Qualification of Alloys for Structural Applications in Fluoride High Temperature Reactor *(FHR)*

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Molten Salt Reactor (MSR) Workshop,
Oak Ridge National Laboratory, ***October 3rd and 4th, 2018***

Georgia Institute of Technology

Part of an Integrated Research Project (IRP) Led by Georgia Tech -

Integrated Approach to Fluoride High Temperature Reactor (FHR) Technology and Licensing Challenges

Academia

Lead Organization: Georgia Institute of Technology, *PI: Farzad Rahnema, co-PIs: Bojan Petrovic, Anna Erickson, Srinivas Garimella, Preet M. Singh*

University of Michigan (UM), *Xiaodong Sun (Co-Pi)*

Virginia Tech (VT), *Jinsuo Zhang (Co-Pi)*

Texas A&M University (TAMU), *co-PIs:* *Pavel Tsvetkov (College Station) and Yousri Elkassabgi (Kingsville)*

Industry

Framatome, Lynchburg, VA, *Kim Stein (Co-PI)*

Southern Company Services, *Nicholas Smith*

Students supported/engaged in this FHR-IRP

Graduate students: 22

Undergraduate students: 14

Post-doctoral researchers: 3

National Laboratories

Oak Ridge National Laboratory (ORNL), *Grady Yoder (Co-PI)*

International Institutions

Politecnico di Milano, Milano, Italy; *co-PIs: Antonio Cammi, Lelio Luzzi , Marco Ricotti*

University of Zagreb, Zagreb, Croatia: *co-PIs: Davor Grgic, Nikola Cavlina, Dubravko Pevec*

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, China; *Kun Chen (Co-PI)*

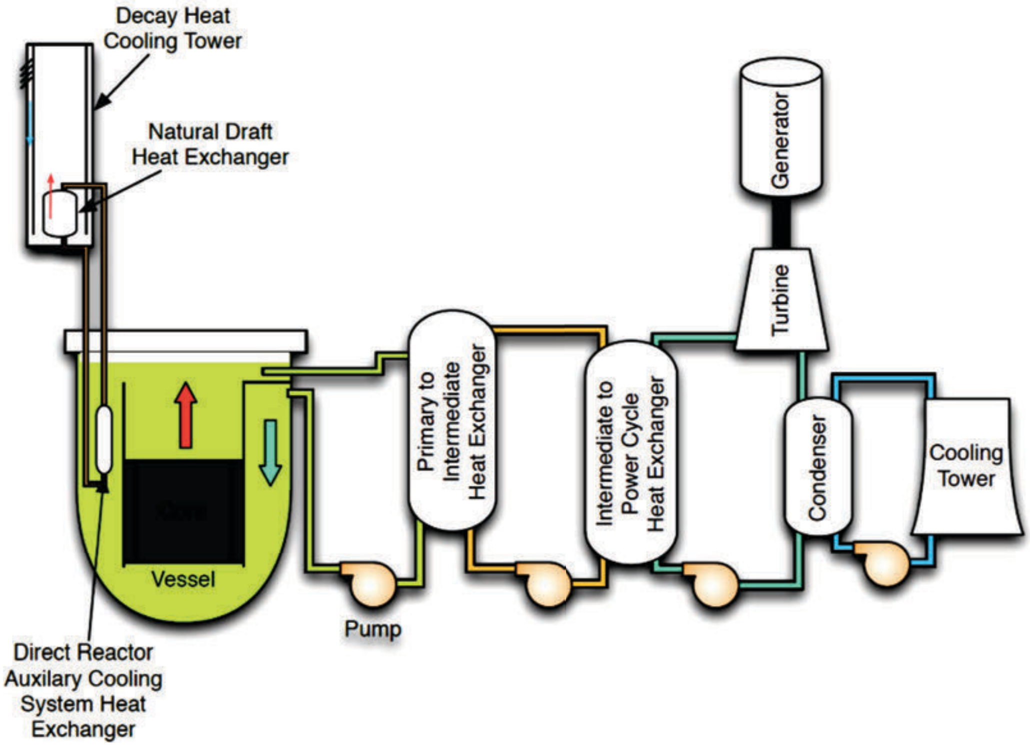
Reference Design: *ORNL AHTR Conceptual Design*

AHTR Overall Design Values*

Thermal power	3400 MW
Electrical power	1500 MW
Top plenum temperature	700 °C
Coolant return temperature	650 °C
Number of primary loops	3
Primary coolant	$2^{7}LiF\text{-}BeF_2$
Primary coolant flow rate	28,500 kg/s
Fuel type	Tri-structural isotropic particles in carbon plates
Fuel plates per assembly	18
Number of fuel assemblies	252
Uranium enrichment	9%
Refueling	2 batch, 6 month interval
Core height (fueled region)	5.5 m
Intermediate coolant salt	$KF\text{-}ZrF_4$
Intermediate salt flow rate	43,200 kg/s

***Taken from "David Holcolmb, et. al., ORNL/TM-2013/401"**

AHTR Plant Overview*



IRP Objectives

- **To address several key technology gaps associated with FHRs – These include challenges surrounding:**
  - **Verification and validation (V&V) of neutronics and thermal hydraulics modeling and simulation tools in support of licensing**
  - **Design, fabrication, testing, demonstration, and modeling of novel heat exchangers**
  - **Tritium management**
  - **Liquid salt coolant impurity removal and redox and corrosion control**
  - **Qualification of alloys for structural applications**
  - **Advanced instrumentation under extreme conditions**
- **Close these gaps to reduce technical uncertainties, facilitating commercialization of FHRs**

Motivation for corrosion study

- **To develop an understanding of corrosion mechanisms**
  - **Enable us to accurately predict the equipment service length**
  - **Prevent unexpected failures**
- **Optimum materials selection**
- **Determining maintenance requirements and service life**

