Plasma-Based Surface Modification and Corrosion in High Temperature Environments

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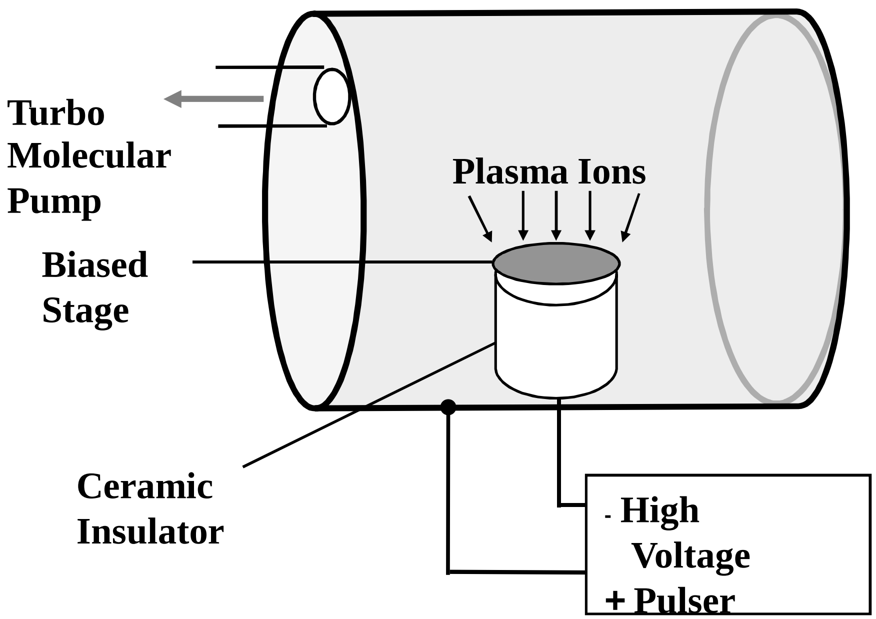
Corrosion research at the University of Wisconsin, Madison

- Plasma Immersion Ion Implantation and Deposition (PIIID), a non-line-of-sight surface treatment technology for improving wear and corrosion resistance of materials
- High temperature corrosion studies in harsh environments aimed at future nuclear reactors; materials corrosion research applicable to DoD applications

Plasma Immersion Ion Implantation and Deposition (PIIID)

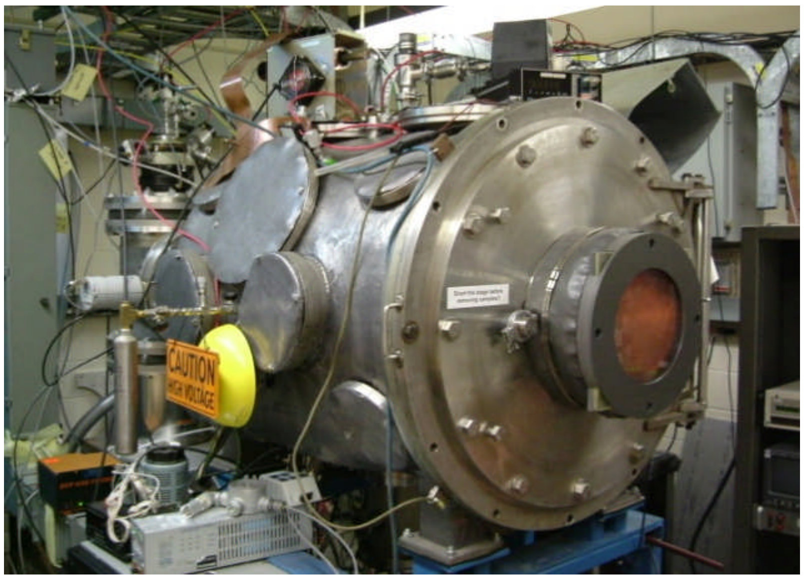


- Vacuum chamber pumped down to 10^{-6} Torr using roughing and turbo pumps
- Gas containing surface modification species introduced
- Gas ionized to create a plasma
- Sample stage pulse biased to high negative potential
- Positive ions in the plasma accelerated to sample materials' surface at high velocities to change properties

