Oak Ridge National Laboratory

Module 6: Materials

David E. Holcomb, Ph.D.

Nuclear Energy and Fuel Cycles Division

November, 2022

MSR Structural and Functional Materials Performance Issues Are Technically Distinctive

- Elevated temperature, extended operation, corrosive chemistry, and radiation flux are the primary materials stressors
- MSR operating parameters are far from fuel salt limits
  - Hundreds of degrees of margin to fuel salt boiling
  - Molten fuel salts are not vulnerable to radiation damage
- Structural and functional material performance limits directly impose reactor performance limits — for example
  - Lower temperatures result in lower thermodynamic efficiency
  - Shorter material lifetimes result in higher replacement costs and more frequent outages
- First generation commercial MSRs are likely to employ higher maturity materials in less stressful environments (e.g., SS316 at 600 °C) to increase confidence in adequate performance
  - Improved materials would increase MSR performance

Materials Selection, Reactor Configuration, and Reactor Operations Are Interrelated

- Materials credited to perform safety functions can depend on the state of the reactor
- Under normal operations the fuel salt wetted boundary provides radionuclide containment
- Normally wetted fuel salt boundary may not be credited to provide containment under design basis accident conditions
- Material performance requirements can be substantially different if they only need to withstand salt contact for the duration of an accident
- Reactor configuration also substantially change material performance requirements
  - Fuel salt removal from critical region during accidents (e.g., to a passively cooled tanks)
  - Internal shielding to reduce radiation damage to reactor vessel
  - Early removal of fission gases from reactor vessel necessitates higher temperature tolerant gas container materials (or improved heat transfer)
  - Cooling fuel salt tubes with a higher pressure coolant changes accident progression for a fuel salt container leak

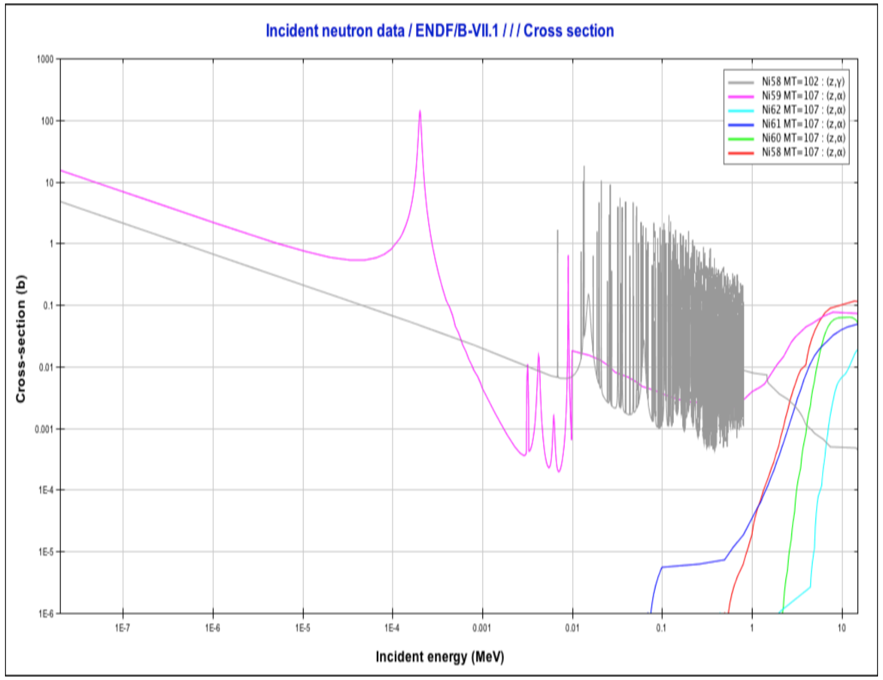
Combination of Lower Pressure and Liquid Fuel Changes Design Optimization

- Less massive components are easier to replace
  - Several design variants feature periodic replacement of all salt-contacting components – including reactor vessel
  - Storage and disposal of activated and contaminated components needs to be considered
  - 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 potential design element to minimize radiation damage to vessel
  - Both fast and thermal spectrum reactors
  - Unfueled coolant salt may provide the vessel shielding – similar to downcomer in LWRs

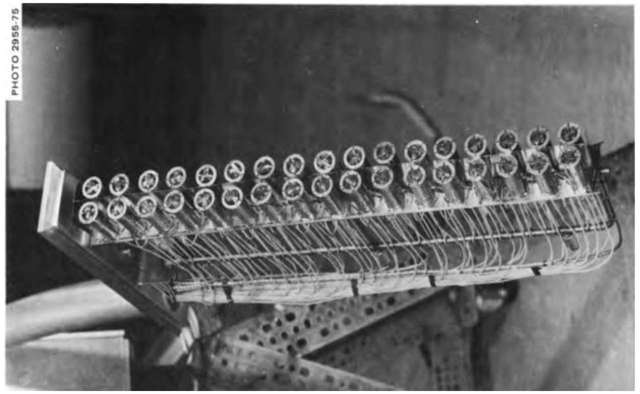
Neutron Fluence Will Be a Significant Stressor for Container Materials

- Nickel-based alloys embrittle when subjected to significant neutron fluxes at high temperatures especially at low strain rates
  - 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
  - Helium trapping at nanoscale precipitates within grains key to inhibiting embrittlement
  - 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

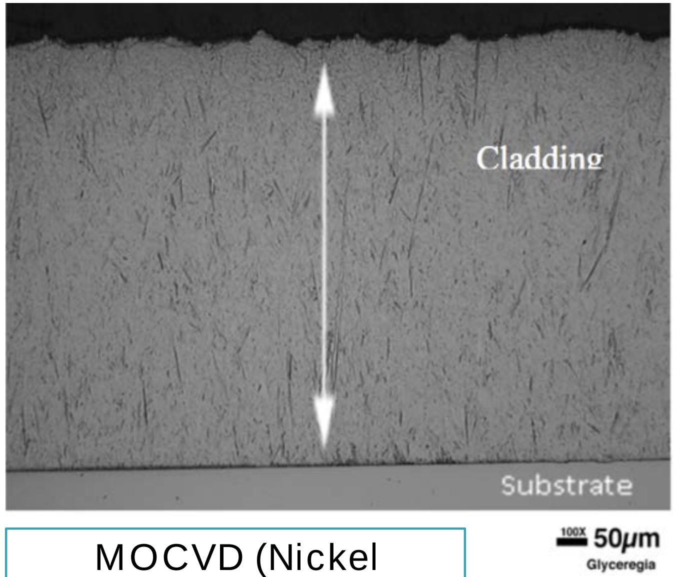


Source: ORNL-5132

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
- Thermal cycling can cause coatings to crack or delaminate
  - Coefficient of thermal expansion (CTE) mismatch is a key phenomenon as is formation of intermetallics due to reaction of cladding and substrate
  - 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

Source: ORNL/TM-2011/95



MOCVD (Nickel Carbonyl Process) Nickel on 617 Substrate

Historic MSR Program Provides Substantial Technical Basis for Understanding Halide Salt Corrosion

Studies on molten fluoride mixtures for reactor applications began in the early 1950's and gave primary consideration to the compatibility of these salt mixtures with structural materials. In the intervening 15 years, an extensive corrosion program has been conducted at ORNL with several families of fluoride mixtures using both commercial and developmental high-temperature alloys. As a consequence, the corrosion technology for the molten-salt reactor concept is' now in an advanced stage of development. Furthermore, container materials are available that have shown extremely low corrosion rates in fluoride mixtures at temperatures considerably above the 1000 to 1300°F range proposed for the MSBR.

