Module 5: Materials

Presentation on Molten Salt Reactor Technology by:

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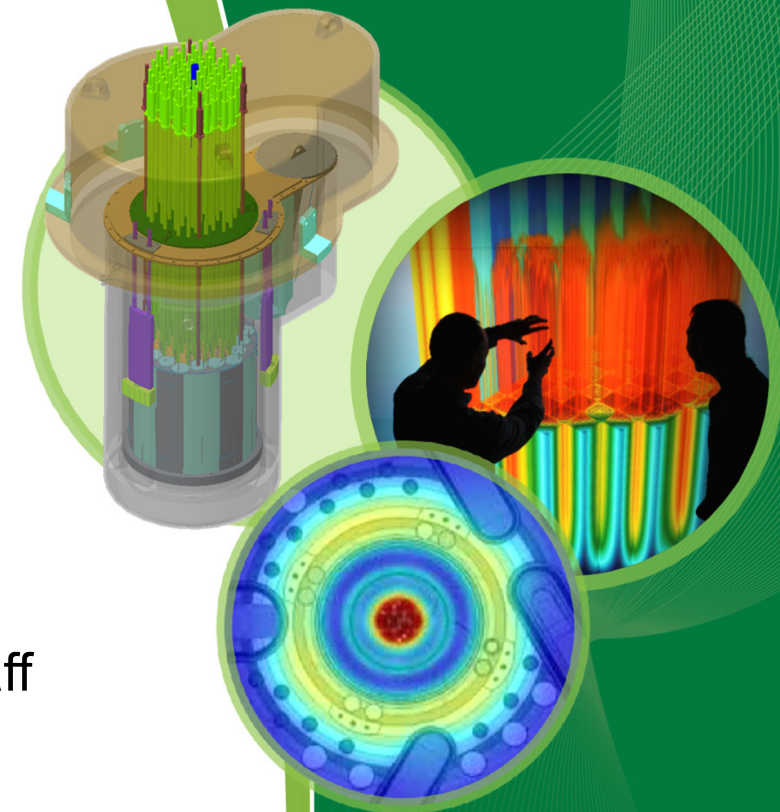

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Plant Design Options Have Significant Implications on Materials Requirements

Denatured Thermal Burner

- *Structural Alloy* – Nickel or clad iron-based alloy
- *Moderator* – Fine-grained, nuclear-grade graphite
- *In-Core Functional Materials* – Carbon or carbide composite based guide tubes and supports
- *Reactivity Control* – Neutron absorber rods in or near core
- *In-Vessel Shielding* – Moderator and neutron absorber possible to reduce vessel flux

Fast Chloride Breed & Burn

- *Structural Alloy* – Nickel (clad?) or clad iron-based alloy
- *Moderator* – No moderator materials in core
- *Reactivity Control* – Only shutdown rods (fuel displacement) in core. Control reactivity likely provided by reflection control (e.g. rotating reflector)
- *In-Vessel Shielding* –High atomic number reflector/shielding materials surrounding core to reduce vessel radiation damage

Thorium Thermal Breeder

- Similar material set as denatured thermal burner
- Liquid bismuth-based reductive separations materials required (likely molybdenum, carbon, or carbide composite-based)

Fast Fluoride Breeder

- *Structural Alloy* – Nickel or clad iron-based alloy
- *Moderator* – No moderator materials in core
- *Reactivity Control* – Only shutdown rods (fuel displacement) in core – control reactivity by in-core sparging rate (fuel displacement).
- Liquid bismuth-based reductive separations structural materials required (likely molybdenum, carbon, or carbide composite-based)
- *In-Vessel Shielding* – Breeding blanket surrounding core to improve neutron economy and reduce vessel radiation damage

No Fully Qualified Structural Alloys Exist for MSRs

- NRC has not endorsed compliance with the high temperature nuclear power section of the ASME BPVC as an adequate demonstration of structural material performance
- ASME BPVC focuses on mechanical performance
  - Includes time and temperature dependence of material properties
  - Does not address corrosion or radiation damage
- Multiple MSR structural material design options are possible
  - Cladding or coating a qualified material
  - Completing a limited term code case for Alloy N (aka Hastelloy® N, and initially known as INOR-8)
  - Employing a guard vessel to perform containment function while not crediting the salt-wetted vessel
- First wall material separating fuel salt from reflector or breeder blanket will have separate safety/performance requirements
  - Will require accident progression models to understand implications of leaks

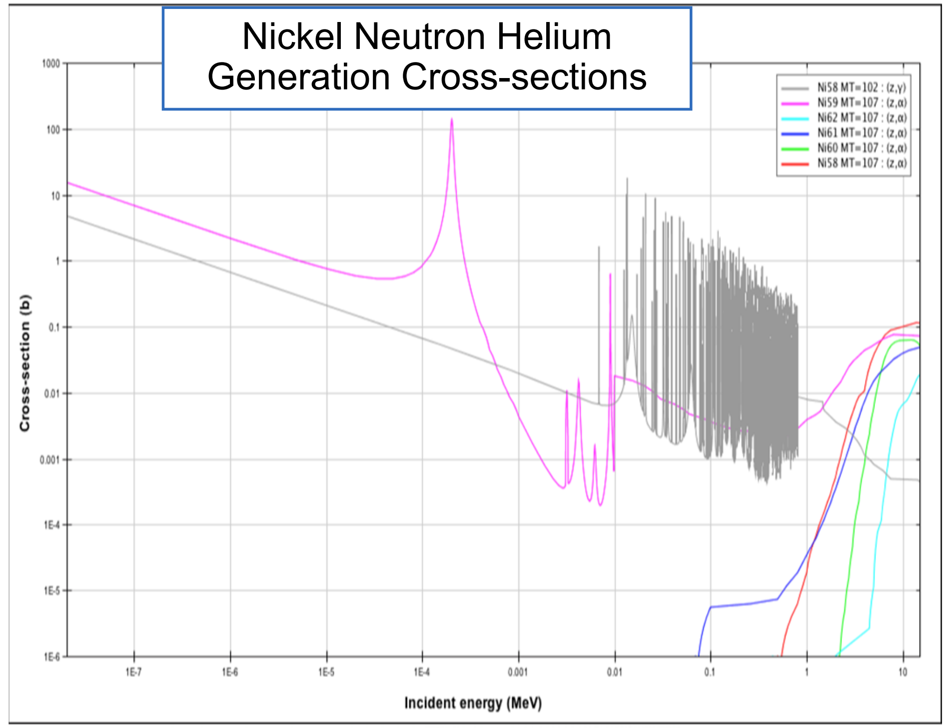
Limited Component Lifetimes Decreases Required Material Testing Duration

