Corrosion and Crack Growth Studies of Heat Exchanger Construction Materials for HI Decomposition in the Sulfur-Iodine Hydrogen Cycle

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General Atomics

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Overview

Timeline

- Project start: Jan 2004
- Project end: Sep 2007
- Percent complete: 85%

Barriers

- Corrosive chemicals at elevated temperatures: HI_x, conc. H_3PO_4
- Stress corrosion issues
- Cost of construction materials

Budget

- Total project funding
  - DOE: 989k
- Funding FY06: $471k
- Funding FY07: $159k (6/07-9/07)

Partners

- Collaborators: Profs. Ajit Roy & Allen Johnson (UNLV) for mechanical testing and analytical support
- Project management: Dr. Tony Hechanova (UNLV)

Objectives

Overall

Develop heat exchanger construction materials for the HI Decomposition process

2004-2006

Screening of materials candidates in HI_x, $HI_x + H_3PO_4$, conc. H_3PO_4, $HI + I_2 + H_2$ (gaseous)

2006-2007

- Stress corrosion and long term testing of qualified candidates
- Effect of chemical contaminations on corrosion
- Testing of components with Ta cladding

Approach

Screening FY04-06 → **Development** FY05-FY07 → **Prototype** FY06-FY09

Screening (FY04-06)

- Construction of Test Systems
- Immersion Testing of Metallic and Ceramic Coupons up to 120 hours in a Static Environment

Development (FY05-FY07)

- Long Term Testing of Qualified Candidates in both Static and Flow Environments
- Stress Corrosion Testing to Study Crack Initiation & Growth
- Testing the Effect of Chemical Contaminations

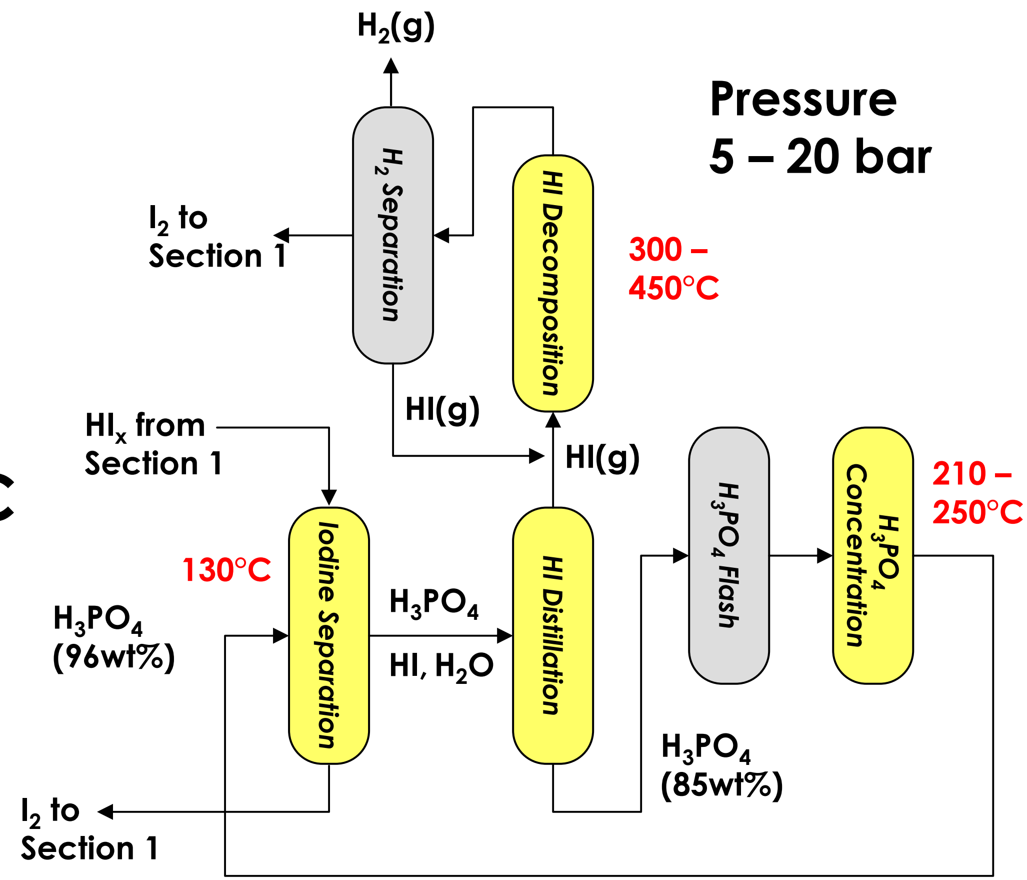
Prototype (FY06-FY09)