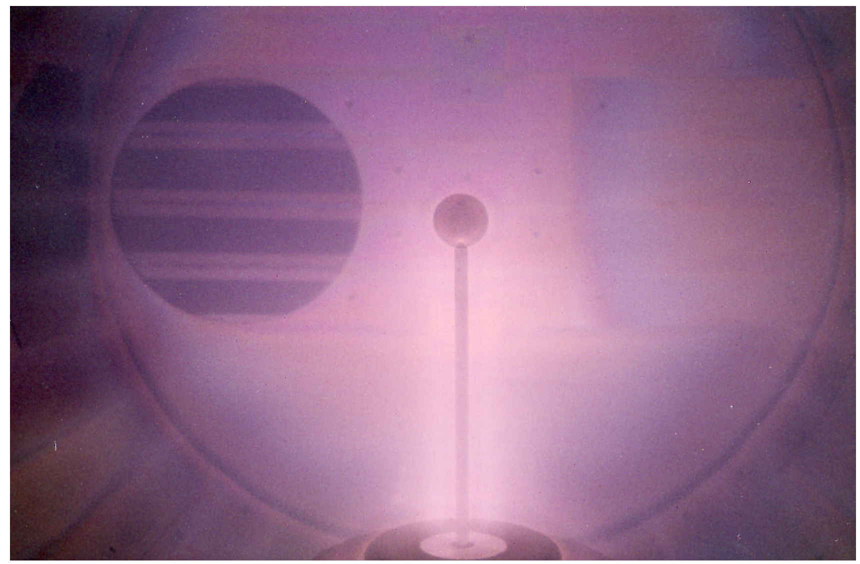
Types of PIIID surface treatments

- Ion implantation of species from gaseous precursors (~50kV, N,O, Ar, C etc.)
- Coating deposition (e.g., wear-resistant, hydrophobic coatings such as diamond-like carbon (DLC) and Si-DLC, performed at < 5kV)
- Energetic ion mixing of thin nano-multilayers
- Enhancing coating-substrate adhesion by ion implantation prior to deposition
- Materials removal (e.g. environmentally benign plasma cleaning)
- Cross-linking thin polymer coatings for mechanical strength

PIIID process system and picture of a nitrogen plasma

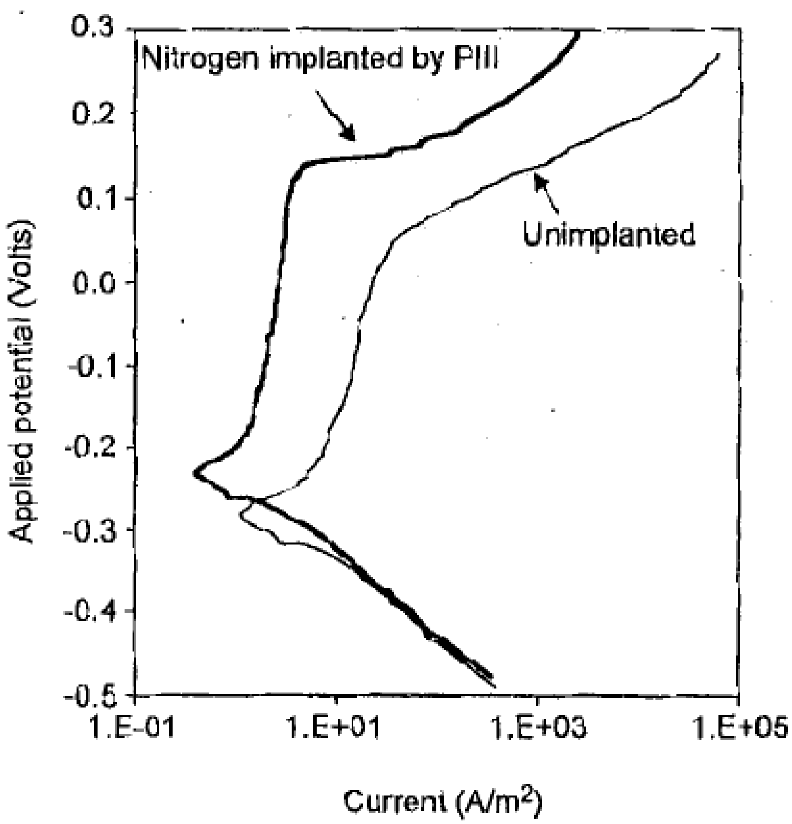


~ 2.5’ diameter x 3’ length



Nitrogen plasma

Nitrogen ion implantation of 17-7PH stainless steel (with Alison Gas Turbines)