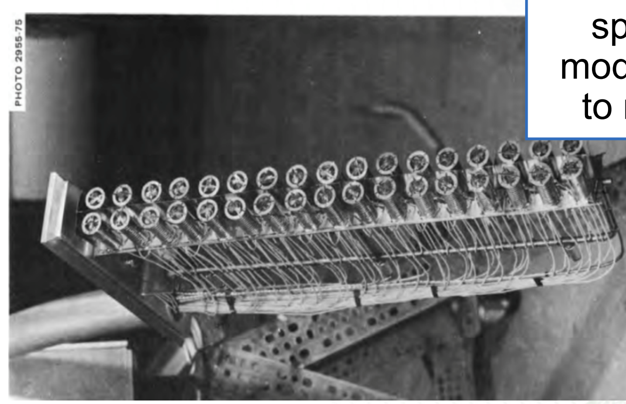
- Several design variants feature periodic replacement of all salt-contacting components – including reactor vessel
  - Storage for activated and contaminated components will be required
  - Incorporating radiation and corrosion damage into design codes and standards could provide useful guidance on remaining useful life
  - Much higher levels of maintenance automation (potentially including component replacement) are anticipated
- Limited term code cases can be developed using shorter duration testing
  - May enable use of higher-performing alloys that are currently less mature
- Interior shielding is a common design element to minimize radiation damage to vessel
  - Generally serves a dual purpose to improve reactor physics
- Establishing component remaining useful life is a key safety issue
  - Guard vessels (and/or drains and collection tanks) are a potential design element to minimize the consequences of a fuel containment system rupture
  - Accident sequences and consequences of large-break loss of fuel and coolant accidents are a distinctive issue for MSRs

Neutron Fluence Will Be a Significant Stressor for Container Materials

- Nickel-based alloys embrittle when subjected to significant neutron fluxes at high temperatures
  - Neutron interactions with nickel generate helium
  - At high temperatures helium migrates to grain boundaries
- MSRE was ~1 year from shutdown due to decrease in vessel fracture toughness
- Niobium-modified Alloy N showed marked improvement up to ~700°C
  - Formed finely dispersed carbide helium sinks
  - Ductility of specimens irradiated and tested at 650°C was the same as unirradiated specimens
- Other radiation-induced degradation mechanisms remain important

Nickel Neutron Helium Generation Cross-sections





102 creep test specimens of Nb-modified Alloy N prior to reactor insertion

Source: ORNL-5132

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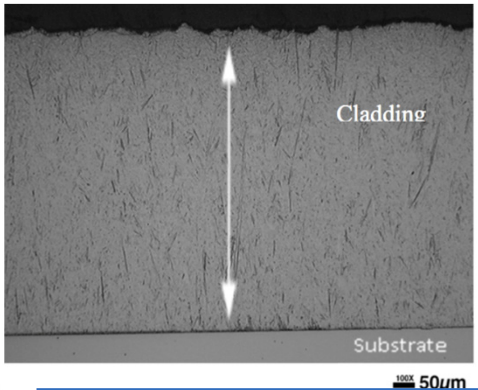
Temperature and Thermal Cycling Are Significant Material Stressors

- Metallic components must operate at temperatures where creep occurs and where time-dependent behavior must be considered
  - Similar to other high temperature reactors

Source: ORNL/TM-2011/95

- Thermal cycling can cause coatings to crack or delaminate
  - Coefficient of thermal expansion (CTE) mismatch is a key phenomenon
  - Thin coatings minimize the tendency of CTE mismatch to result in delamination or cracking but are more vulnerable to imperfections (e.g., pinholes and non-hermeticity)
  - Solid state interdiffusion becomes important for thin coatings – intermixing will be enhanced by fast neutrons
  - Maintaining temperature stability can be a key element in control design (i.e., requiring separate reactivity control rather than relying on thermal feedback for power level changes)
  - Very limited ASME BPVC information on applicability of cladding to high temperature reactors



MOCVD (Nickel Carbonyl Process) Nickel on 617 Substrate

Corrosion Behavior of Halide Salts Is Reasonably Well Understood

- Corrosion by halide salts is dominated by oxidation of the structural metal atoms which are in their most reduced state
  - Structural metal atoms have low solubilities
- Fluoride salts (and most chloride fuel salts) will readily dissolve protective oxide coatings off surfaces
  - Other protective coatings (e.g., Ni, Mo, carbides, etc.) remain a potential design approach
  - Salt-wetted materials must be thermodynamically stable
- MSRE's fuel salt loop experienced intergranular corrosion caused by the presence of tellurium in the fuel salt – $CrF_2 + Te + 2UF_3 \rightarrow 2UF_4 +$"CrTe"
  - Maintaining the salt in a mildly reducing condition prevents tellurium cracking and substantially reduces generalized corrosion
  - Generalized corrosion for Alloy N and SS316 specimens exposed to fuel salt under reducing conditions in poly-thermal loops was < 5 μm/year
- MSRE's graphite and its coolant loop structural alloys remained pristine

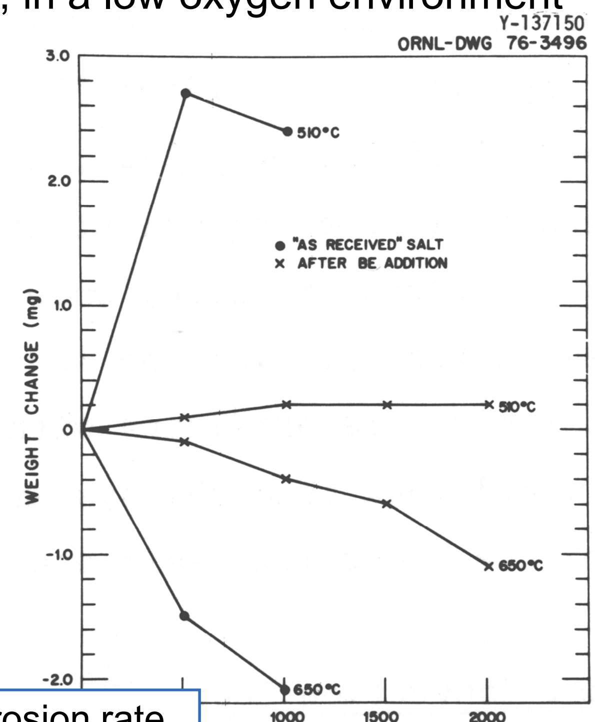
Bottom graphite stud of MSRE before (large photo) and after (inset) operation

Source: ORNL-TM-4174

Key Step in Structural Alloy Corrosion Is Dissolution of Constituent Atoms into Salt

- Maintaining mildly reducing salt conditions is key to minimizing oxidative corrosion
  - Electronegative impurities (e.g., S^{2-} or O^{2-}) increase salt oxidation potential
- Salts will preferentially oxidize least *noble* component from poly-component alloys (generally chromium or aluminum)
  - While aluminum oxide can be stable in chloride salts, in a low oxygen environment aluminum will readily form $AlCl_3$