- Testing of Process Components Fabricated with Qualified Materials
- Explore Means for Cost Reduction e.g. Cladding
- S-I Corrosion Test Loop to Study Cross Contamination Effects

Construction materials are needed for four different chemical environments in Section III of the S-I Cycle

- **Iodine Separation**
  HI_x-H_3PO_4 – 140°C
- **H_3PO_4 Concentration**
  85-96wt% H_3PO_4 – 250°C
- **HI Distillation**
  H_3PO_4-H_2O-I_2-HI – 190°C
- **HI Decomposition**
  H_2-I_2-HI (g) – 450°C

<u>Upper Corrosion Limits</u>
Tubing/Valves – 2.95 mpy
Vessel – 19.7 mpy

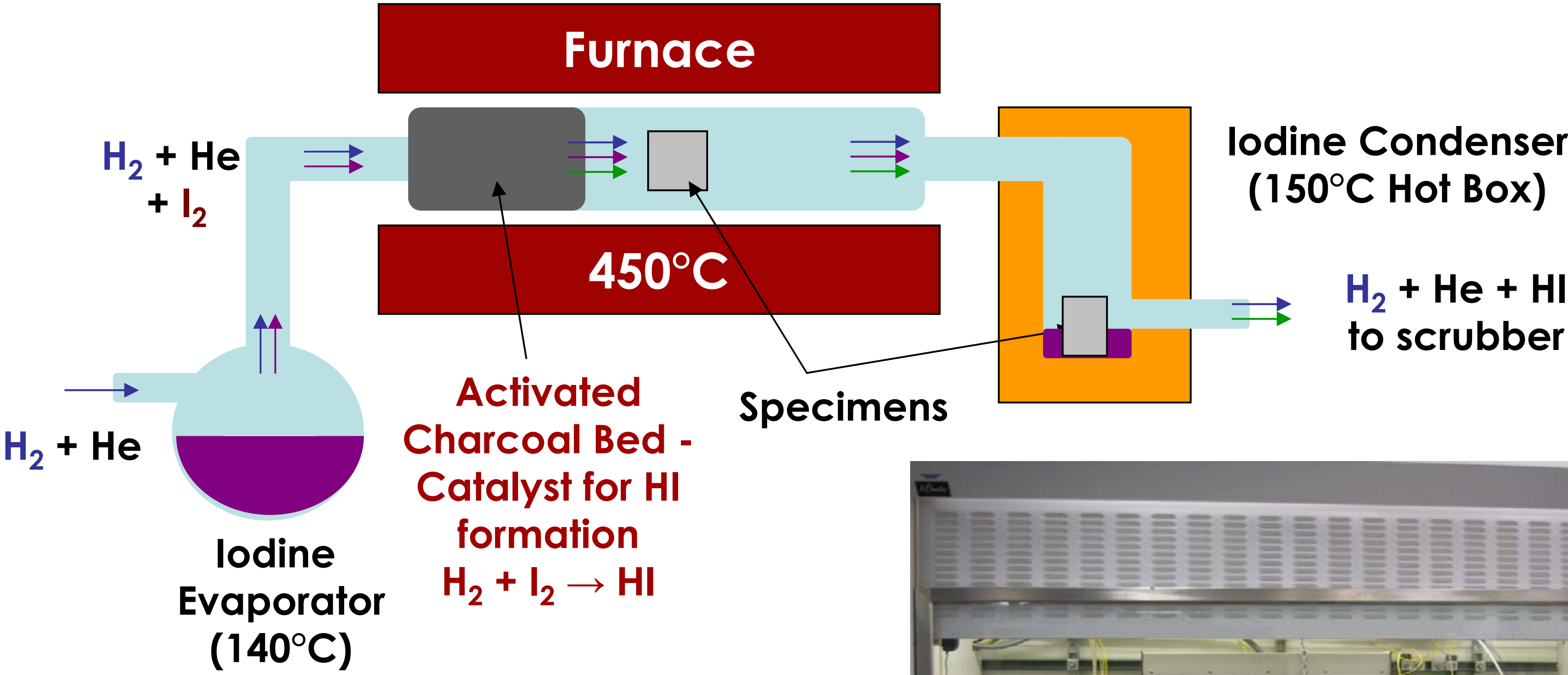


Pressure
5 – 20 bar

A total of six test systems have been constructed to help qualify materials for the different environments

