NE 795-014: Advanced Reactor Materials

Fall 2023

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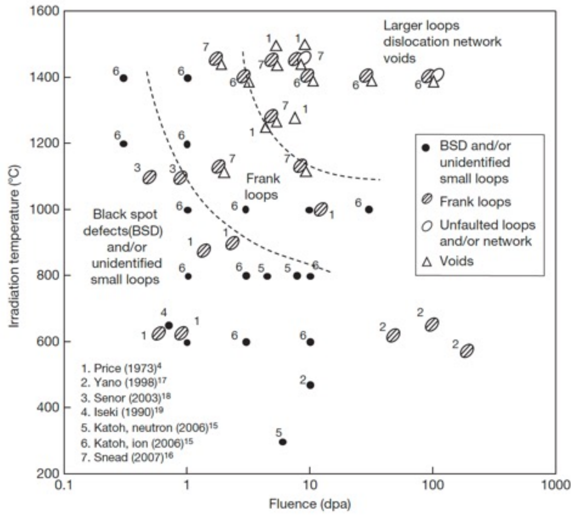
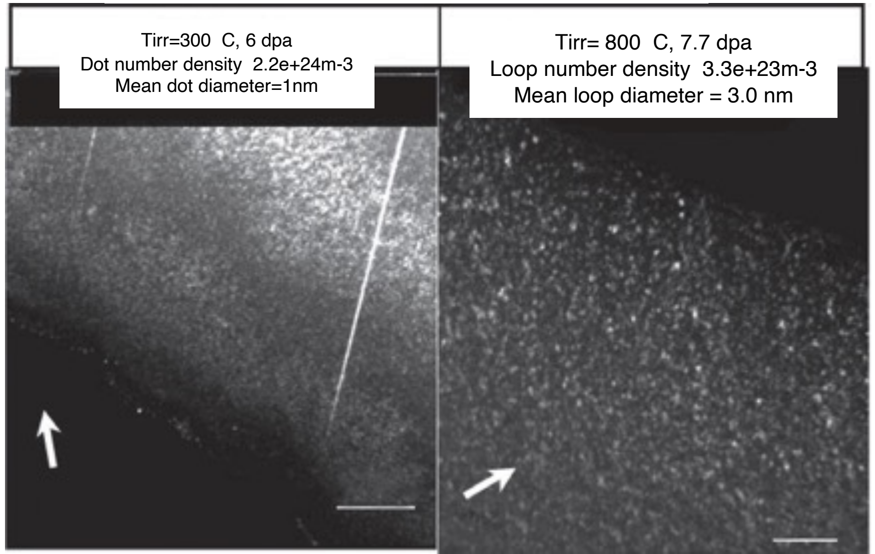
Last Time

- TRISO particle intro, evolution into current TRISO design
- Fuel kernel – UO_2 and UCO
  - UO_2 retains fission products, but generates CO
  - UC_2 limits CO formation, but poorly retains fission products
  - Oxygen potential controls which compounds form, transitioning UC into UO_2, while some FPs form oxides and other carbides
- 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

Low-Med T Radiation Effects in SiC

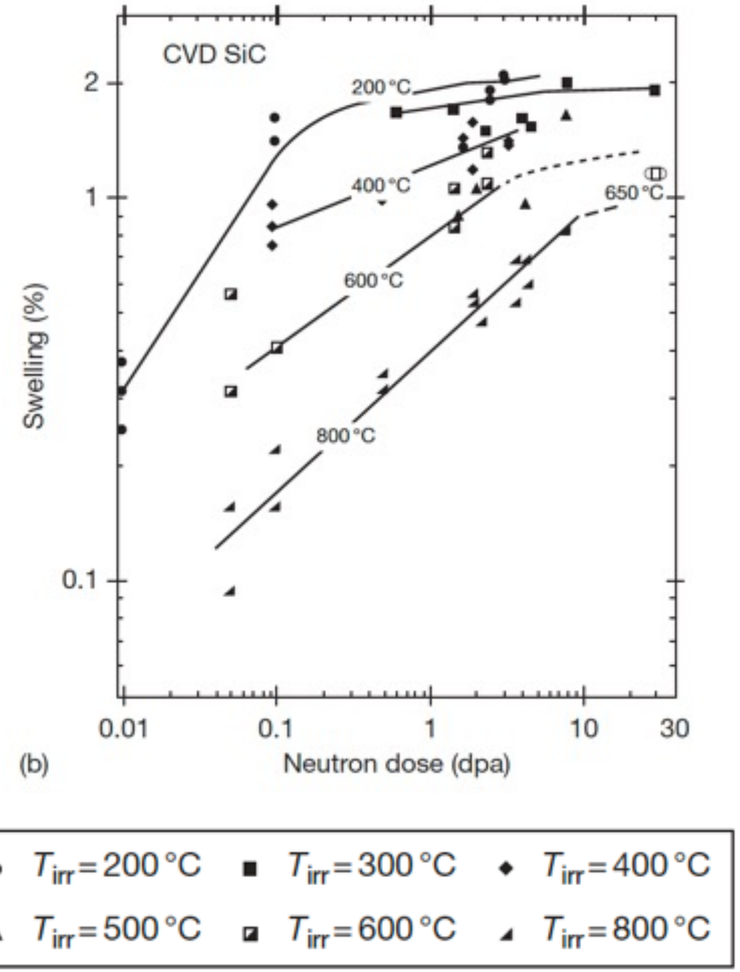
- Above the critical amorphization temperature (423 K), the swelling increases logarithmically with dose until it reaches saturation
- The saturation level decreases with increasing irradiation temperature
- The dose exponents of swelling during the log period are often close to 2/3, in line with assumptions based on interstitial clusters
- This temperature regime is referred to as the point-defect swelling regime and goes from critical amorphization temperature to about 1273 K





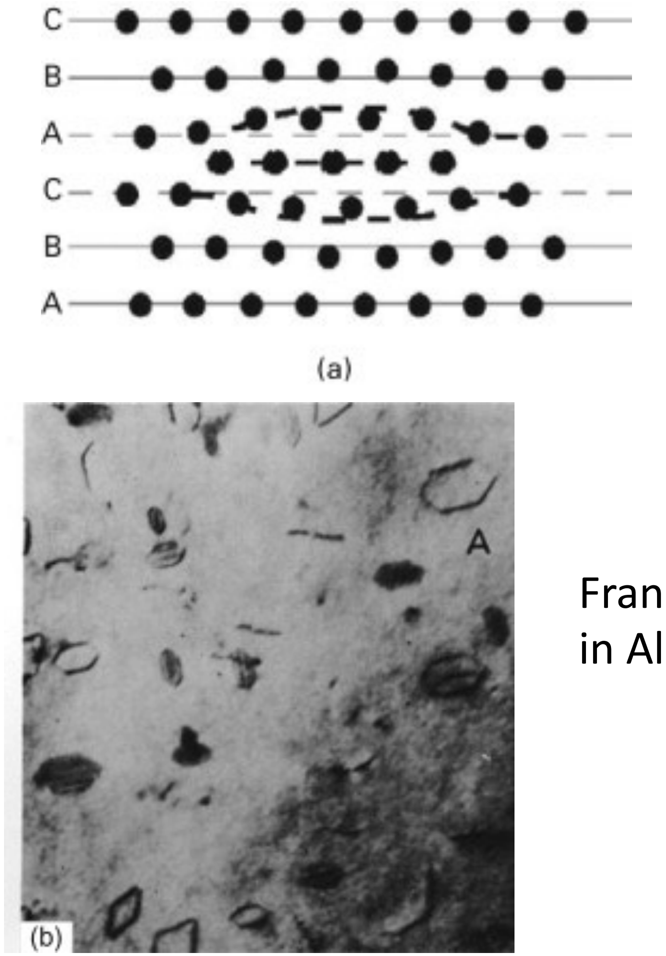
Saturation Swelling in SiC

- Log swelling vs dose shown at right for CVD SiC irradiated in HFIR
- The swelling of SiC is highly temperature dependent
  - at 1 dpa, saturation values from 200 C to 800 C vary by a factor of 5
- The decrease in saturation with increasing T is due to increased recombination of defects
- Swelling saturates at relatively low doses, less than 10 dpa