Inconel 601 exposed to MSBR fuel salt showing Cr voids



Change in corrosion rate of SS316 with redox

Source: ORNL/TM-5783

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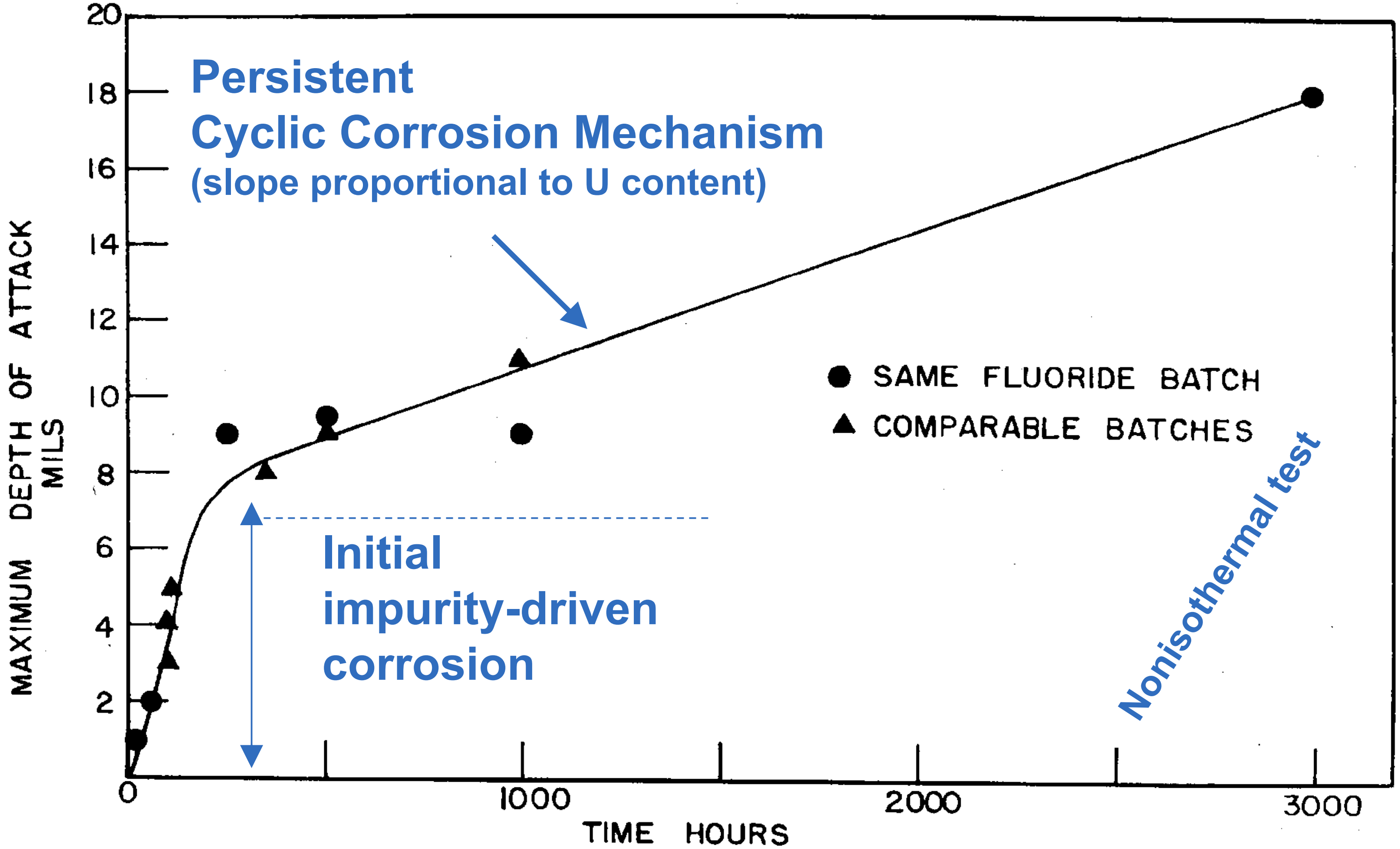
Corrosion in Halide Salts Shows a Characteristic Pattern



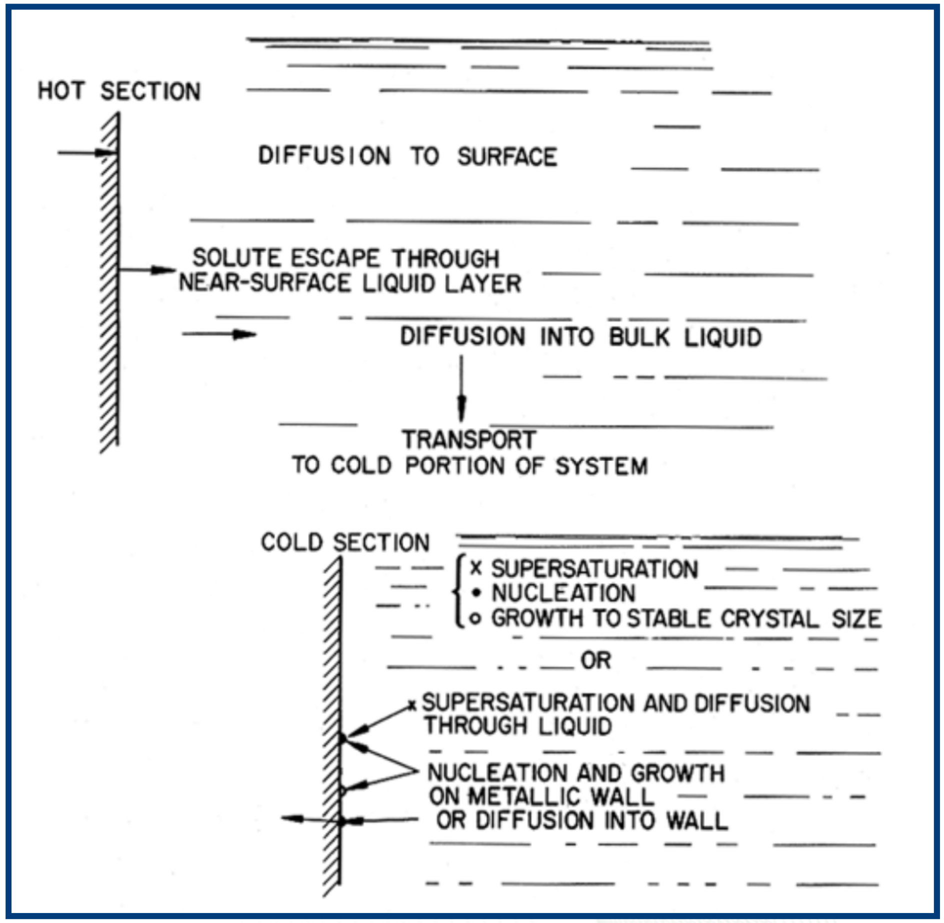
- Salt impurities initially react to form stable compounds

Source: ORNL-2349

Mass Transfer Corrosion Can Occur Because of Oxidation and Deposition

- Oxidation of Cr on surface
  - Reactions with impurities or salt constituent
- Cr diffuses to surface
- Void formation occurs if there is a salt constituent whose reaction with Cr is temperature sensitive
  - In the case shown, UF_4

    $Cr + 2UF_4 \rightarrow 2UF_3 + CrF_2$



Source: ORNL-TM-3488

Corrosion Issues Arise from Solubility Variance with Temperature

- Hastelloy N loop after 9 years
  - T_{max} 700°C, T_{min} 560°C
- Attack and void formation in hotter area
  - Higher solubility at higher temperature
  - 50 µm (2 mils) into matrix
- Deposition in cooler regions
  - Lower solubility at lower temperature

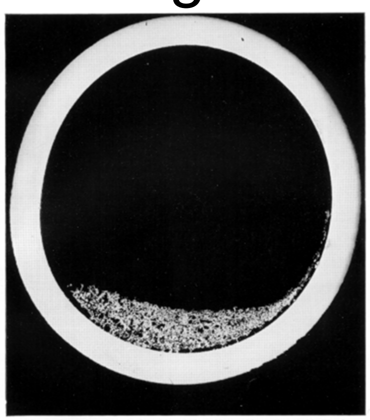


Fig. 7. Chromium deposits found in cold leg of Inconel loop discussed in Fig. 5.

