IV.G.4 High Temperature Heat Exchanger Project*

Anthony Hechanova
University of Nevada, Las Vegas
4505 Maryland Parkway, Box 454009
Las Vegas, NV 89154-4009
Phone: (702) 895-1457; Fax: (702) 895-2354; E-mail: hechanova@unlv.nevada.edu

DOE Program Manager, Nuclear Hydrogen Research: David Henderson
Phone: (301) 903-3097; Fax: (301) 903-5057; E-mail: David.Henderson@nuclear.energy.gov

DOE Project Officer: Carl Sink
Phone: (301) 903-5131; Fax: (301) 903-5084; E-mail: Carl.Sink@nuclear.energy.gov

Technical Advisor: Steven Sherman
Phone: (208) 533-7327; Fax: (208) 533-7735; E-mail: steven.sherman@inl.gov

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**Congressionally directed project*

Objectives

- Identify candidate materials for heat exchanger components.
- Test candidate materials for heat exchanger components.
- Design critical components in the interface between the reactor and hydrogen production plant and within the sulfur iodine thermochemical process.
- Fabricate prototypical components.
- Test prototypical components.

Technical Barriers

This project addresses the following technical barriers of the Nuclear Hydrogen Initiative:

- Development of high-temperature, corrosion resistant materials
- Development of high-temperature, high-activity, stable catalysts
- Development of compact, cost-effective heat exchanger components
- Achievement of reasonable performance of small-scale experiments

Approach

- Identify candidate metallic and ceramic materials based on reasonable expectations of the material properties.
- Identify candidate structural alloys for self-catalytic material.
- Fabricate testing coupons from candidate materials.
- Screen candidate metallic and ceramic materials for compatibility in hydrogen iodide using short-term corrosion performance experiments.
- Test candidate metallic and ceramic materials in long-term corrosion performance experiments.
- Test candidate metallic materials for corrosion resistance and mechanical properties using tensile, constant load, and slow strain rate machines.
- Perform fractographic evaluations and surface analysis of candidate metallic materials using spectroscopy. Perform helium permeation testing on candidate ceramic materials.
- Demonstrate fabrication methods of ceramic heat exchangers.
- Design compact and efficient heat exchangers for challenging components, in particular, the intermediate heat exchanger, the sulfuric acid decomposition heat exchangers, and the hydrogen iodide decomposition heat exchangers.
- Generate computer simulation model of candidate heat exchanger designs.
- Perform hydrodynamic and heat transfer simulations on candidate heat exchanger designs to develop baseline designs.
- Perform computational fluid dynamic parametric studies to optimize heat exchanger designs.
- Perform computational stress analyses on candidate heat exchanger designs.

Accomplishments

- Tensile properties of Alloy C-22, C-276, and Waspaloy were determined in temperatures up to 600^{o}C in the presence of nitrogen. Waspaloy outperformed the other candidates in these tests.
- Stress corrosion cracking susceptibility studies of Alloys C-22, C-276, and Waspaloy in sulfuric acid and sodium iodide at 90^{o}C were completed.
- Computational fluid dynamics (CFD) modeling for pressure drop and thermal performance was completed for a baseline ceramic compact off-set strip fin heat exchanger. Results indicate that satisfactory performance is expected.
- Stress analyses for the baseline ceramic compact off-set strip fin heat exchanger were performed. Results are still under evaluation.
- A micro-channel plate design heat exchanger was designed for helium-to-sulfuric acid heat transfer.
- 22 coupons from four classes of materials (refractory and reactive metals, superalloys, and ceramics) were screened for 100 hours or more each in liquid blends of hydrogen iodide (HI), iodine (I_2), and water. Suitable candidates for the HI decomposition heat exchanger include Nb-1Zr, Ta-7.5Nb, and SiC.
- High pressure helium permeation testing was performed on ceramic composite materials. Very good helium hermeticity was observed for melt infiltration SiC splint-based material and melt infiltration pitch based carbon fiber reinforced SiSiC.
- Chemical vapor deposition coating of C/SiC coupons was demonstrated, which can be applied to the interior heat exchanger surfaces after fabrication is complete. The resulting coupons showed very good helium hermeticity and high strength.
- Microstructural and electrochemical characterization of self-catalytic materials using Alloy 800HT and Alloy 617 as the base material with the addition of 2, 5, 15 and 30 weight percent Pt were completed.