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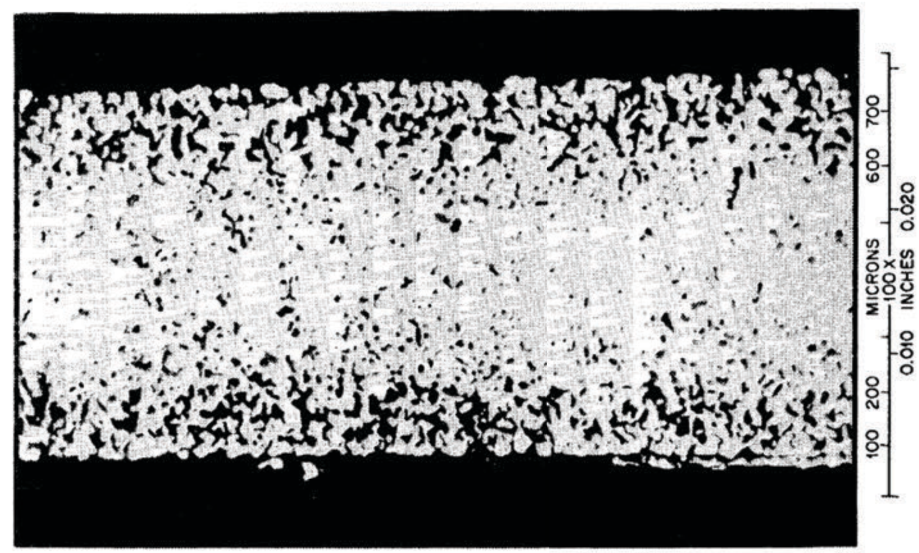


Fig. 6. Type 304L Stainless Steel Specimen from Loop 1258 Exposed to $LiF-BeF_2-ZrF_4-ThF_4-UF_4$ (70-23-5-1-1 mole %) for 45,724 hr at 685°C.

304L tested in flow-loop for ~5.2 Years at 685^oC

Keiser et al. "The Corrosion Resistance of Type 316 Stainless Steel to Li_2BeF_4", ORNL/TM-5782 (1977)

Qualification of Alloys for Structural Applications

- ***Corrosion resistance of alloys in Molten FLiNaK and FLiBe***
- ***Effect of molten salt impurities and redox conditions on corrosion of alloys***
- ***Effect of flow on corrosion behavior of alloys –*** *Coordinated with ORNL team*
- ***Performance of commercial grade SiC and CFC***

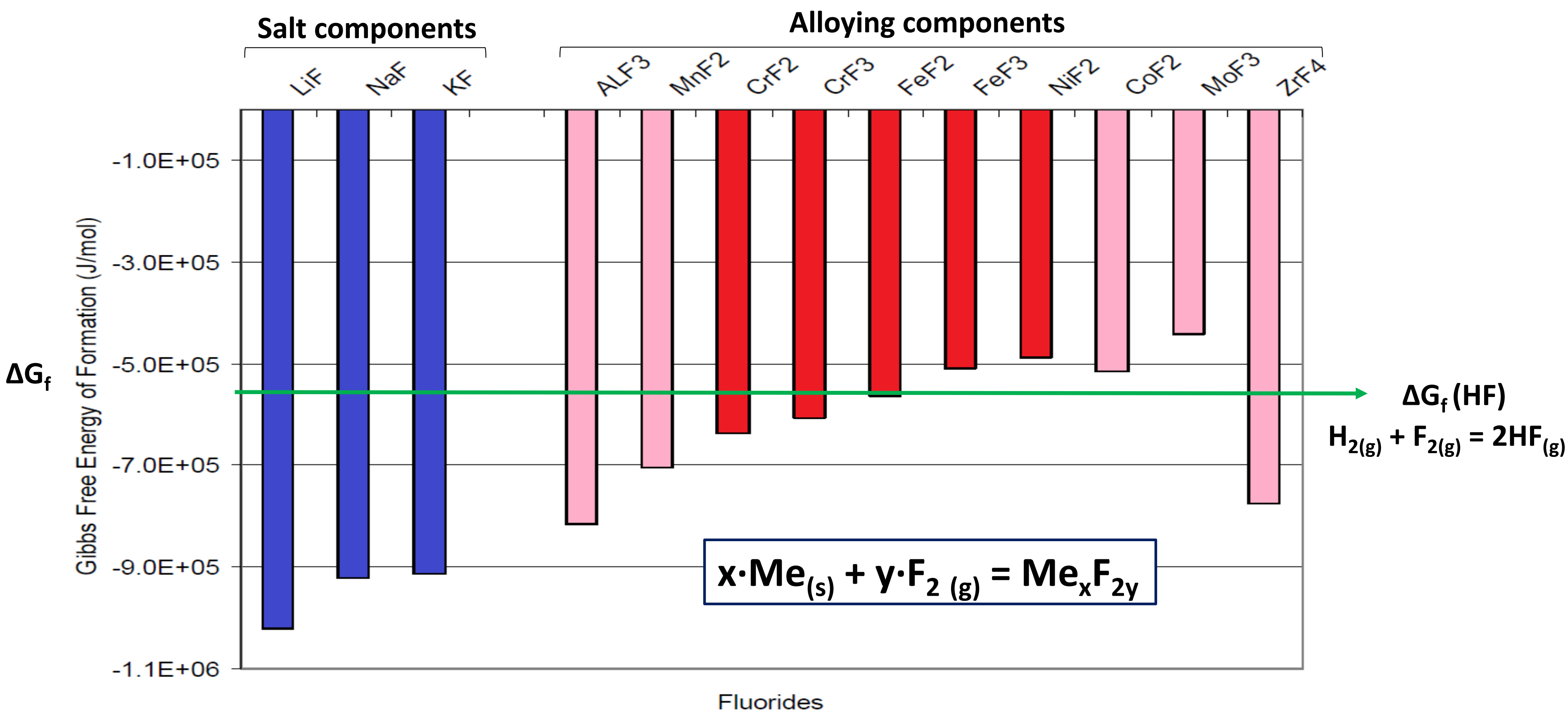
Project Activities - *Done*

- **Effect of Alloy Composition**
- **Effect of Salt Purity**
  - **Effect of Added Impurities**
    - ***Water***
    - ***Metal Fluorides (NiF_2)***
    - ***Effect of Salt Volume***
- **Effect of Pre-Oxidation Treatment on Corrosion**
  - **Performance of "oxide-forming" alloys**
- **Electrochemical behavior of alloys in molten salts**
  - **Dynamic Reference Electrode**
  - **Electrochemical Tests with Pseudo-Reference Electrode**
    - ***Potentiodynamic Polarization***
- ***FHR Material-PIRT Exercise – report issued***