H. E. McCoy, Jr. and J. R. Weir, Jr. - 1967

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 + $2UF_3$ → $2UF_4$ +"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

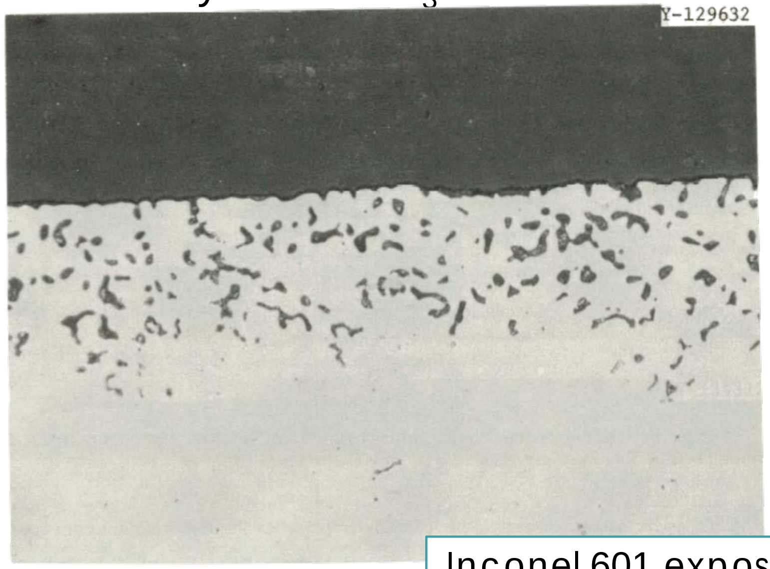
Bottom graphite stud of MSRE before (large photo) and after (inset) operation

Source: ORNL-TM-4174

OAK RIDGE National Laboratory

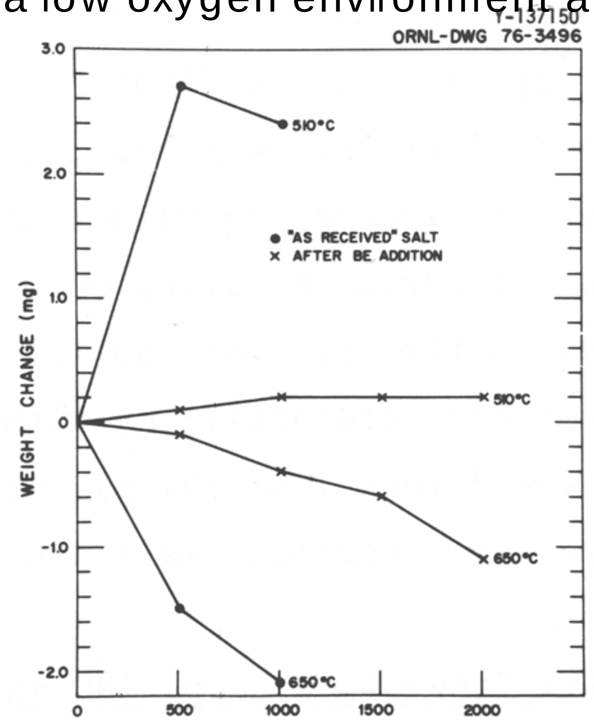
Key Step in Structural Alloy Corrosion is Dissolution of Constituent Atoms into Salt

- 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 with higher generalized (non-oxidative) corrosion can produce flow path blockages in cold regions due to temperature dependent solubility
- 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 $AlCl_3$



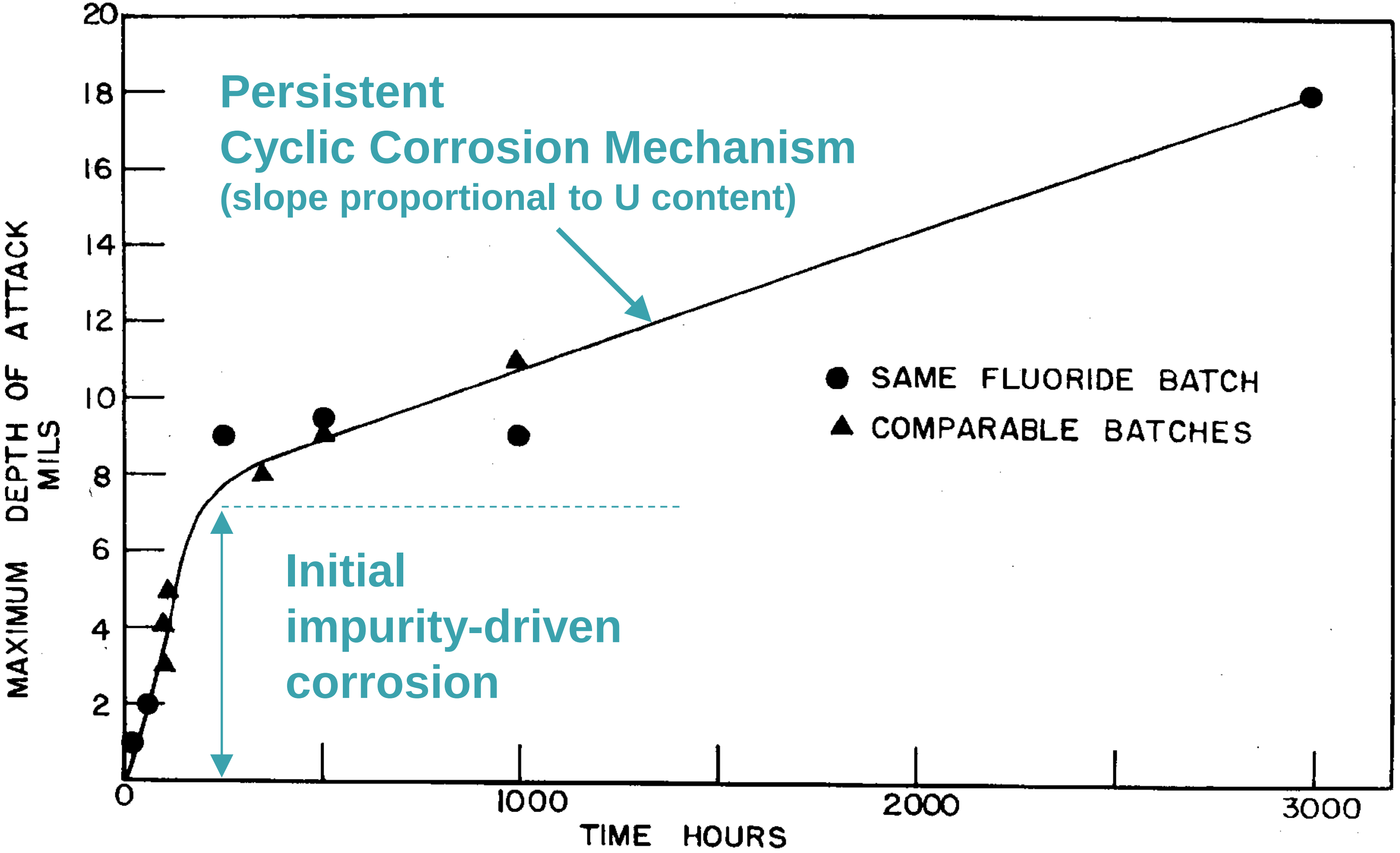
Inconel 601 exposed to MSBR fuel salt showing Cr voids