Results indicate that the materials will be effective catalysts for the reduction of hydrogen approaching that of Pt. The results also imply potential use for high temperature electrolysis applications.

Future Directions

- Test candidate metallic materials (Incoloy 800H, Nb-1Zr, Nb-7.5Ta, and Zr 705) for high temperature corrosion and material properties.
- Perform optimization studies using CFD techniques on heat exchanger designs.
- Perform thermo-structural analysis of heat exchangers for different materials with larger elastic moduli.
- Complete sulfuric acid decomposition heat exchanger design.
- Perform experimental testing to validate numerical modeling of the heat exchangers.
- Perform long-term coupon testing in blends of hydrogen iodide, iodine, and water (HIx).
- Conduct tests to study the effect of HIx on stress corrosion behavior of materials.
- Study the effects of crack growth in candidate materials.
- Evaluate material cost reduction through cladding.
- Demonstrate fabrication of small plate heat exchanger.
- Perform advanced analyses and design of ceramic heat exchangers including transient and mechanical/ thermal stress analyses of complete system (including manifolds) and safety analyses for applications with sulfur-iodine (S-I) process fluids.
- Design a flow-loop for testing materials with liquid salts.
- Complete characterization of self-catalytic materials from small heats.
- Fabricate and characterize larger heats of Alloy 800HT and Alloy 617 with 2% weight Pt.
- Design and construct a system to determine catalyst effectiveness.

Introduction

The University of Nevada Las Vegas Research Foundation (UNLVRF) assembled a research consortium for high temperature heat exchanger design and materials compatibility and performance comprised of university and private industry partners under the auspices of the DOE Office of Nuclear Energy, Science & Technology's Nuclear Hydrogen Initiative in October 2003. The objectives of the consortium were to conduct investigations of candidate materials for high temperature heat exchanger components in hydrogen production processes and design and perform prototypical testing of heat exchangers. The initial research of the consortium focused on the intermediate heat exchanger (located between the nuclear reactor and hydrogen production plant) and the components for the hydrogen iodine decomposition process and the sulfuric acid decomposition process. These heat exchanger components were deemed the most challenging from a materials performance and compatibility perspective.

Approach

The research was divided into three technical areas: metallics, ceramics, and catalysts. Materials were identified through communications and consensus among the UNLVRF consortium members and researchers within the Nuclear Hydrogen Initiative materials group (led by Bill Corwin). Short-term corrosion testing in hydrogen iodide was conducted at General Atomics. Materials evaluation and characterization were conducted at UNLV (for metallic materials), UC Berkeley (for ceramic materials), and MIT (for catalytic materials). Heat exchanger design was conducted by UNLV and Ceramatec, Inc. The consortium met quarterly to update collaborators on research progress and exchange information.

Results

Materials Characterization and Testing

Selection of structural metallic materials and alloys for high-temperature heat exchangers (HTHX) to generate hydrogen using a nuclear power source poses a major challenge to scientific and engineering communities. The materials must possess excellent resistance to numerous environment-induced degradation and superior high-temperature metallurgical properties. Since the inception of this project, experimental work involving three nickel-base alloys, namely Alloy C-22, Alloy C-276 and Waspaloy has been ongoing. Tensile properties of all three alloys have been determined at ambient temperature, 450 ^{o}C, and 600^{o}C in the presence of nitrogen at UNLV. Further, the evaluations of the stress corrosion cracking (SCC) susceptibility of all three alloys in a 90^{o}C aqueous solution containing sulfuric acid and sodium iodide at constant load and slow-strain-rate, respectively, have been performed. More recently, the evaluations of the tensile properties and SCC susceptibility of Incoloy 800H have been initiated. Fractographic evaluations of the tested specimens by scanning electron microscopy are also ongoing.

