NE 795-014: Advanced Reactor Materials

Fall 2023

Dr. Benjamin Beeler

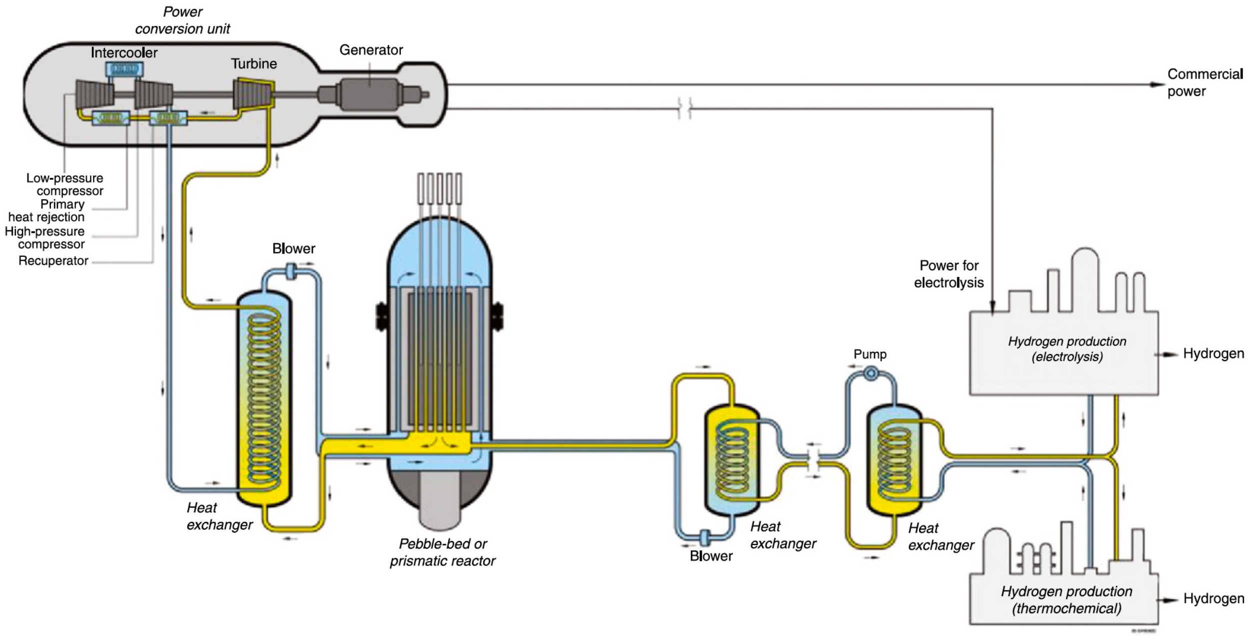
Last Time

- Graphite radiation damage: point defects and Mrozowski cracks lead to shrinkage
- Shrinkage and creep are dependent upon stress state
- Large temperature and stress gradients in graphite structural components
- Irradiation creep is very important in graphite and relieves large induced stresses
- Fuel fabrication processes for particles and pebbles/compacts
- Covered key fuel failure mechanisms
  - Overpressure; IPyC cracking; IPyC and SiC debonding; Kernel migration; Fission product attack; Creep failure of PyC; SiC decomposition; KCMI
- TRISO-coated fuel is usually designed such that none of the fuel failure mechanisms are expected to be significant

MATERIAL PERFORMANCE IN HE

High Temperatures

- Current designs target 750 C coolant outlet temperatures
- Process heat requirements may require outlet temperatures up to 950C
- The most critical metallic component in the VHTR system is the intermediate heat exchanger (IHX)
- The high temperatures and long duration of operation restrict IHX material selection



Flow and Impurities

- In the reactors under consideration, the gas pressure is typically between 5 and 7 MPa
- The coolant is circulated at high velocity, sometimes over 100 m/s
- Operating experience has shown that the primary He coolant tends to contain H_2O, H_2, N_2, CO, CO_2, and CH_4 at concentrations of a few parts per million
- These are the primary drivers of corrosion in He-cooled systems
- Reactor systems need to have extensive gas cleanup systems associated with the helium coolant flow to keep the total impurity levels in the helium below typically 10 ppm
- Active control should be maintained on the H_2O and CO concentrations to reduce oxidation of the graphite
- Molecular sieves are effective in capturing most of the gaseous impurities

IHX Materials

- The desire for higher temperature operation led to selection of nickel-based alloys
- These alloys rely on the formation of a chromia layer for long-term protection from environmental degradation
- The alloys are primarily solid-solution strengthened with carbides on the grain boundaries to improve creep resistance

Table 3 Compositions of potential high-temperature alloys for VHTR (compositions in wt%)

Alloy	*Ni*	*Fe*	*Cr*	*Co*	*Mo*	*Al*	*W*	*Ti*	*C*	*Si*	*Mn*
Alloy 617 UNS N06617	44.5	3	20–24	10–15	8–10	0.8–1.5		0.6	0.05–0.15	1	1
Alloy 230 UNS N06230	Bal	3	20–24	5	1–3	0.2–0.5	13–15		0.05–0.15	0.25–0.75	0.3–1
Alloy 800H UNS N08810	30–35	39.5	19–23			0.15–0.6		0.15–0.6	0.05–0.1		
Alloy X UNS N06002	Bal	17–20	20.5–23	0.5–2.5	8–10	0.1	0.2–1	0.03	0.05–0.15	<1	<1

