NE 591: Advanced Reactor Materials

Fall 2021
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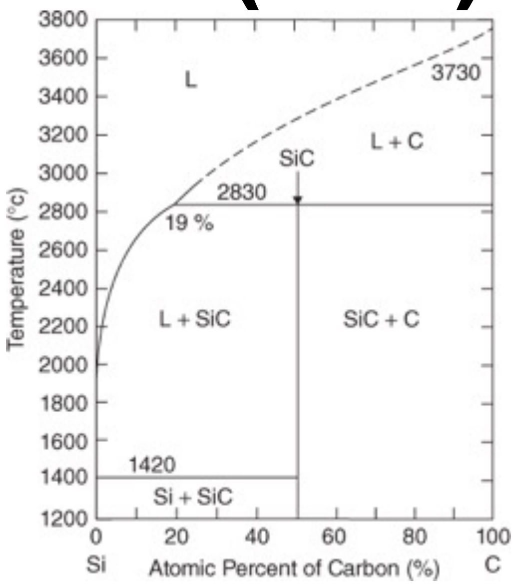
Last Time

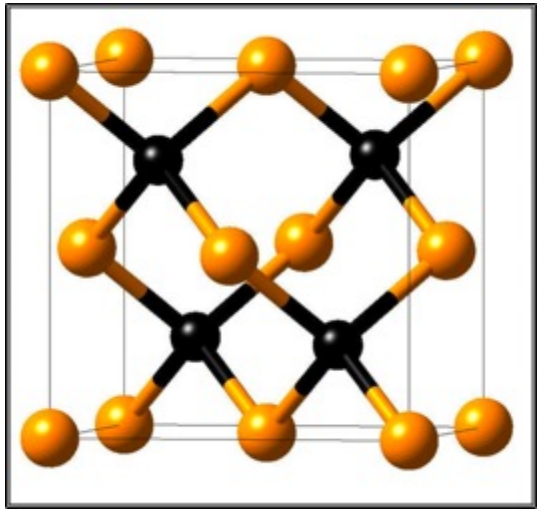
- Background and history of HTGRs/TRISO particles
- Difference from LWRs
  - helium cooled; much higher temperatures; thermal/fast options; extensive utilization of graphite; flexibility of fuel
- Fuel Kernel
  - oxides and carbides
  - oxides have better fission retention, carbides don't produce CO
  - US uses UCO, UC2 being consumed over time
  - oxygen potential will govern CO production
  - CO production can cause failure

SILICON CARBIDE

Silicon Carbide (SiC)

- SiC is a very hard and strong non-oxide ceramic that possesses unique thermal and electronic properties
- Polycrystalline SiC has a strength of 15 GPa and has excellent creep resistance
- SiC's upper limit of stability is around 2500C and has a melting temperature of around 2830C
- SiC also has excellent thermal conductivity
- SiC is a highly covalent material that forms tetrahedra that are centered around either carbon or silicon atoms





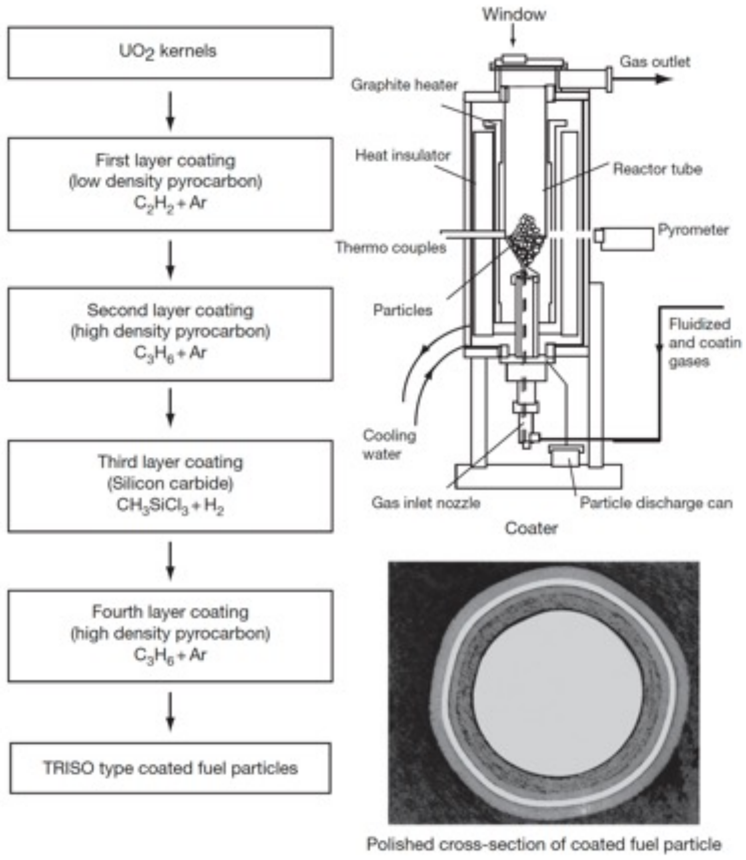
- β-SiC takes the diamond cubic structure with half of the carbons being replaced with silicon; this is a very stable structure that is conducive to phononic heat conduction

Silicon Carbide (SiC)

- Silicon carbide (SiC) has been studied and utilized in nuclear systems for decades, primarily as the micro pressure vessel for high-temperature gas-cooled reactor fuels
- The SiC must be strong enough to withstand the pressure buildup from the fission product gas liberated and CO produced
- The SiC layer must withstand chemical attack from metallic fission products such as palladium
- The SiC must be able to handle the mechanical loads derived from irradiation-induced dimensional changes occurring in the pyrolytic graphite
- The SiC must maintain its properties during irradiation

