II.J.11 Corrosion and Crack Growth Studies of Heat Exchanger Construction Materials for HI Decomposition in the Sulfur-Iodine Hydrogen Cycle

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Contract Number: DE-FC07-04ID14566

Subcontractor:
General Atomics, San Diego, CA

Project Start Date: January 1, 2004
Project End Date: September 30, 2007

Objectives

- Identify heat exchanger construction materials candidates for use in HI_x, $HI_x + H_3PO_4$, concentrated H_3PO_4 and HI (hydrogen iodide) + I_2 +H_2 (gaseous) environments within Section III of the sulfur-iodine (S-I) cycle.
- Study the stress corrosion and long-term general corrosion characteristics of qualified candidates from the screening process.
- Investigate the effect of chemical contamination on corrosion performance of qualified candidates.
- Test the corrosion performance of parts and components that have been coated with corrosion resistance materials such as Ta.

Technical Barriers

The project addresses the following technical barriers:

- Corrosive chemicals at elevated temperatures – HI_x, I_2, HI acid, concentrated H_3PO_4 and a mixture of these.
- Stress corrosion issues – system will be operated in a pressurized environment and materials may be susceptible to crack formation and growth under stress.
- Cost of construction materials – qualified materials are expensive.

Contribution to Achievement of DOE Milestones

This project contributed to achievement of the following DOE Nuclear Hydrogen Initiative (NHI) 2006 and 2007 milestones:

FY 2006: Construct major components for the S-I cycle reaction sections in preparation for integrated laboratory-scale system operation in FY 2008.

FY 2007: Complete assembly of integrated laboratory-scale S-I thermochemical system and pre-operational testing.

Accomplishments

- A total of 59 candidates have been screened in the various chemical environments within Section III and a list of preliminary materials candidates were selected for further evaluation. Six test systems, replicating the various process environments, have been constructed for this work.
- From the preliminary candidates, materials of construction were qualified based on testing of preliminary candidates with i) long term immersion in both static and flow environments, and ii) chemical contaminants in the process fluids.
- The use of Ta coated components has been successfully demonstrated and this will lead to a reduction of material cost.

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Introduction

The chemical streams within the HI decomposition section (Section III) of the S-I cycle are extremely corrosive at operating temperatures. They include a mixture of HI_x ($HI + I_2 + H_2O$), concentrated phosphoric acid, and HI and I_2 gases. In addition, contaminants such as H_2SO_4 and corrosion products from the other two sections are also expected to be present. In order to realize a stable, safe and functional nuclear hydrogen production plant, careful selection of materials used to fabricate the heat exchangers and other components for the HI decomposition process must be taken.

Materials of construction candidates have been identified for all the chemical environments within Section III through preliminary testing. The selected materials were used to fabricate components for the NHI S-I Integrated Laboratory Scale demonstration experiment. The performance of these materials in a stress corrosion environment and avenues for cost reduction are being investigated.

Approach

The project is divided into three stages. In Stage I, potential material candidates were chosen based on previous data in the literature. These materials were then screened in the various applicable environments for a minimum of 100 hours. Those with general corrosion rate less than 20 mpy were selected for testing in Stage II. In this stage, the long-term corrosion rate of materials was established. In addition, stress corrosion effects and the effect of chemical contaminants were also investigated. In the final stage, process components constructed with the qualified materials were tested in the proper working environment at ambient pressure. Means to reduce component cost such as Ta cladding and coating were also evaluated. These results will be used to construct a corrosion loop operating at working pressure and temperature for long-term evaluation of component performance.

Results

We had previously qualified Ta-based and Nb-based alloys for use with liquid HI_x up to a temperature of 310°C. However, it was found that Nb alloys are not compatible with phosphoric acid as a phosphate scale forms on the surface after test (Figure 1). This prevents it from being used in the extractive distillation process.

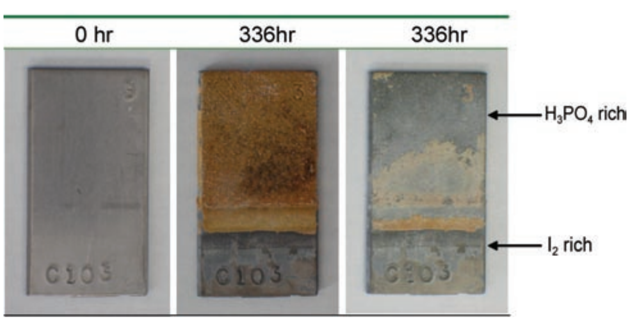

FIGURE 1. Nb-10Hf Coupon Tested in HI_x-H_3PO_4 at 140°C for 336 Hours: (a) New, (b) Post-Test, and (c) Post-Test with Scale Removed

In FY 2006, based on long-term immersion testing in regular settings and with chemical contaminants, materials have been qualified for heat exchanger and other process component fabrication for the various environments within Section III. A summary is given in Table 1. The targeted upper corrosion limit is 2.95 mpy for use in valves and tubing and 19.7 mpy for use in vessels.