Ceramic Materials

To meet cost targets, candidate ceramic materials must have relatively low bulk costs, and fabrication methods must extrapolate to low-cost mass manufacturing. Researchers at UC Berkeley surveyed candidate heat exchanger materials and fabrication methods with a focus on low-cost chopped-carbon fiber reinforced silicon carbide, where the silicon carbide is infiltrated by either melt (MI) or polymer infiltration and pyrolysis, and where additional low-cost filler materials may be used. Additionally, sintered silicon carbide materials have relatively low bulk costs and Ceramatec, Inc. has demonstrated a process for fabrication using a tape-casting, lamination and sintering methods that extrapolate to low-cost production.

Research conducted at UC Berkeley focused on inexpensive chopped carbon fiber based ceramic composite. Helium permeation testing and mechanical property testing were conducted. Young's moduli of carbon fiber reinforced SiSiC (FR-SiSiC), splint based SiSiC (SB-SiSiC) and pitch based carbon fiber reinforced SiSiC (BioKer) were tested by using a strain gauge. The material properties and measured values are given in Table 1.

Table 1. Properties of Melt Infiltration Materials

MI Material	Density kg/m^3	Young's modulus GPa	Failure stress MPa
Carbon fiber reinforced SiSiC with coating	2523	325	270
Splint based SiSiC	2932	450	224
Pitch based SiSiC	2600	298	200
Short fiber reinforced SiC	2000	60	90 - 140

Construction Materials Screening

In order to identify the material of construction candidates for the HI decomposition process, immersion corrosion coupon test in HIx was used to screen potential candidates. Materials that perform well in this test will be put through developmental testing which will gauge material processing effects on their corrosion and mechanical properties. A test system capable of handling HIx at the reaction temperature was set up at General Atomics. Twenty-two different material coupons were tested at the boiler conditions from January 2004 through March 2005. A summary of the results is listed in Table 2.

The Nb and Ta based alloys all performed well and will undergo further testing. Another refractory, Mo, did not exhibit adequate corrosion resistance as it lost weight during test. Weight loss of MoRe was acceptable but it is still not as good as Ta and Nb alloys. Both zirconium coupons, Zr702 and Zr705 showed signs of corrosion pitting and some dissolution. The normally corrosion resistant superalloys such as Hastelloy C-276 and Haynes 188 showed severe weight loss through dissolution. Hence, these materials are not suitable for this application.

Table 2. Summary of all the Coupons Tested in HIx

	Materials	Boiler	Feed
1	Ta	Good	Good
2	Ta-10%W	Excellent	Excellent
3	Ta-40%Nb	Excellent	Excellent
4	Nb	Good	-
5	Nb-1%Zr	Excellent	Good
6	Nb-7.5%Ta	Fair	Good
7	Nb-10%Hf (C103)	Excellent	Excellent
8	Zircalloy 702	Poor	Poor
9	Zircalloy 705	Poor	-
10	Mo	Poor	-
11	Mo-47Re	Fair	-
12	graphite	Poor*	-
13	C-276	Poor	-
14	Haynes 188	Poor	-
15	SiC (sintered)	Good	-
16	Ceramatec SiC (sintered)	Excellent	-
17	SiC (CVD)	Excellent	Excellent
18	Bioker 29 Si-SiC	Good	-
19	Splint Si-SiC	Good	Good
20	Fused Si-SiC	Good	-
21	Alumina	-	Fair
22	Mullite	Excellent	-

Poor: severe corrosion - dissolution and pitting
Fair: mild corrosion - localized oxidation, uneven passivation
Good: distinguish color change due to passivation
Excellent: very minor change in color due to passivation

The SiC based ceramic materials demonstrated that they are also suitable for HI decomposition heat exchanger applications. Three different varieties of SiC were tested: two sintered samples and one fabricated by chemical vapor deposition (CVD). They all performed well in the liquid HIx environment and will undergo more long term testing. The Si-inflitrated SiC coupons also are resistant to HIx liquid but there is minor absorption of HIx by the specimens during the test.

Although the extruded graphite rod that was tested HIx did maintain its structural integrity, it absorbed a large amount of liquid and resulted in a final weight gain of 20%. The application of graphite will be extremely limited.