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

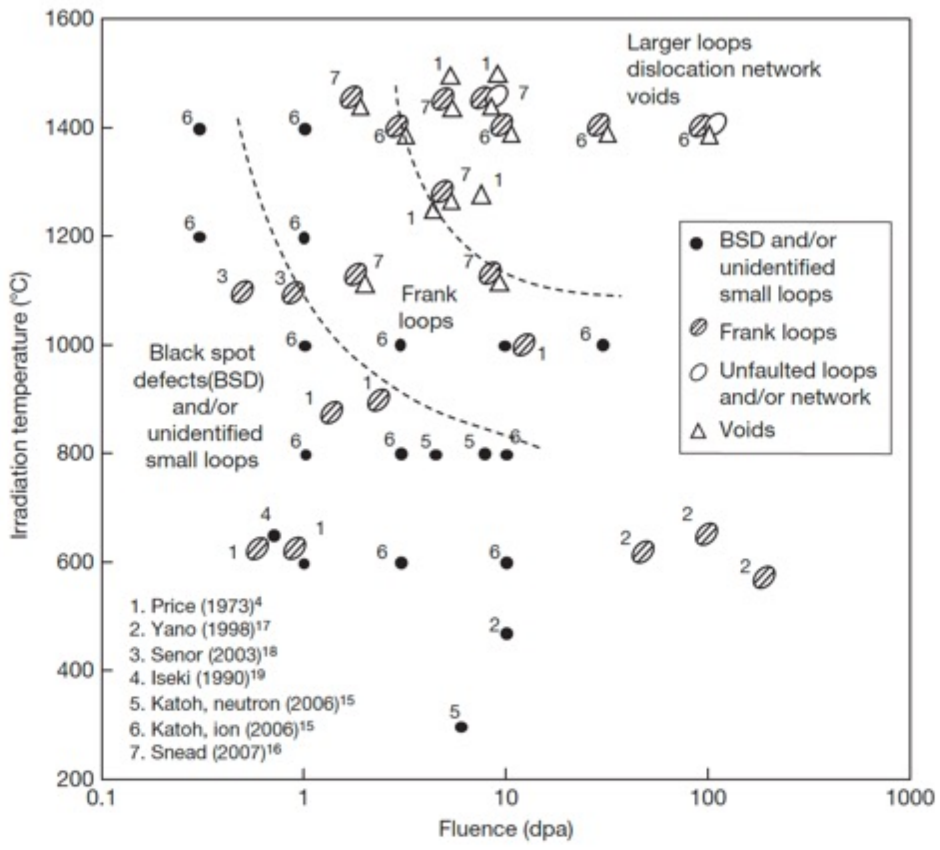


Radiation Effects in SiC

- The neutron-induced swelling of SiC has been well studied for low and intermediate temperatures (up to 1000 C)
- It is well understood that the presence of significant second phases and/or poorly crystallized phases in these materials leads to unstable behavior under neutron irradiation
- While high purity, stoichiometric, near-theoretical density SiC can show excellent radiation resistance
- Here I will be talking about the good SiC, assuming that the fabrication process has produced appropriately clean coatings

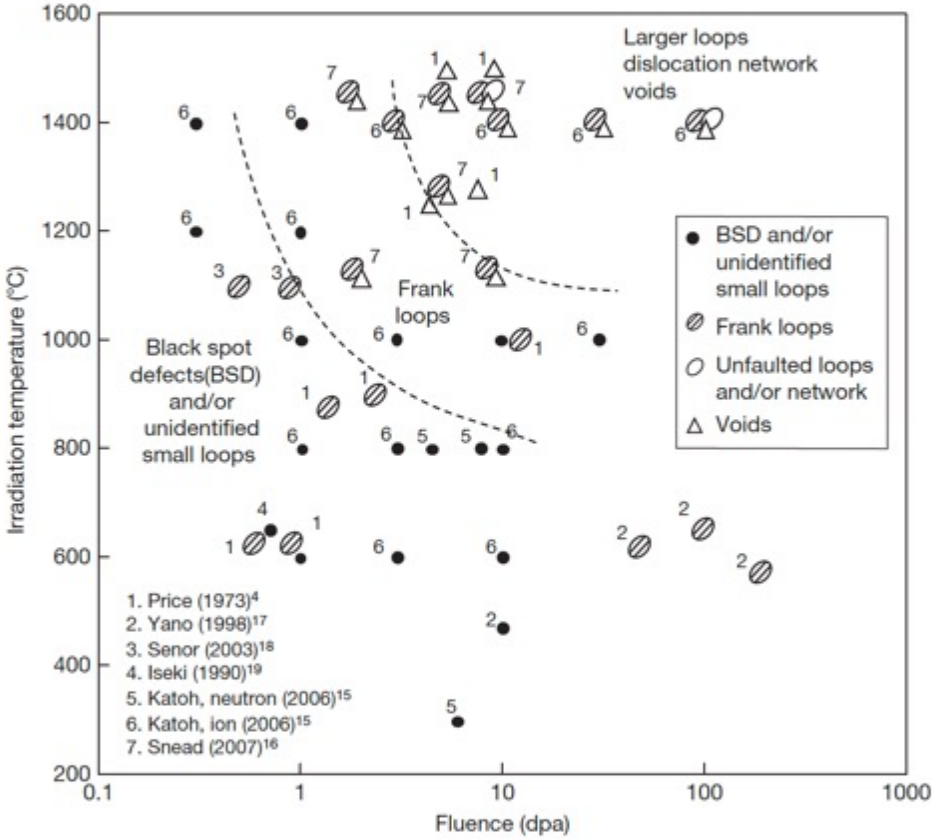
Radiation Effects in SiC

- The microstructural evolution map is shown on the right
- The contribution of the defects themselves to the swelling in SiC is not well understood



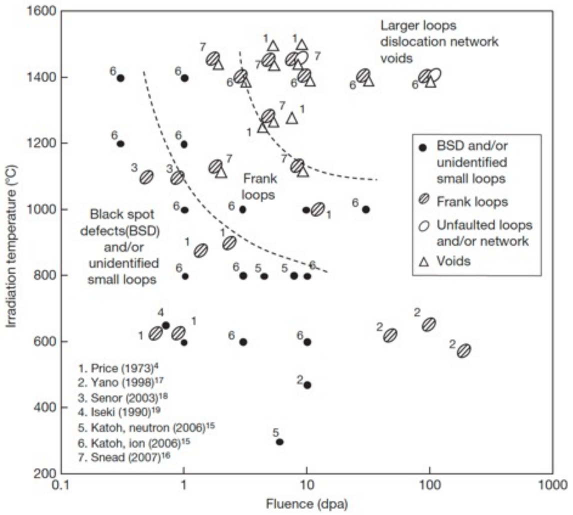
Low T Radiation Effects in SiC

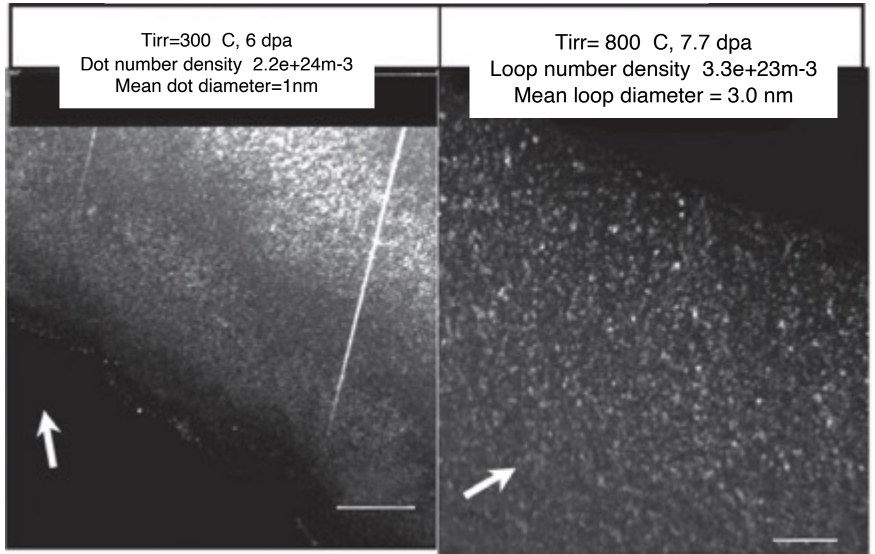
- Below 400 K, neutron irradiated SiC microstructure is described as black spot defects, which are most likely clusters of self-interstitial atoms
- For irradiation temperatures less than about 423 K, accumulation of strain due to the irradiation-produced defects can exceed a critical level above which the crystal becomes amorphous
- The swelling under self-ion irradiation increases logarithmically with dose until amorphization occurs
- The swelling of neutron- and ion-amorphized SiC has been reported to be as high as 10.8% at 343K