High T Radiation Effects in SiC

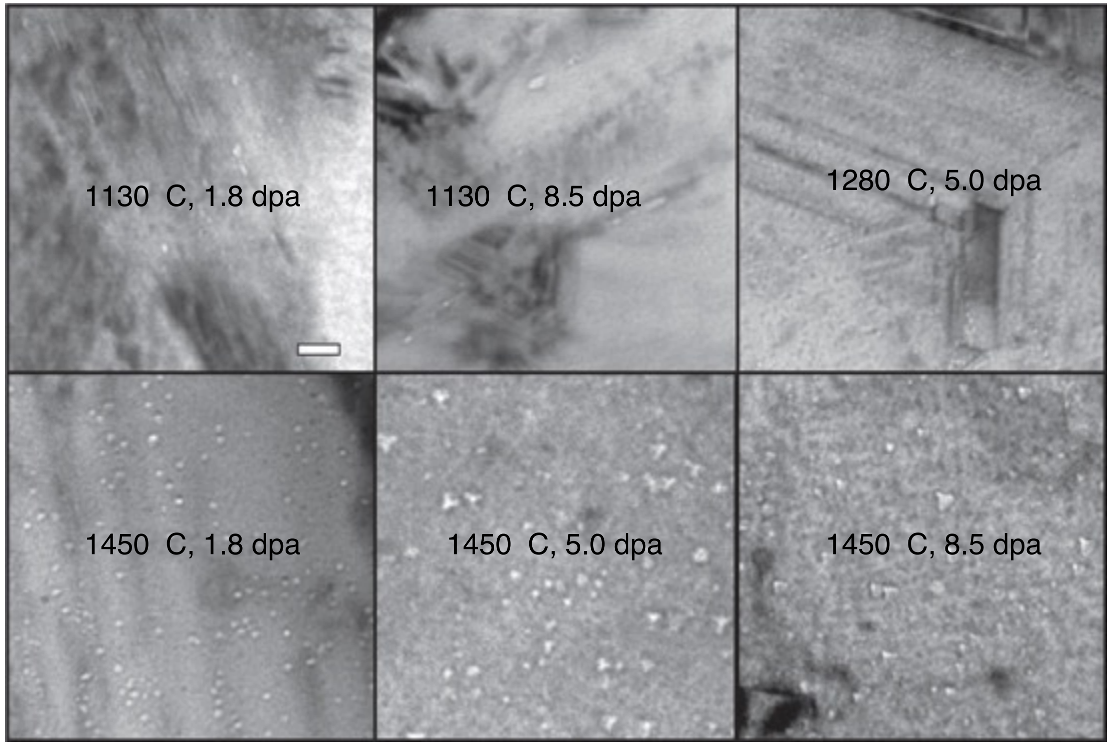
- Above 1000C, Frank loops of the interstitial type become the dominant defects observed by TEM
- Interstitial Frank loops are faulted, in that they include a stacking fault
- Consequently, these loops cannot glide and will not move under an applied stress or temperature, and are therefore considered as sessile
- At high temperature, the development of Frank loops into dislocation networks through unfaulting reactions at high doses is reported



Frank loops in Al

High T Radiation Effects in SiC

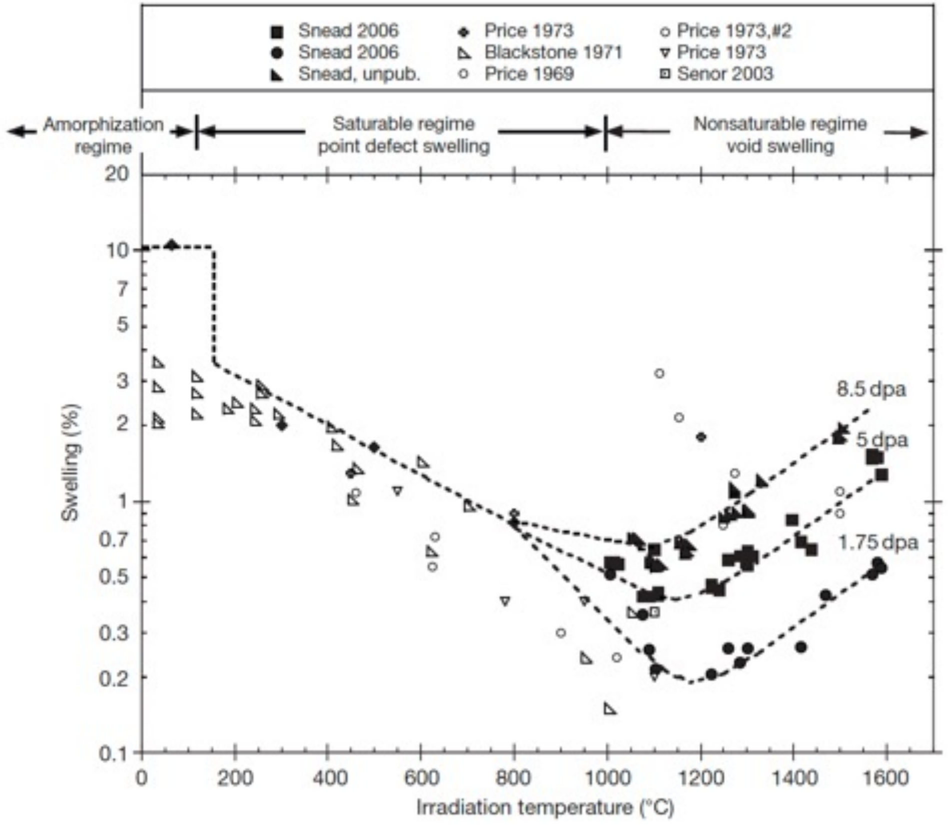
- The volume associated with dislocation loops in irradiated SiC has been estimated to be on the order of 0.1%
- At high T (greater than about 1500 K) vacancies are sufficiently mobile and vacancy clusters can be formed
- This high T regime is the void swelling regime



Evolution of voids in high-temperature irradiated CVD SiC

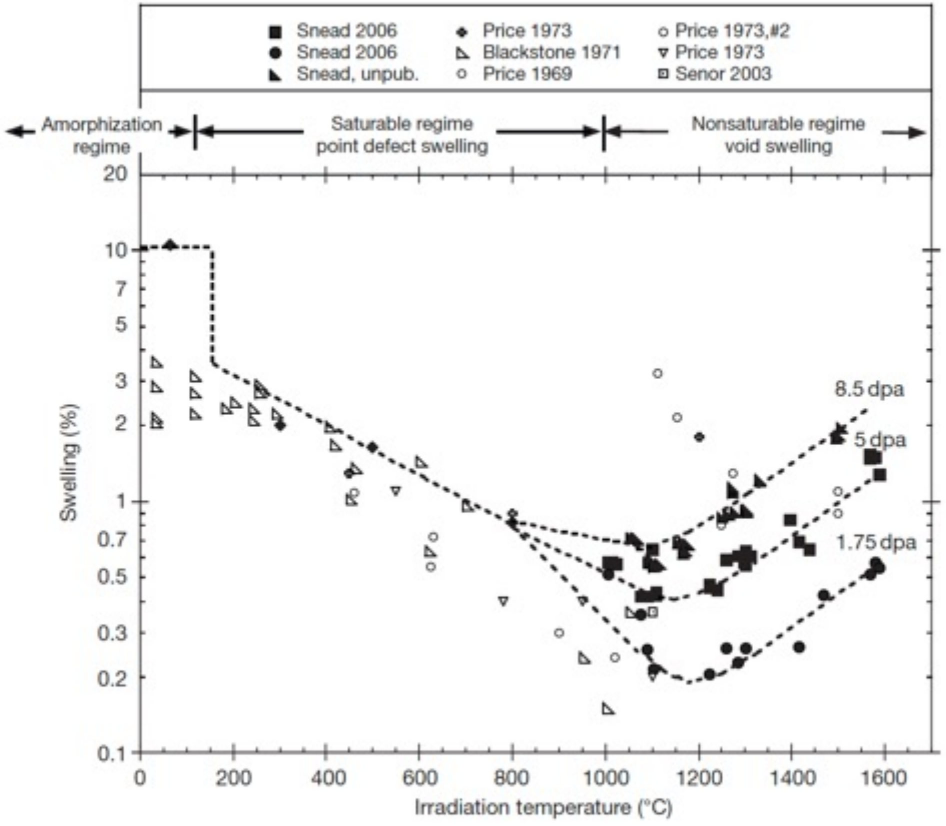
Irradiation-Induced Swelling in SiC

- The transition from point-defect saturated swelling to void swelling occurs above 1000C
- Void swelling increases as a function of dose, and is not known to saturate
- The swelling near the critical amorphization temperature is described as the differential strain between the single interstitial, or tiny interstitial clusters, immobile vacancies, and antisite defects