Source: ORNL/TM-5783



Change in corrosion rate of SS316 with redox

Polythermal Corrosion in Halide Salts Shows a Characteristic Pattern



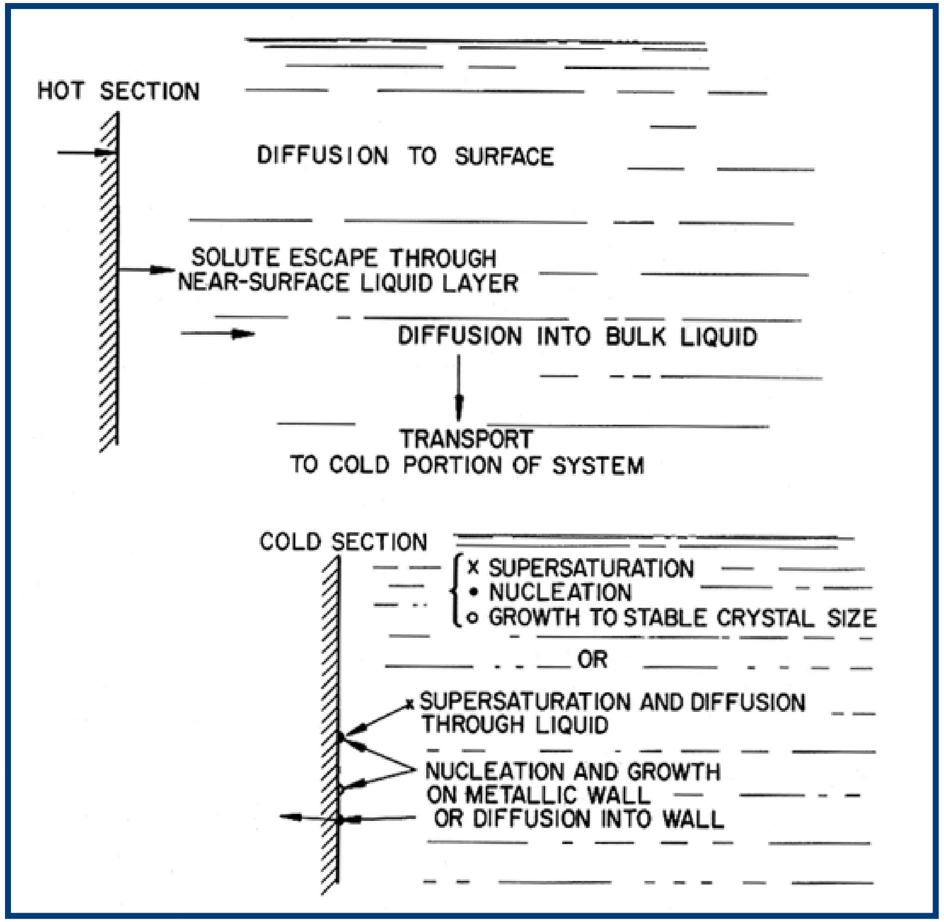
Source: ORNL-2349

- Salt impurities initially react to form stable compounds
- Longer-term corrosion dominated by mass transfer from hot to cold leg

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

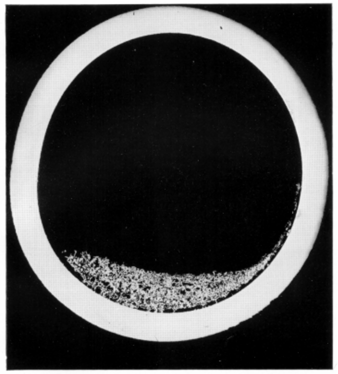


Fig. 7. Chromium deposits found in cold leg of Inconel loop discussed in Fig. 5.