On-going Research Activities – *cont.*

- **Corrosion of Alloys in Purified Salts – *Tests at ORNL***
  - ***In purified FLiNaK LSTL test-loop at ORNL***
  - ***In purified FLiBe – capsule tests***
- **Degradation of SiC in FLiNaK**
- **Role of Graphite on Metallic Corrosion in Molten FLiNaK**
- **Electrochemical behavior of alloys in molten salts**
  - **Ni/NiF_2 Reference Electrode for Molten FLiNaK**
    - **Redox of salts as a function of impurities**
    - **Potentiodynamic Polarization, EIS**
- **FLiNaK Purification for Corrosion Tests**
  - **Using ammonium bifluoride (NH_4HF_2)**

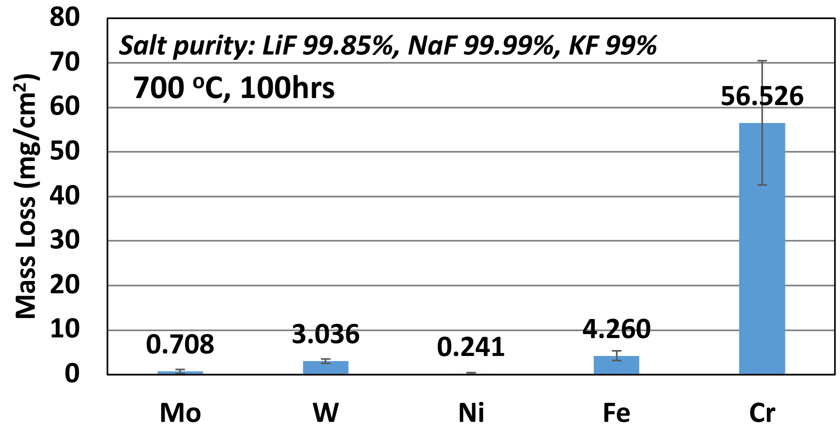
Thermodynamic driving force as a predictor of corrosion in molten fluorides



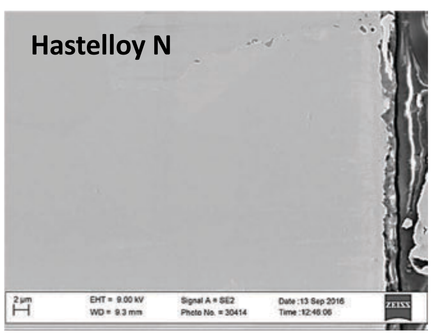
Adapted from L.C. Olson, Ph.D. dissertation, University of Wisconsin-Madison (2009)

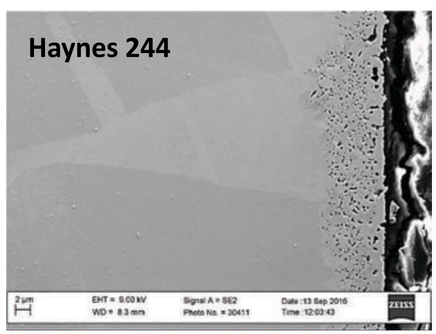
Corrosion of Pure Metals and Alloys in Molten FLiNaK

Corrosion of Pure Metals

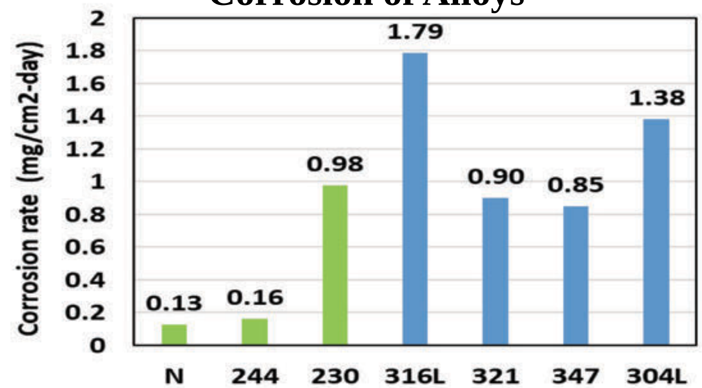


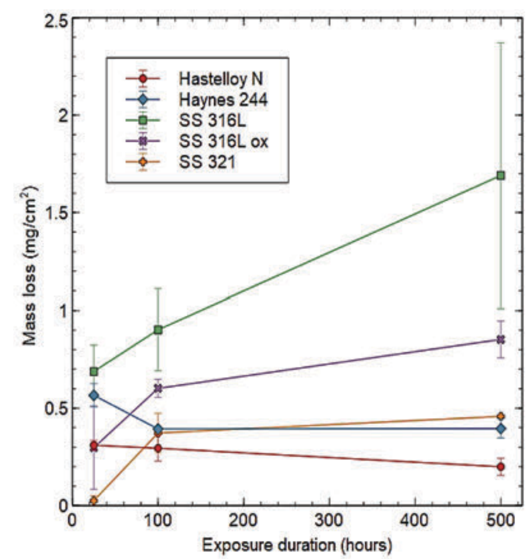
ΔG$_f$ (kcal/mol F)	MoF_3	WF_4	NiF_2	FeF_2	CrF_2
	-54.9	-58.0	-60.4	-69.4	-78.1