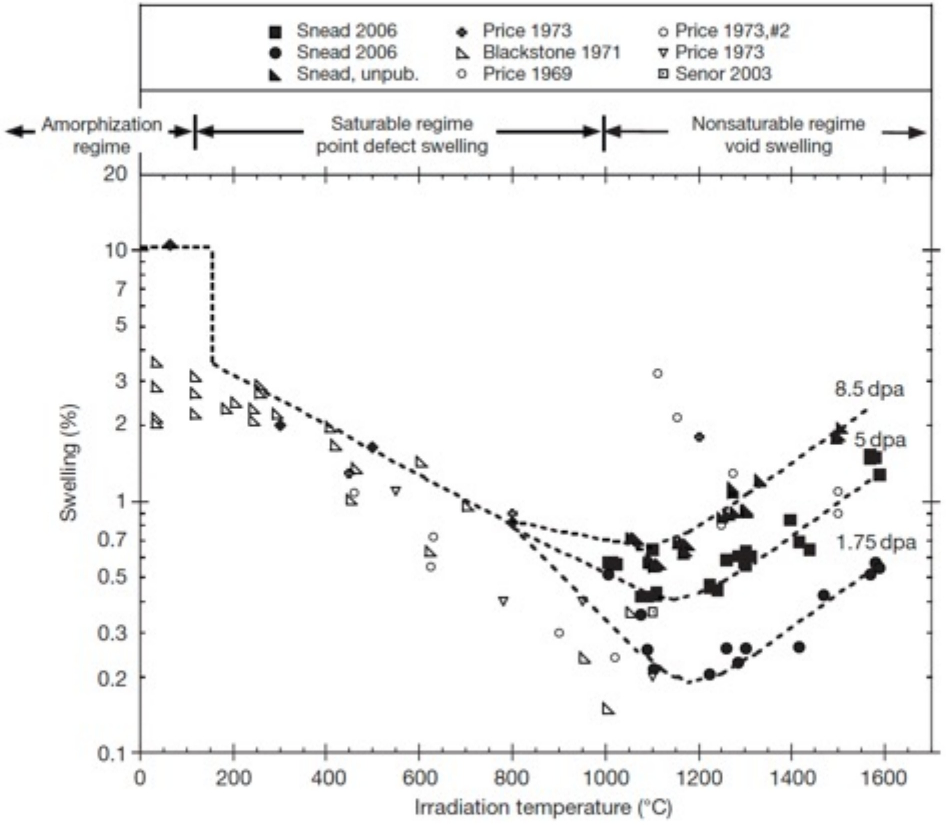
Irradiation-Induced Swelling in SiC

- Above the critical amorphization temperature, the number of defects surviving recombination is reduced and the mobility of both silicon and carbon interstitials becomes significant
- Above 1000 C microstructural studies have noted the presence of both Frank loops and tiny voids, indicating limited mobility of vacancies
- The max irradiation temperature shown is 0.65 T_{melt}



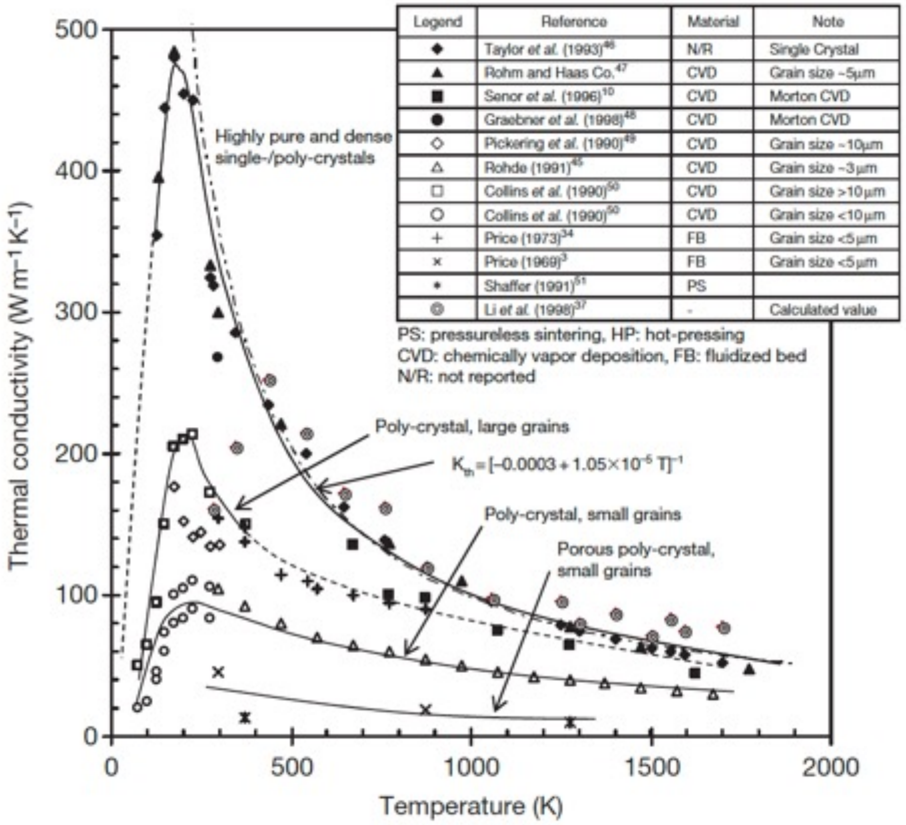
Irradiation-Induced Swelling in SiC

- In typical fcc metal systems void swelling typically begins at ~0.35Tm, goes through a maximum value, and decreases to nil swelling by ~0.55Tm
- The voids in SiC are continuing to grow in SiC irradiated to 1773 K, thus the energies for diffusion of either the Si or C vacancy or both must be quite high
- This has been confirmed through DFT methods
- It is unclear how swelling will increase as a function of dose above 10 dpa



Thermal Conductivity Degradation

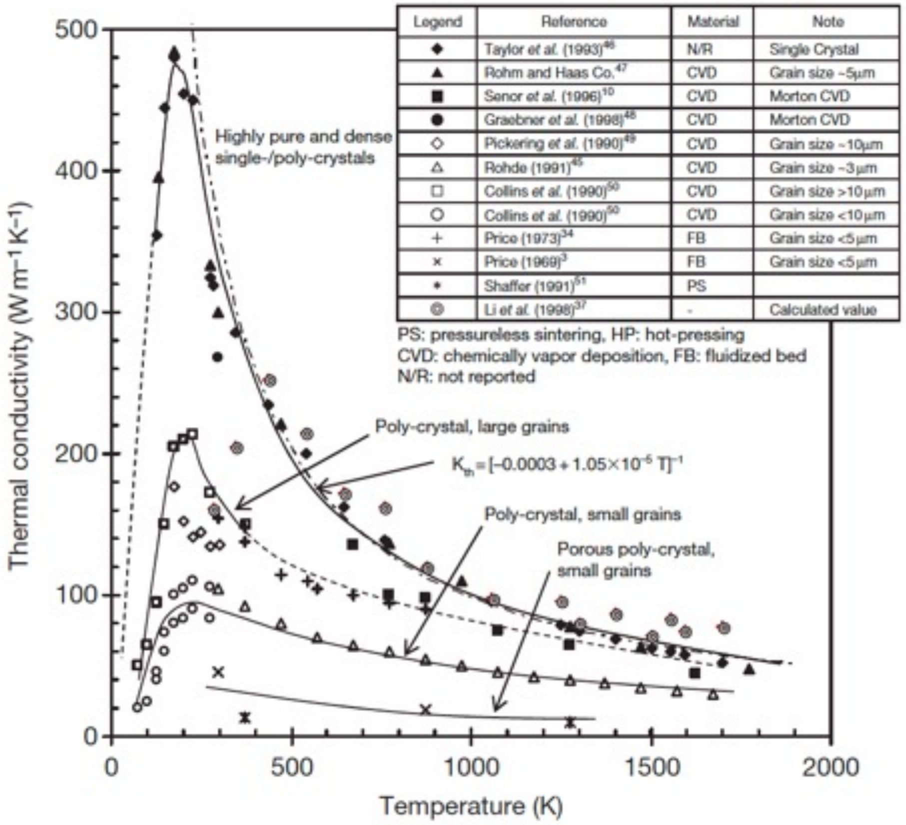
- SiC is a ceramic with a band gap, and thus thermal conductivity is based on phonons
- The conduction heat can be generally described by the strength of the individual contributors to phonon scattering: grain boundary scattering; phonon–phonon interaction; and defect scattering
- Each of these types occurs at differing phonon frequencies and can be considered separable