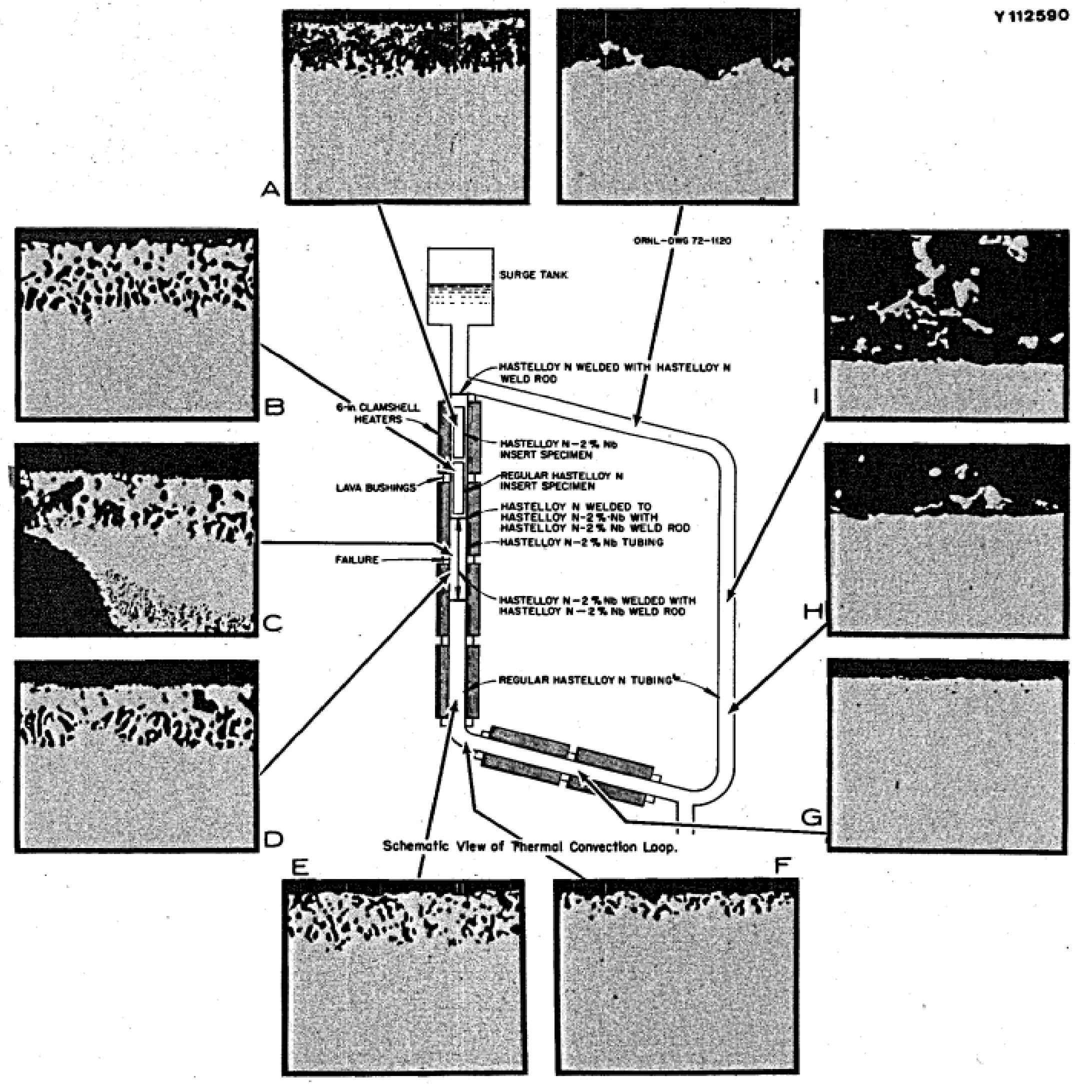


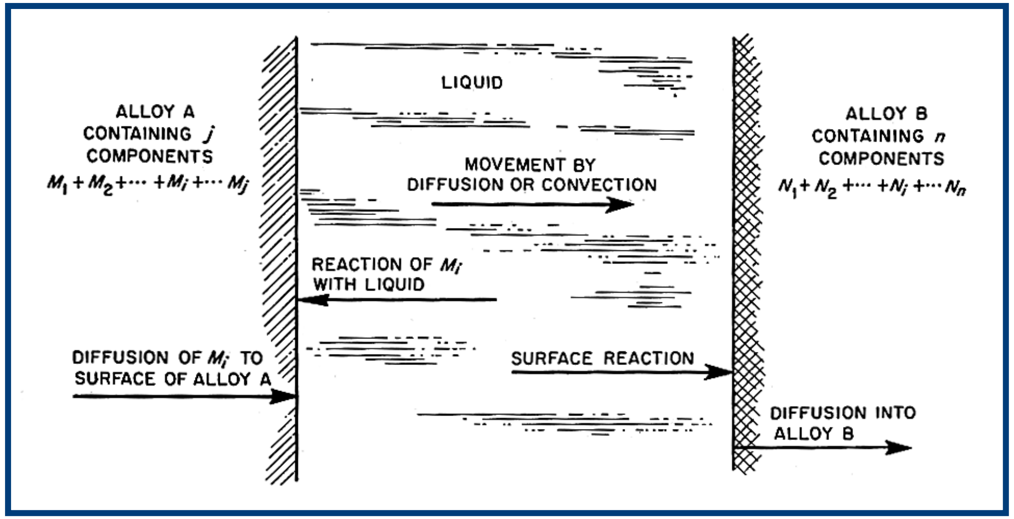
Fig. 11. Micrographs of tubing and specimens from loop 1255 exposed to LiF–23 mole % BeF_2–5 mole % ZrF_4–1 mole % ThF_4–1 mole % UF_4 molten salt at 560–700°C for 9.2 years. As polished. 500×. Reduced 15%.

Source: ORNL-TM-4189, Fig. 11

OAK RIDGE National Laboratory

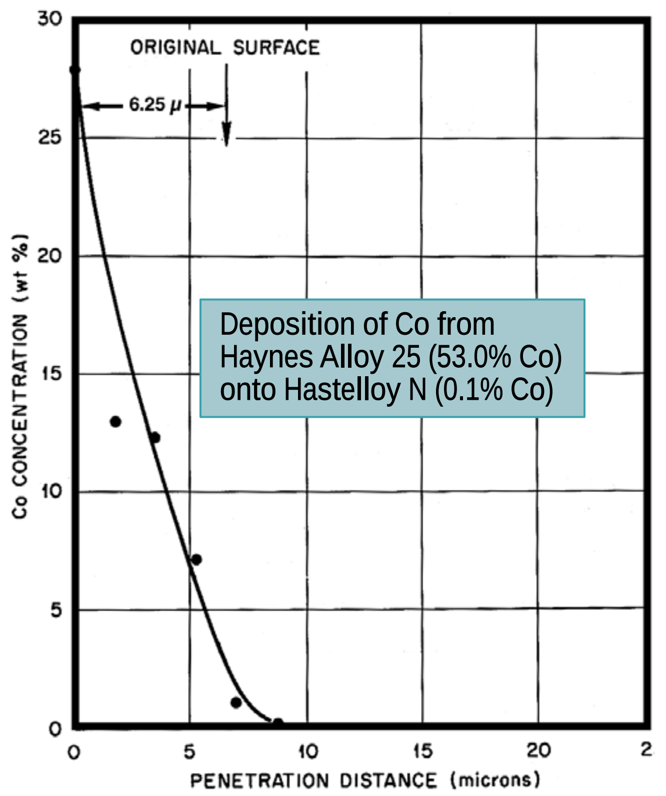
Mass Transfer Can Also Occur Due to Differences in Chemical Activity (Dissimilar Materials)

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



Deposition of Co from Haynes Alloy 25 (53.0% Co) onto Hastelloy N (0.1% Co)

OAK RIDGE National Laboratory

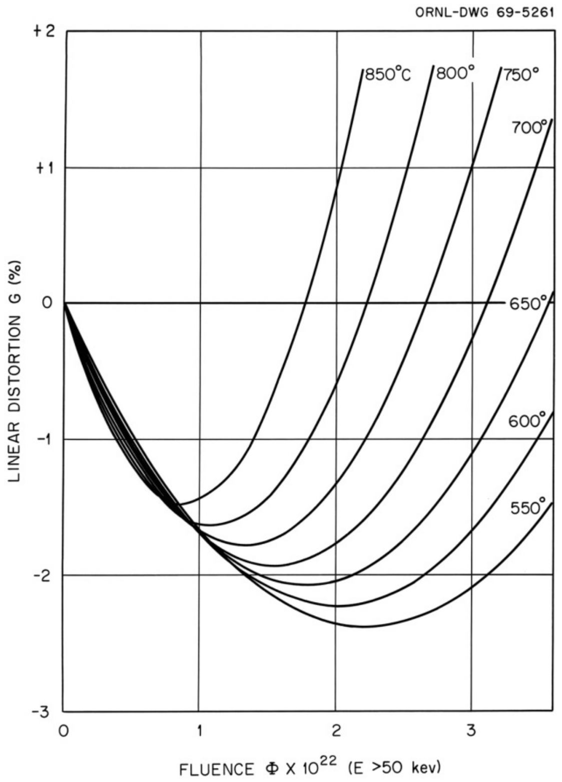
Most Traditional Alloy Coating Technologies Are Potentially Applicable to Molten Salts

- 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
  - Previous 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 Thermal Spectrum MSRs