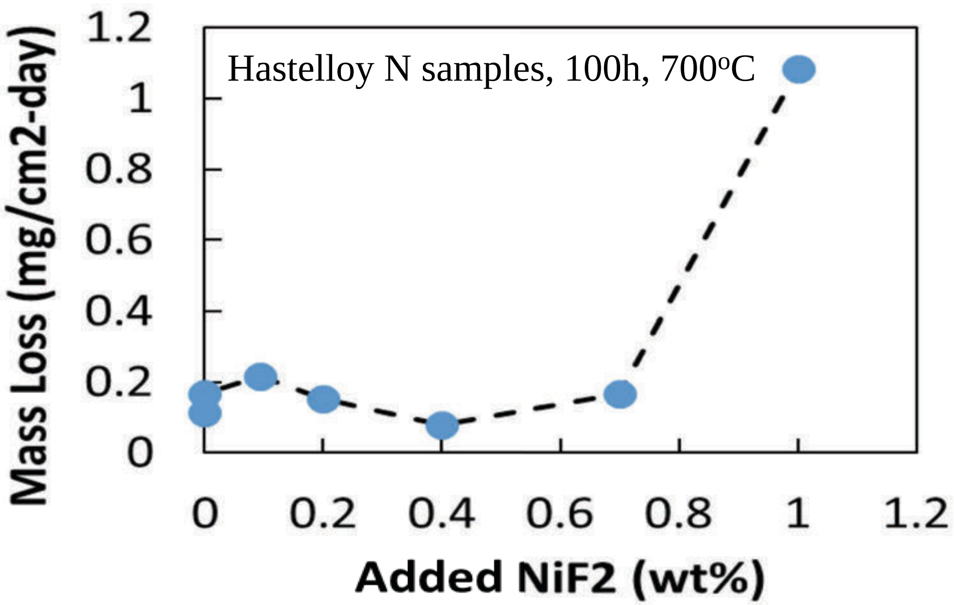
Corrosion of Alloys

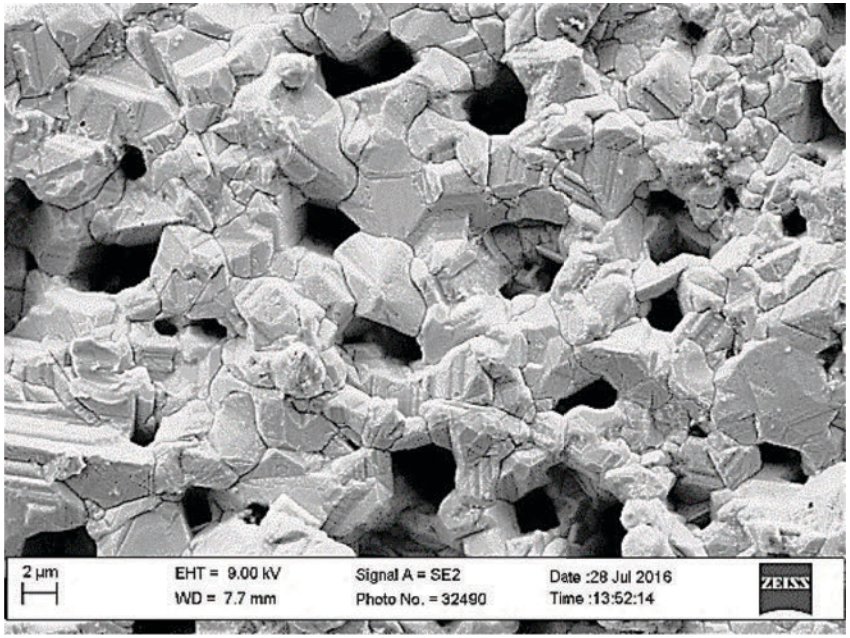




Effect of Impurities – *Metal Fluorides*

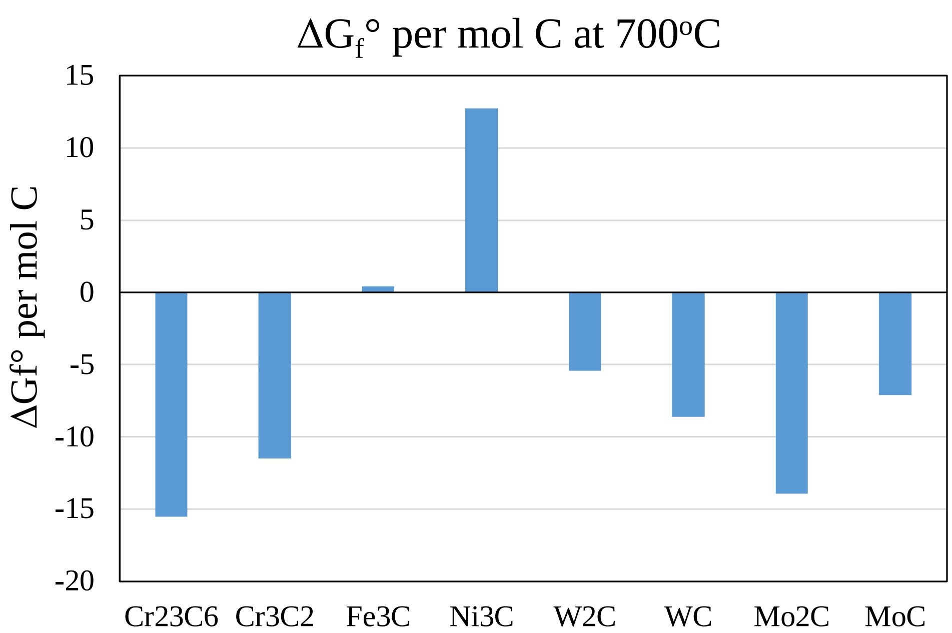
- **Metal Fluoride Impurities**
  - **NiF_2 impurity experiment**
    - **0.1%wt and 1%wt NiF_2 in FLiNaK added prior to exposure.**





Intergranular Attack on Hastelloy N Surface - *after 100 hour Exposure in FLiNaK with NiF_2 Impurities*