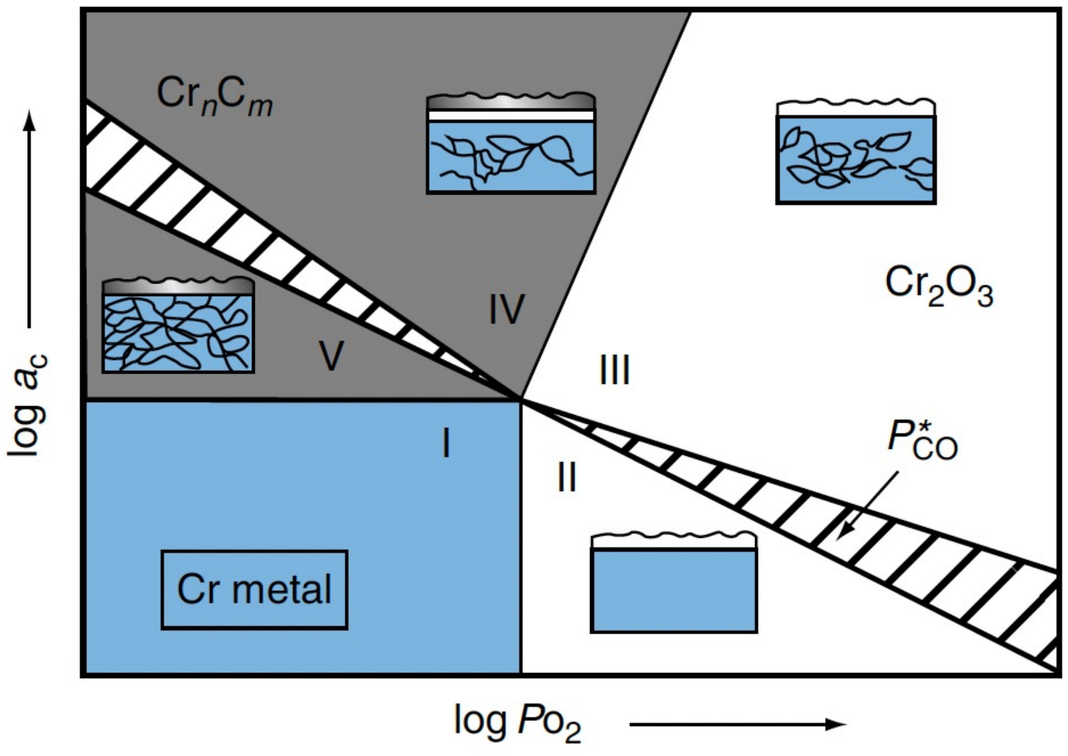
IHX Corrosion in VHTR

- Interplay between the alloy surface, temperature, and gas composition determines whether corrosive oxidation, carburization, or decarburization occur
- Carburization is associated with low-temperature embrittlement, and decarburization is linked to reduced creep rupture strength
- Ideally, a continuous self-healing, impermeable passivating oxide layer is needed to establish the most corrosion resistant alloy
- There is a critical temperature above which the oxide layer is unstable and CO evolution will occur

$$2Cr_2O_3 + Cr_{23}C_6 = 6CO + 27Cr$$

Alloy 617 Stability

- Alloy 617 is the leading candidate for use in the VHTR heat exchangers because it has the highest creep strength of the solid-solution alloys under consideration for temperatures above 850C
- Five conditions: I – strong reduction; II – decarburization; III – stable external oxide; IV – mixed surface oxide and carbide; and V – strong internal and external carburization
- Zone 3 is optimal for stability



TRISO FUEL PERFORMANCE

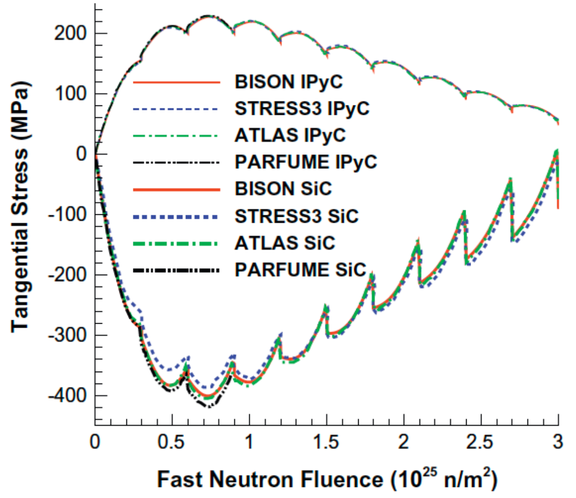
TRISO Fuel Performance

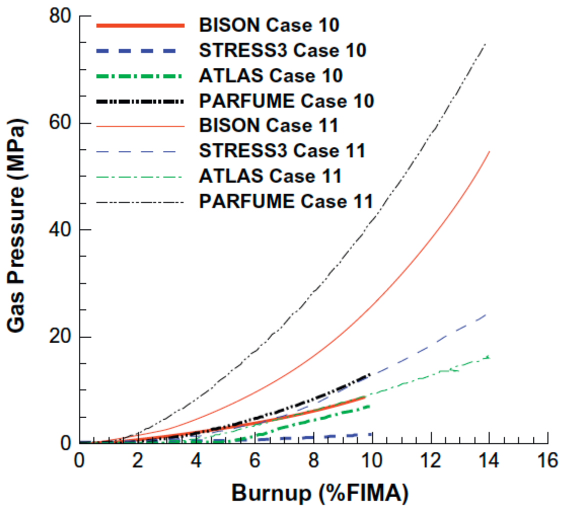
- Fuel performance models need to be able to account for numerous inter-related phenomena that affect temperatures, stresses, and failure of the material systems
- Must be multiphysics, incorporating thermodynamics, chemistry, kinetics, microstructure, mechanics, etc.

