel Failure Mechanisms

- Matrix-OPyC interactions and OPyC irradiation-induced cracking

- During manufacture, infiltration of the liquid graphitic matrix into the porosity of OPyC caused mechanical weakening
- During subsequent dimensional change under irradiation this caused OPyC layer to fail by cracking and debonding from the SiC layer
- This has largely been addressed through specifications on the matrix material and on the microstructure of the OPyC

- Non-retentive SiC

- There are situations where the SiC layer becomes functionally failed or degraded in some way and is no longer retentive of fission products
- Diffusive release through intact layers
  - If fuel temperatures during normal operation approach 1300C, then some of the fission products that are usually retained by the TRISO coating (e.g., cesium) will be able to diffuse out of the particle during normal operation
- SiC degradation resulting in permeability
  - Cesium attack of the SiC and/or CO corrosion of the SiC can allow fission products to be released at high burnup

Fuel Failure Mechanisms

- Creep failure of PyC

- Under stress, thermal creep of the PyC will occur
- In some post-irradiation heating tests, photomicrographs reveal a thinning and failure of the PyC
- Such failure has not led to failure of the SiC layer

- SiC thermal decomposition

- At very high temperatures (> 2000C) the SiC layer undergoes thermal decomposition
- The phenomenon is primarily a function of temperature and time and has not played a major role in fuel failure at lower accident temperatures

Fuel Failure Mechanisms

- Kernel-coating mechanical interaction (KCMI)

- At sufficiently high burn-up values, it is inevitable that all gas gaps between the kernel and coatings will close, thereby resulting in a mechanical interaction between the two
- Modelling studies predict that the SiC layer will fail shortly after the onset of KCMI
- This failure mechanism could be of increasing importance as attempts are made to achieve higher burn-up values

Fuel Failure Mechanisms

Failure mechanism	Reactor service conditions	Particle design and performance parameters that affect the failure mechanism	Comments
Pressure vessel failure	Temperature Burnup Fast fluence	Strength of SiC Buffer density (void volume) Fission gas release CO production Layer thicknesses Kernel type (UO_2, UCO)	
Irradiation-induced PyC failure	Fast fluence Temperature	Dimensional change of PyC Irradiation-induced creep of PyC Anisotropy of PyC Strength of PyC PyC thickness PyC density	Can be ameliorated by proper coating conditions
IPyC partial debonding	Temperature Fast fluence	Nature of the interface Interfacial strength Dimensional change of PyC Irradiation-induced creep of PyC	Can be ameliorated by proper coating conditions
Kernel migration	Temperature Burnup Temperature gradient	Layer thicknesses Kernel type	UO_2 only. Not important for UCO. Reasonably well understood
Fission product attack	Temperature Burnup Temperature gradient Time at temperature	Fission product transport behavior Diffusion Buffer densification and cracking Chemical state/transport behavior of fission products Microstructure of PyC and SiC	Could be more important at high burnup in LEU fuels because of greater yields of palladium from plutonium fissions
Non-retentive SiC Layer: Diffusive release through intact layers	Temperature Burnup Temperature gradient Time at temperature	Chemical state/transport behavior of fission products Microstructure of SiC SiC thickness	More important at higher temperatures (> 1200*C) where existing data suggest diffusion will contribute to the source term.
Non-retentive SiC layer:	Burnup Temperature Fluence	Kernel type (UO_2, UCO)	CO is generated in particles with UO_2 kernels.
SiC Corrosion by CO	Time at temperature	IPyC performance	At elevated temperatures, CO can attack the SiC layer if the IPyC layer is porous or has failed.
SiC degradation by cesium		Microstructure of SiC Thickness of SiC	Exact mechanism is unclear but limited data suggest cesium may degrade SiC layer
PyC thermal creep	Time at temperature	Thickness of PyC and stress state of PyC	Not important in traditional accident envelope (peak temperature < 1600°C)
SiC thermal decomposition	Temperature Time at temperature	SiC thickness Microstructure of SiC	Not important in traditional accident envelope (peak temperature < 1600°C)
Kernel Coating Mechanical Interaction (KCMI)	Burnup Fast Fluence Temperature	Initial Kernel – Coating Gas Gap Buffer properties IPyC Properties Kernel Swelling Rate	Failure of SiC Layer shortly after Gas Gap closed at sufficiently high Burn-ups

Fuel Failure Summary

- Overpressure
- IPyC cracking
- IPyC and SiC debonding
- Kernel migration
- Fission product attack
- Creep failure of PyC
- SiC decomposition
- KCMI

- These failure mechanisms have been observed to some extent in TRISO-coated fuel testing activities conducted around the world
- They are in general functions of temperature, burnup, fluence and temperature gradient in the particle and details of the particle design
- TRISO-coated fuel is usually designed such that none of the fuel failure mechanisms are expected to be significant