$$1/K = 1/K_{gb} + 1/K_u + 1/K_d.$$

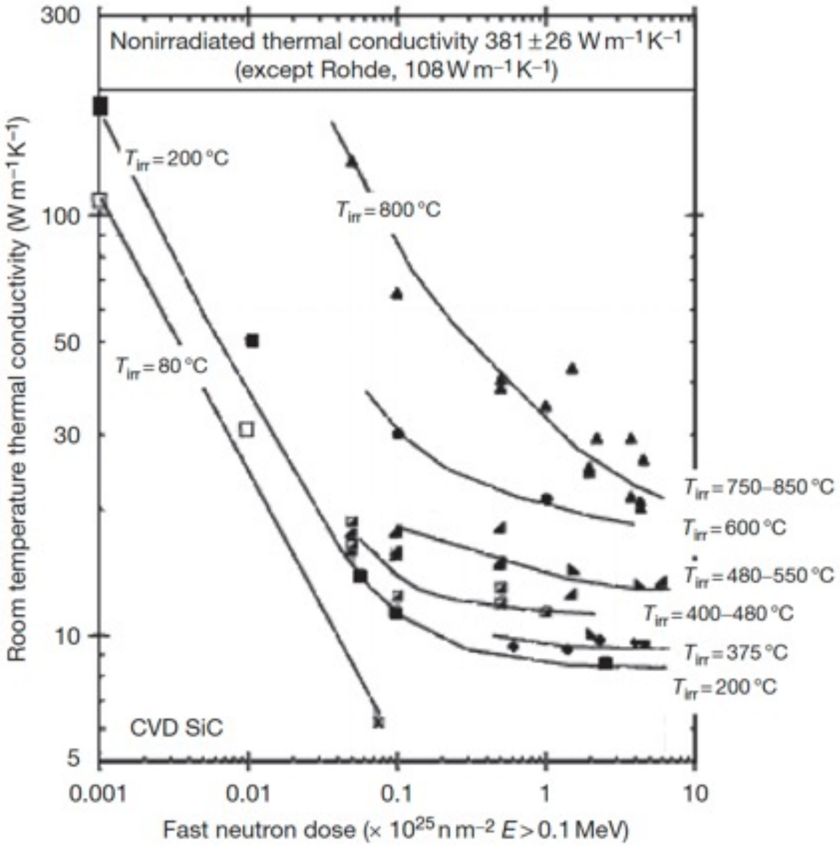
Thermal Conductivity Degradation

- The unirradiated k_{th} is highly dependent upon initial microstructure and temperature
- Initial microstructure can be tailored, but the temperature dependence cannot be removed
- For reference, Zr thermal conductivity is about 22 W/m-K at 1000 K



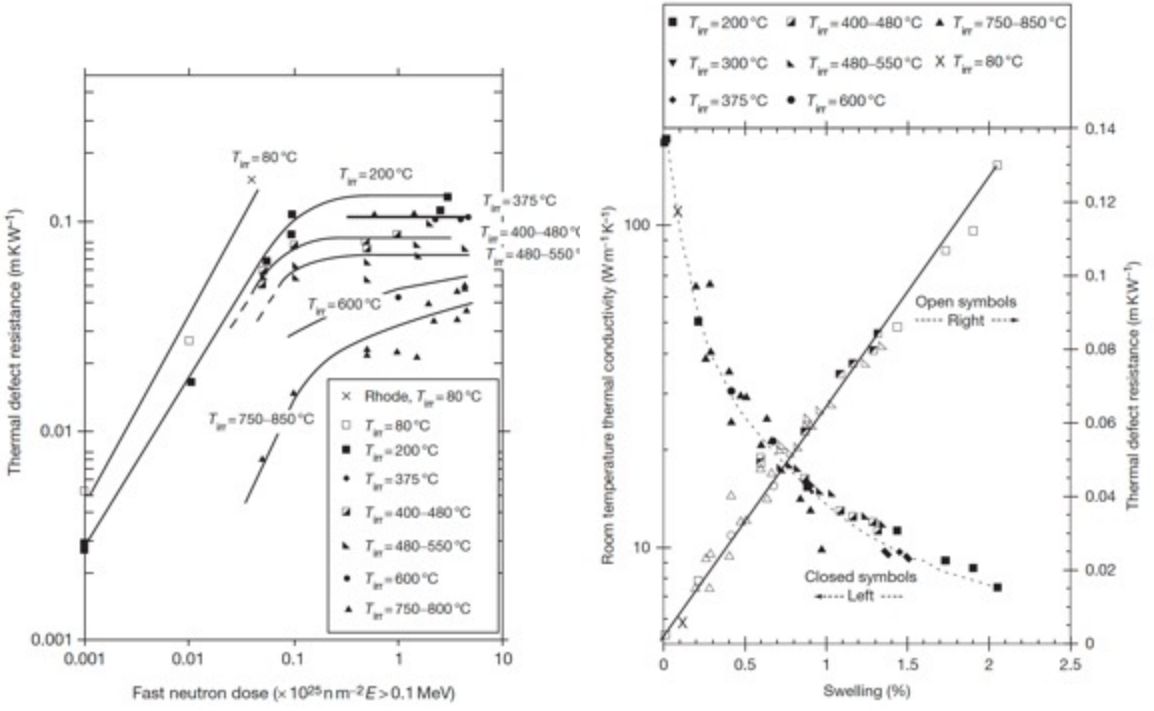
Thermal Conductivity Degradation

- At low temperatures irradiation produces simple defects and defect clusters that very effectively scatter phonons
- In this case, defect scattering quickly dominates, with saturation thermal conductivity typically achieved by a few dpa
- Defect scattering is sufficiently present to eliminate the temperature dependence