Effects of Carbon *(Graphite)* on Corrosion in a FHRs

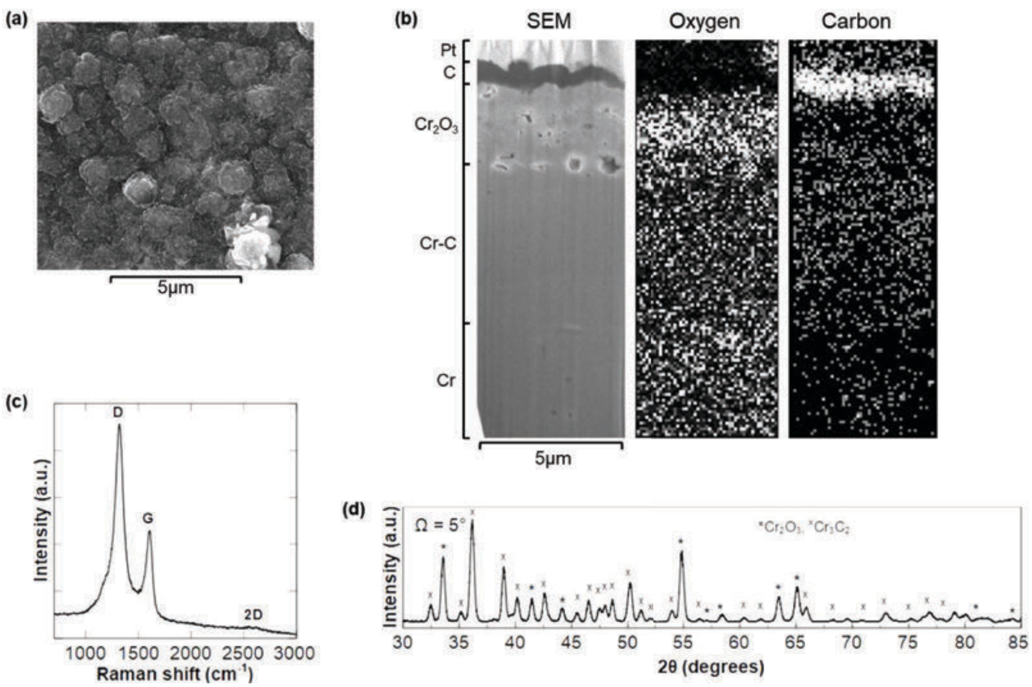


Gibbs free energies of formation for metal carbides at 700°C, *calculated per mole C*

- **In FHRs, structural alloys and graphite will be in contact with molten fluoride**
  - **Alloy-graphite interaction is expected – *metal carbides are formed***
  - **Unless alloys are in contact with graphite, transport of the metal or carbon through the salt is required for metal carbide formation**
- **The stability of the carbides of alloying elements augments their corrosion**
- **However the same tendency can be useful if a continuous layer of stable carbides is formed to reduce corrosion in molten fluoride salts.**

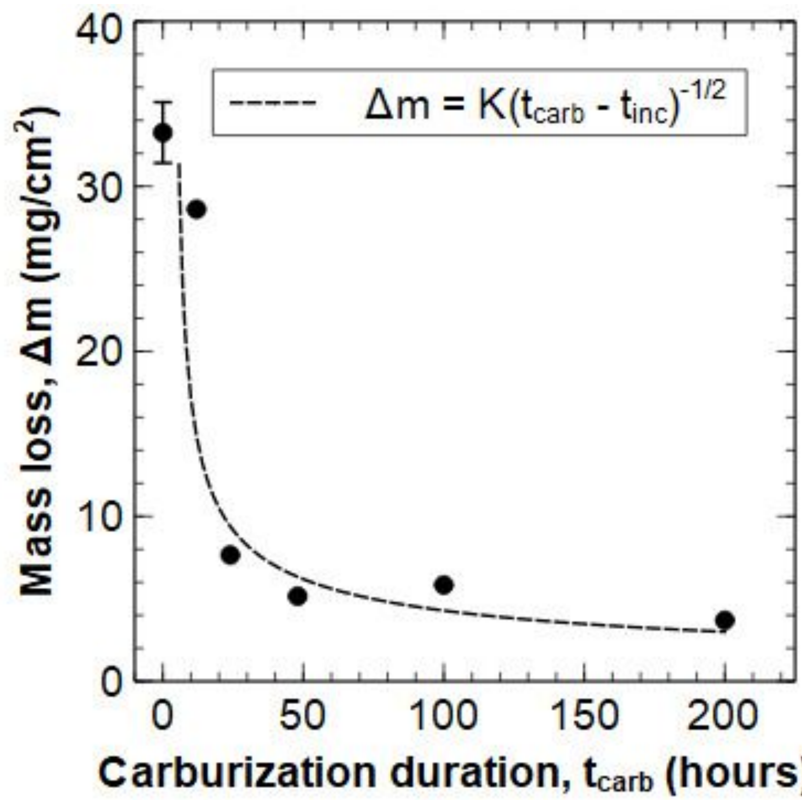
Carburization of Pure Chromium

- **Pure Cr Substrate**
- **200h @ 800°C**
- **116 SCCM H_2 + 84 SCCM C_3H_4**



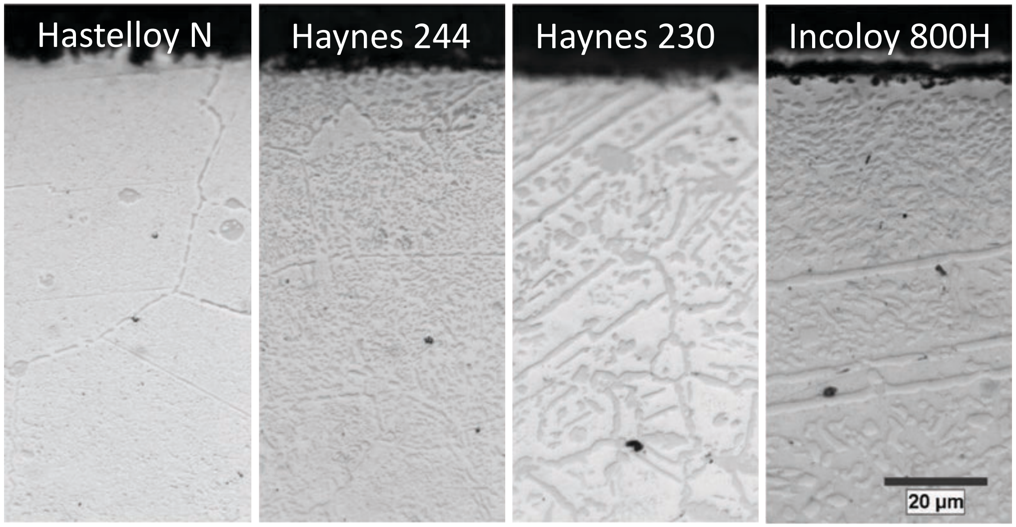
A Dense Layer of *Chromium Carbide* was Generated at the Surface of Pure Cr Samples

Corrosion Tests in FLiNaK at 700 °C for 100 hrs



Effect of Pre-carburization on corrosion of Ni-based alloys

- **Alloys:** Haynes 230, Incoloy 800H, *Hastelloy N, Haynes 244*
- **Sample sets:**
  - (1) carburized only
  - (2) carburized & exposed
  - (3) exposed only
- **Carburization conditions:**
  - 200 hours @ 900°C
  - 116 SCCM H_2, 84 SCCM C_3H_8
- **Salt:** FLiNaK *(LiF-NaF-KF, 46.5-11.5-42 mol%)*
- **Exposure Conditions:**
  - 100 hours @ 700°C
  - Graphite crucibles (<5ppm ash, baked 8h @ 900C under Ar-4%H_2).
  - Ar atmosphere (<2ppm O_2,<1ppm H_2O)