Low-Med T Radiation Effects in SiC

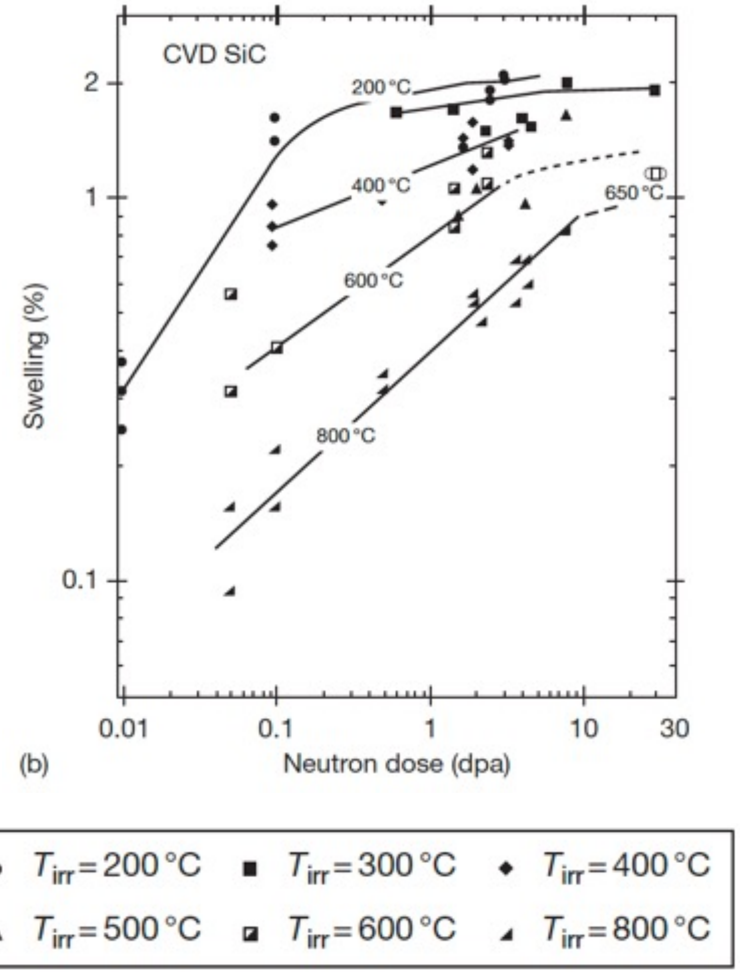
- Above the critical amorphization temperature (423 K), the swelling increases logarithmically with dose until it reaches saturation
- The saturation level decreases with increasing irradiation temperature
- The dose exponents of swelling during the log period are often close to 2/3, in line with assumptions 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





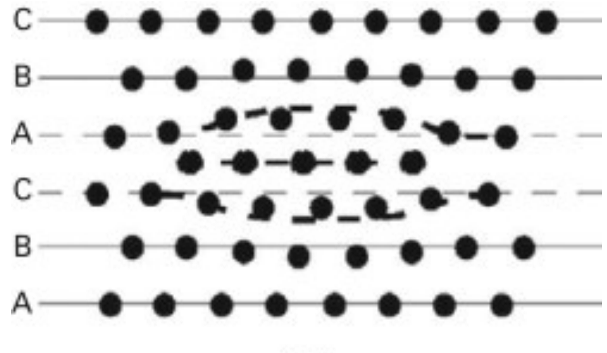
Saturation Swelling in SiC

- 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

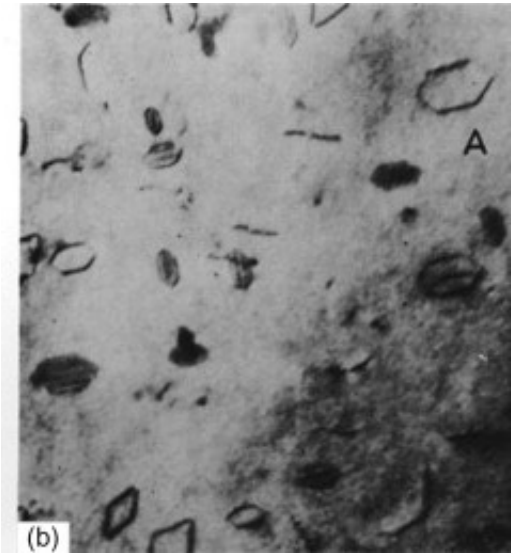


High T Radiation Effects in SiC

- 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



(a)

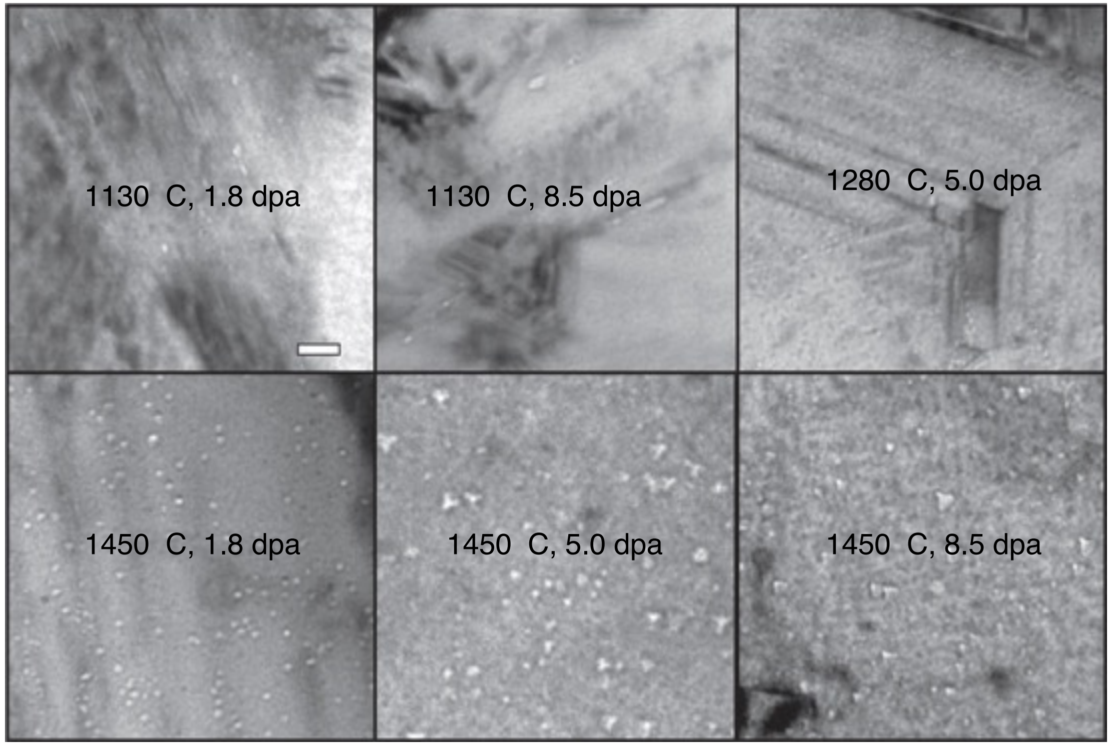


(b)