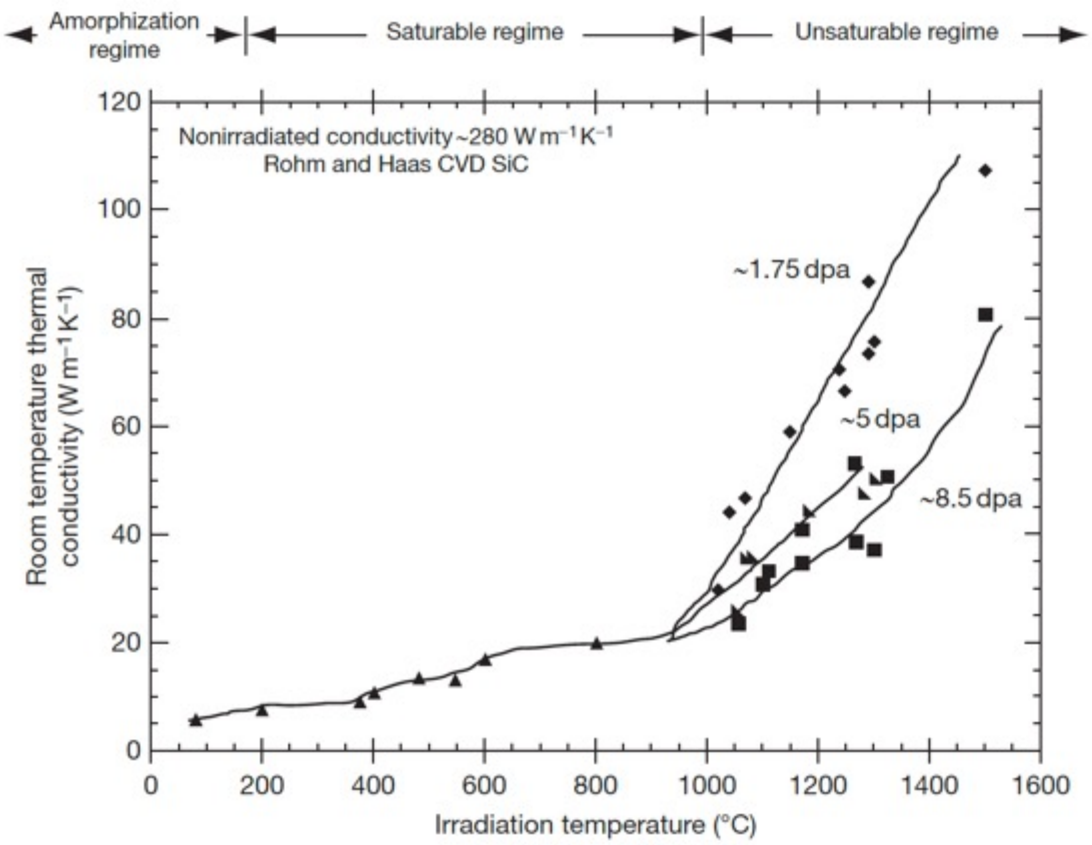
Thermal Conductivity Degradation

- The thermal defect resistance is defined as the difference between the reciprocals of the irradiated and nonirradiated thermal conductivity ($1/K_{rd} = 1/K_{irr} - 1/K_{nonirr}$)
- This term can be related directly to the defect type and concentration present in irradiated ceramics
- The thermal defect resistance is directly proportional to the irradiation-induced swelling in SiC
- This allows an indirect determination of thermal conductivity by measurement of the density change in the TRISO SiC shell



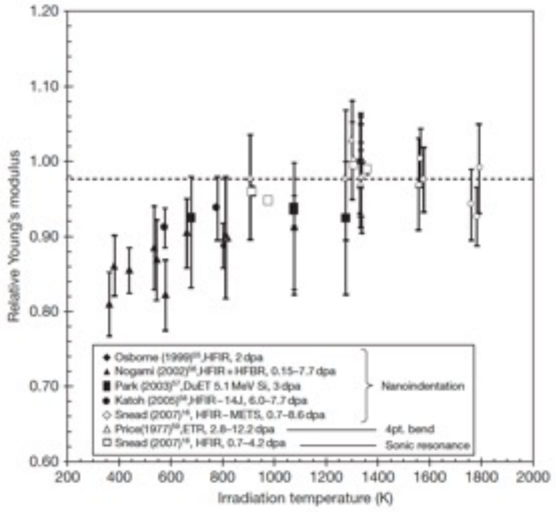
Thermal Conductivity Degradation

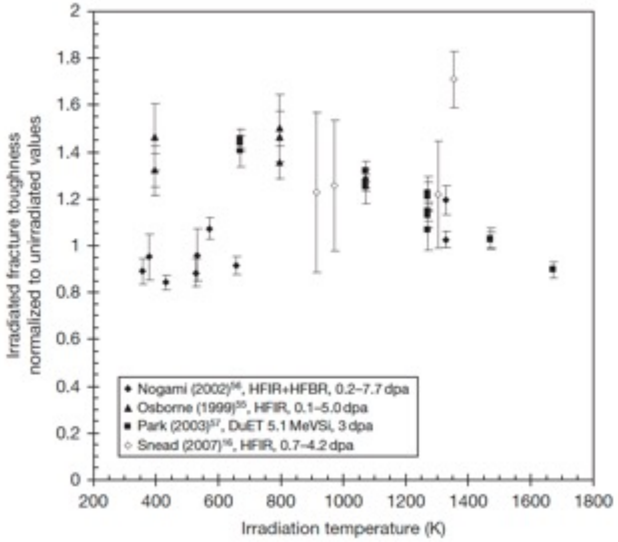
- In the high temperature void swelling regime, thermal conductivity degradation is not expected to saturate, as voids continue to grow and scatter phonons
- Additionally, the linear relationship between swelling and thermal defect resistance does not exist at high temperature
- Generally, void swelling does not degrade thermal conductivity as severely as point defects, but data at high T is quite limited



SiC Mechanical Properties

- Irradiation generally reduces modulus to a greater extent for lower temperature irradiation, while the modulus reduction becomes negligible when irradiation temperature reaches or exceeds 1273 K
- Irradiation-induced toughening (increase in fracture toughness) seems to be significant at 573–1273K in spite of the decrease in elastic modulus
- However, there is significant scatter in the data
- Reminder: toughness is related to the area under the stress–strain curve





SiC Creep

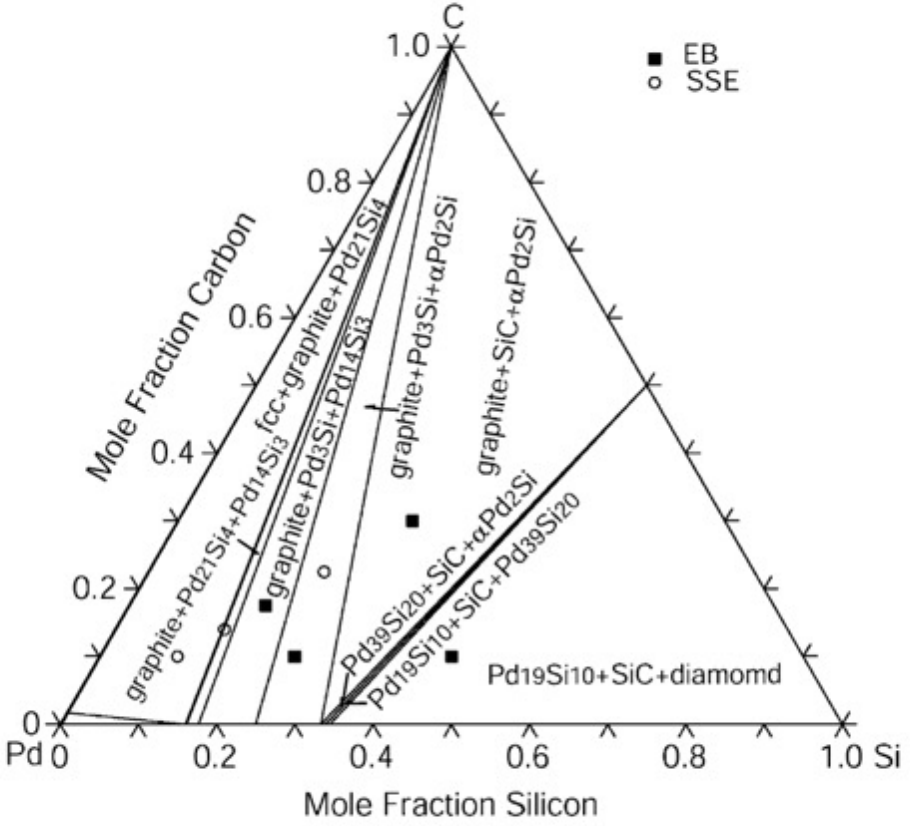
- Irradiation creep is defined as the difference in dimensional changes between a stressed and an unstressed sample irradiated under identical conditions
- Studies on irradiation creep of SiC have been limited, although it is of high importance for SiC in TRISO particles
- The creep strain for CVD SiC exhibited a weak temperature dependence at <0.7 dpa whereas a major transition at higher doses likely exists at higher temperatures
- Note: 3C-SiC is beta-SiC

Table 1 Irradiation creep data for CVD SiC from bend stress relaxation experiments