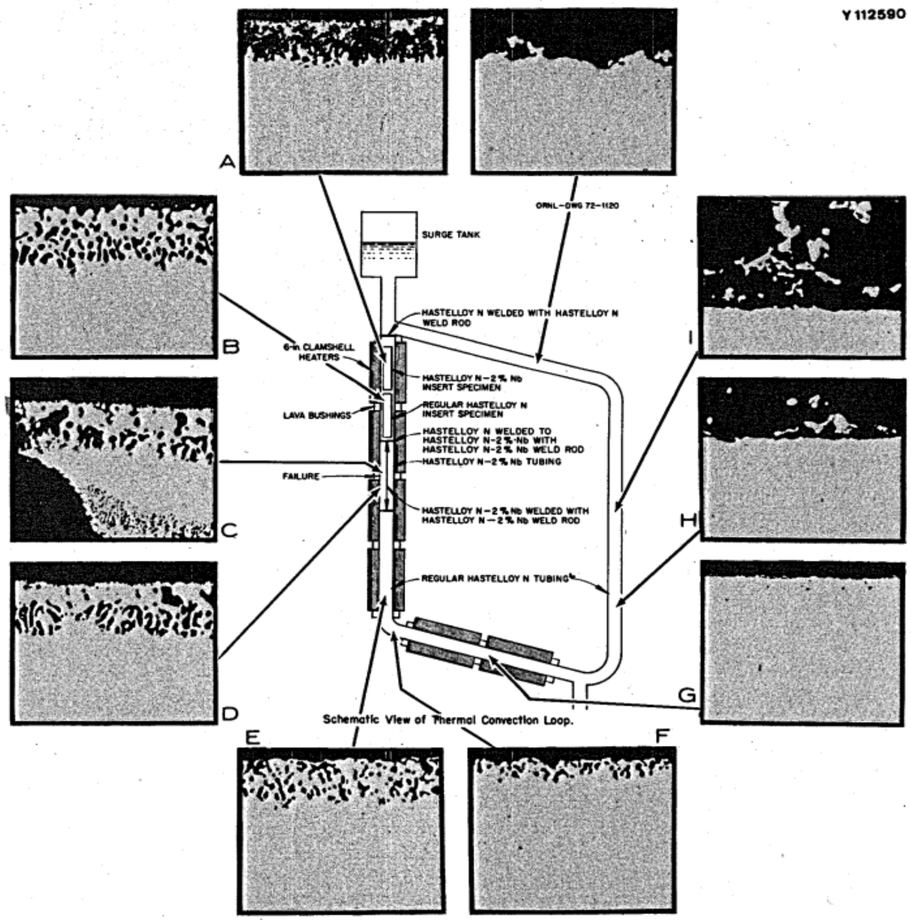
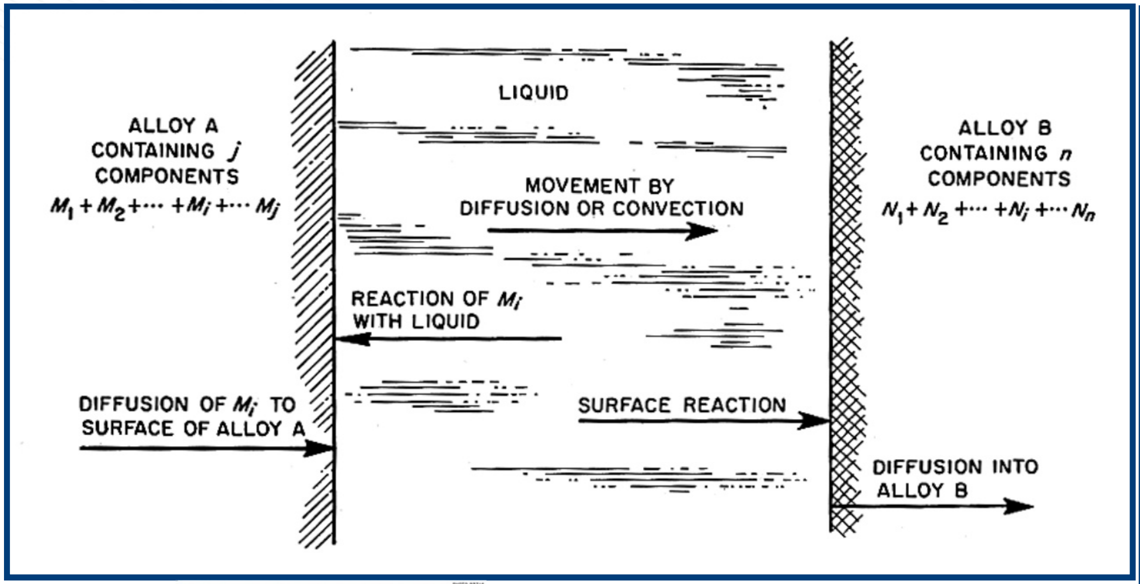


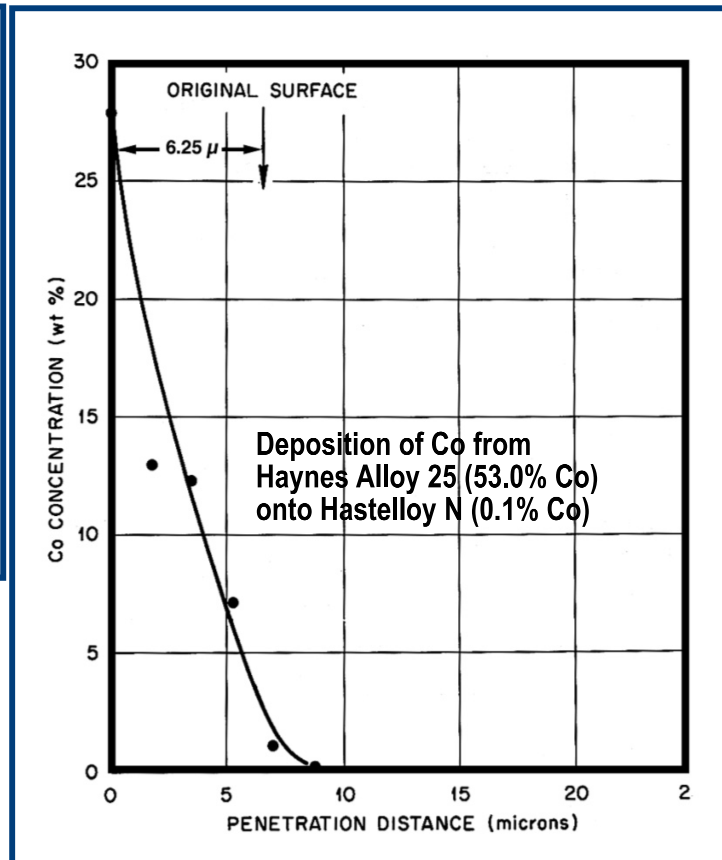
Fig. 11. Micrographs of tubing and specimens from loop 1255 exposed to LiF–23 mole % BeF_2–5 mole % ZrF_4–1 mole % ThF_4–1 mole % UF_4 molten salt at 560–700°C for 9.2 years. As polished. 500×. Reduced 15%.