Frank loops in Al

High T Radiation Effects in SiC

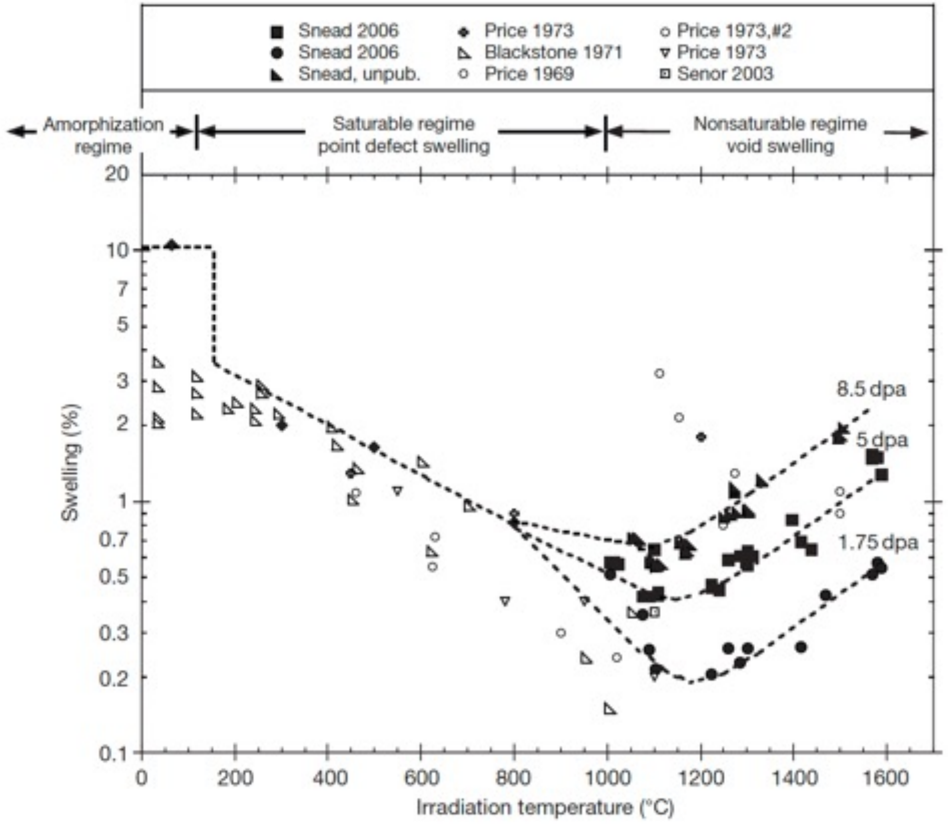
- The volume associated with dislocation loops in irradiated SiC has been estimated to be on the order of 0.1%
- At high T (greater than about 1500 K) vacancies are sufficiently mobile and vacancy clusters can be formed
- This high T regime is the void swelling regime



Evolution of voids in high-temperature irradiated CVD SiC.