T_{irr} (°C)	*Fluence (dpa)*	*Reactor*	*Initial/final bend stress (MPa)*	*Initial/final bend strain ($\times 10^{-4}$)*	*Creep strain ($\times 10^{-4}$)*	*BSR ratio m*	*Average creep compliance $\times 10^{-6}$ (MPa dpa)$^{-1}$*
CVD SiC							
400	0.6	JMTR	82/60	1.80/1.39	0.41	0.77	0.97
600	0.2	JMTR	81/57	1.80/1.31	0.49	0.73	3.5
600	0.6	JMTR	81/46	1.80/1.05	0.75	0.58	2.0
640	3.7	HFIR	87/36	1.95/0.83	1.12	0.42	0.50
700	0.7	HFIR	102/72	2.27/1.64	0.63	0.72	1.1
750	0.6	JMTR	80/55	1.80/1.27	0.53	0.71	1.3
1030	0.7	HFIR	85/61	1.94/1.42	0.52	0.73	0.97
1080	4.2	HFIR	101/8	2.29/0.19	2.10	0.08	0.91
3C–SiC							
640	3.7	HFIR	87/30	1.94/0.68	1.26	0.35	0.59
700	0.7	HFIR	102/90	2.27/2.06	0.21	0.87	0.34
1030	0.7	HFIR	86/57	1.94/1.31	0.63	0.67	1.2
1080	4.2	HFIR	101/1	2.29/0.02	2.27	0.01	1.1

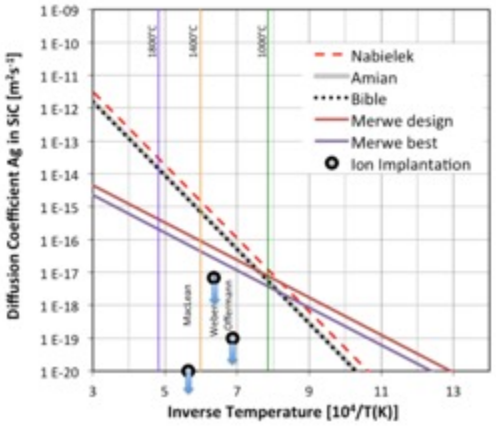
SiC Corrosion

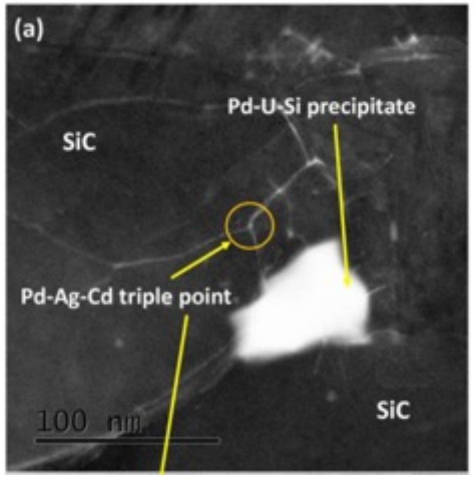
- The silicon carbide layer serves as a critical fission product barrier, but can be corroded by fission products, in particular palladium
- Additionally, silver can be transported through intact SiC layers
- For Pd, the reaction with SiC can be qualitatively explained by the phase-diagram, where a number of intermetallic structures are present
- To prevent corrosion by Pd, new combinations of coating layers have been proposed, and means of trapping Pd in the fuel are explored

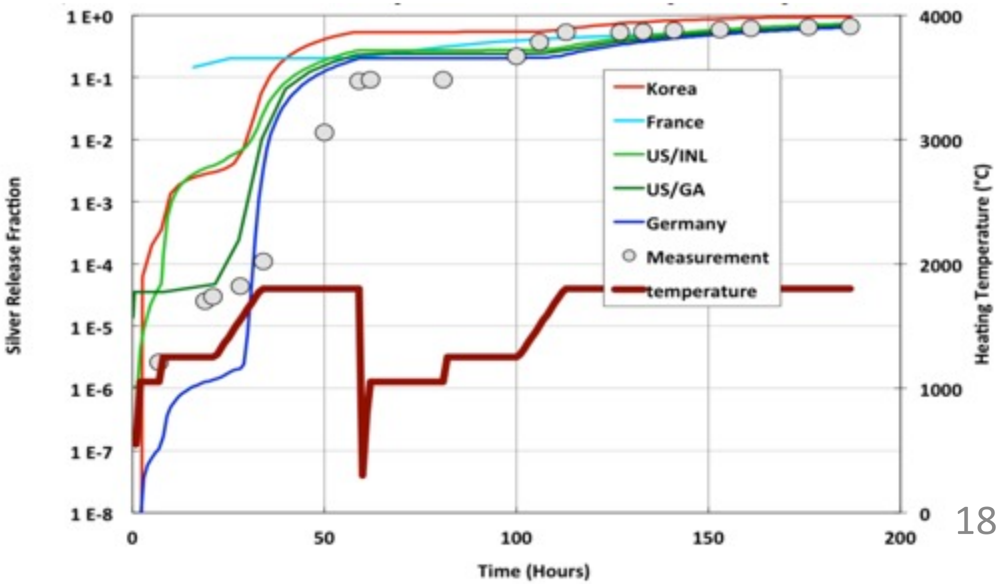


SiC Corrosion

- Silver release has been observed from undamaged particles suggesting that Ag migrates through intact SiC layers at temperatures >1100 C
- The Ag migration mechanism remains not fully understood, and is still an active area of research
- Ag release has a temperature dependence, pointing towards a diffusive mechanism
- From microstructural analyses, it seems possible that Ag, Cd, and Pd cluster and transport together at grain boundaries and triple points because of their common chemical properties







SiC Corrosion

- Once cesium has migrated into the buffer, it can react with carbon
- At nominal temperatures, cesium may be released and associated with carbon of the buffer layer to form compounds
- These compounds, if they are not stable with increasing temperatures, may become a potential source of cesium release
- Typically, cesium-graphite compounds are not stable at 923 K under vacuum and decompose to give cesium vapor and graphite

TABLE II. Heats and entropies of formation.

Reaction	ΔH_f^0 cal/mole Cs	ΔS_f^0 cal/mole Cs-°K
8 C(s) + Cs(g) = C_8 Cs(s)	-33 800	-23.8
10 C(s) + Cs(g) = C_{10}Cs(s)	-31 300	-18.9
24 C(s) + Cs(g) = C_{24}Cs(s)	-34 000	-18.2
36 C(s) + Cs(g) = C_{36}Cs(s)	-35 400	-18.8
48 C(s) + Cs(g) = C_{48}Cs(s)	-35 600	-18.6
60 C(s) + Cs(g) = C_{60}Cs(s)	-35 900	-18.7

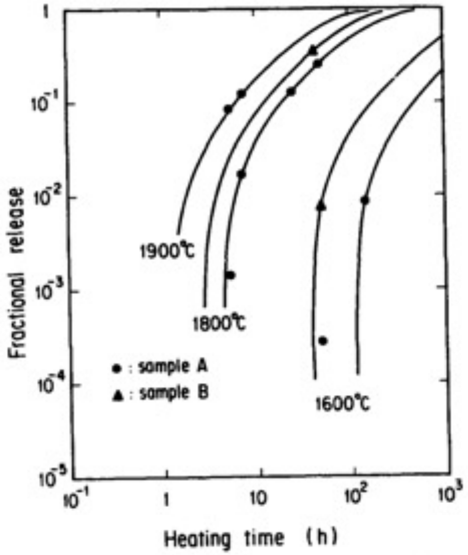


Fig. 5. Fractional release of ^{137}Cs during postirradiation heating as a function of heating time and temperature. Solid lines are diffusive release curves calculated by a simple diffusion model assuming a one-layer coated particle.