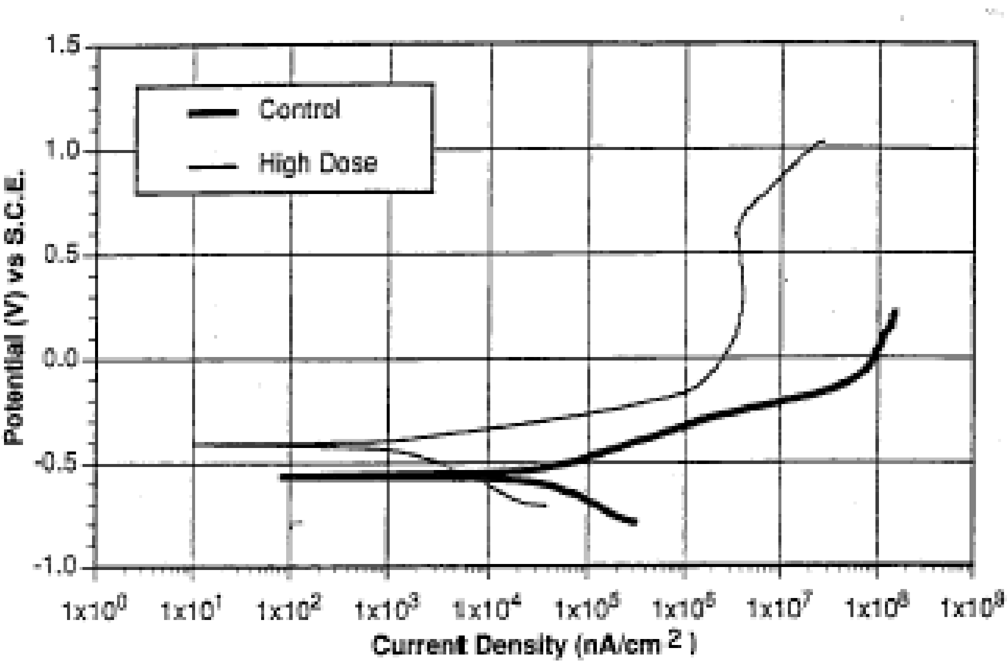


Corrosion testing in 3.5% NaCl solution; lower corrosion current and higher pitting potential

Also a 11% decrease in erosion rate for the N^+ implanted sample (compared to the as-received sample) under an accelerated test 90 mesh alumina powder at 20psi at 30º incidence

Corrosion and erosion tests performed at Alison Gas Turbines, IN

Nitrogen ion implantation of Cr-plating (in collaboration with Rock Island Arsenal, IL)



Improvement in wear resistance was also observed in pin-on-disk wear tests due the formation of hard CrN phase

Corrosion testing in 3.5% NaCl solution; lower corrosion current due to the formation of CrN

PIIID surface modification for gyroscope bearings for Navy (with Kearfott Guidance & Navigation)

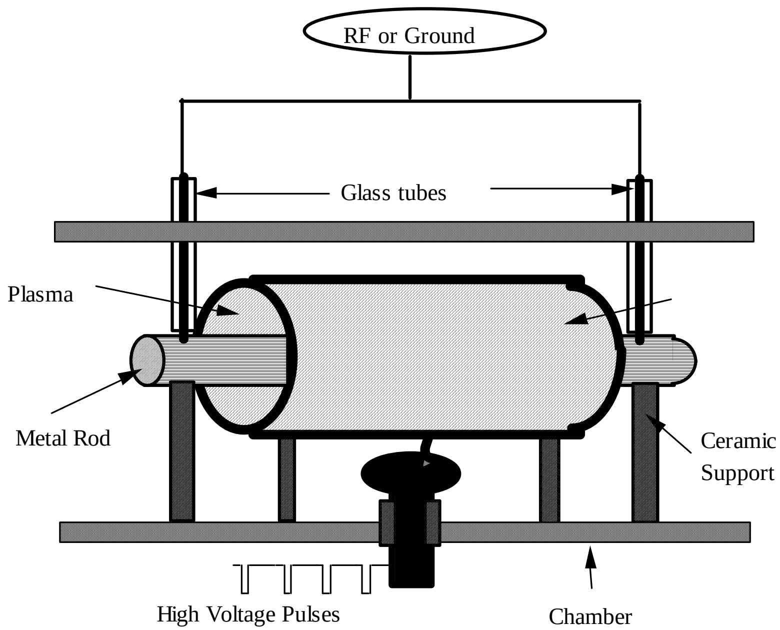
Bearings (~ 3mm dia.) made of AISI 52100 Bearing Steel