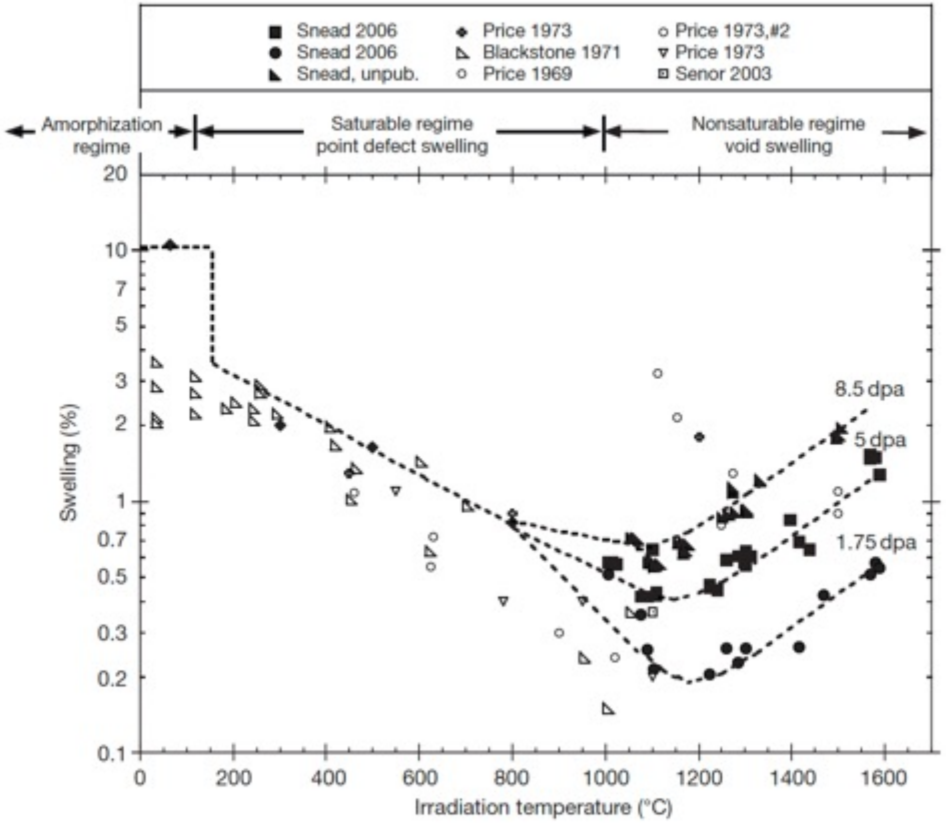
Irradiation-Induced Swelling in SiC

- 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



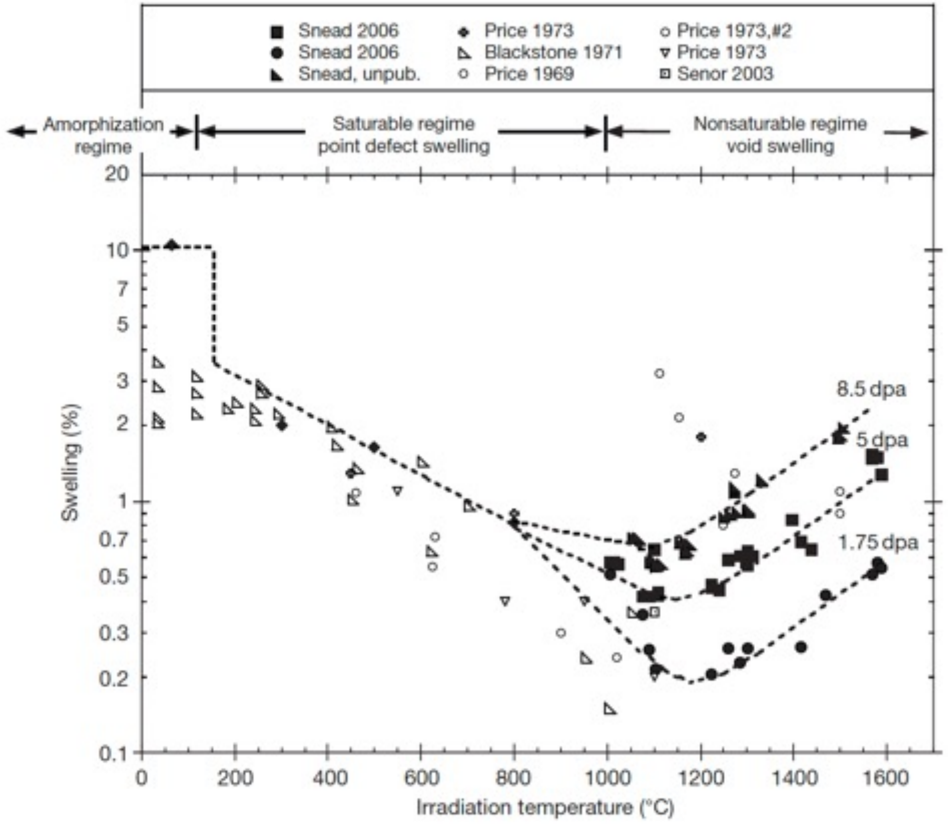
Irradiation-Induced Swelling in SiC

- 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}



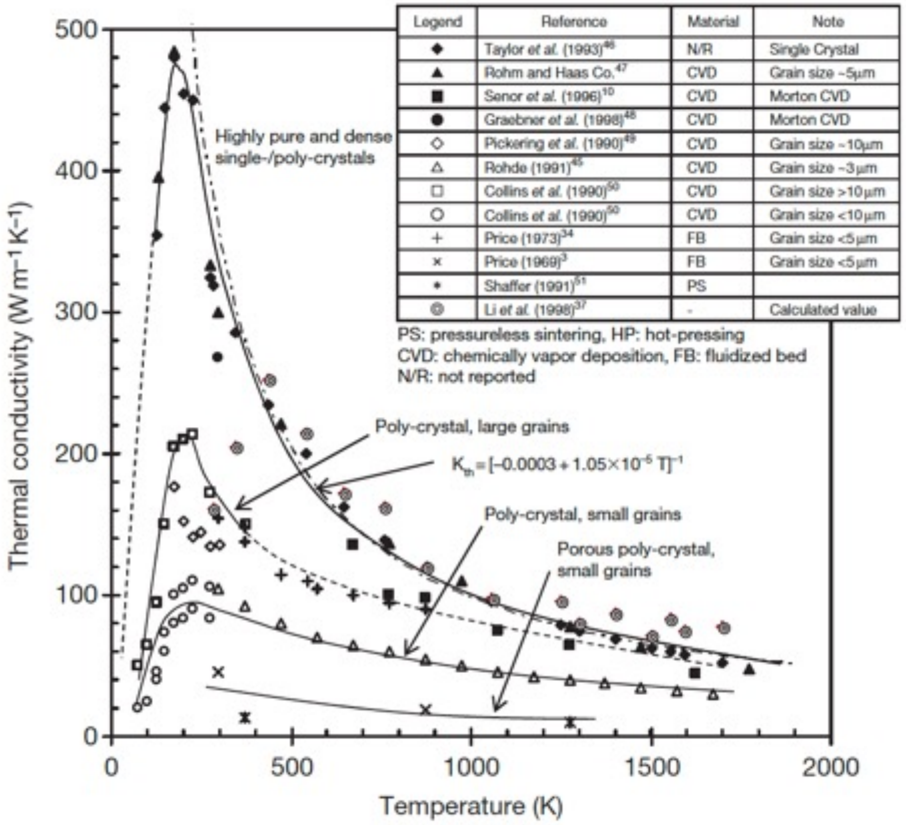
Irradiation-Induced Swelling in SiC

- 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

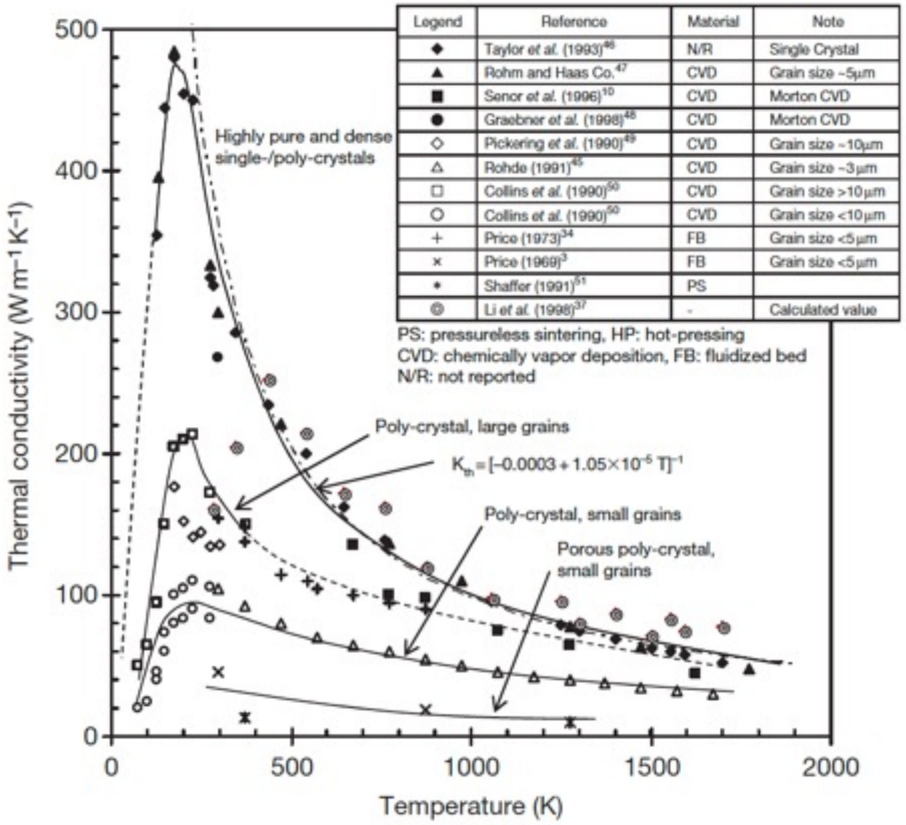


$$1/K = 1/K_{gb} + 1/K_u + 1/K_d.$$

Thermal Conductivity Degradation

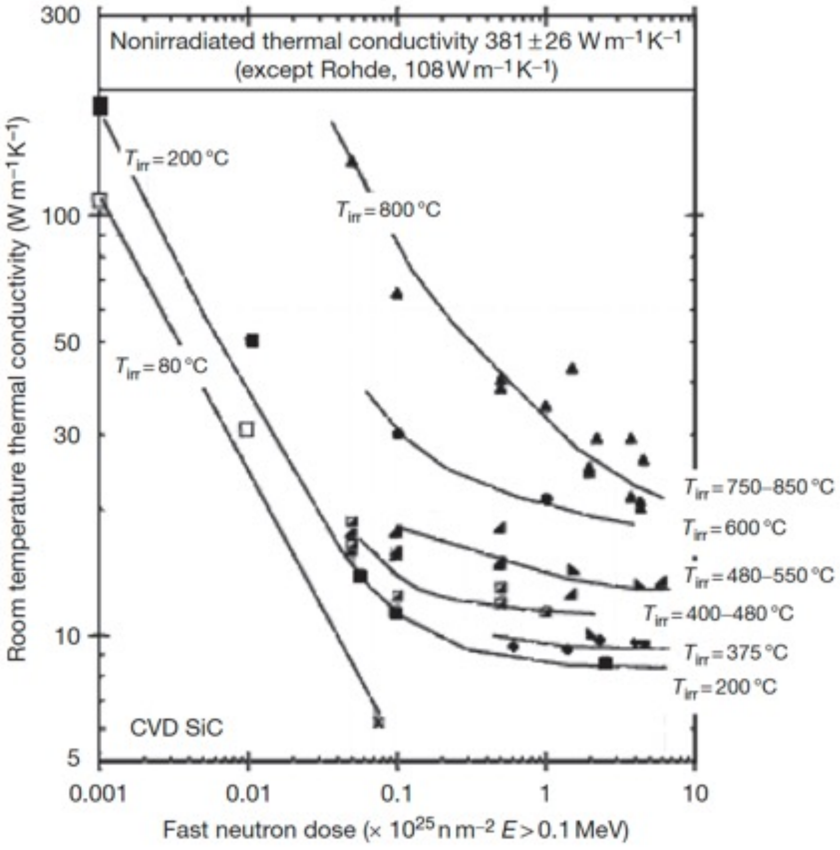
- The unirradiated k_{th} is highly dependent upon initial microstructure and temperature