Source: ORNL-TM-4189, Fig. 11

Mass Transfer Can Also Occur Due to Differences in Chemical Activity (Dissimilar Materials)

Alloy	Ni	Mo	Cr	Fe	Co	W	Si	Mn
Alloy N	70.8	16.5	6.9	4.5	0.1	0.1	0.4	0.5
Haynes Alloy #25	9.0	0.5	19.0	1.0	53.0	14.0	0.3	0.5





Source: ORNL-TM-2741

Tip of a SS304 probe inadvertently used in an Inconel 600 salt loop for 192 hours

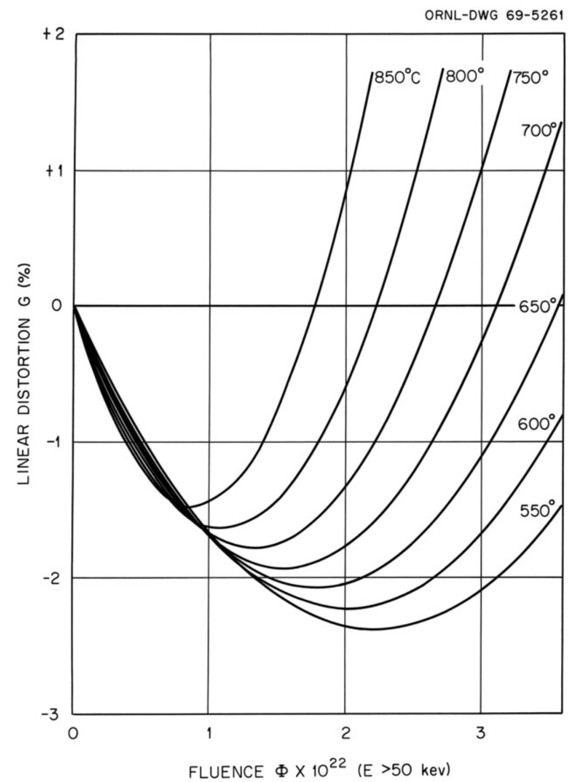
Most Traditional Alloy Coating Technologies Are Potentially Applicable to Molten Salts

- Carbides, nitrides, borides, phosphides, and sulfides as well as refractory coatings may provide increased chemical compatibility
  - Very little information is available on coating performance in molten salts
  - Radiation enhanced intermixing will be a significant issue for thin coatings
  - Coating of joints and welds would also be required
- Carbides appear interesting for protection against fluoride salts due to chemical stability
  - Recent NEUP project was not successful in forming a hermetic layer resulting in undercutting and delamination
- Chemical vapor deposition of molybdenum and tungsten onto nickel-based alloys was demonstrated during MSBR program (for protection from liquid bismuth in reductive fission product extraction process)
  - Coatings (125 μm) "adhered tenaciously" to nickel-based alloys (required nickel flash layer to adhere to iron-based alloys)

Inconel 600 bend specimens showing coating cracks
Source: ORNL-TM-3609

Graphite Remains Leading Candidate Moderator Material for Future MSRs

- Compatible with both fluoride and chloride salts
  - Movable fuel displacement moderator rods were the baseline for reactivity control in the MSBR design
- Substantial knowledge base on its radiation-induced degradation
- BeO was employed at the ARE
  - Not included in any modern MSR design
- ZrH is employed as an alternative moderator in some modern designs
  - Primary advantage would be to decrease required moderator volume
  - Primary technical challenge is retaining hydrogen high temperatures
  - ZrH moderator pins were an element of the fast spectrum, solid fuel MSR design concept developed at MIT in 2006–8



Graphite Fast Flux Induced Distortion

Source: ORNL-4541, Fig. 3.10

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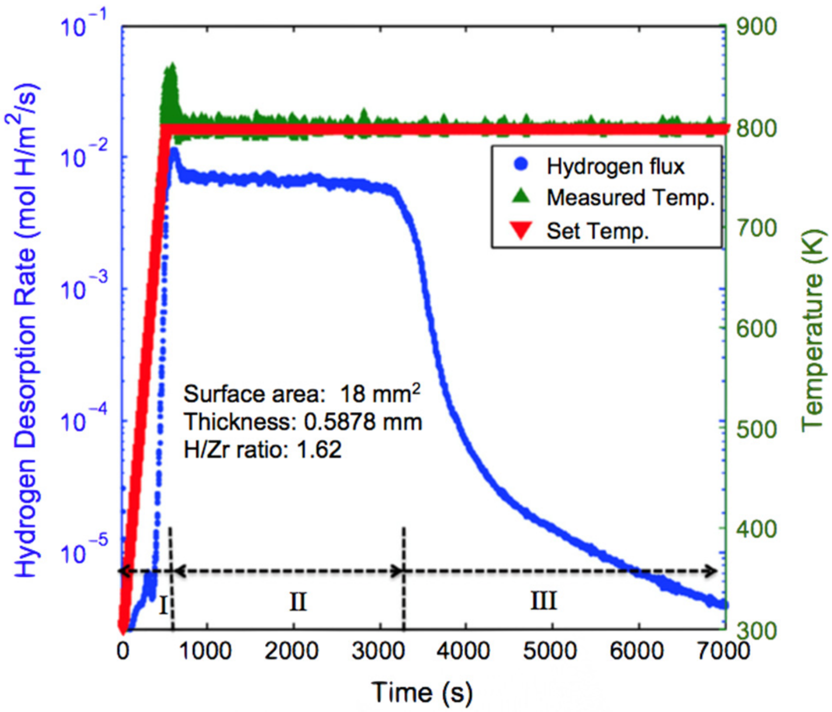
Hydrogen Retention of Zirconium Hydride at Operating Temperature Is a Key Challenge

- Hydrogen readily desorbs from ZrH at high temperatures
- At lower temperatures, uranium-zirconium-hydride fuel is employed by TRIGA reactors
- SNAP reactor program was unsuccessful at developing a high temperature hydrogen barrier cladding that would endure thermal cycling
- Substantial improvements in ceramic composites over the intervening decades may enable retaining hydrogen at temperature while enduring thermal cycles