SiC vs ZrC Corrosion

- An approach to counteract SiC fission product corrosion is to replace the SiC coating by a ZrC layer
- Experimental observations showed neither Pd attack nor thermal degradation of ZrC up to 1600C
- ZrC was also shown to have a high capacity to retain Cs, but poor retention of Ru
- At higher T, the deterioration of the ZrC particle is caused by failure of the IPyC
- The development of TRISO with ZrC-coating is at an early stage compared to the SiC-coated design

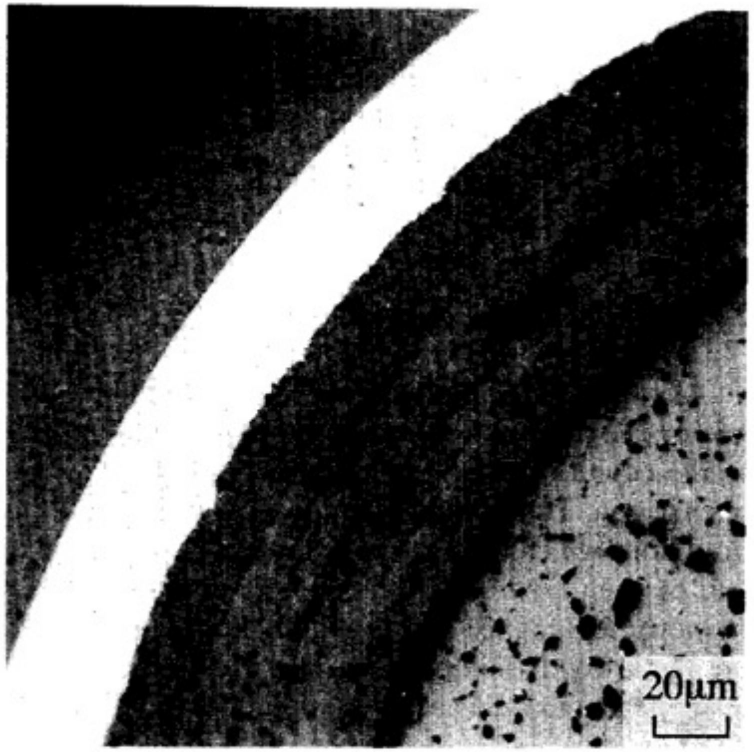


Fig. 2. Optical micrographs of polished section of ZrC-coated fuel particles after heating at 1600°C for 4500 h.

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

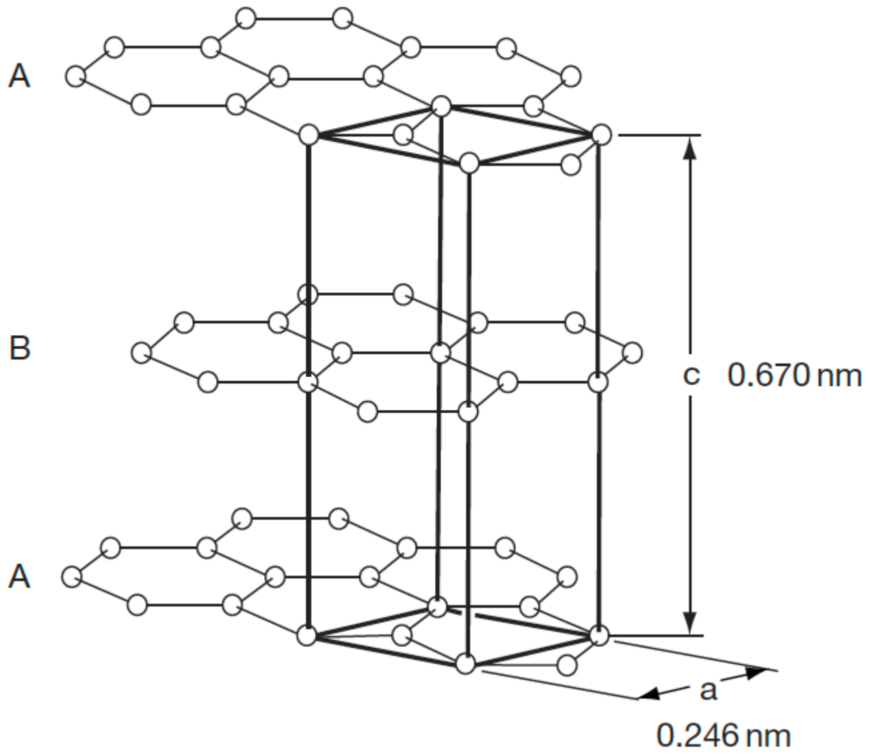
Delineate Types of Graphite

- TRISO Graphite (PyC)
  - 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

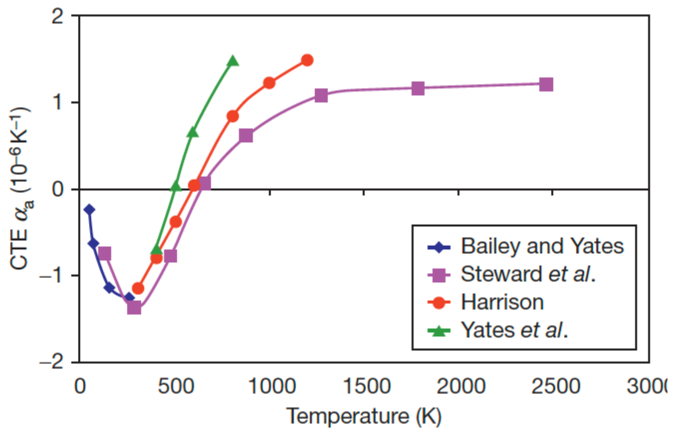
Graphite Structure

- 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

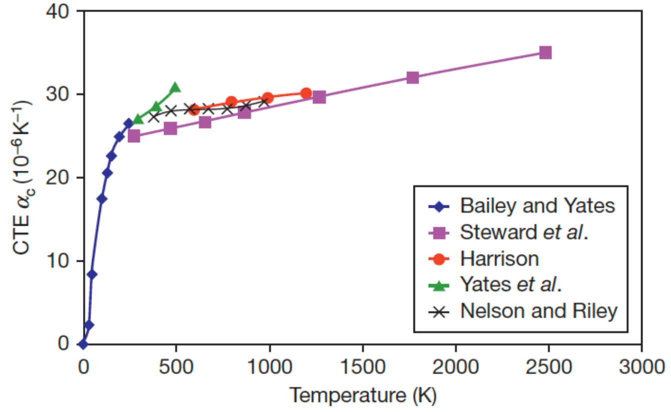


Fundamental Properties

- 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



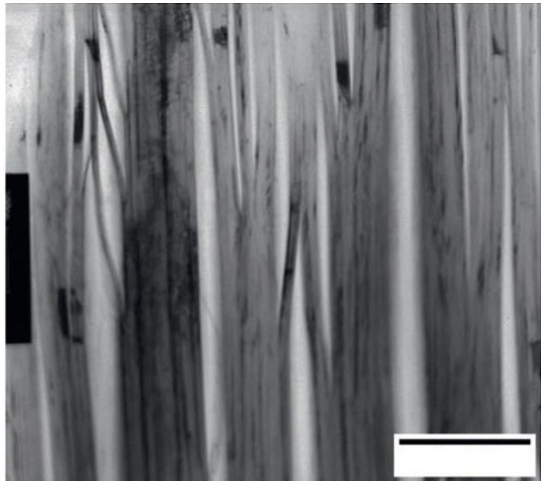
‘c’ direction



‘a’ direction

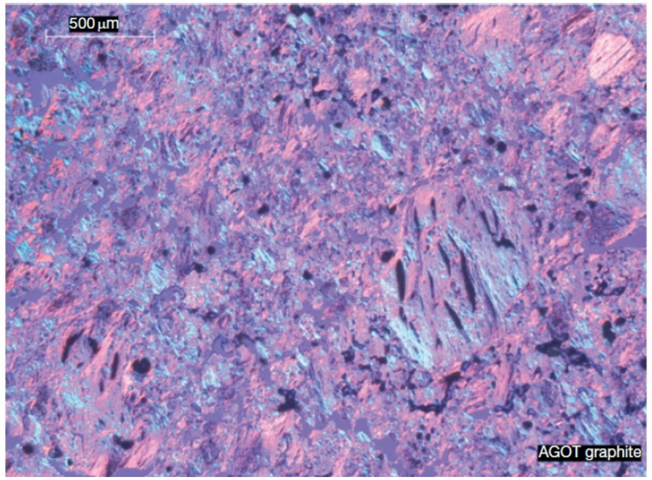
Mrozowski Cracks

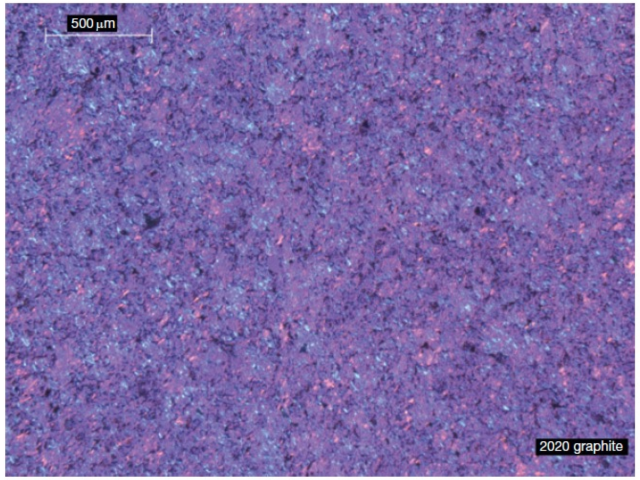
- During the manufacture of artificial graphite, very high temperatures (2800–3000 C) are required
- Upon cooling, the anisotropy in thermal expansion coefficients leads to the formation of long, thin microcracks parallel to the basal planes, often referred to as ‘Mrozowski’ cracks
- The presence of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