- Initial microstructure can be tailored, but the temperature dependence cannot be removed

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



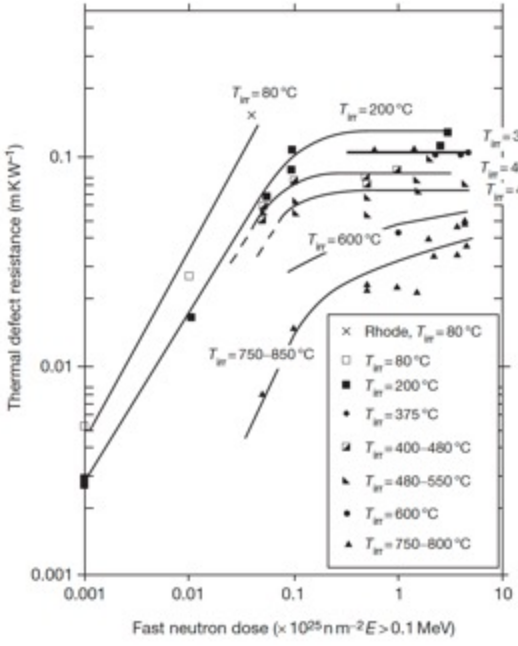
Thermal Conductivity Degradation

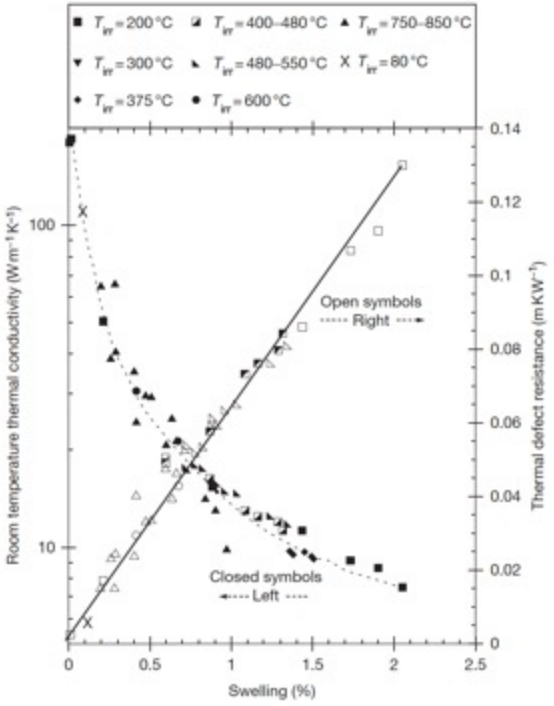
- At low temperatures irradiation produces simple defects and defect clusters that very effectively scatter phonons
- In this case, defect scattering quickly dominates, with saturation thermal conductivity typically achieved by a few dpa
- Defect scattering is sufficiently present to eliminate the temperature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