Hydrogen Desorption Timeline from $ZrH_{1.6}$ at 525°C

X. Hu et al.2014. "Hydrogen desorption kinetics from zirconium hydride and zirconium metal in vacuum," *Journal of Nuclear Materials* 448: 87-95, Fig. 6a.
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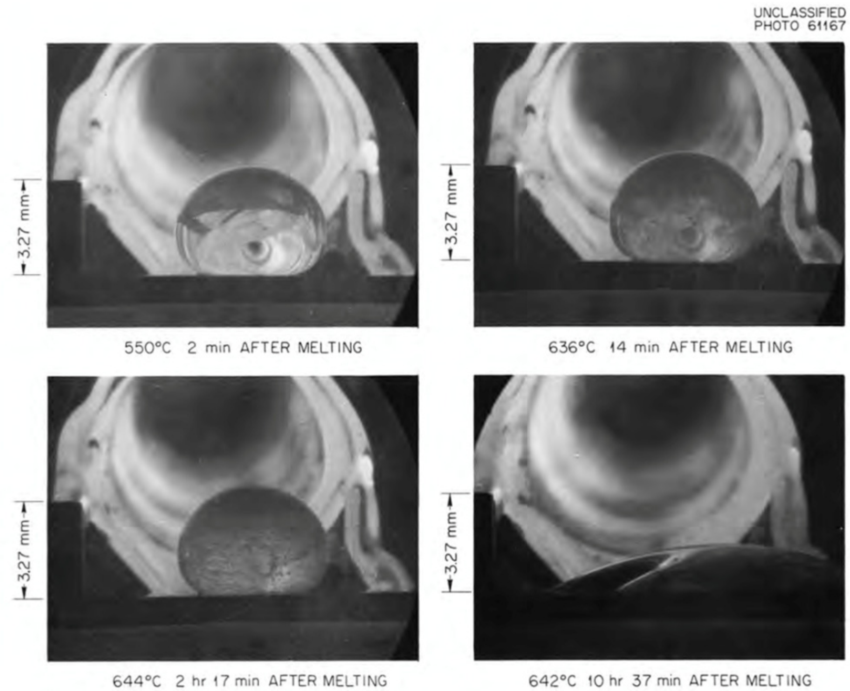
Fluoride Salts Have Limited Permeation into Graphite



Source: ORNL-3529

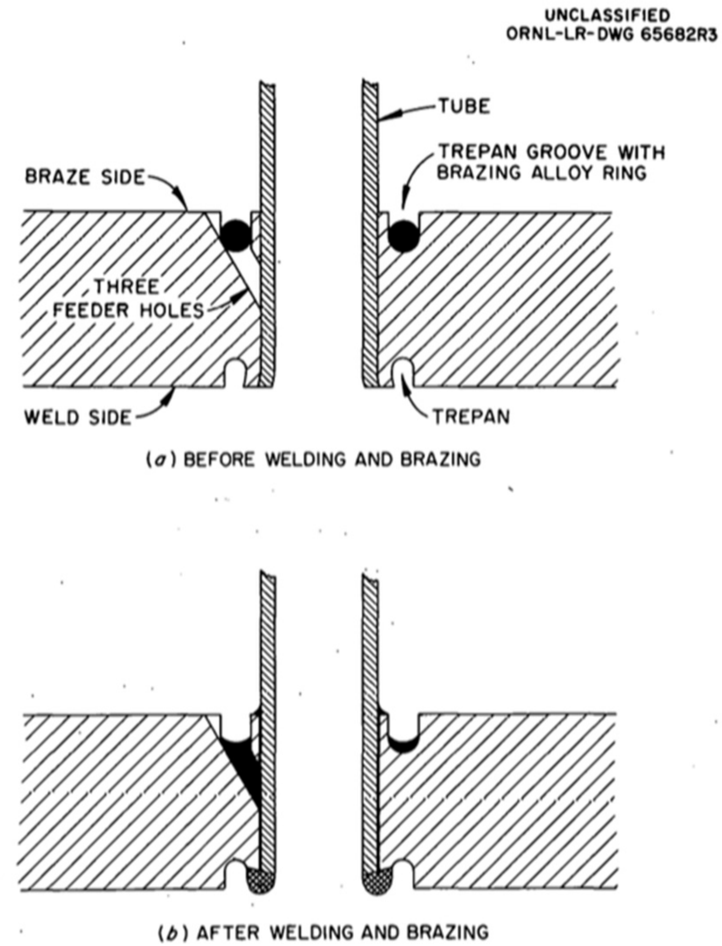
- Clean fluoride salts do not wet graphite
- Small amounts of moisture changes wetting behavior
  - FLiBe and MSRE fuel salts were studied with multiple graphite grades
  - Initially a BeO scum shell forms in moist He (or H_2)
  - Virtually no graphite penetration
- Droplets are indefinitely stable in dry helium
- Details of fuel salt penetration into reactor graphite is not well known
  - High surface fission product concentrations dropping by several orders of magnitude to low interior concentrations
  - Noble gas fission product daughters have highest concentrations
  - Fuel penetration was concluded to *not be a serious problem*
  - Significant tritium trapping in first ~1½ mm
    - Substantial increase in tritium trapping due to irradiation damage

Reflectors and/or Shielding Reduce the Radiation Damage to Reactor Vessel

- Optimal reflector depends on neutron spectrum
  - Graphite for thermal spectrum
    - Neutron absorber lining of reactor vessel
  - High atomic mass material for fast spectrum
    - Lead or tungsten preferred (^{208}Pb has best neutronic performance)
    - Nickel or iron-based alloys may provide acceptable reactor physics with significantly lower material compatibility and radiation damage challenges
    - Substantial gamma heating load
    - Fuel salt bypass for cooling reflector will be a significant element for evaluating lower plenum designs
    - Lead would be liquid and resulting in significant corrosion issues
      - Requires first wall material that is compatible with both lead and fuel salt
- Subcritical breeding blanket performs similar shielding role

Structural Alloy Joins Will Be Necessary in Any Realistic Design

- MSR alloy weld procedures were developed in the MSBR program
- Welds would need to be coated to provide chemical compatibility
- Brazing is anticipated to play a larger role in MSRs due to the lower temperature necessary to form braze joints resulting in less damage to the base material microstructure
  - Gold-based brazes can be compatible with halide salts and functional with iron and nickel-based alloys
  - May enable joining precoated materials
- Brazing is not addressed in nuclear portion of ASME BPVC



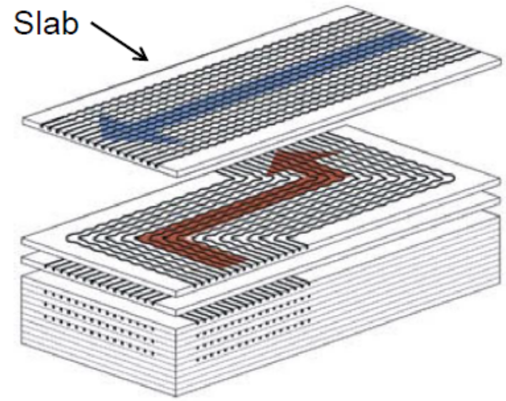
Source: ORNL-3500, Fig. 2

MSRE Tube-to-Tube Sheet Joints – weld and back braze

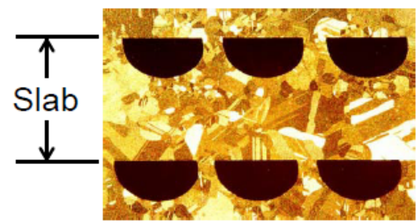
Advanced Manufacturing Methods Can Result in Components with Increased Performance Uncertainty