- Phosphoric Acid Boiler (x2) FY05 and FY06
  testing of samples in *boiling H_3PO_4 acid* and *HI distillation liquid*
- HI Decomposer FY06
  gas flow system to test sample in *$HI + I_2 + H_2$* and *condensing I_2*
- Iodine Separator with Circulating Acid FY06
  testing of samples in *$H_3PO_4 + HI_x$* and *HI_x*
- Component Test System FY06
  testing of valve, tubing and other components in *$H_3PO_4 + HI_x$* and *HI_x*
- Static High Pressure Test System FY04
  testing of sample in static *$H_3PO_4 + HI_x$* and *HI_x*

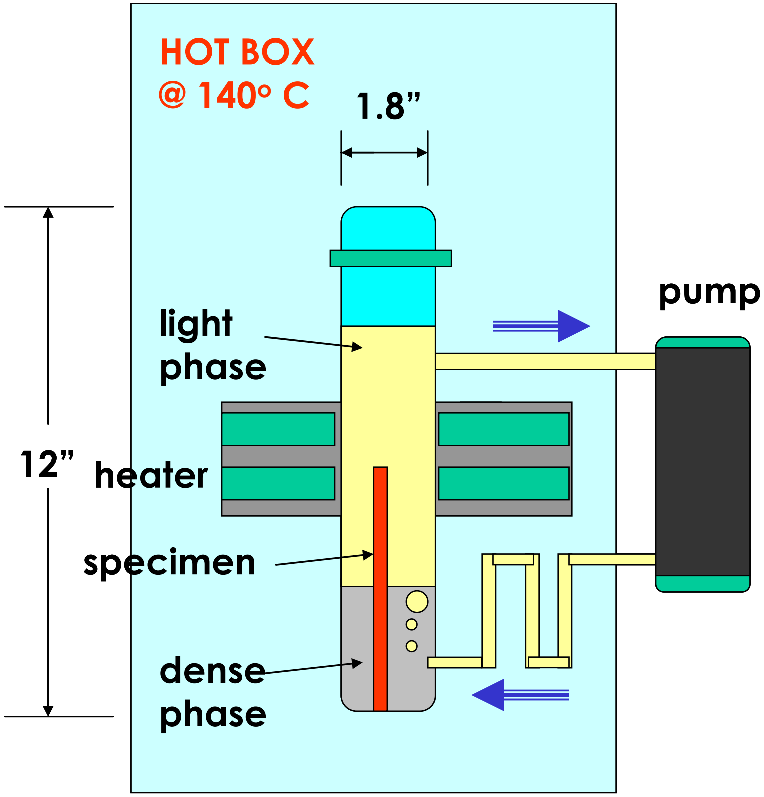
The HI decomposition materials test system replicates the HI gaseous decomposition environment



- Eliminates the need to procure expensive HI gas
- Test materials for both HI decomposition and Iodine condensation

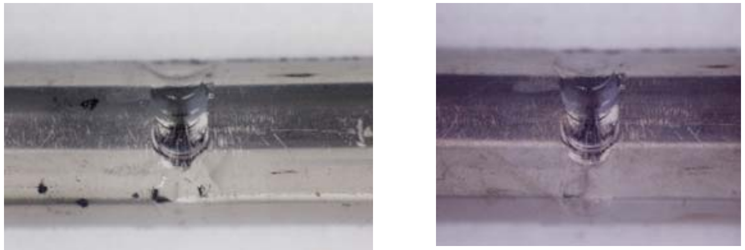
The acid (HI_x; $HI_x + H_3PO_4$) circulating system enable materials testing in a dynamic environment

- Corrosion behavior can be radically affect by agitation
- System can handle two phase liquids: H_3PO_4-HI-H_2O (light) I_2 rich (dense)



- The light phase is pumped into the bottom of the capsule. It rises to the top due to density difference
- Processed and Ta coated parts, stress corrosion and tensile specimens have been tested in this set up