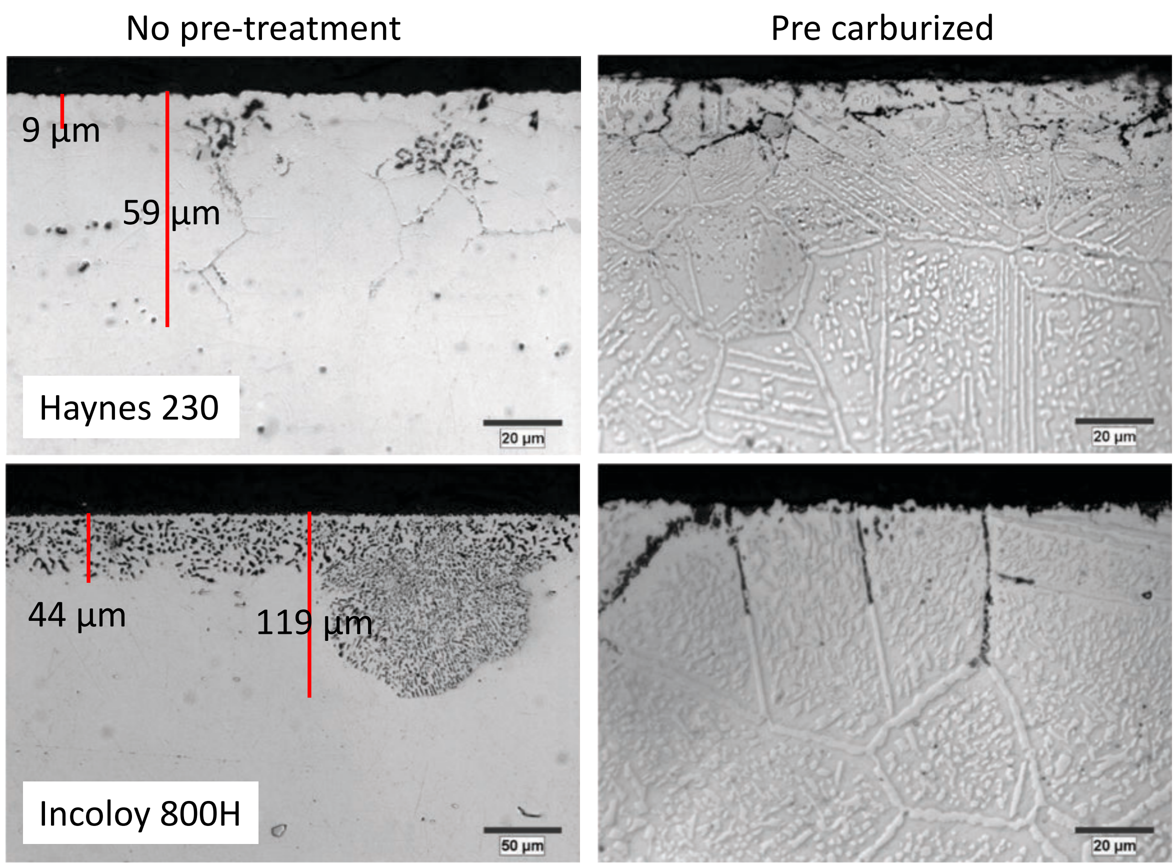


Post-carburization microstructure

Effect of Pre-carburization on corrosion of Ni-based alloys

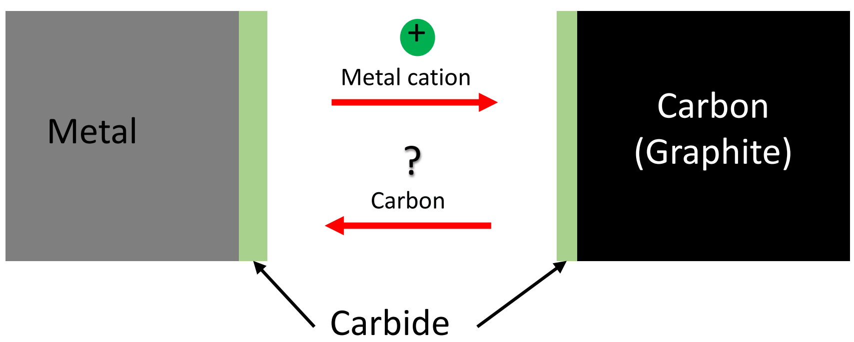
Alloy	Corrosion Attack Depth (μm)			
	No pre-treatment		Pre-carburized	
	GB	*Matrix*	*GB*	*Matrix*
Hast. N	NM	NM	NM	NM
Hay. 244	90	30	NM	NM
Hay. 230	59	25	20	NM
IN 800H	NM	119	40	NM

NM – No Measurable Attack



Carbon transport mechanism from graphite to metal

Unless alloys are in contact with graphite, transport of the metal or carbon through the salt is required for carbide formation

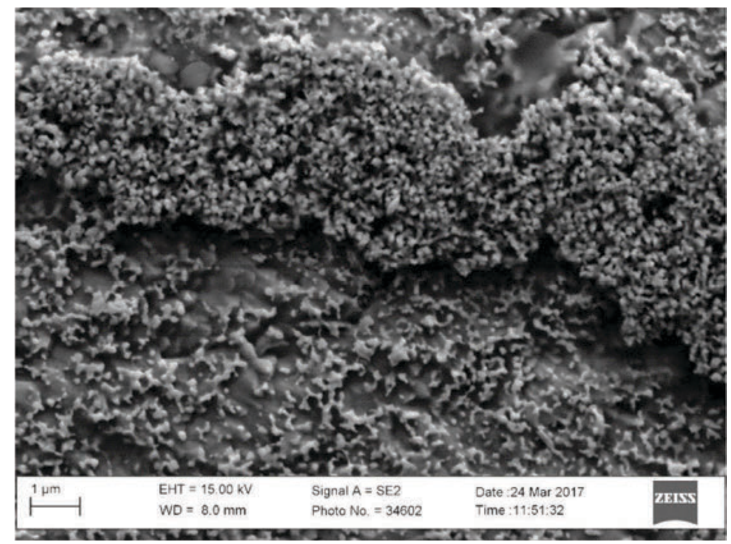


Elemental carbon is not soluble in molten fluoride, so how does carbon travel from graphite to metal?