Thermal Conductivity Degradation

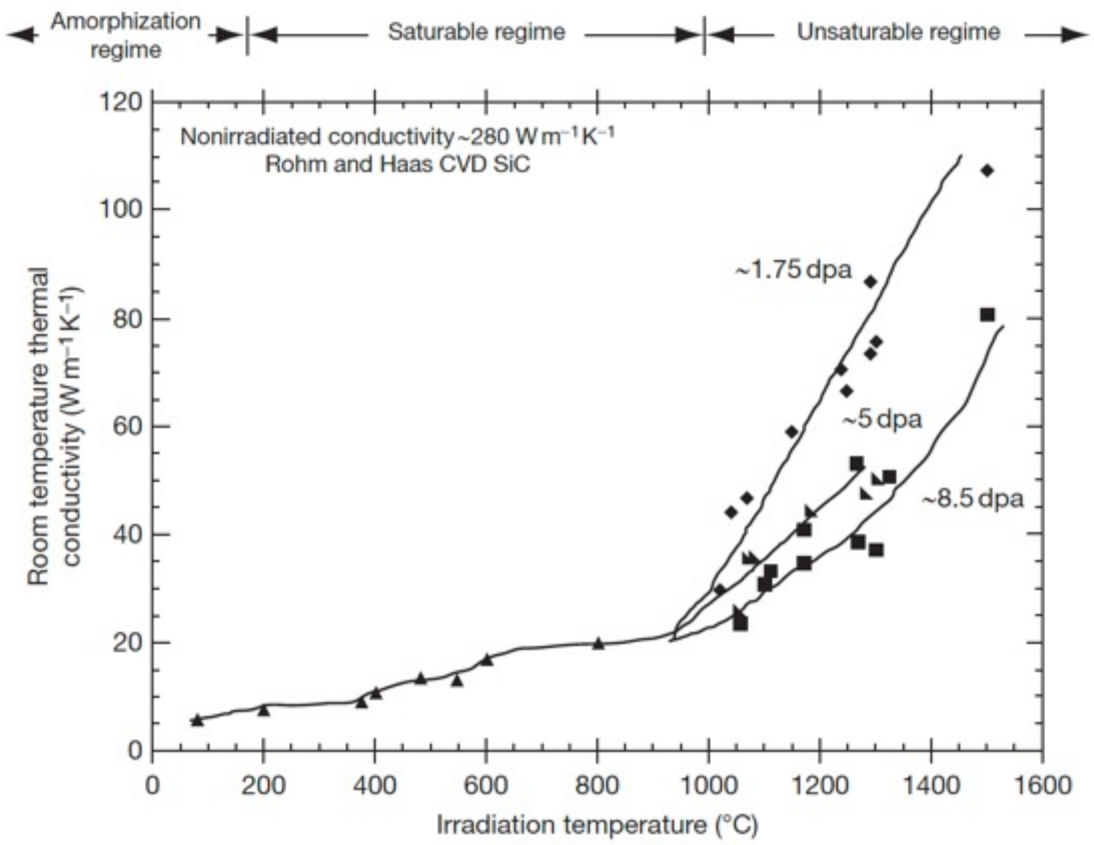
- The thermal defect resistance is defined as the difference between the reciprocals of the irradiated and nonirradiated thermal conductivity ($1/K_{rd} = 1/K_{irr} – 1/K_{nonirr}$)
- This term can be related directly to the defect type and concentration present in irradiated ceramics
- The thermal defect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





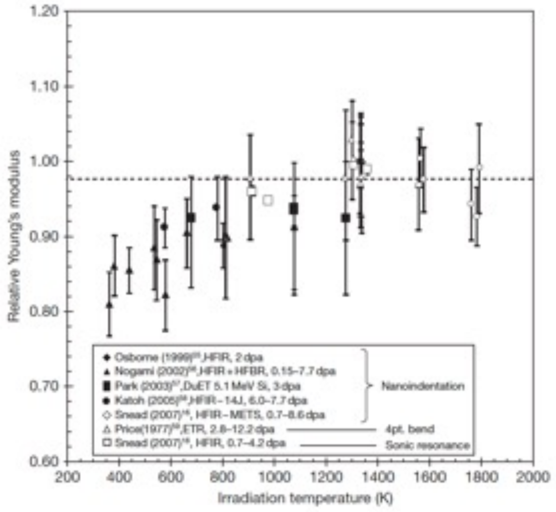
Thermal Conductivity Degradation

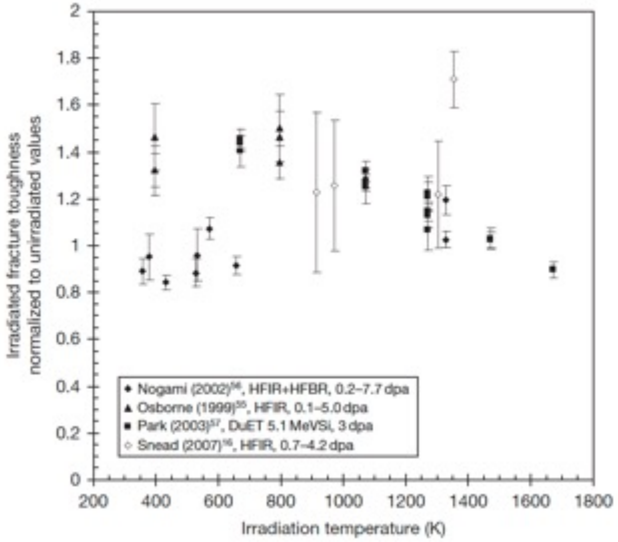
- In the high temperature void swelling regime, thermal conductivity degradation is not expected to saturate, as voids continue to grow and scatter phonons
- Additionally, the linear relationship between swelling and thermal defect resistance does not exist at high temperature
- Generally, void swelling 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





SiC Creep

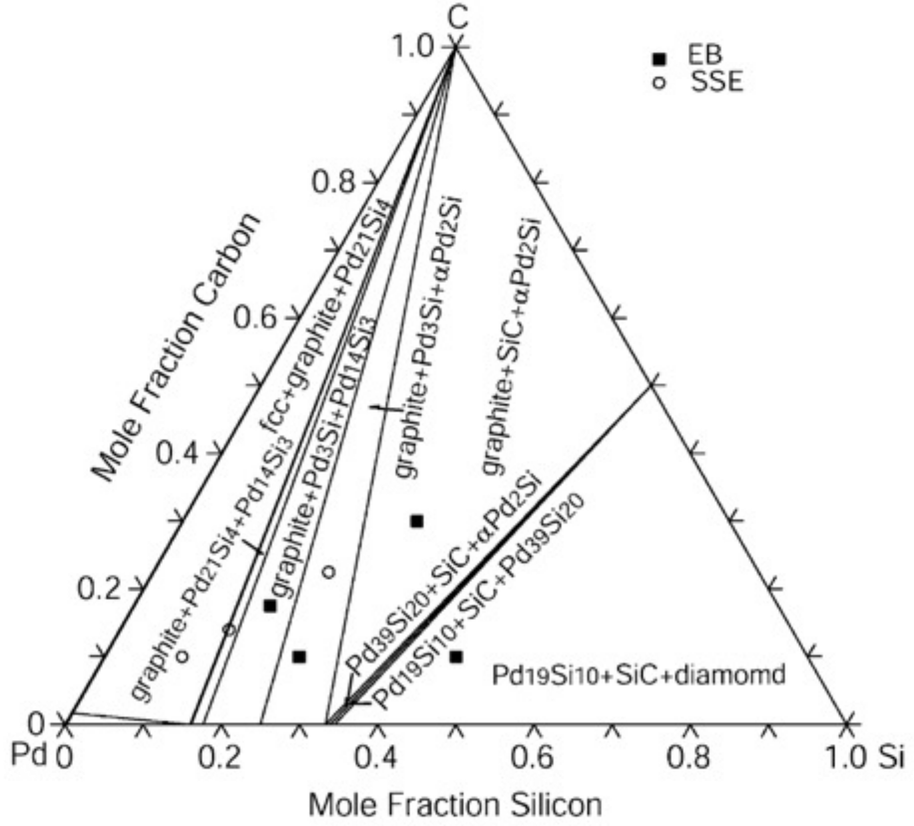
- Irradiation creep is defined as the difference in dimensional changes between a stressed and an unstressed sample irradiated under identical conditions
- Studies on irradiation creep of SiC have been limited, although it is of high importance for SiC in TRISO particles
- The creep strain for CVD SiC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