- Solid fission product swelling
- Gaseous fission product swelling
- Densification
- Thermal conductivity
- Fission gas release
- CO production
- Oxygen transport
- PyC layer dimensional change
- Kernel migration
- SiC failure
- Fission product attack

Fuel Performance Codes

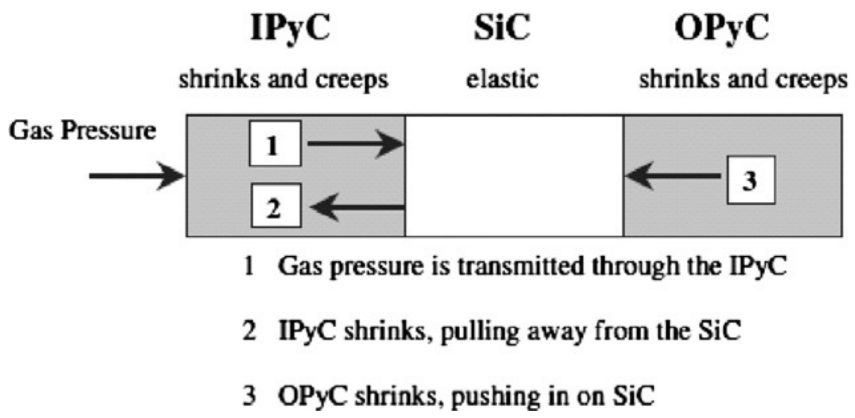
Code	PARFUME	PASTA	ATLAS	STRESS3	TIMCOAT	GA/KFA	JAERI
Developer	INL (US)	TU Delft (NL)	CEA (FR)	BNFL/NS (UK)	MIT (US)	GA/KFA (US)/(DE)	JAERI (JP)
References	[9,18,45–47]	[44,48,49]	[9,17]	[9,17,50]	[16]	[17,52]	[17,51]
Mission	NPR/AGR, NGNP	PUMA (EU)	FBR MOX	None specified	HTRs	Multiple	HTTR
Assumed geometry	Pebble bed, prismatic	None	None?	None	Pebble bed, prismatic	None	None
Pressure calculation	R-K EOS	R-K EOS	R-K EOS	Unknown	IGL	R-K EOS	IGL
CO production method	HSC-based yield	Custom (Nabielek?)	unknown	Martin	Karsten (KFA)	None, LEU, HEU	Proksch
Heat transfer calculation	1D finite difference with buffer/IPyC gap	THERMIX calculation with buffer/IPyC gap	Finite element	Unknown	Full-core then particle	Single irr. temp. used	Single irr. temp. used?
Phenomena modeled	Pressure, PyC IIDC, PyC irr. creep, thermal expansion, SFP swelling, FP diffusion	Pressure, PyC IIDC, PyC irr. creep, Thermal expansion	Pressure, PyC IIDC, PyC irr. creep, SFP swelling, GFP swelling	Pressure, PyC IIDC, PyC irr. creep, SFP swelling, SiC elasticity	Pressure, PyC IIDC, PyC irr. creep	Pressure, PyC IIDC, PyC irr. creep, SFP swelling	Pressure, PyC IIDC
Failure mechanisms modeled	PV, IPyC cracking, debonding, asphericity, SiC thinning, SiC thermal decomposition, kernel migration	PV, IPyC cracking	PV, IPyC cracking, debonding, asphericity	PV, IPyC cracking, debonding	PV, IPyC cracking via fracture mechanics	PV	PV
PyC shrinkage correlation	Custom	FZJ	Unknown	Custom	Unknown	Unclear	Unknown
PyC irr. creep coefficient $(\mathrm{MPa\ n\ m^{-2}})^{-1}$	$c = 5 \times 10^{-29}$/ $\nu = 0.5$ or $c = 4 \times 10^{-29}$/ $\nu = 0.4$	3.0×10^{-29}	Unknown	4.9×10^{-29}	CEGA function	2.0×10^{-29}	Unknown
Fission gas release model (s)	Recoil + booth	Modified booth (cyclic situation)	Unknown	Unknown	UT/KFA (booth-based?)	Booth	Booth (single species)
Displacement calculations?	Yes	Yes	Yes	Yes	Yes	No	No





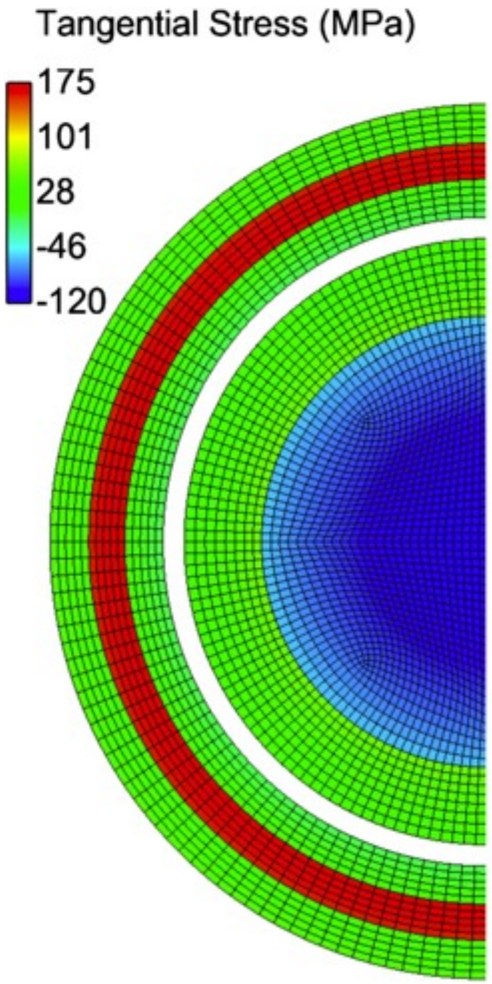
SiC Failure

- The dominant 1D failure mechanism for TRISO fuel particles involves pressure vessel failure, where the SiC layer develops a through-thickness crack resulting from a tensile stress that exceeds the fracture strength of the material
- Modern approaches to pressure vessel failure explicitly calculate separate stresses and through-layer crack probabilities for the SiC layer and each PyC layer