1) Physical mechanism: *Suspended graphite particles*

2) Chemical mechanism: *Dissolved carbon-bearing ion*

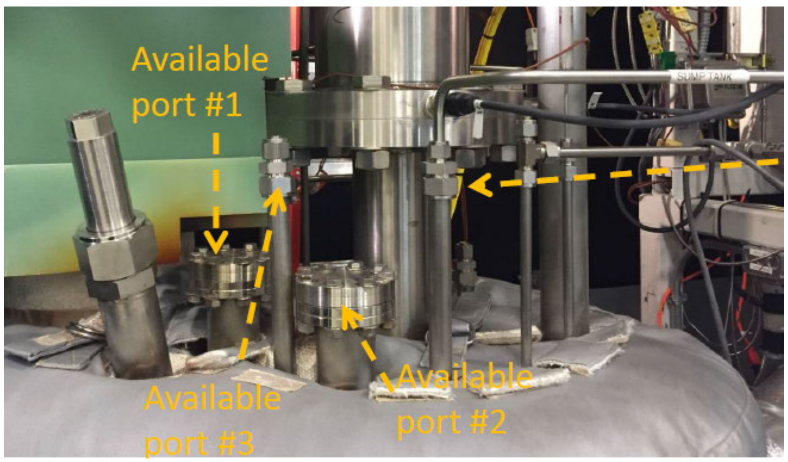
K.J. Chan et al. *Annals of Nuclear Energy* (2018)



Carbon film on W sample after FLiNaK exposure in presence of graphite.

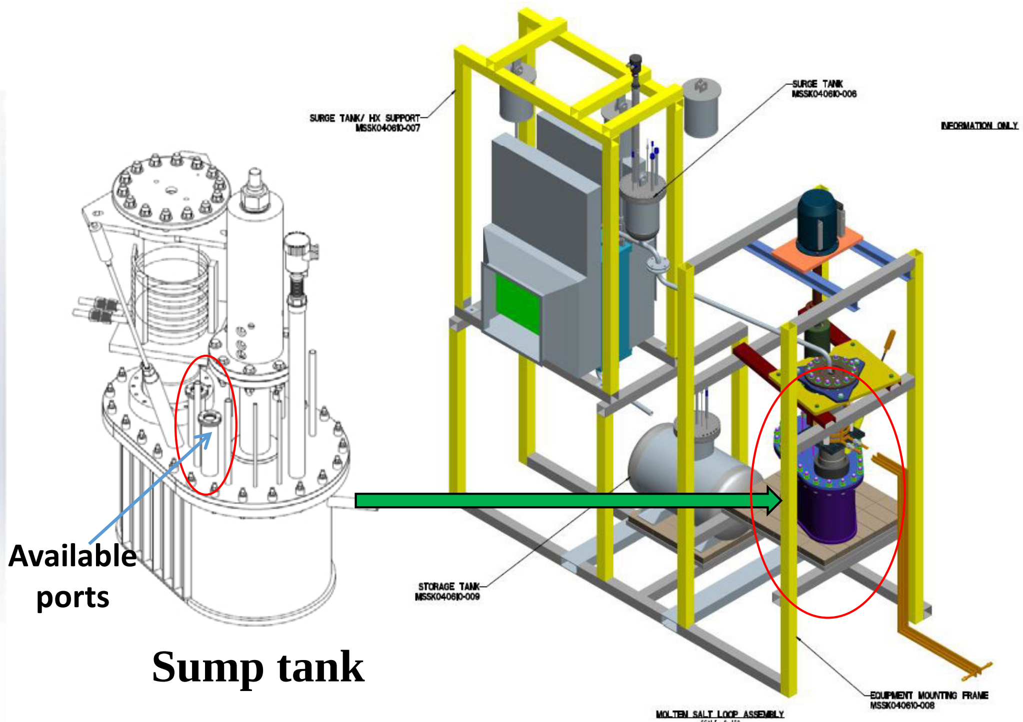
Tests in LSTL at ORNL – *To Study Flow Effects on corrosion*

- **Liquid Salt Test Loop (LSTL) @ ORNL**
  - Elvis Domingues-Ontiveros/Grady Yoder
  - Kevin Robb and Jim Keiser
- **Purified FLiNaK @ 650-700°C**
- **Location: Sump tank**
  - **2” tube port (1.87” ID)**



picture taken by Elvis Dominguez-Ontiveros

Corrosion Test Rack for LSTL



Liquid Salt Test Loop (LSTL)

Corrosion Test Samples were Placed in *ORNL-LSTL* on 9/21/18

PC: Kevin Robb

- 316L SS
- 321 SS
- Ni 200
- Hastelloy N
- Haynes 244
- Inconel 600
- Inconel 625
- Inconel 625 (pre-carburized)

FHR Material-PIRT

- **FHR Materials PIRT panel meeting was held at Georgia Tech on November 28th to 30th, 2016**

•**Panelists:**

- •David Diamond (BNL, Facilitator)
- •Preet M. Singh (Georgia Tech)
- •Grayon Yoder (ORNL)
- •Weiju Ren (ORNL)
- •Vinay Deodeshmukh (Haynes Int.)
- •Jinsuo Zhang (Ohio State Univ.)
- •Jim Keiser (ORNL)
- •Dane Wilson (Thorcon Power)
- •Sam Sham (ANL)
- •William Corwin (DOE, Nuclear Energy) (WebEx)
- •Chaitanya Deo (Georgia Tech

•**Students:**

- •Kevin Chan (Georgia Tech), Rebecca Ambrecht

Final report was issued and posted on SMARTech on April 15, 2017

https://smartech.gatech.edu/bitstream/handle/1853/56668/fhr-materials_pirt_report-final-4-16-2017.pdf?sequence=1&isAllowed=y

"Phenomena Identification and Ranking Tables (PIRTs) Report for Material Selection and Possible Material Degradation Mechanisms in FHR"

Summary Paper in *Annals of Nuclear Energy*

Preet M. Singh, Kevin J. Chan, Chaitanya S. Deo, Vinay Deodeshmukh, James R. Keiser, Weiju Ren, T.L. Sham, Dane F. Wilson, Graydon Yoder, Jinsuo Zhang, Phenomena Identification and Ranking Table (PIRT) study for metallic structural materials for advanced High-Temperature reactor, *Annals of Nuclear Energy 123 (2019) 222–229*, https://doi.org/10.1016/j.anucene.2018.08.036