TABLE 1. Corrosion Rate of Qualified Materials of Construction for Various Process Chemical Environments

Chemical Environment	Materials	Corrosion Rate (mpy)
Iodine Separation- $HI_x + H_3PO_4$ 120°C	Ta-10W	0.018
	Ta-2.5W	0.029
	SiC	0.081
	Ta	0.113
HI Distillation- $HI + H_3PO_4 + H_2O$ 200°C	Ta-10W	0.688
H_3PO_4 Concentration- 84-95 wt% H_3PO_4 260°C	Ta-2.5W	1.361
	Si-SiC	3.104
HI Gaseous Decomposition- $HI(g)+I_2(g)+H_2(g)$ 450°C	Hastelloy B2	2.549
	Hastelloy C22	10.70
	Hastelloy C276	13.50

The qualified materials were tested in a stress corrosion set up to study their crack formation and crack growth characteristics as they will be used to manufacture pressure components. Results from pre-stressed C-ring and U-bend Hastelloy specimens submerged in the $HI(g)+I_2(g)+H_2(g)$ have not shown any susceptibility of crack formation (Figure 2). Crack growth studies are currently ongoing.

The project also explored the effectiveness of various Ta coating techniques in addition to testing the performance of components with Ta coatings. It was found that stainless steel parts plated with Ta in a molten salt bath or chemical vapor coated with Ta have good corrosion resistance in contrast to sputtered Ta. Based on these results, parts from a ball valve were chemical vapor deposition coated with Ta and reassembled for testing. It is the first study of the actual working performance of a Ta coated component in the S-I environment. Preliminary results after 1,000 cycles of testing show generally good corrosion characteristics except in areas whereas excessive stress concentration is present due to incorrect installation (Figure 3).

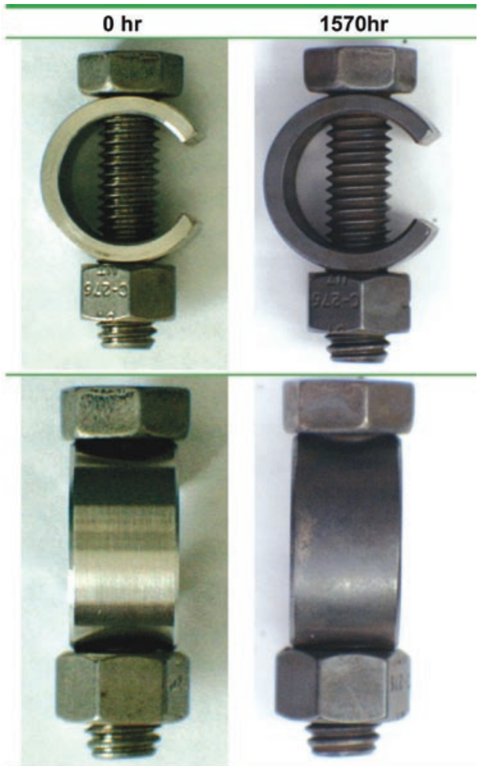

FIGURE 2. C22 C-Ring Specimen Coupon Tested in the Gaseous HI Gaseous Decomposition Environment ($HI + I_2 + H_2$) at 450°C

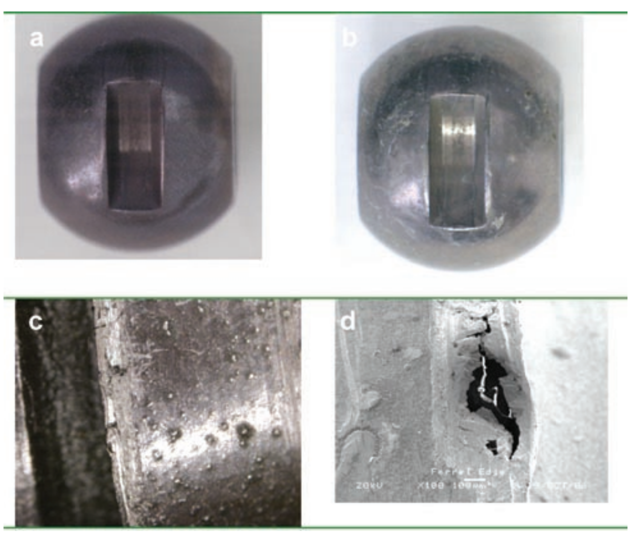

FIGURE 3. Components from a Ball Valve that has Undergone 1,160 cycles: (a) Before, and (b) After, (c) and (d) Cracked Ta Coating due to Incorrect Installation of the Drive Bolt

Conclusions and Future Directions

- Ta, Ta-2.5W, Ta-10W and SiC have been qualified for use and further testing in the liquid streams in Section III. Hastelloy B2, C22 and C276 all met the performance criteria for use in the HI decomposition environment.
- Stress corrosion studies of Hastelloy specimens in the HI gaseous decomposition environment have not shown any stress corrosion effect.
- We have demonstrated that Ta coated parts are suitable for manufacturing of heat exchanger and process components.
- The effect of chemical environments (HI_x + H_3PO_4 and concentrated H_3PO_4) on the tensile properties of the qualified materials will need to be characterized.
- The effect of chemical contaminants and corrosion products in the process streams on corrosion properties will need to be studied.
- Identify failure conditions associated with components geometry and base materials with various forms of Ta coating techniques.

FY 2007 Publications/Presentations

1. “Construction materials development in sulfur–iodine thermochemical water-splitting process for hydrogen production,” B. Wong, R.T. Buckingham, L.C. Brown, B.E. Russ, G.E. Besenbruch, A. Kaiparambil, R. Santhanakrishnan and Ajit Roy, *International Journal of Hydrogen Energy*, *Volume 32, Issue 4*, *March 2007*, *Pages 497-504.*