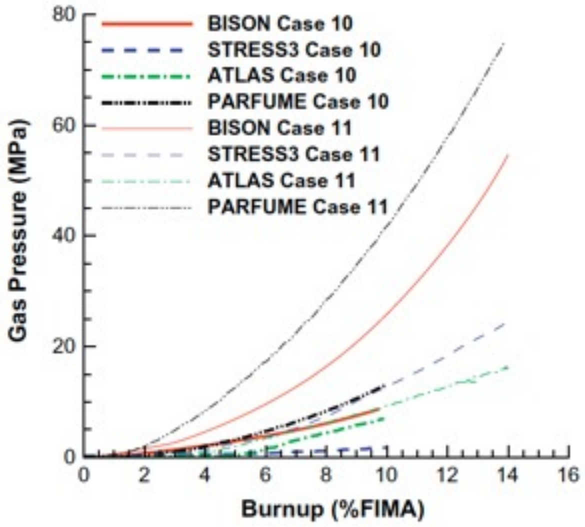
TRISO Stresses

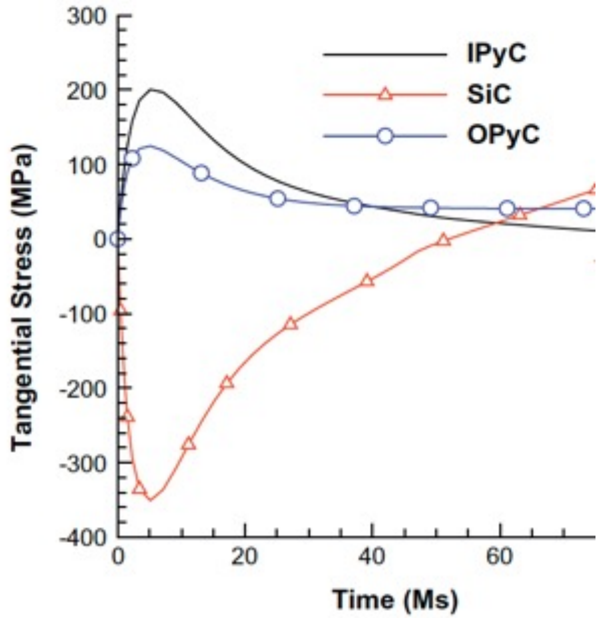
- The irradiation causes the kernel to swell and the buffer layer to shrink, thereby modifying the internal void volume available to the fission and reaction gases
- The porosity of the buffer leads to the gas pressure being the only force on the load-bearing layers
- If the IPyC and OPyC were absent, the gases produced in the fission process would simply stress the SiC layer and, if the pressure were high enough, cause it to fail
- However, these tangential stresses are reduced by the presence of the two PyC layers because; under unrestrained conditions they would shrink during irradiation



TRISO Stresses

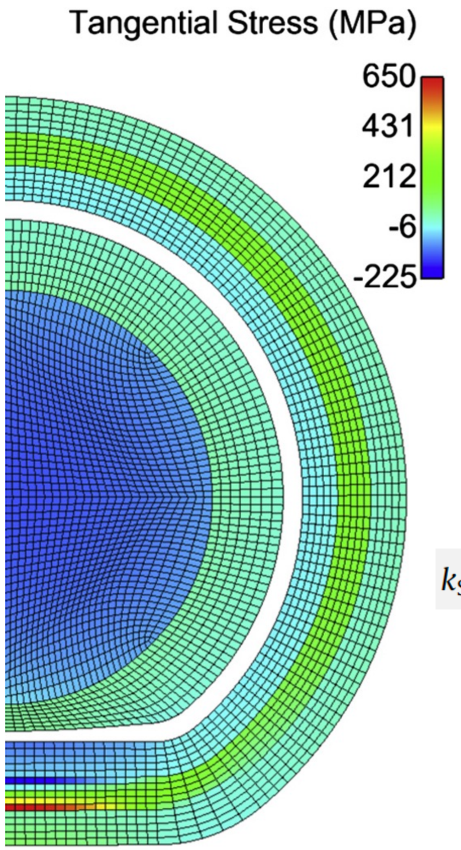
- PyC shrinkage will be largely restrained by the SiC layer, and tangential stresses will be generated in both PyC layers, with radial (inward) acting forces imposed on the two surfaces of the SiC layer
- In practice, these tangential stresses in the two PyC layers will attain a quasi-equilibrium stress state because their shrinkage is counter-balanced by irradiation creep
- The SiC elastic modulus is at least an order of magnitude greater than that of PyC and thus, the dimensional changes and creep strains of SiC are comparatively much smaller than for PyC





Material Evolution

- Ideally, would be able to model and describe 3D modes of failure
  - Shrinkage cracks within the IPyC layer
  - IPyC/SiC debonding
  - Particle asphericity
  - Kernel migration
  - SiC coating thinning
  - Fission product attack



$$k_{\text{fuel}} = K_{1d} K_{1p} K_{2p} K_{4r} k_{0,\text{fuel}}$$

$$K_{1d} = \left(\frac{1.09}{\tau^{3.265}} + \frac{0.0643}{\sqrt{\tau}}\sqrt{T_{\text{kern}}}\right) \arctan\left(\frac{1}{\frac{1.09}{\tau^{3.265}} + \frac{0.0643}{\sqrt{\tau}}\sqrt{T_{\text{kern}}}}\right)$$

$$K_{1p} = 1 + \frac{0.019}{3 - 0.019\tau} \frac{1}{\left(1 + \exp\left(-\frac{T_{\text{kern}} - 1200}{100}\right)\right)}$$

$$K_{2p} = \frac{1 - P}{1 + 2P}$$

$$K_{4r} = 1 - \frac{0.2}{1+\exp\left(\frac{T_{\text{kern}} - 900}{80}\right)}(1 - \exp(-\tau))$$

$$k_{PyC} = 10.98222\left(\frac{1 - P}{1 + 2P}\right) + 0.00444$$

$$k_{\text{SiC}} = k_{0,\text{SiC}}(3.91112 \times 10^{-2} \cdot \exp(2.24732 \times 10^{-3} \cdot T_{\text{SiC}}))(1 - P)$$

$$k_{0,\text{SiC}} = 42.58 + \frac{-1.5564 \times 10^{4}}{T_{\text{SiC}}} + \frac{1.2977 \times 10^{7}}{(T_{\text{SiC}})^2} + \frac{-1.8458 \times 10^{9}}{(T_{\text{SiC}})^3}$$