- Compatible with both fluoride and chloride salts
  - Movable fuel displacement moderator rods were the baseline for reactivity control in the MSBR design
- Radiation degradation of graphite identified by both historic MSR program and AEC technology review as key technology issue
  - Historic program halved design power density to extend graphite lifetime to decades
- Moderation length of carbon ~10x water
  - Equivalent moderation require ~10x volume
  - Spreads out radiation damage
- BeO was employed at the ARE
  - Fuel salt contained in tubes – did not contact moderator
  - Multiple vendors considering high-temperature moderators not in contact with fuel salt
- Development of improved high temperature moderators is an active research area
  - DOE-NE currently sponsoring evaluation of Be_2C – non fuel salt compatible, but may capture tritium



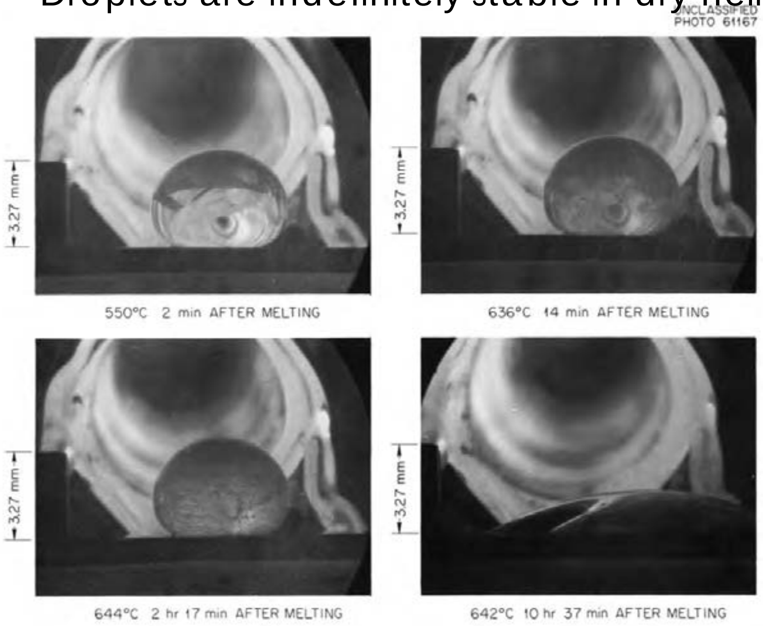
Graphite Fast Flux Induced Distortion

Source: ORNL-4541, Fig. 3.10

OAK RIDGE National Laboratory

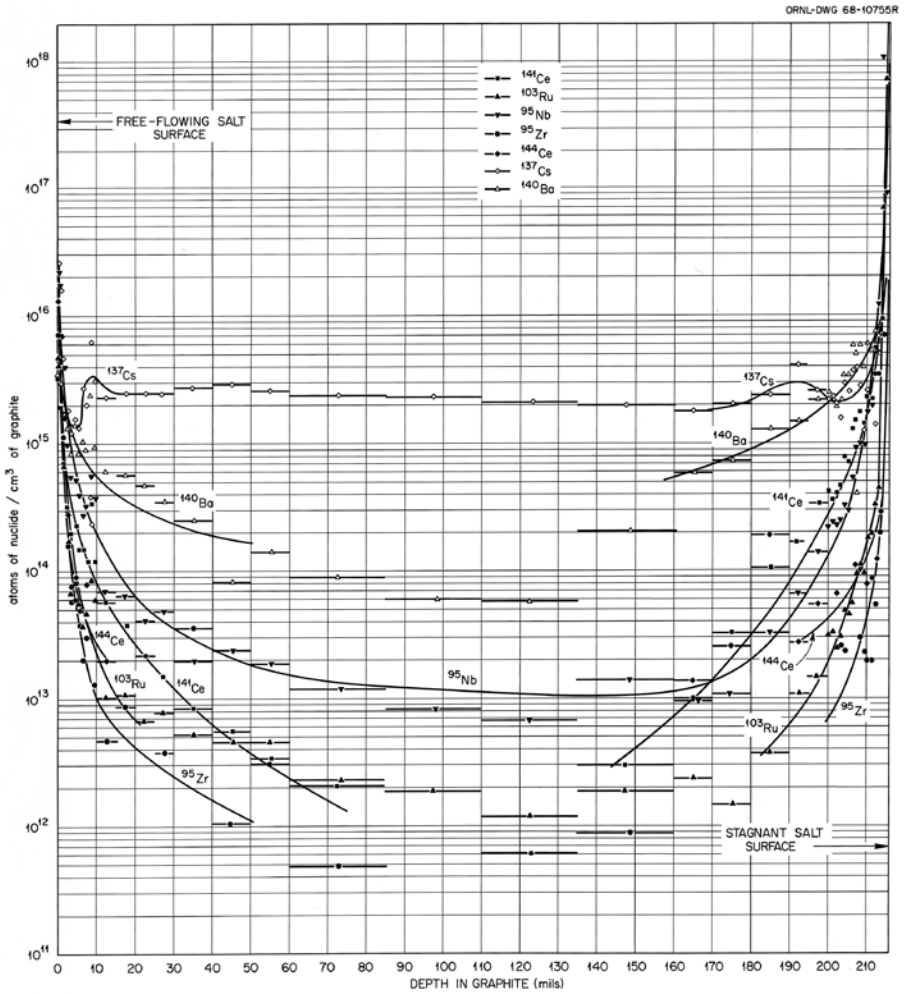
Fluoride Salts Have Limited Permeation into Graphite

- 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



Source: ORNL-3529

- Details of fuel salt penetration into reactor graphite are 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*
  - Key issue is change in fuel salt penetration with radiation damage
  - Significant tritium trapping in first ~1½ mm
    - Substantial increase in tritium trapping due to irradiation damage