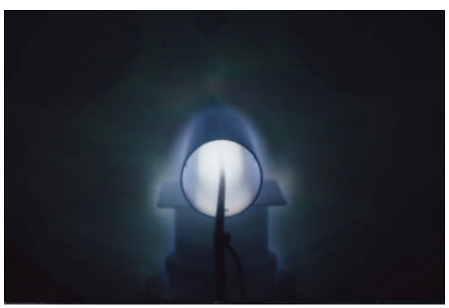
Goal to improve wear and rust resistance

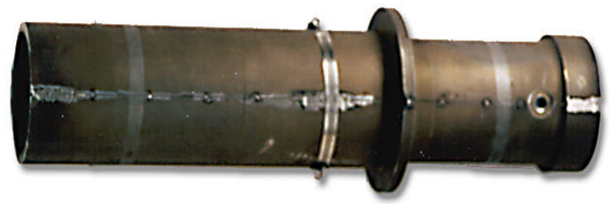
Carbon ion implantation with methane plasma: SIMS and Auger depth of surface modification: ~120nm

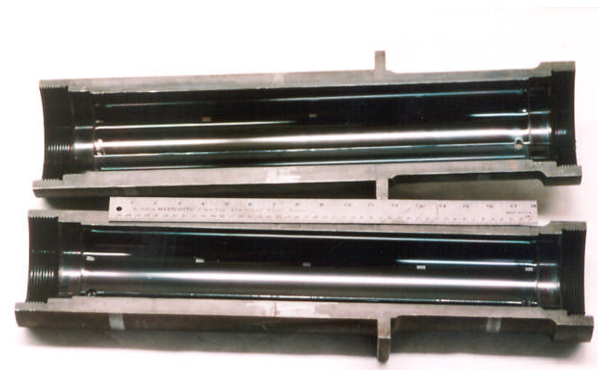
Test	Untreated 52100 steel	C^+ implanted
Wear scar after 4-ball wear test (0.65 max Mil. req.) (ASTM-D-4172)	0.69mm	0.32mm
Humidity test 14 day/90F/75 %RH	Rust observed (SEM 200x)	No rust

Deposition of coatings inside of tubes to reduce wear and oxidation (with Rock Island Arsenal, IL)









Diamond-like carbon (DLC) coating deposited on the inside surface of a cylinder (3.5” ID x 18” L) using acetylene plasma

High temperature corrosion: Supercritical Water

Supercritical water:

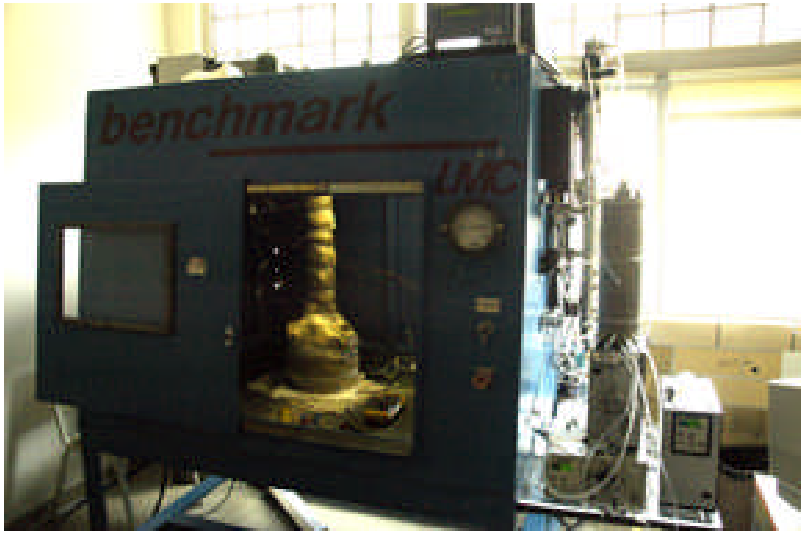
- Water at temperatures greater than 374^{o}C <u>and</u> pressures greater than ~ 3600psi