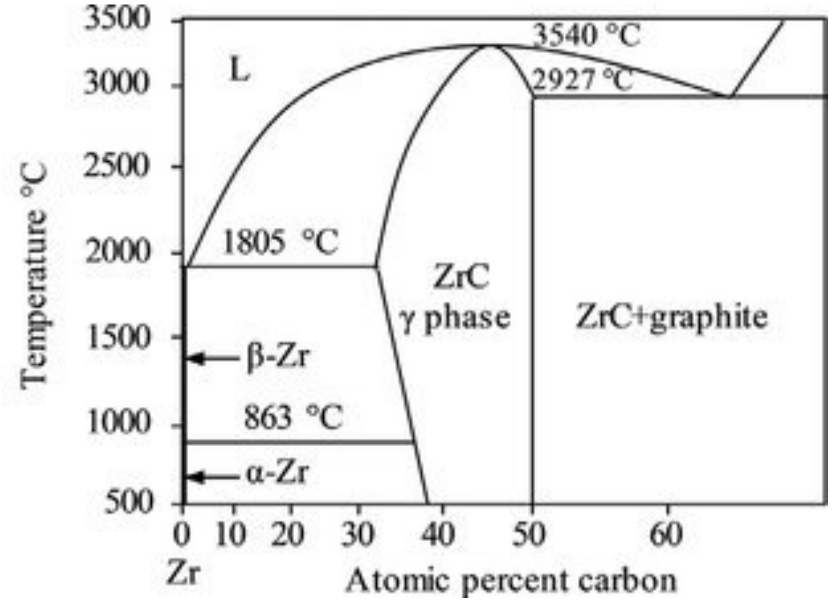
Data needs

- There are a number of areas where we lack requisite data, either behavioral or fundamental properties, in order to accurately describe TRISO particle evolution
- High-quality high burnup data on TRISO particles is generally lacking, which would enable benchmarking of fuel performance models
- Uncertainties and unknowns in fundamental material properties are also abundant, especially with regard to how properties vary as functions of temperature, fast fluence, and burnup
- There is significant uncertainty in the irradiation creep constant, the value of Poisson's ratio in irradiation creep models, and the thermal conductivity of PyC
- Predictions for the chemical attack of SiC require effective diffusion coefficients of key fission products in various fuel materials, which are unknown
- Fuel properties are the least well understood, especially as the fuel evolves during operation

ADVANCED CONCEPTS IN TRISO

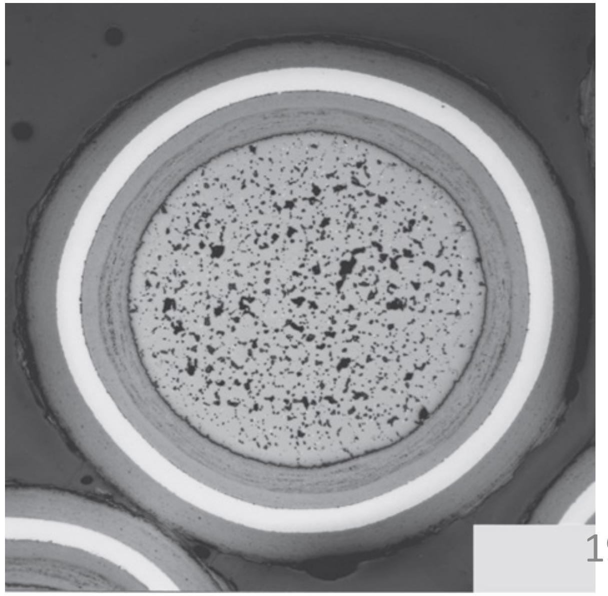
ZrC replacing SiC

- Zirconium carbide (ZrC) is a refractory and chemically stable compound, which melts eutectically with carbon at 3123 K
- ZrC can potentially improve the high-temperature stability, the resistance to chemical attack by fission products, and the retention of fission products
- However, ZrC is significantly less oxidation resistant than SiC