0 hr 178 hr



A Ta-10W tube section with a Ta weld

In FY05, a total of 25 materials have been screened in HI_x at 310°C; Ta and Nb alloys meet the criteria

Materials Performance Requirements

- Corrosion resistant to the working environment
- Good thermal conductivity - heat exchangers
- Suitable mechanical properties - high pressure
- Good fabricability, weldability, and availability

Upper Corrosion Limit

- Tubing, Valves – 2.95mpy
- Vessel, Pipe – 19.7 mpy
- Minimize crack initiation and growth

	Corrosion Rate (mm/yr)	
Material	**Boiler (310°C)**	**Feed (262°C)**
Nb-7.5Ta	-3.911	0.391
Splint Si-SiC	-3.301	0.000
SiC (sintered)	-2.584	
Mo-47Re	-0.664	
SiC (CVD)	-0.565	-0.565
Ta	-0.513	0.086
Ta-2.5W	0.000	
Ta-10W	0.040	-0.234
Nb-10Hf	0.051	0.000
Ta-40Nb	0.274	-0.091
Nb	0.417	0.000
Zr702	467.094	0.504
C-276	1083.060	
Haynes 188	411.957	

Qualified Candidates

Ta, Ta-2.5W, Ta-10W, Nb-10Hf

In FY06, we have identified construction materials for the different environments in Section III

- Qualification is based on long term immersion in regular settings and that with chemical contaminations

Iodine Separation

Ta-10W	0.018
Ta-2.5W	0.029
SiC	0.081
Ta	0.113

(mpy)

HI Distillation

Ta-10W	0.688

HI Decomposition

B2	2.549
C276	13.497
C22	14.438

H_3PO_4 Concentration

Ta-2.5W	1.361
SiSiC	3.104

Tubing/Valves – 2.95 mpy
Vessel – 19.7 mpy

13 different materials have been tested in the static Iodine Separation ($HI_x+H_3PO_4$) environment

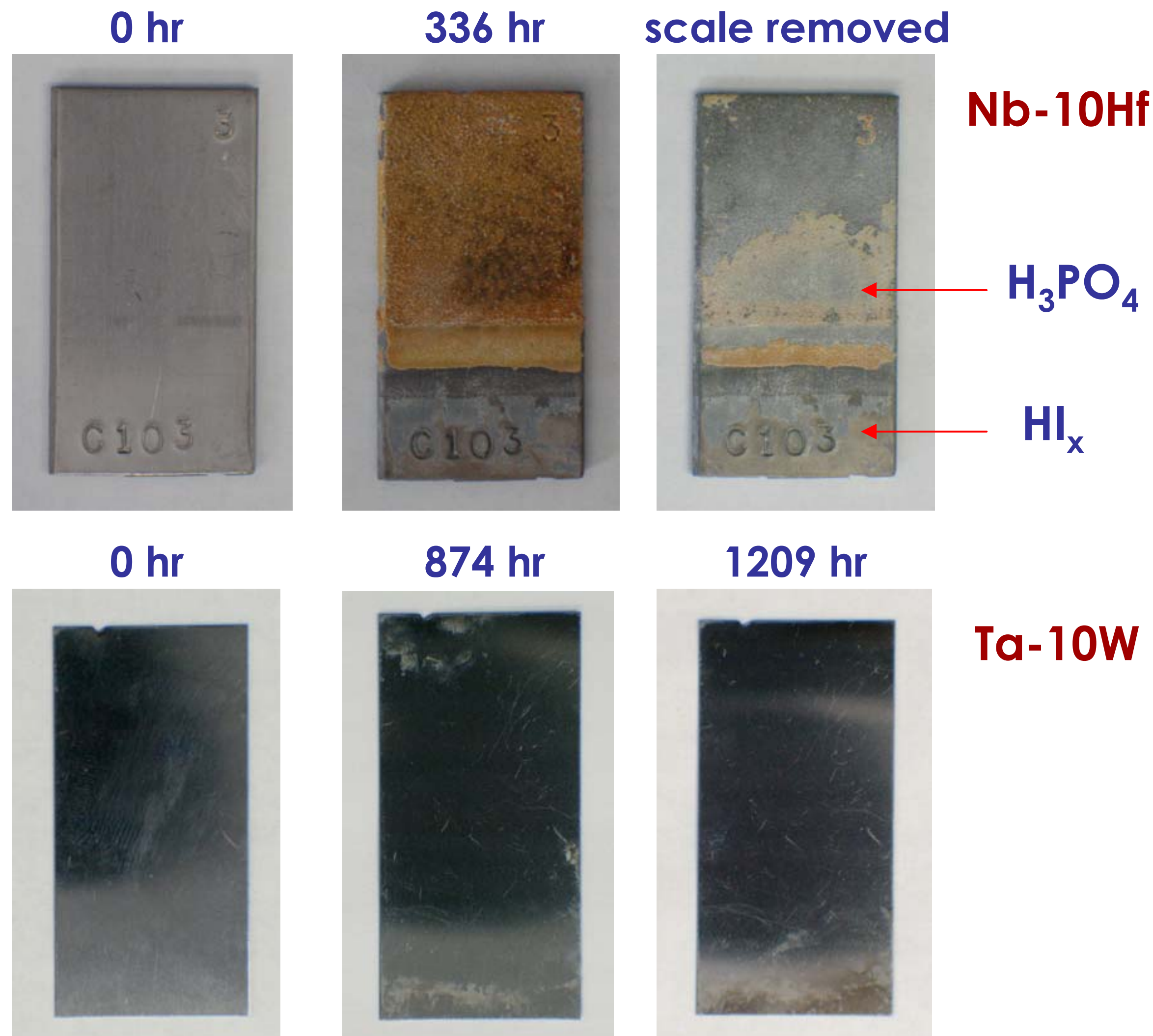
Sample	Hours	Corr. Rate (mpy)
Nb-1Zr (1)	120	-0.92
Ta-2.5W	1000	0.029
Ta-10W	336	0.045
SiC	120	0.239
Mo	160	0.45
Ta	336	0.902
Hastelloy B2	336	19.94
Nb-7.5Ta	336	22.97
Nb-1Zr (2)	120	27.7
Nb	336	38.91
Nb-10Hf	336	40.49
Zr705	120	91.32
C-276	120	139.88
C-22	120	147.07