Material Degradation - *Categories*

- **Chemical Degradation**
- **Microstructural Change *(Thermal Aging)***
- **Mechanical Property Degradation**
- **Radiation**
- **Synergistic Effects**

Chemical Degradation Mechanisms

- **Temperature-Gradient Driven Corrosion/deposition**
- **Galvanic Corrosion**
- **Selective Dissolution**
- **Intergranular Corrosion**
- **Flow Accelerated Corrosion (isothermal)**
- **High Temperature Oxidation**
- **Hydrogen (Tritium) Related Degradation**
  - **Hydride formation - embrittlement**
  - ***Interstitial hydrogen related embrittlement (Solid solution hardening)***
  - ***Accumulation of Hydrogen in voids, leading to blistering***
- **Impurity effects**
  - **Fission products**
  - **Tritium Fluoride (TF)**
- **Fluorine attack under solidification conditions**

Mechanical / Thermal Degradation Mechanisms

- **Thermal Aging [Microstructural Changes at Operating temperature]**
  - Decrease in strength and ductility at higher temperatures (function of time, temperature, and stress)
  - Decrease in impact strength
- **Creep**
- **Fatigue**
  - **Low cycle mechanical fatigue (LCF)**
  - **Thermal fatigue**
- **Creep-Fatigue**
- **Erosion/Wear**
- **Crack Growth**
- **Stress relaxation cracking (SRC)**
- ***Inter-diffusion in Cladding Materials***
- ***Delamination of Cladding Materials***

Components and Materials Considered

- **Vessel and Primary Piping** ***(700^{o}C steady state, up to 760^{o}C transient; 40-60 years; ??? stress level)***
  - **800-H Alloy with Ni cladding**
  - **800 H Alloy with Alloy-N cladding**
  - **IN 617 with Ni cladding**
  - **316H with Ni cladding**
  - **Alloy-N**
  - **Alloy-N variants (existing commercial alloys and new alloys)**
- **Core Barrel** ***(700^{o}C steady state, up to 760^{o}C transient; 40-60 years; ??? stress level, ??? DPA, ??? fabrication method)***
  - **C-C**
  - **SiC-SiC**
- **Primary Heat Exchanger** ***(700^{o}C steady state, up to 760^{o}C transient; 40-60 years; ??? stress level; replaceable)***
  - **Alloy-N**
  - **Alloy-N variants (existing commercial alloys and new alloys)**
- **DRACS** ***(700^{o}C steady state, up to 760^{o}C transient; 40-60 years; ??? stress level)***
  - **Alloy-N**
  - **Alloy-N variants (existing commercial alloys and new alloys)**
- **Pump/Valves** ***(700^{o}C steady state, up to 760^{o}C transient; 40-60 years; ??? stress level; wear resistance)***
  - **Alloy-N**
  - **Alloy-N variants (existing commercial alloys and new alloys)**
  - **Boron Nitride (seals)**
  - **SiC (seals)**

Materials Considered – Cont.

- **Bearings- Non-salt contact**
- **Seals Non-salt contact**
  - **Commercially available metallic seals**
- **Welds**
  - **All Metallic Materials**
- **Intermediate Salt Loop Piping** ***(<=675^{o}C steady state, up to 735^{o}C transient; 40-60 years; ??? stress level)***
  - **Alloy-N**
  - **Alloy-N variants (existing commercial alloys and new alloys)**
- **Steam Generator tubes** ***(650^{o}C steady state, up to 715^{o}C transient; 40-60 years; 24MPa)***
  - **Alloy 800-H with Alloy-N cladding inside**
- **Steam Generator vessel** ***(650^{o}C steady state, up to 715^{o}C transient; 40-60 years; 24MPa)***
  - **Alloy 800-H**
- **Control Rod** ***(700^{o}C steady state, up to 760^{o}C transient; 40-60 years; ??? stress level, ??? DPA)***
  - **Molybdenum-hafnium-carbon (MHC)**

Example –*Vessel and Primary Piping - (Alloy 800-H with Ni-Cladding)*

Component: Vessel and Primary Piping					
Environment: 700C steady state, up to 760C transient; 40-60 years; stress levels will vary; 10^20 n/cm^2					
Material: Alloy 800-H with Ni cladding			Comment:		
Phenomenon	**Importance Score (Final)**	**Comments**	**Knowledge Level**	**Comments**	**Path Forward**
Chemical Degradation Mechanisms					
Temperature-Gradient Driven Corrosion/deposition	L	Higher impurity levels will exacerbate this phenomenon. Thickness dependent (interdiffusion)			
Galvanic Corrosion	L				
Localized Selective Dissolution	L				
Intergranular Corrosion	L	Thickness and interdiffusion dependent.			
Flow Accelerated Corrosion	L				
High Temperature Oxidation	M	Outside surface	K		
Hydrogen (Tritium) Related Degradation [Hydride formation - embrittlement]	L				
Impurity effect [Fission products, Tritium Fluoride (TF)]	L	Assuming redox control			
Fluorine attack under solidification conditions	L	No solidification expected			
Cladding Interdiffusion	H	Thickness dependent	P		Literature search for interdiffusion data and identify known interdiffusion models. Need validation experiments for different process conditions and temperatures.
Cladding Delamination	H	Dependent on fabrication process and QC	P		Literature search, and get information from Sandvik, Special Metals, WSI welding services, Sumitomo, and Klad. Also look at work from LANL, ORNL, UNLV, Univ. of Florida, and MIT. Review ASTM specification. Review in service examination methods [changes in microstructure over time or radiation effects]. Develop experimental techniques for this material.

PIRT-Panel identified following as important areas in metallic material degradation in FHR environments and its control

- **Impurity control and property measurement are very important**
- **Electrochemical measurement techniques must be created/recreated for molten fluoride environment.**
- **Chemical measurement methods of low level impurities must be developed.**
- **Correlations between low level impurity content and corrosion must be created.**
- **Chemical form of fission products in the salt environment must be determined. Fission products may not only exist as fluorides.**
- **Need to determine salt impurity level at startup of reactor.**

Thanks