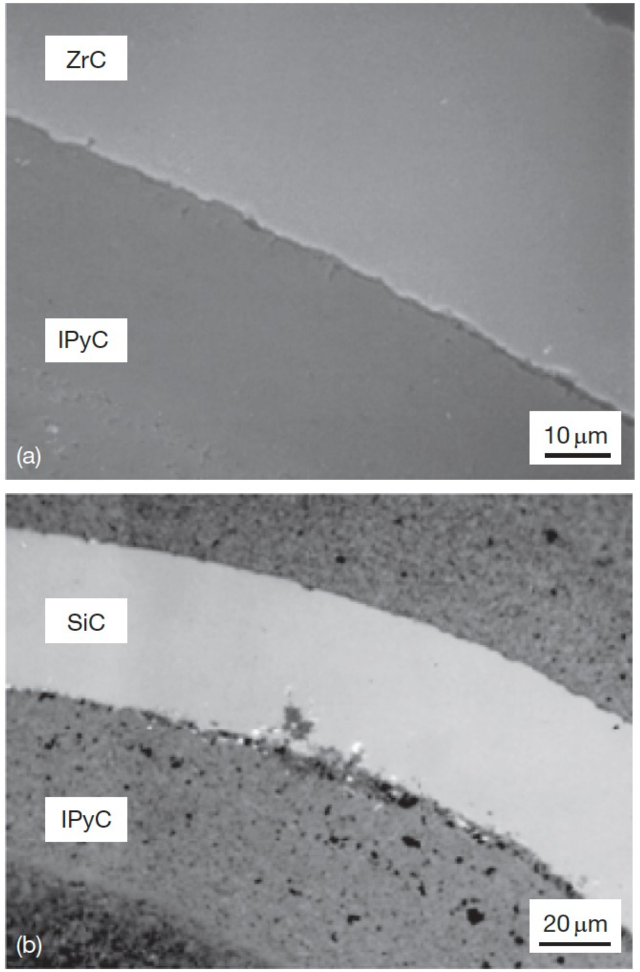
ZrC replacing SiC

- Four types of ZrC inclusions have been studied (1) ZrC-TRISO coated particles, (2) ZrC-TRISO type coated particles without OPyC layer, (3) ZrC-coated particles with ZrC-doped OPyC layer, and (4) ZrC coated particles with graded C–ZrC layer(s)
- All four types have been fabricated and irradiated
- Primary focus has been on option 1, however usage of ZrC started from option 2 in the 1970s
- ZrC-TRISO-coated UO2 particle after irradiation at 1673–1923K to 4.5% FIMA



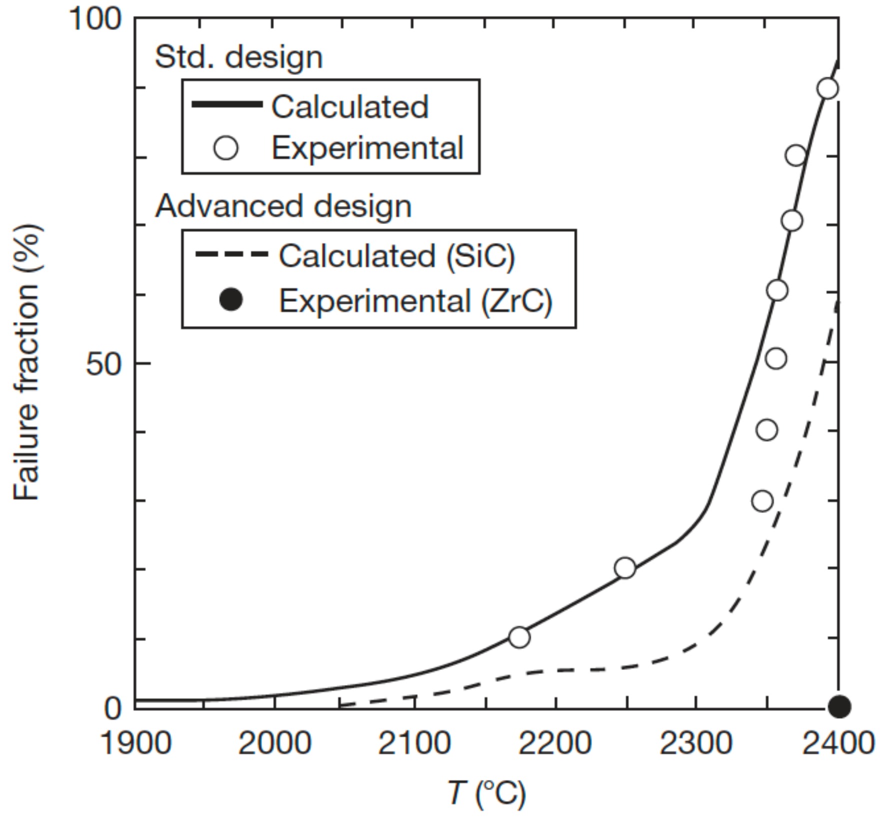
ZrC replacing SiC

- The improved performance of the ZrC coating layer against chemical attack by Pd has been demonstrated in both out-of-reactor experiments and irradiation tests
- ZrPd3 can form in lab conditions, but insufficient Pd exists in fuel particles to cause formation and thus degradation
- ZrC does not seem to solve the silver problem
- Ruthenium release might be an issue, which it is not for SiC