- Ta, Ta-W and SiC showed no sign of corrosion after test
- Long term testing up to 1000 hrs has been completed
- Ta alloy bulk components were tested in a system with circulating acid
- Effect of chemical contamination (H_2SO_4 trace) showed no effect so far

Materials that can handle HI_x at high temperature may not be suitable for Iodine Separation

- **Nb alloys showed noticeable corrosion in the $HI_x + H_3PO_4$ mixture at 120°C**

- **Ta alloys are the only metals which can handle the iodine separation acid complexes**



11 candidates were tested in boiling 95 wt% phosphoric acid

- Based on post test specimen state and corrosion rate, Ta-2.5W, Ag, Cu-Ni and Si-SiC all showed good corrosion resistance in this environment
- SiO_2 and alumina based ceramics have been severely etched in this acid

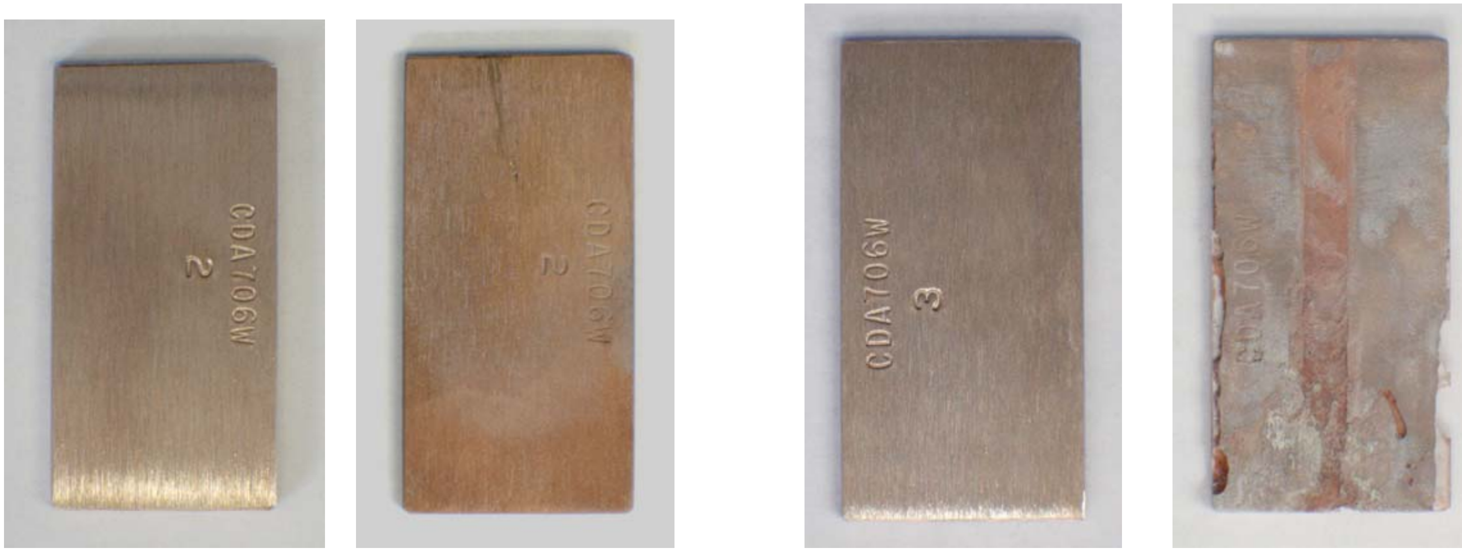
	hours	mpy
Si-SiC	96	-1.37*
Ta-2.5W	456	-0.541
Ag	336	2.583
Cu-Ni	336	0.65
B2	336	-4.51

-ve: weight gain after test due mainly to a phosphate layer that is attached to the specimen

However, contaminants (I_2, HI) additions lead to unanticipated corrosion of materials

C706 Cu-Ni

0 hr | 380 hr | 0 hr | 490 hr



H_3PO_4-3HI-5H_2O (wt%) at 250°C

H_3PO_4-14.4HI-0.7I_2-16.1H_2O (wt%) at 190°C

- Only Ta based alloys were not affected by HI and I_2 additions in H_3PO_4
- Cross contamination of chemicals and corrosion products will be the key issue in the longevity of components