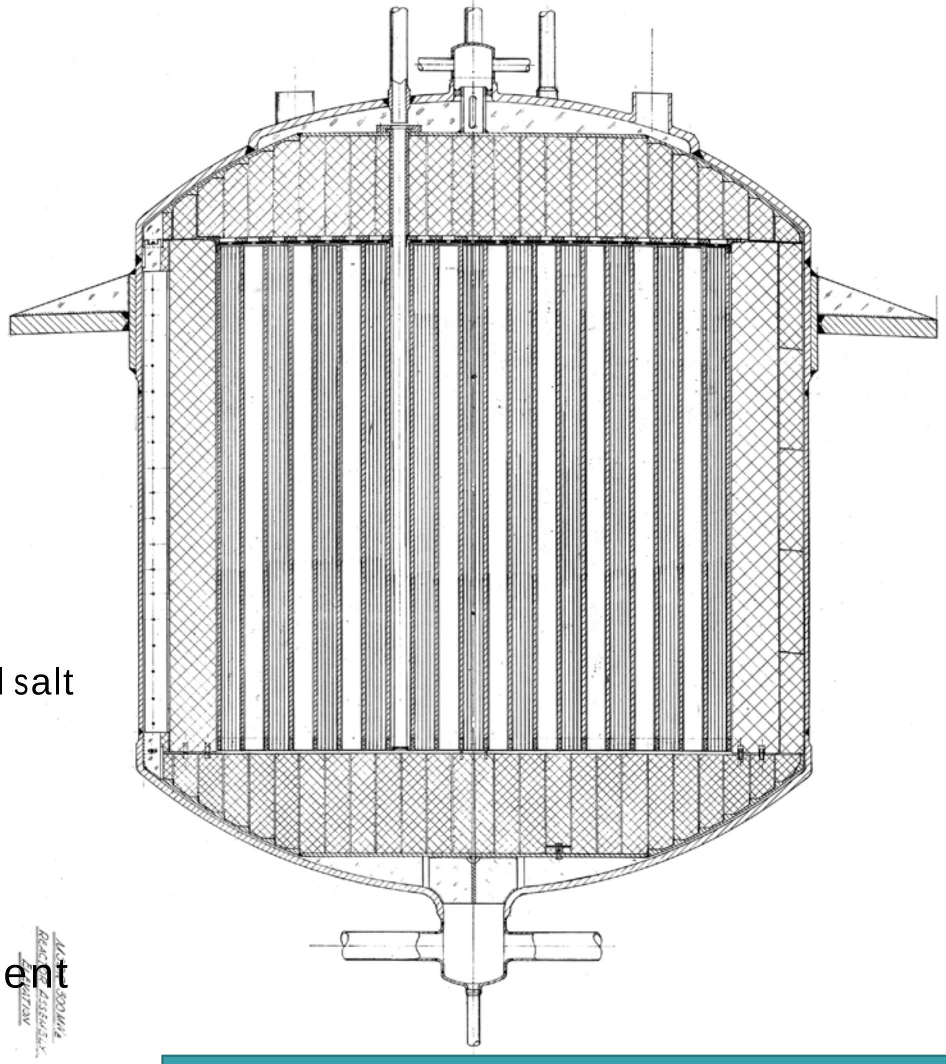
Fission product penetration into MSRE graphite

ORNL DWG 68-10755R ORNL-4568

OAK RIDGE National Laboratory

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

- Optimal reflector depends on neutron spectrum
  - Graphite for thermal spectrum
    - Key lesson learned from MSRE
      - All subsequent designs had thick graphite liner
    - Neutron absorber lining of reactor vessel
  - High atomic mass material for fast spectrum
    - Lead or tungsten preferred (^{208}Pb has best neutronic performance)
      - Requires first wall material that is compatible with both lead and fuel salt
    - 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
- Subcritical breeding blanket performs similar shielding role



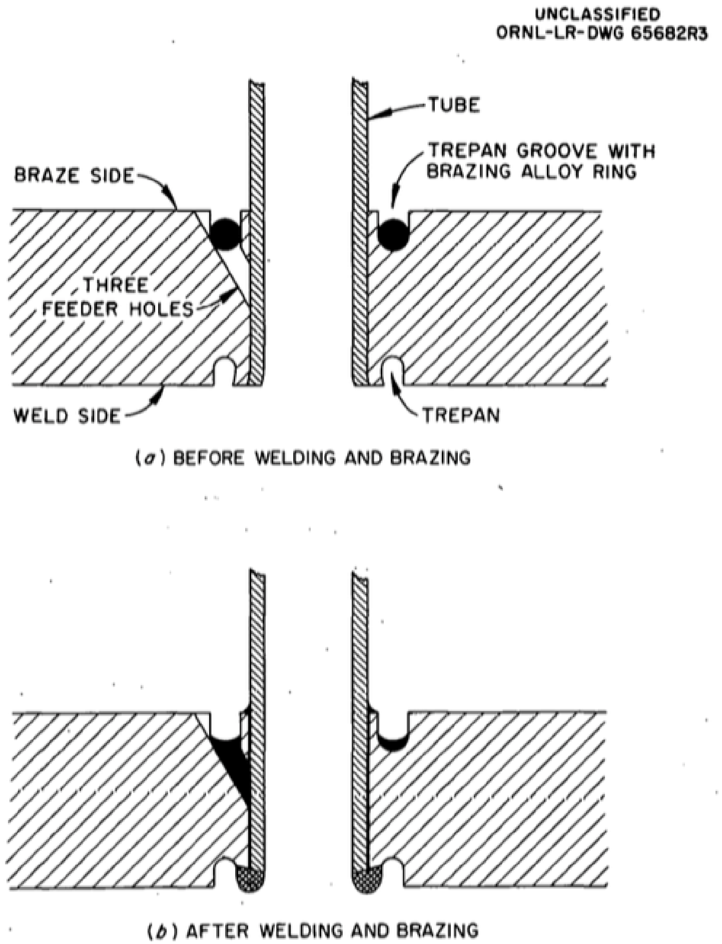
Molten Salt Demonstration Reactor cross section showing thick graphite reflector

ORNL DWG 72-2829 - ORNL-TM-3832

OAK RIDGE National Laboratory

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
- Helium content / radiation embrittlement would be substantial impediment to repair welding



Source: ORNL-3500, Fig. 2

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

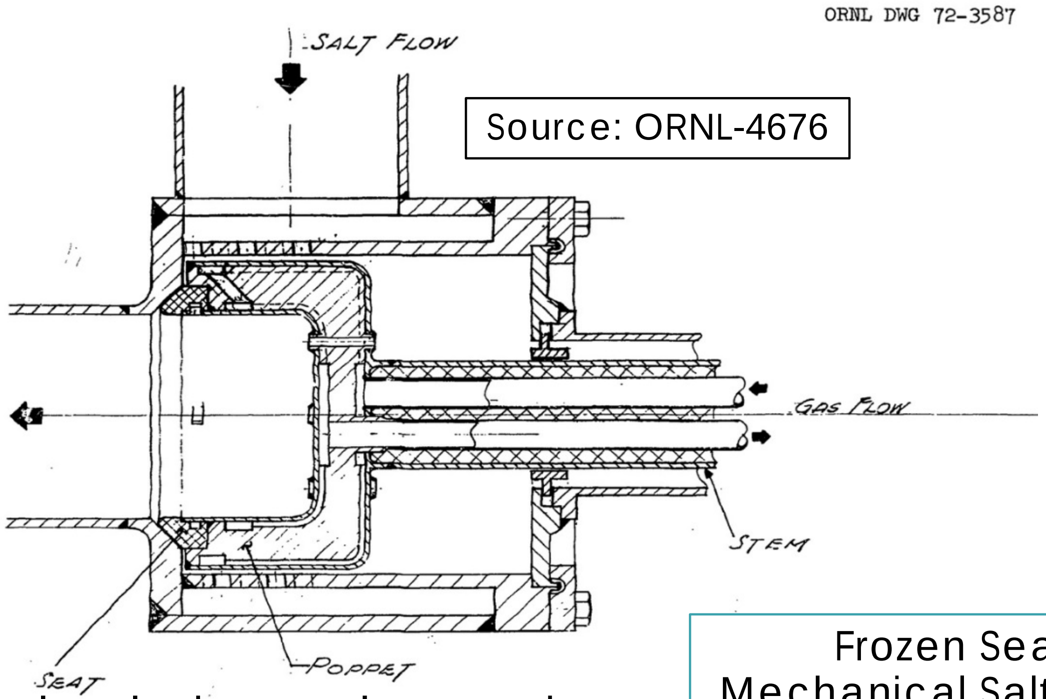
Flanges and Gasket Materials

- 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 soft-metal plated resilient metal gaskets (spring or pressure energized) are current leading candidates
  - Employ spring loaded bolts to maintain compression
  - Resilient metal seals are now common