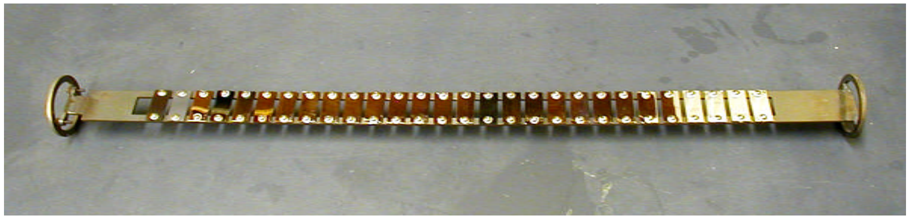
- Being considered for coolant for nuclear reactors and has been used in fossil fuel power plants for decades

- Very corrosive

- Has been investigated by the Army for toxic waste disposal [Dr. Robert Shaw, U.S. Army (retd.) will give a talk on this topic at the March 2009 NACE conference]

University of Wisconsin supercritical water corrosion testing system





Temperatures: Up to 600^{o}C

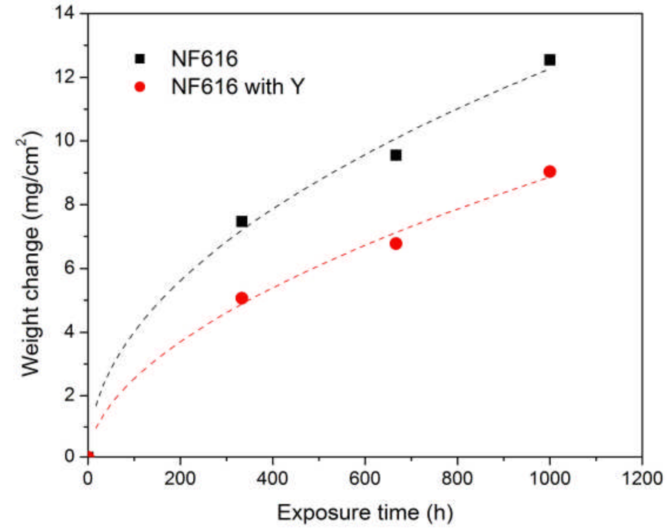
Exposure times: Up to 3000 hours (~ 4 months)

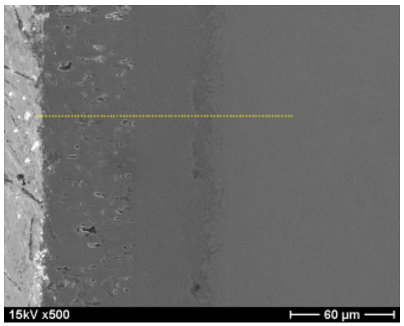
Sample Dimensions: 1.25" length, 0.5" wide and ~0.02" thick

Alloys studied include a wide range of high temperature ferritic and austenitic steels and superalloys (625, 718 etc.)

Novel Approaches – Surface Treatments
600ºC SCW exposure (NF 616 9% Cr ferritic steel)

Yttrium surface treatment reduces the thickness of the oxide layer formed on ferritic steel

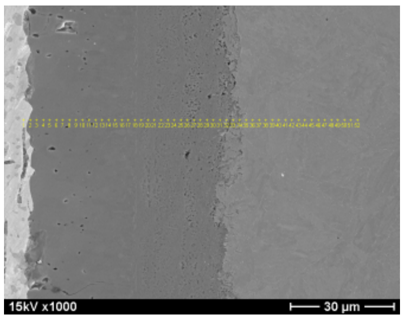




96 µm

NF616 after 6 weeks in 600ºC SCW (taken at 500x)

~ 44% Improvement



53 µm

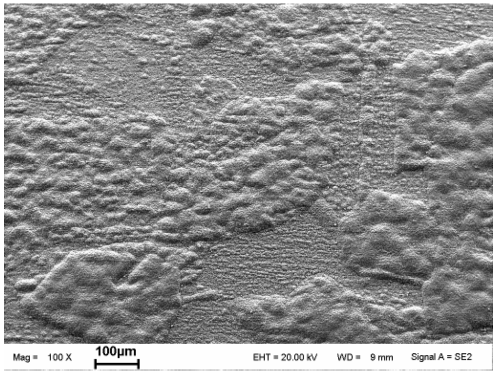
Y-surface treated NF616 after 6 weeks in 600ºC SCW (taken at 1,000x)