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

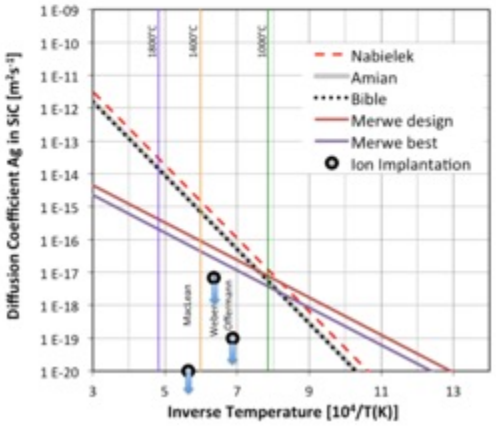
SiC Corrosion

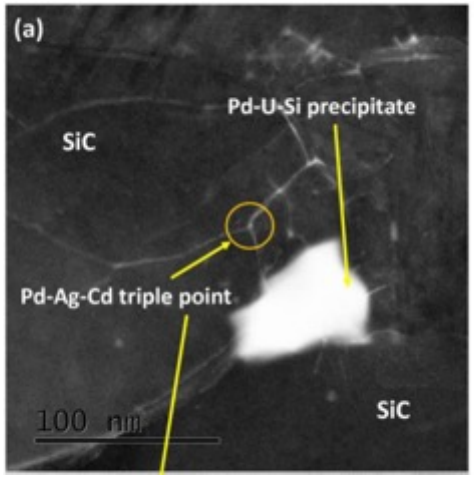
- The silicon carbide layer serves as a critical fission product barrier, but can be corroded by fission products, in particular palladium
- Additionally, silver can be transported through intact SiC layers
- For Pd, the reaction with SiC can be qualitatively explained by the phase-diagram, where a number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

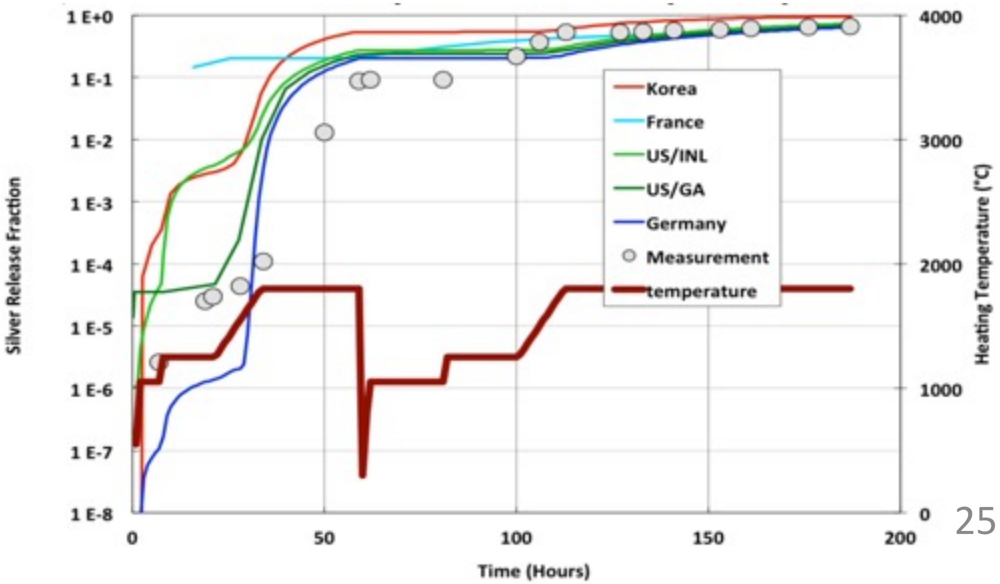


SiC Corrosion

- 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, but 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
$8\,C(s) + Cs(g) = C_8Cs(s)$	-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

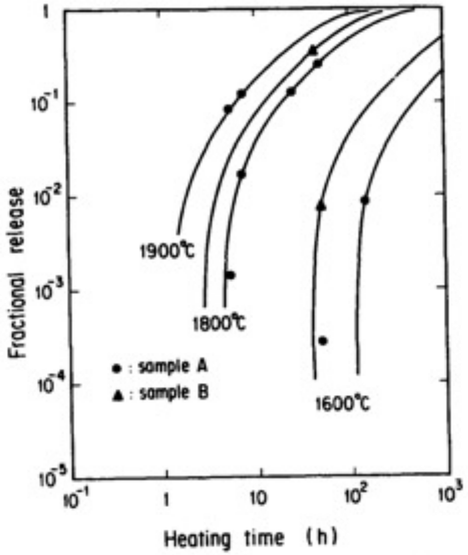


Fig. 5. Fractional release of ^{137}Cs during postirradiation heating as a function of heating time and temperature. Solid lines are diffusive release curves calculated by a simple diffusion model assuming a one-layer coated particle.

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

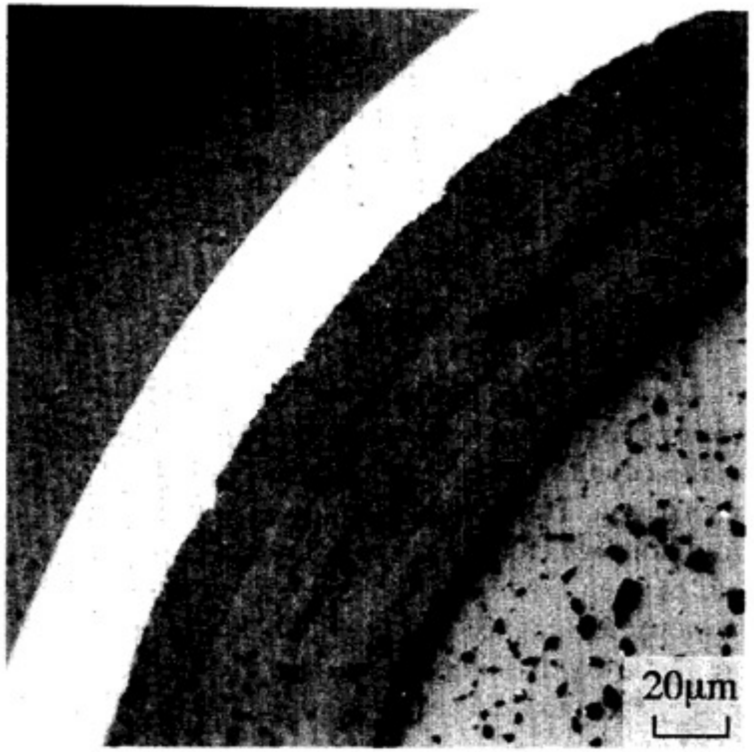


Fig. 2. Optical micrographs of polished section of ZrC-coated fuel particles after heating at 1600°C for 4500 h.

QUESTIONS?

Project Assignments

- Mahmoud: The role and effect of silver on SiC in TRISO particles

- Hamdy: High temperature materials for gas reactor heat exchangers

- Khadija: SiC as a cladding material (non-TRISO applications)

- 15-20 minute PowerPoint presentation on Sept 9
- Summarize what and why and key aspects