Spiral wound nickel-grafoil gasket

Valves and Bearings

- MSBR program was not successful in developing purely mechanical shut-off valves due to self-welding (galling) of the sealing surfaces
  - Frozen seal mechanical poppet valve developed as alternative
  - Bellows-sealed, sleeve-type, mechanical throttling valves were also demonstrated



Source: ORNL-4676

Frozen Seal Mechanical Salt Valve

- 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

Freeze/Melt Point Triggers

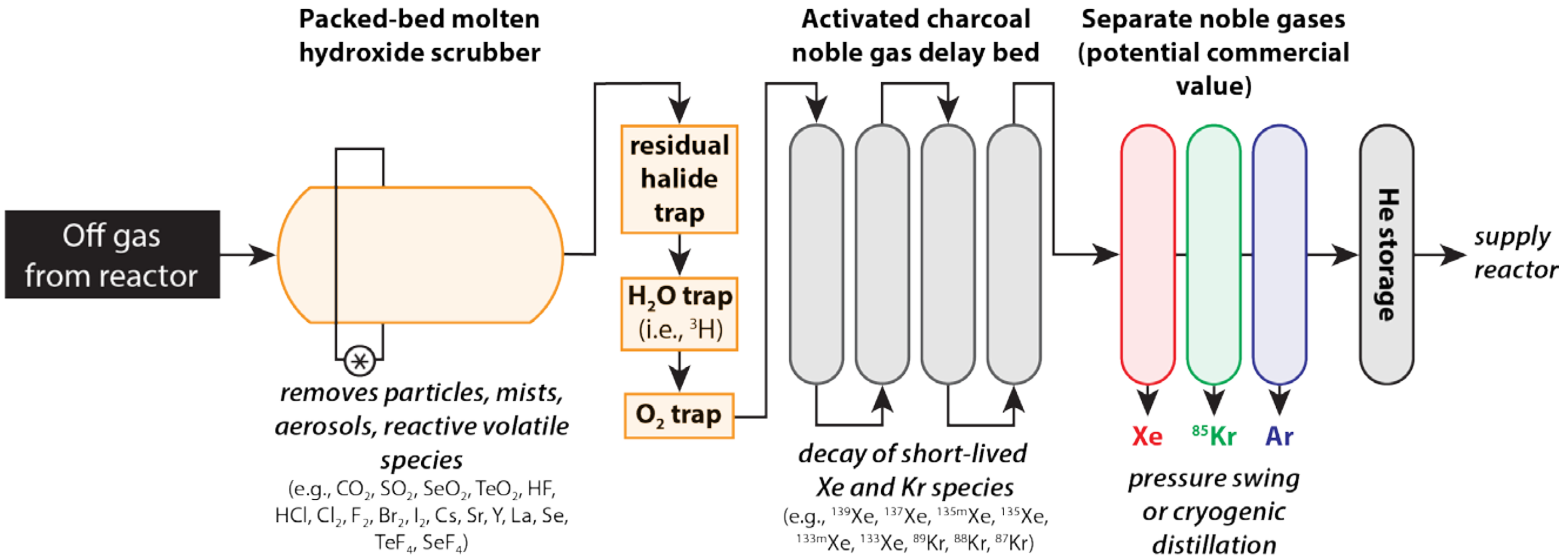
- Ability of MSRs to tolerate temperature excursions enables use of melt point triggers to activate safety mechanisms
  - 10 CFR 50 Appendix A Criterion 21 requires ability to periodically test protection system functionality while in service
  - Freeze valves can be cycled
  - Materials other than salts can be employed
    - Au-Sn alloys are candidate material system – likely with Au plating

Salt Cleanup and Cover Gas Handling Systems

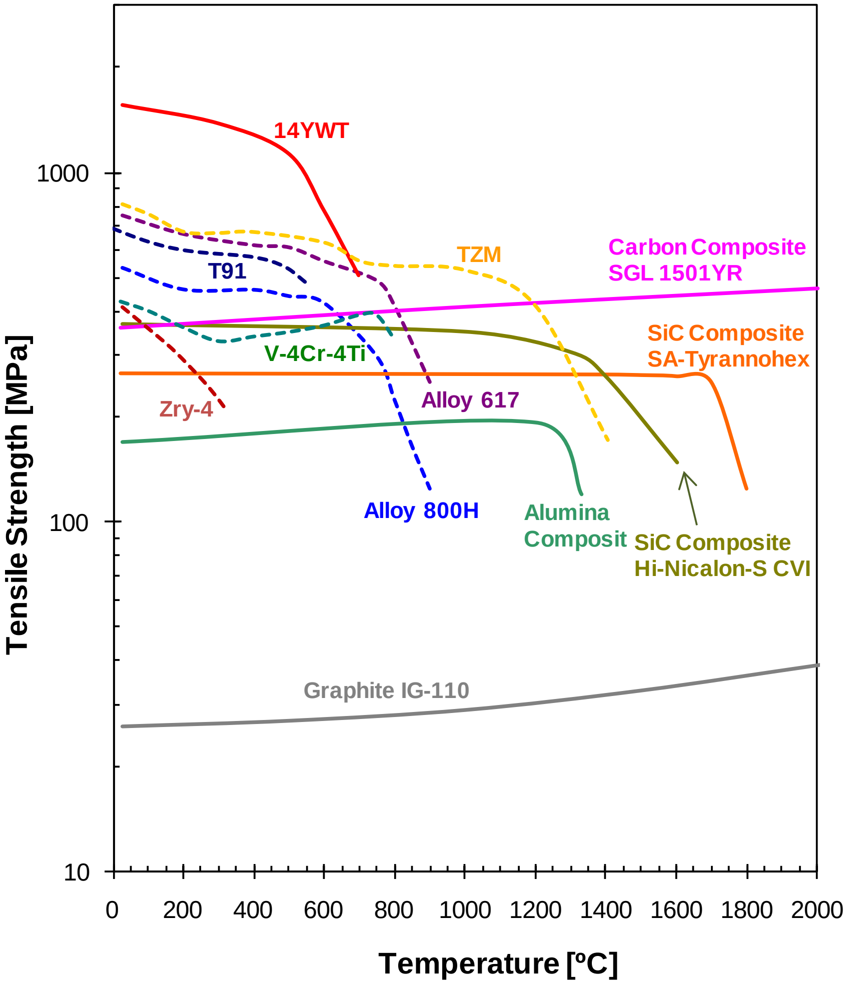
- Mechanical filtering for liquid salt treatment
  - Sintered porous nickel filters employed for MSBR program
  - Porous carbon filters are a modern alternative
  - Filters will become highly activated requiring remote handling
  - Filters will need to be assayed to assure that they have not trapped fissile materials