Novel Approaches
Grain Boundary Engineering e.g. Incoloy 800H

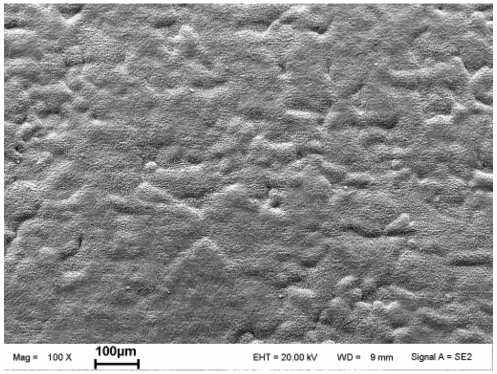
- **<u>Grain Boundary Engineering</u> (GBE) to address oxide spallation in austenitic steels:**

- **A combination of deformation and annealing steps, that enhances the population of low energy grain boundaries**

- **Incoloy 800H is a high temperature ASME code certified alloy used in fossil and nuclear power industry**



Alloy 800H after 6 weeks exposure in 600°C SCW



Alloy 800H after 6 weeks exposure in 600°C SCW

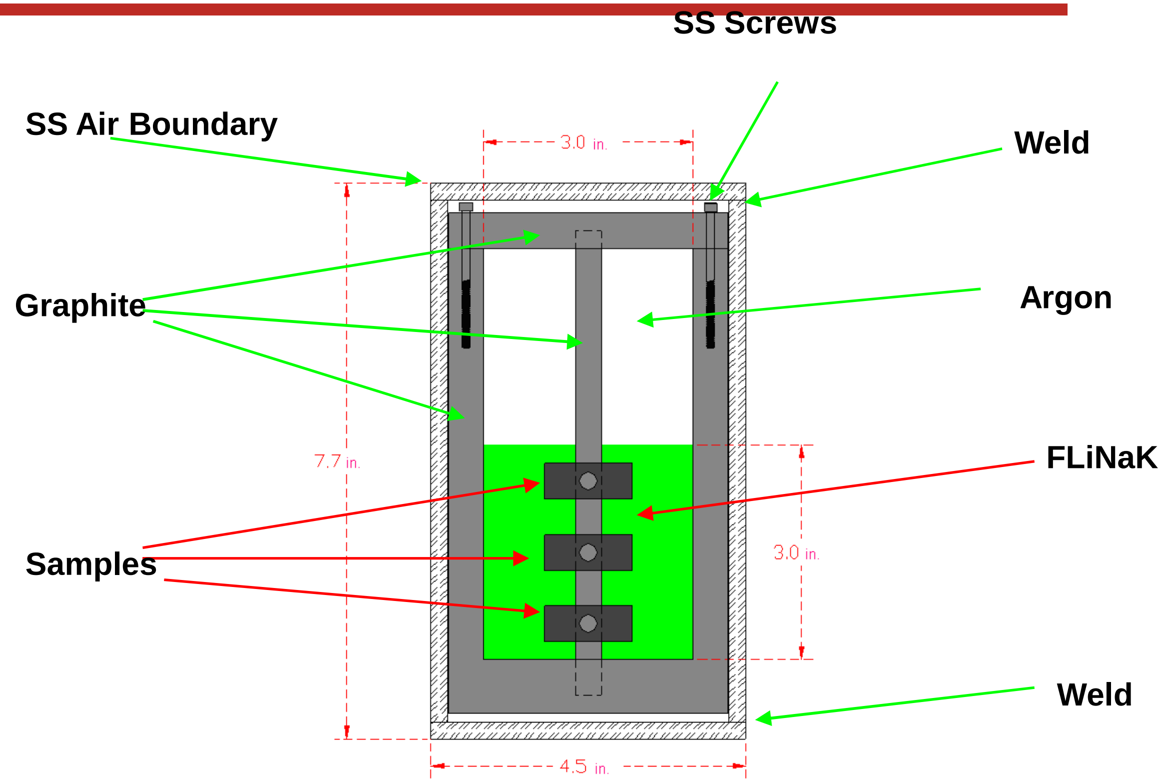
High temperature corrosion: Molten Salts