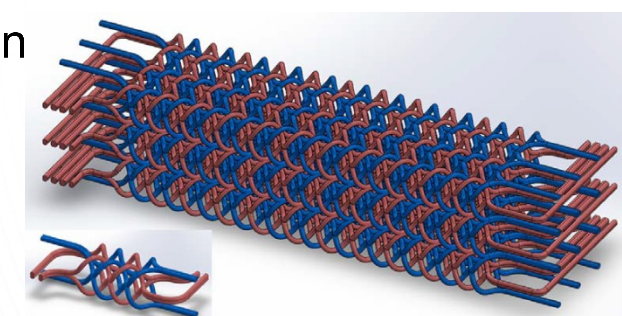
- Low thermal conductivity and high viscosity of molten salts provides incentive to add surface heat transfer enhancement features to heat exchangers
- Printed circuit heat exchangers with diffusion bonded layers have significant remaining issues
  - Multiple weld and brazed joints and potential for defects
  - Mechanically rigid structure with poor performance in deep thermal cycling (as in shutdowns)
- Investment cast heat exchangers require alloys that form proper microstructure

Heat Exchanger Core



Diffusion Bonding





Images Courtesy M. D. Carlson et al.
Sandia National Laboratories

Counter-rotating helical geometry proposed for cast metal heat exchanger

Flanges and Gasket Materials

- Flanges would significantly decrease maintenance time and difficulty
  - Freeze valves are a safety element in some designs
  - Enabling technology for remote maintenance
- Gaskets for molten salts have been challenging due to tendency to develop leaks over time
  - Bolt creep
  - Gasket corrosion
  - Sealing-surface deformation
- Double gaskets employing intermediate overpressure and leak detection force leaks to be inwards
- Indent gaskets (gold-plated) were developed under MSBR program
- Nickel-grafoil spiral wound and plated metal C-ring type gaskets are current leading candidates
  - Employ spring loaded bolts to maintain compression

Spiral wound nickel-grafoil gasket

Valves and Bearings

- MSBR program was not successful in developing mechanical shut-off valves due to self-welding (galling) of the sealing surfaces
  - Fluoride salts dissolve hard oxide surfaces
  - Bellows-sealed mechanical throttling valves were demonstrated
  - Hard-face-sealing surfaces and/or flexible metallic seats (such as plated C-ring gaskets) remain to be developed
- Salt-wetted bearings would significantly simplify the design and operation of coolant pumps
  - Neither ceramic bearings nor dry gas seals were available in the 1960s
  - MSRE experienced oil leakage down pump shaft resulting in foaming and salt redox shifting
    - MSRE bearings were above sealing ring (cantilever pump)
  - Diamond and cubic boron nitride bearings are commercially available and chemically compatible with halide salts
  - Dry gas seals (gas-lubricated, mechanical, noncontacting, end-face seals) are widely used commercially

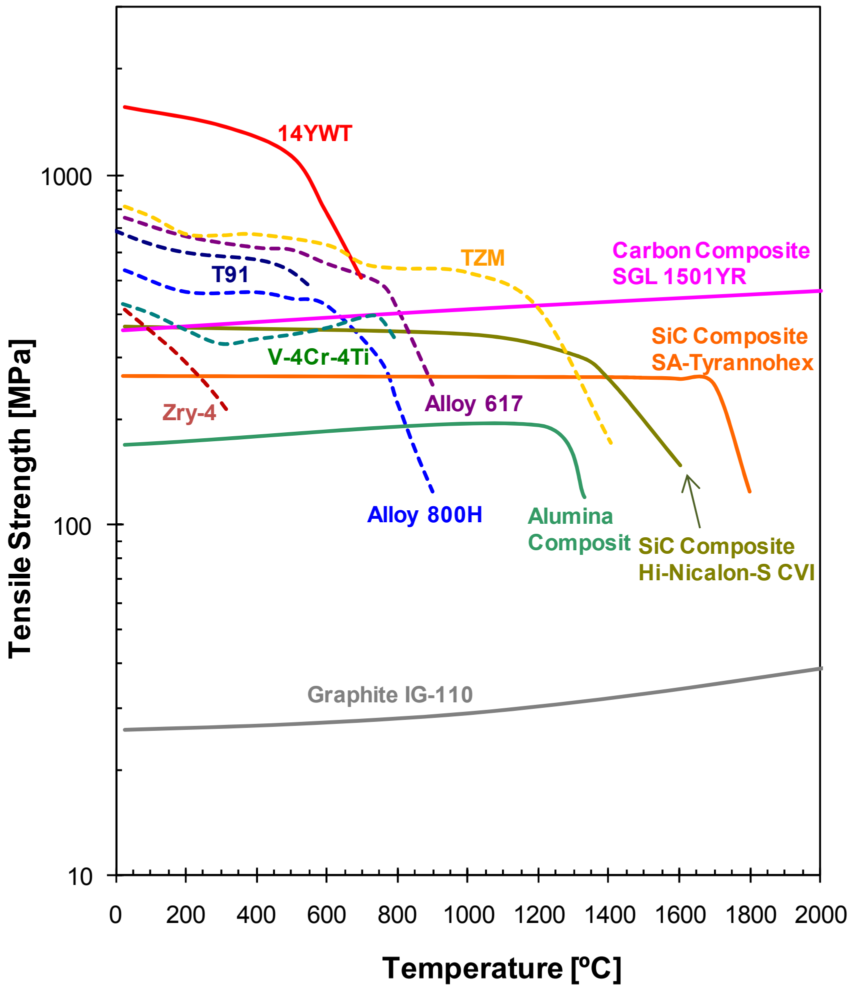
Melt Point Triggers

- Ability of MSRs to tolerate temperature excursions enables use of melt point triggers to activate safety mechanisms
- Melt point triggers are anticipated to be employed in reactivity control mechanisms (links in shutdown rod drives or seals in poison salt injectors)
  - Au-Sn alloys are candidate material system – likely with Au plating
  - Will require testing of safety function

Salt Cleanup and Cover Gas Handling Systems

- Mechanical filtering
  - Sintered porous nickel filters employed for MSBR program
  - Porous carbon filters are a modern alternative
  - Filters will become highly activated requiring remote handling
  - Filters will need to be assayed to assure that they have not trapped fissile materials
- Thermal treatment
  - Heat salt to drive out volatiles
  - Filter offgas lines
- Inert gas sparging
  - Plating out fission gases
- Snow traps
  - All cover gas lines are vulnerable to plugging
  - Likely to be metal plate structures