Hastelloys showed the best corrosion performance in the HI decomposition environment ($HI + I_2 + H_2$)

	hours	mpy
B-2	1172	2.55
C-22	1570	10.70
C-276	1220	13.50

0 hr

1172 hr

B-2

0 hr

1570 hr

- Stress corrosion testing of C-22 and C-276 U-bend and C-ring specimens did not show any crack initiation

Ta coated components can be an effective means to reduce equipment cost

- Testing of Ta coated parts with different deposition means is on going

0 hr

294 hr

- Ta plated washer showed no sign of corrosion after immersion in $HI_x + H_3PO_4$

- Cr-Mo steel coupon coated with sputtered Ta and then anodized. Severe corrosion took place after immersion in $HI_x + H_3PO_4$

0 hr

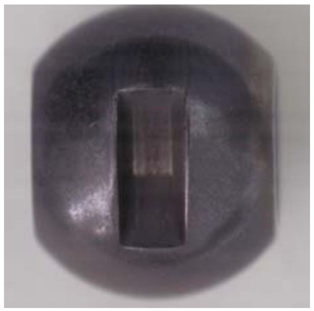
399 hr

Performance of Ta coated components such as fittings and valves have also been evaluated

- Most valves parts did not show any sign of corrosion

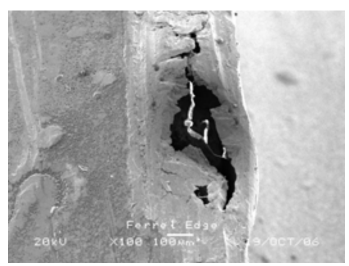
0 hr | 1160 cycles (88 hr) | 0 hr | 1160 cycles

Valve ball



Valve housing

- Testing did reveal incorrect assembly can lead to damage in the Ta coating



Damaged fitting during installation

Incorrectly installed valve drive bolt

Future Work

- Study the effect of chemical environments (HI_x + H_3PO_4 and conc. H_3PO_4) on the tensile properties of Ta-10W
- Crack growth studies of Hastelloy DCB specimens in the HI gaseous decomposition environment
- Testing on the effect of chemical contaminants on Ta-alloys used in Section III
- Identify failure conditions associated with components with Ta cladding