Molten Salts:

- Excellent heat capacity and thermal conductivity
- Used for storing solar energy, and transport of process heat from a nuclear reactor for hydrogen production
- Very corrosive
- At Wisconsin research has been performed on high temperature fluoride and chloride salts and low temperature nitrate salts
- In the 1950s the Army, under the Aircraft Reactor Experiment program, tested nuclear powered aircraft using U-fuel dissolved in molten salts)

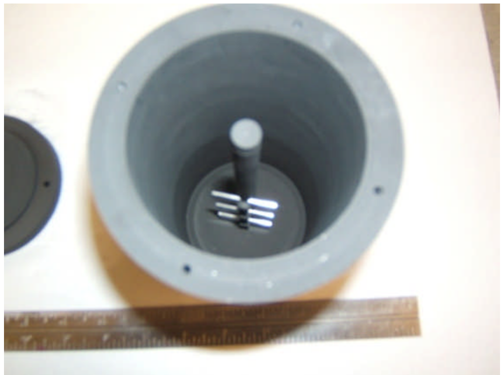
Experimental system for evaluation of corrosion in molten salts

- Graphite crucible
- Graphite central rod for fixturing samples
- Stainless steel outer shell for additional purity and safety
- One crucible/alloy/test
- Alloys tested in triplicate
- Minimal interfaces between materials and environment
- Argon space large enough for FLiNaK when flipped for sample retrieval