Graphite Texture

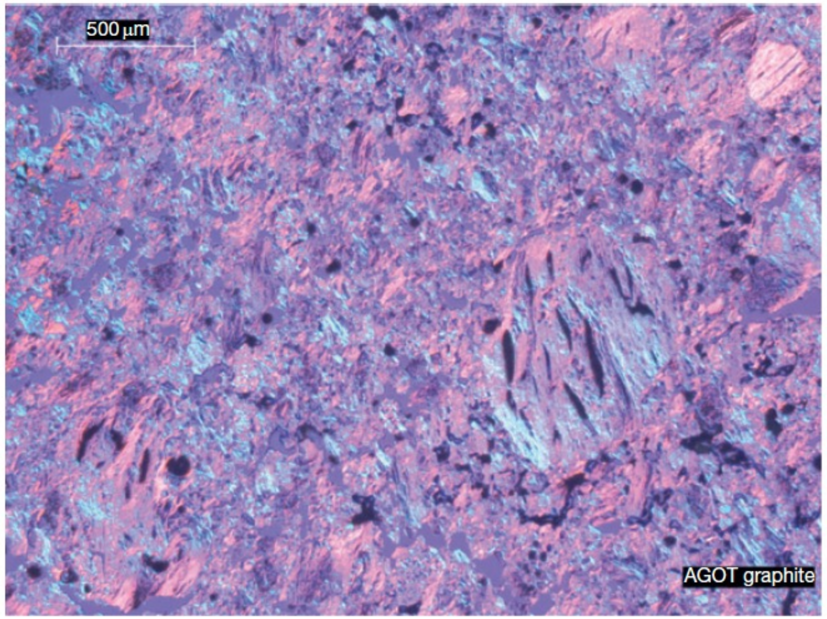
- Graphite structure is largely dependent upon the manufacturing process
- Graphites are classified according to their grain size from coarse-grained (containing grains in the starting mix that are generally >4mm) to microfine-grained (containing grains in the starting mix that are generally <2 mm)
- 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

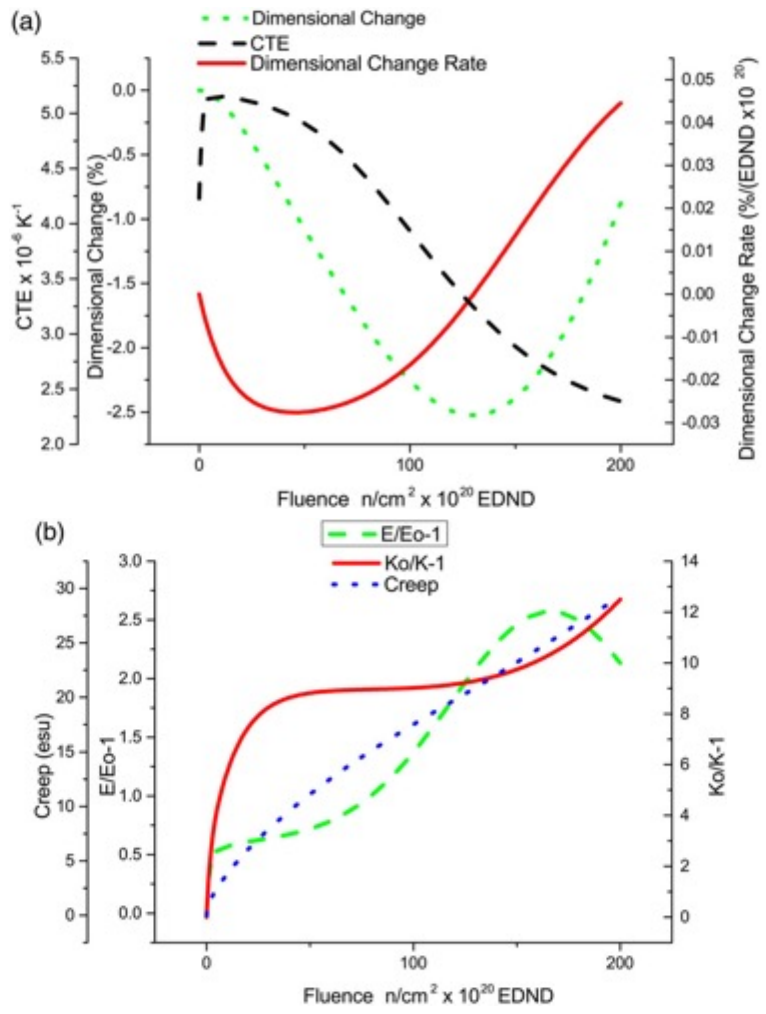


RADIATION EFFECTS IN GRAPHITE

Graphite Shrinkage

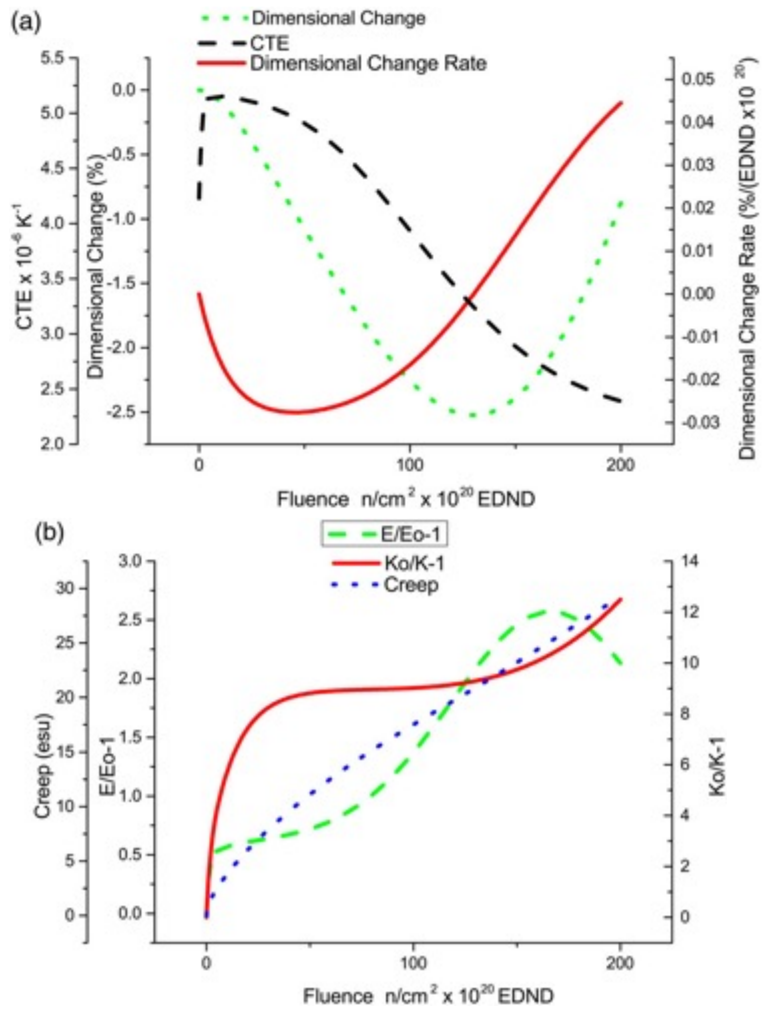
- When graphite components are irradiated in a reactor, significant changes to their dimensions and properties occur
- The unit of irradiation exposure EDND used in the figures is particular to nuclear graphite technology
- EDND = Equivalent DIDO Nickel Dose
- EDNF = Equivalent DIDO Nickel Flux
- They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