- Multistage off-gas treatment system
  - Decay cooling likely required for first stage

Source: PNNL-27723



Structural Composites Are an Alternative Functional Material for MSRs

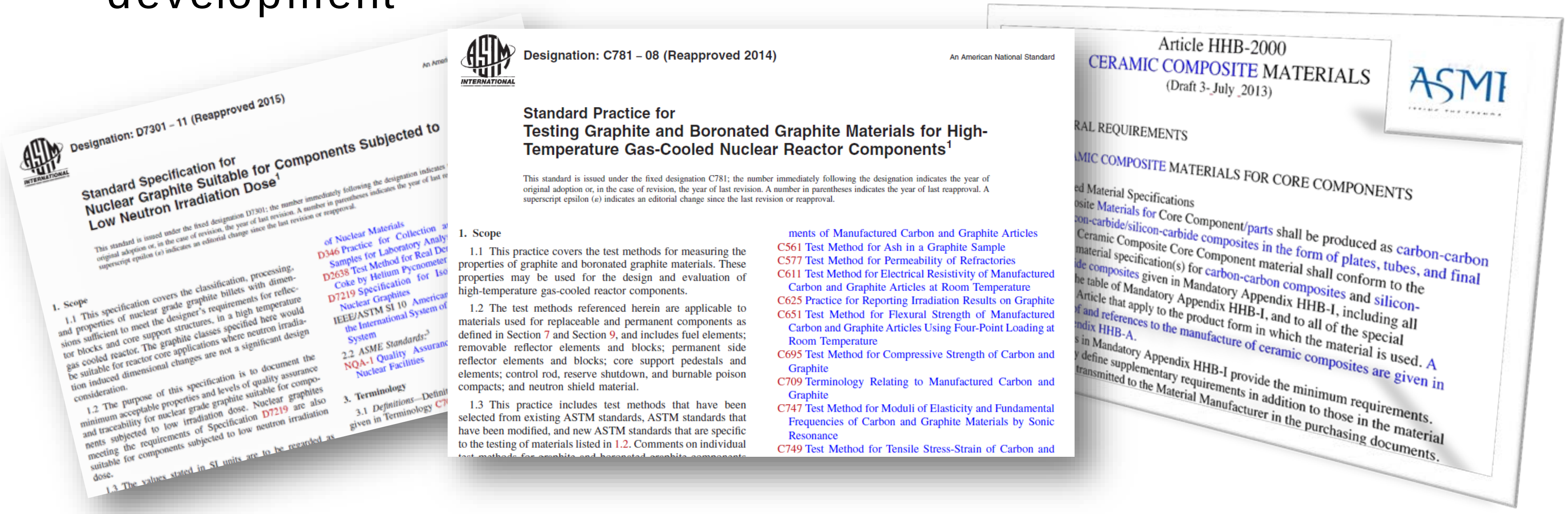


- Carbon has good chemical compatibility with both chlorides and fluorides
- Carbides have good compatibility with fluorides
- Unparalleled high temperature strength
- Practically no irradiation embrittlement
  - Limited irradiation effects for C/C (cf. heat resistant alloys); very minor, nonprogressive 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



Silicon Carbide Compatibility with Fluorides Depends on Purity and Stoichiometry

- Free silicon readily forms SiF_4
  - Radiolysis can enhance corrosion
- Uranium is a strong carbide former
  - Carbides may be stable in coolant salts, but not in fuel salts
- Binder phase oxides readily dissolve in fluoride salts

Cast & fired

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.

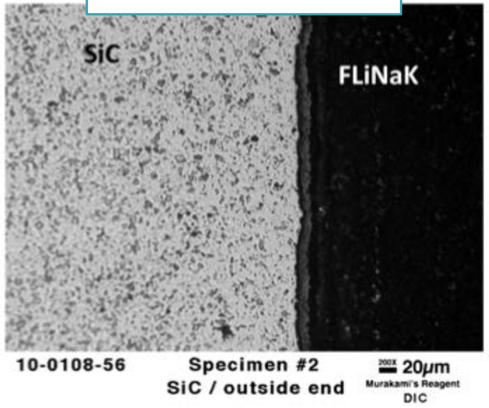
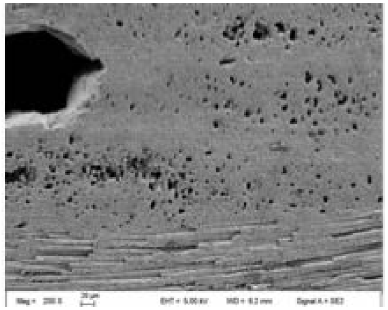
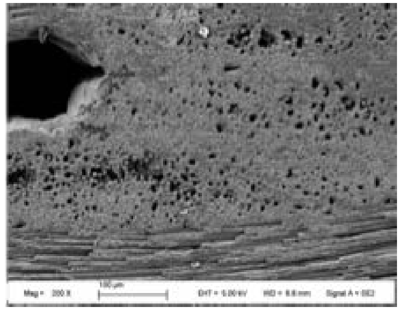
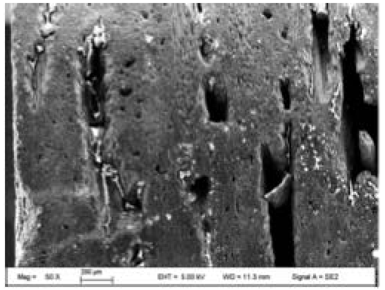


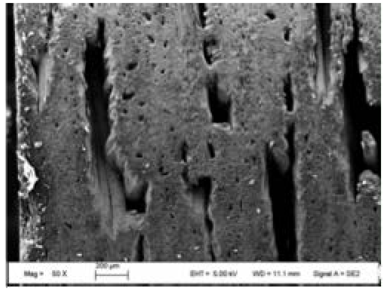
Fig. 6. SiC specimen after 90 day exposure to 700 °C FLiNaK salt.





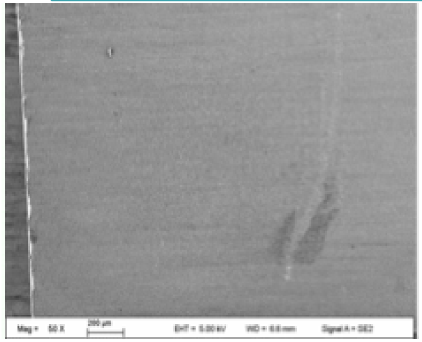
Chemical vapor infiltration SiC composites exhibit small weight loss

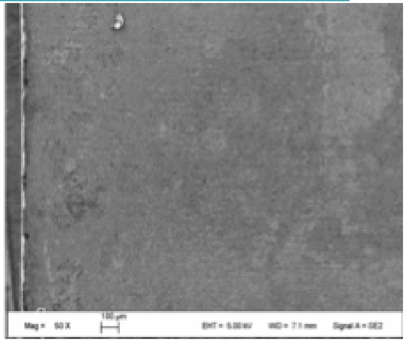




High purity SiC exhibits little corrosion

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

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