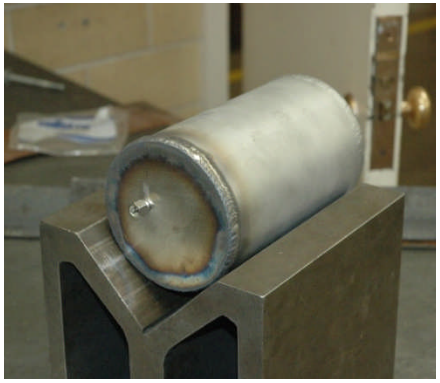


Test Conditions: 850°C for 500 hr

Procedure for preparation of corrosion capsules



Graphite capsule with samples

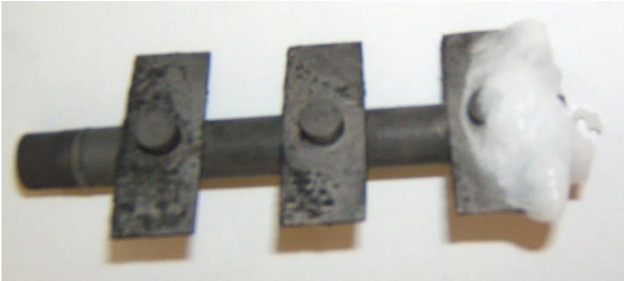


Capsule welded and ready for molten salt introduction

Salt transfer apparatus in glove-box

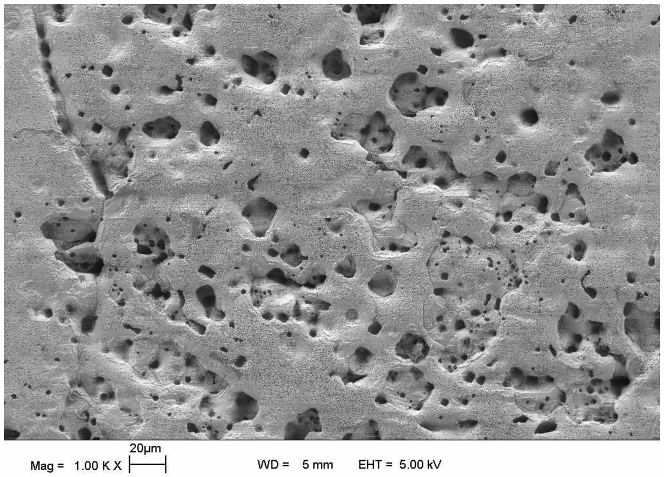
Cutting the capsule

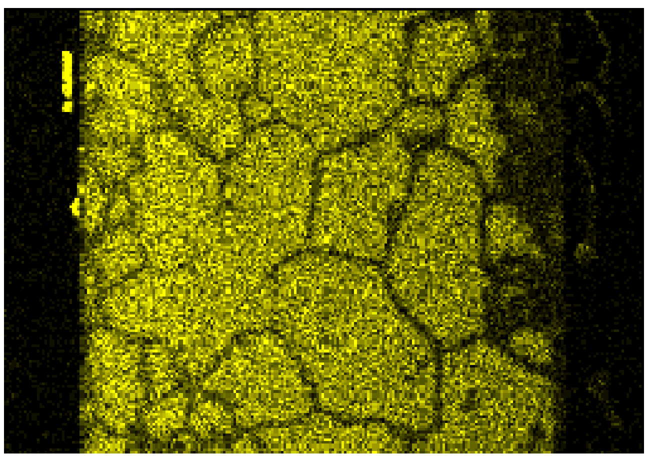
Salt drained away from the samples

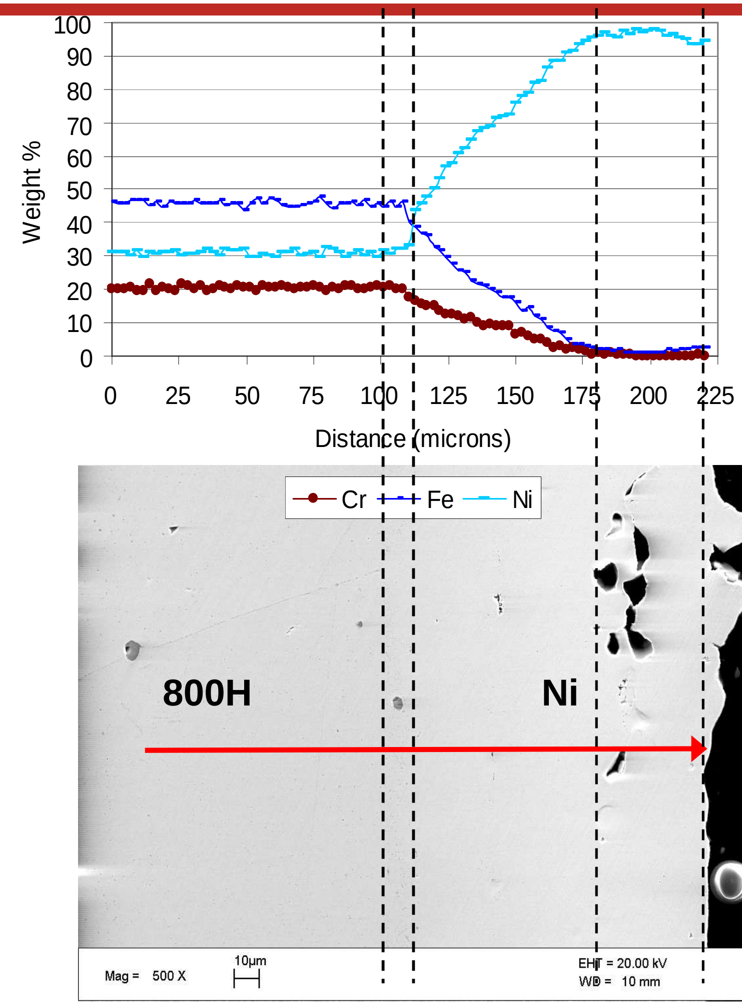


Graphite central rod with samples removed from corrosion cell

Corrosion of Incoloy 800H (20% Cr) and Ni electroplated Incoloy 800H in Na/K/Li fluoride salt: Ni coating greatly mitigates corrosion







Incoloy 800H

Ni electroplated Incoloy 800H

Concluding Remarks

- Corrosion research at the University of Wisconsin is focused on two areas (i) plasma-based surface treatments to reduce corrosion, (ii) high temperature corrosion in harsh environments
- Plasma-based surface treatments (10 to 2000nm depth) have involved ion implantation and thin film deposition and atomic mixing approaches to mitigate corrosion and wear
- Specific testing equipment for corrosion testing in high temperatures and harsh environments such as supercritical water, molten salts, supercritical carbon dioxide (KAPL), and helium have been designed and built
- Room temperature corrosion tests for potentiodynamic corrosion tests, impedance spectroscopy, and salt spray test facilities exists and are being used for research in conjunction with a suite of materials characterization techniques
- Research projects involve the development of a basic understanding of corrosion mechanisms as well as strategies such as surface treatments and grain boundary engineering to mitigate corrosion