Structural Composites Are an Alternative Functional Material for MSRs

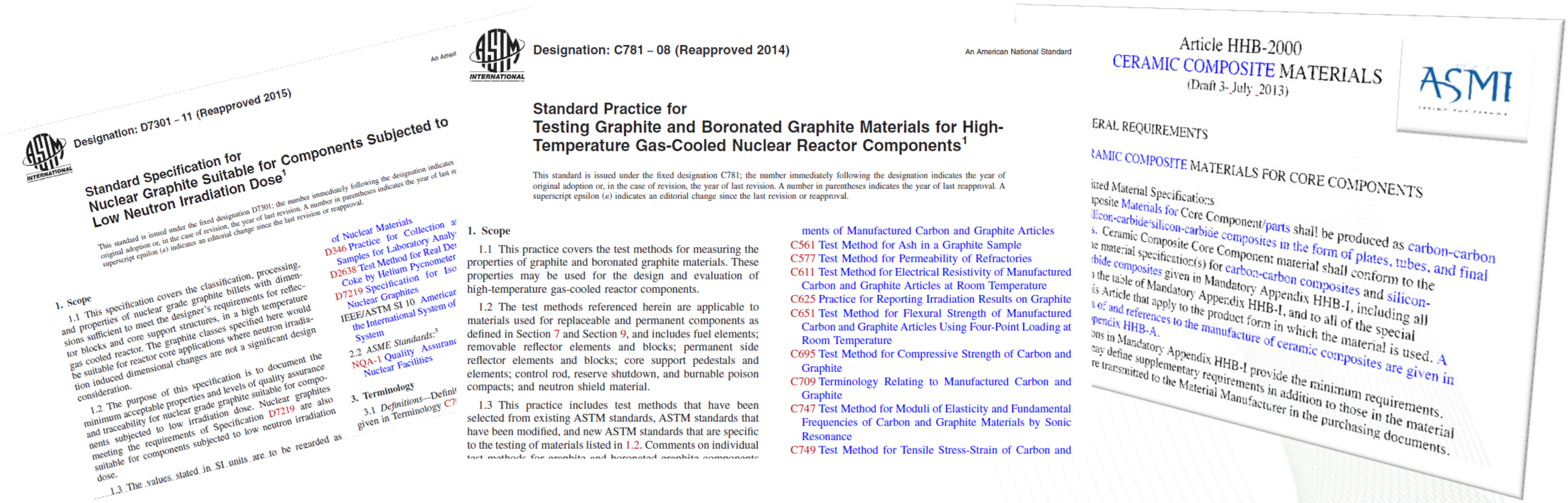


- Carbon has good chemical compatibility with both chlorides and fluorides
- Carbides have good compatibility with fluorides
- Unparalleled high temperature strength
- Practically no irradiation embrittlement
  - Limited irradiation effects for C/C (cf. heat resistant alloys); very minor, nonprogressive irradiation effects for SiC/SiC
- Low neutron absorption
- However, differences from metallic alloys impose new challenges
  - Anisotropy
  - Pseudoductile fracture; small strain to micro-cracking
  - Statistical failure

Source: Y. Katoh. 2013.
"Continuous Fiber Ceramic Composites for Fluoride Salt Systems." US-RF MSR/FHR Workshop. ORNL

Material Standardization Remains a Significant Issue with Composites

- Continuous fiber composites can be formed by several different processes with different precursor materials
- Performance characteristics of different grades of composites varies substantially
- ASME and ASTM standards on ceramic composites remain under development



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Silicon Carbide Compatibility with Fluorides Depends on Purity and Stoichiometry

- Free silicon readily forms SiF_4
  - Radiolysis can enhance corrosion
- Binder phase oxides readily dissolve in fluoride salts

Cast & fired

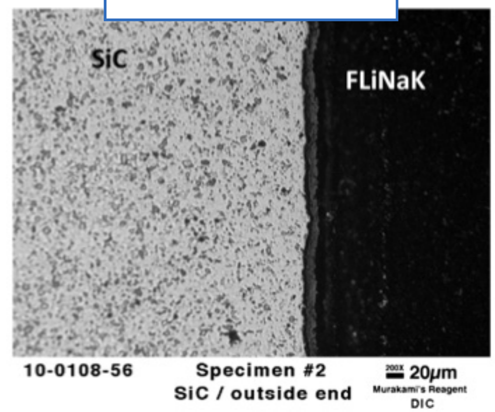
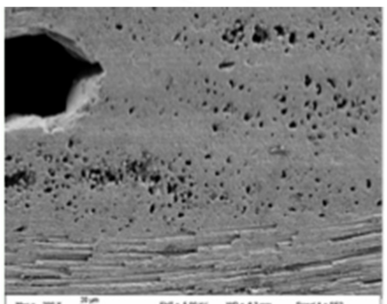
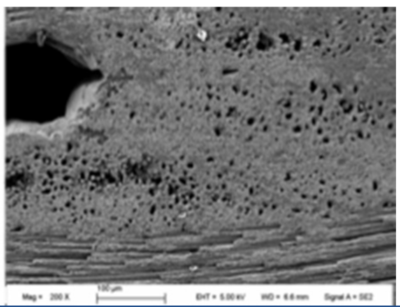


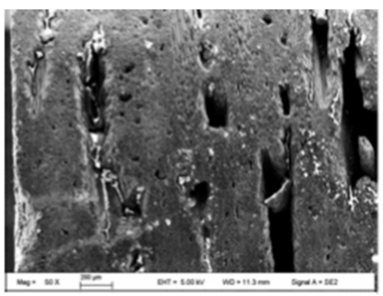
Fig. 6. SiC specimen after 90 day exposure to 700 °C FLiNaK salt.

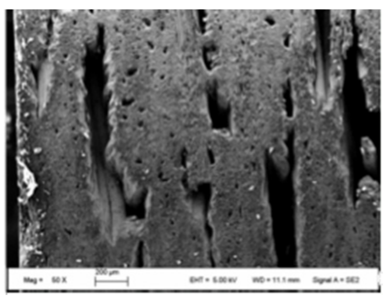
Cast & fired source: G. Yoder et al. ORNL.2014. "An experimental test facility to support development of the fluoride-salt-cooled high-temperature reactor." *Annals of Nuclear Energy* 64:511-517.





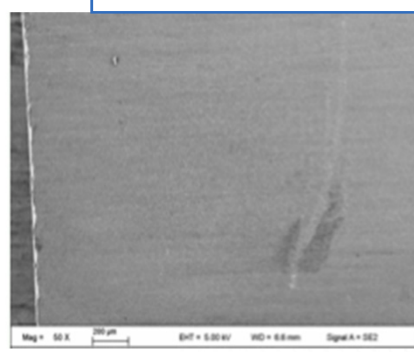
Chemical vapor infiltration SiC composites exhibit small weight loss

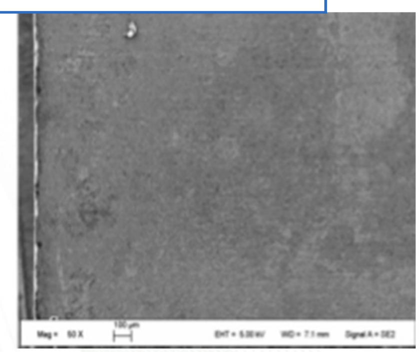




High purity SiC exhibits little corrosion

Chemical Vapor Deposition (CVD)





SiC-SiC & CVD SiC composite data from DOE-NE IRP project University of Wisconsin. K. Sridharan. "Fluoride Salt-Cooled High Temperature Reactor (FHR) – Materials and Corrosion," IAEA, Vienna, June 10-13, 2014

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Maturity of Materials for MSRs Varies Widely

- Radiation damage to reactor vessel is a primary design safety issue
- Proper operations are key to managing salt corrosion
- Coating and/or cladding of structural alloys needs to be codified
- Standardization is a key issue to enabling the use of ceramic fiber composites
- Periodic component replacement substantially changes the qualification testing duration for high temperature alloys
- Joining and forming of alloys and composites is key to maturing MSR designs
  - Brazing needs to be codified for high temperature nuclear applications