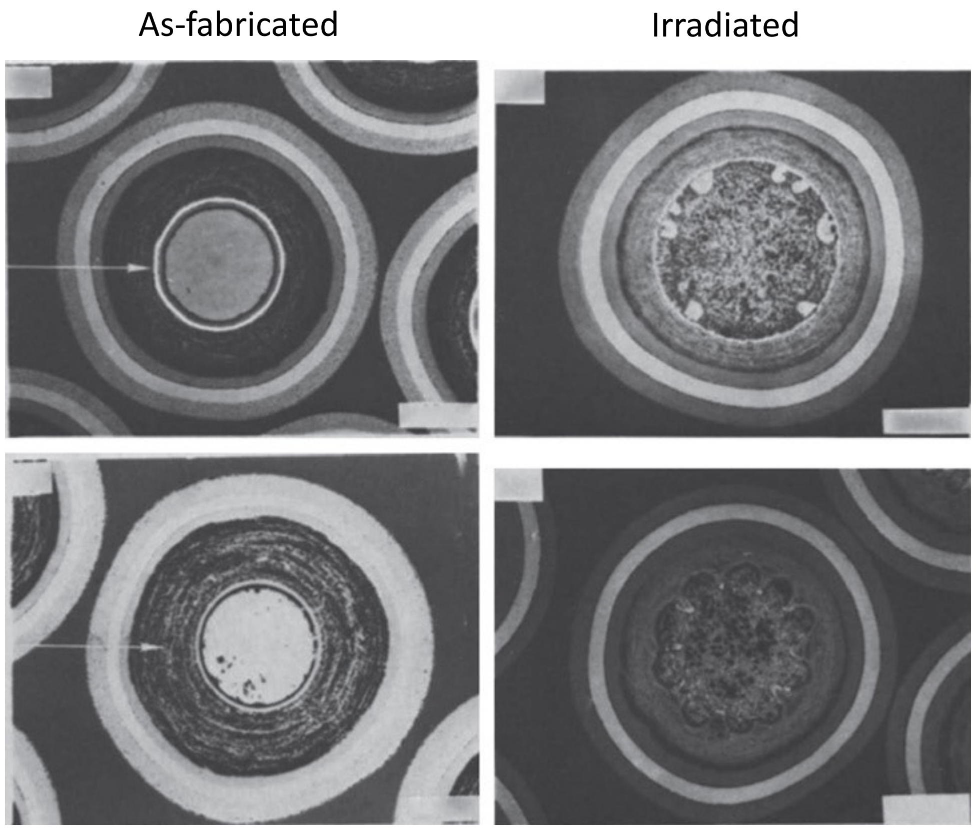
ZrC replacing SiC

- High-temperature behavior of ZrC is superior to SiC
- Right is a heating experiment on irradiated TRISO particles
- No ZrC failures up to 2400C, where an extended hold produced a failure
- At temperatures above 2000C, SiC will decompose into its constituents
- Thus, better stability during fabrication, ability to operate at higher temperatures, better stability in off-normal temperature spikes, better fission gas retention at high temperature



Non-fissile Carbides in Fuel

- To inhibit the buildup of CO gas in UO2 fuel kernels, UC2 is often added to getter oxygen and reduce the oxygen potential
- Similar results can be achieved by the addition of nonfissionable carbides, such as SiC or ZrC around fuel kernel
- Added as a layer around UO2 fuel kernels and/or dispersed within the buffer



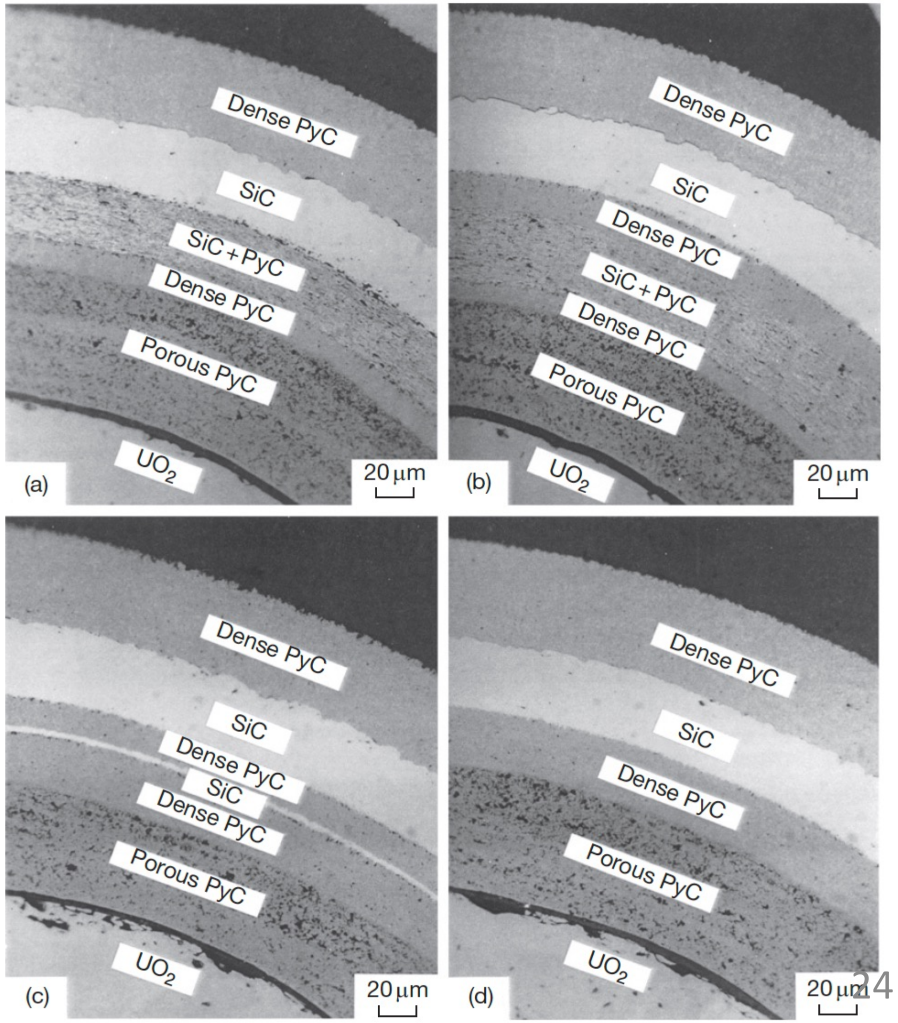
Non-fissile Carbides in Fuel

- Introduction of ZrC around fuel kernel getters released oxygen
- This seems to inhibit fuel kernel migration
- If the layered ZrC is intact, can inhibit fuel swelling as well, potentially reduced stresses on outer layers
- Have performed limited irradiation experiments with no failures

- If the layered ZrC is intact, no release occurs for Ag and Eu
- Release occurs for both species under same conditions for nominal TRISO and for ZrC dispersed in buffer
- An intact ZrC layer seems to be necessary for explaining the outstanding retention of these particles, in addition to the benefits of O gettering

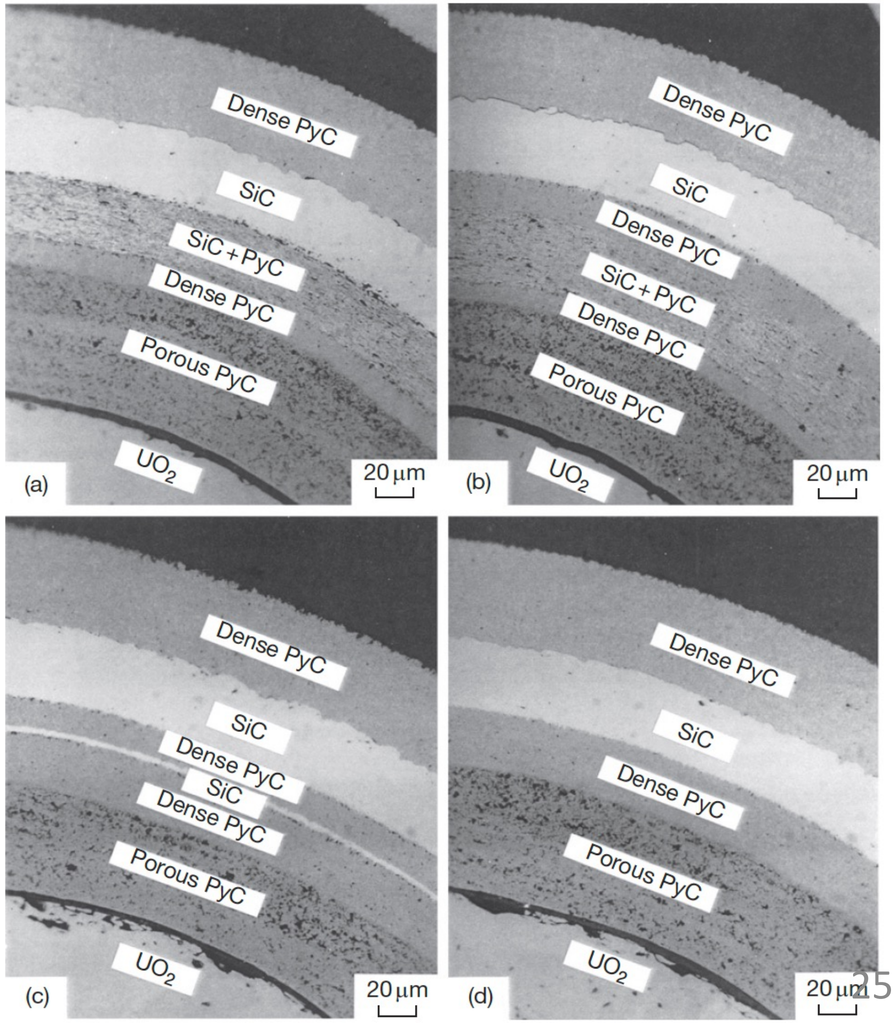
Alternate Layering

- Two methods are available to prevent the corrosion of the SiC layer: (1) to keep the fission products within the fuel kernel and (2) to make a barrier to the diffusion of the fission products to the SiC layer
- Can potentially add a layer that traps palladium by chemical reaction inside the SiC layer of the TRISO coating
- Can add either an additional SiC layer, or a SiC/PyC composite layer



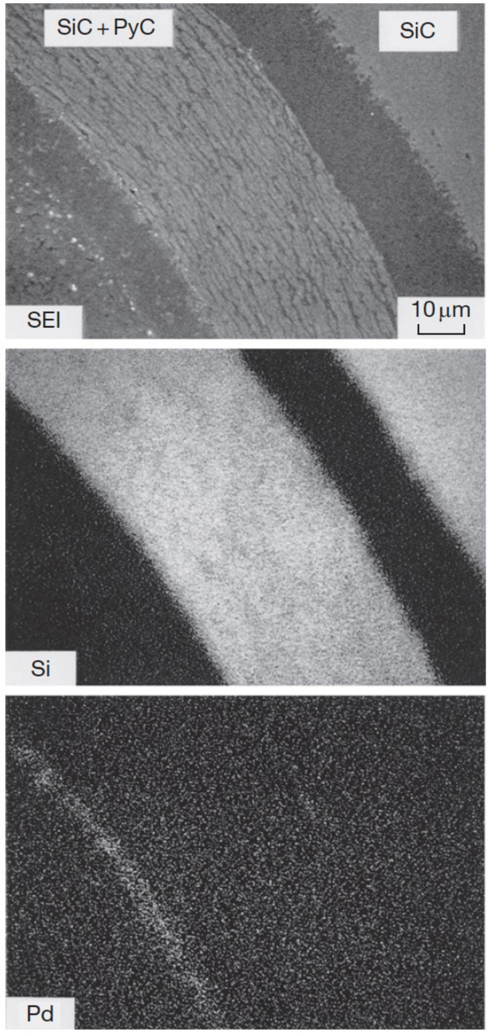
Alternate Layering

- The type-A coating has an additional layer of SiC+PyC adjacent to the inside of the SiC layer; the thickness of the IPyC layer can be reduced
- The type-B coating has the dense PyC layer between the SiC+PyC and SiC layers; the intermediate dense PyC layer will interrupt extension of the corrosion zone from the SiC+PyC layer to the SiC layer
- In the type-C coating, SiC is used for an additional layer; SiC layer will react with fission products and PyC will interrupt corrosion of outer SiC



Alternate Layering

- Irradiation of these advanced coatings was performed in the JRR-2 reactor
- Ceramography revealed no crack in the advanced coating layers or in the TRISO coating layers
- All three types trapped Pd at the inner SiC-based barrier, preventing corrosion of the outer SiC
- At high heating, a PyC layer between the outer SiC and the inner SiC-based layer proved more effective at fission product retention
- Also, the SiC/PyC layer proved more effective than pure SiC
- No new technology needed to fabricate these particles



Type B Coating

Summary

- He environment corrosion
  - impurity driven; primary concern is IHX
  - can control with cleanup systems, tailoring pO2 and carbon activity
- TRISO Fuel performance
  - there are a number of fuel performance codes
  - data needs, and the evolutionary complexity of particles hold back more sophisticated modelling
- Advanced concepts in TRISO particles
  - ZrC instead of SiC
  - ZrC/SiC as a layer around kernel
  - alternate layering of SiC/PyC

QUESTIONS?

Quiz Upcoming!

- Will cover TRISO particle-based fuels
- Quiz will be on Sept 12
- Open ended questions covering the concepts presented in class
- Closed book