Self-Catalytic Materials

Research was conducted at MIT to develop a material that can act as both the structural material for the heat exchanger and the catalyst for the acid decomposition reaction. The general approach for the development of self-catalytic materials was to focus on an alloy system that would normally be considered for the acid decomposition reaction and to modify this chemistry via the addition of a catalytic element. The research focused on alloys 800HT and 617 with the incorporation of platinum as an added element to the base chemistry.

Alloy 800 and 617 plus 2, 5, 15, and 30 wt % Pt with the Fe concentration reduced as Pt is added were characterized in the as-cast condition prior to conversion to wrought material by a series of rolling/annealing steps. Samples of each material were mounted and polished using standard metallographic techniques. The microstructure of each cast sample is composed of a dendritic structure as would be expected. The clarity of the inter-dendritic boundaries decreases as the mass percent of platinum increases within the material. This is indicative of the role that the increasing amount of a noble metal (Pt) is having on corrosion resistance. Relatively few inter-dendritic boundaries were developed in the 30% Pt cast sample compared to the other samples. Orange blocky particles between 1-15 µm in size are present in each microstructure. The size shape and color of these deposits indicate that they are probably titanium carbonitrides. In many cases, these carbonitrides are aligned in rows that indicate solidification patterns within the dendritic microstructures.

The etched microstructure of alloy 617 plus Pt alloys indicated that the interdendritic structure is more pronounced. The clarity of the interdendritic boundaries decreases as the mass percent of platinum increases within the material for the same etching conditions. This is indicative of the role that the increasing amount of a noble metal (Pt) is having on corrosion resistance.

Heat Exchanger Designs

Stress analyses and thermal hydraulic systems numerical modeling to investigate temperature, pressure, and flow rate requirements were completed for an offset strip-fin hybrid plate type compact ceramic heat exchanger by research groups at UNLV and UC Berkeley. Two- and three-dimensional numerical models to predict the overall performance of an advanced high temperature (up to 1000 °C) heat exchanger design with an expected thermal power of 50 MW were completed. The heat exchanger design is shown in Figure 1. The heat exchanger is made from liquid silicon impregnated carbon composite. The offset strip-fin is chosen as a method of heat transfer enhancement due to the boundary layer restart mechanism between the fins that has a direct effect on enhancing heat transfer. The offset strip-fin heat exchanger channels are characterized by the presence of fins located in a staggered fashion in order to interrupt the flow and increase the heat transfer area. The study was conducted with helium gas and molten salt as the working fluids with varied channel dimensions.

Preliminary analysis was performed based on a laminar and incompressible fluid flow model and the CFD results predicted the baseline design will satisfy the required thermal performance. The CFD model was modified to test the use of temperature dependent physical properties in the numerical model in the laminar flow cases. The helium side (gas) had almost no difference while there was only a 10% difference in the results for the molten-salt side (liquid). Thus, the impact of temperature dependent properties was not considered when turbulence modeling. Grid independence studies were performed for three kinds of meshes and the effect of each type on flow and heat transfer was investigated. Turbulence modeling was performed using the standard K-omega model and the when the results were compared to those of laminar models, the curved fin edges seemed to be unaffected while the rectangular fin edge case had a notable difference in results. CFD analysis was also performed to investigate the effect of the fillets (or manufacturing geometrical effects causing rounded corners) at the channel surfaces on the fluid flow and heat transfer. The results showed that the effect was significant only for the molten salt side due to the constriction in flow area.

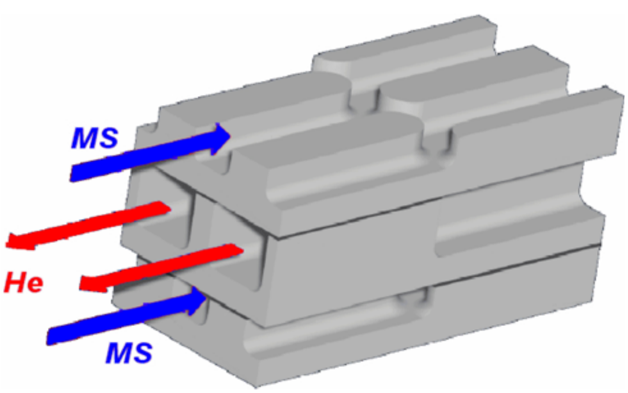

Figure 1. Offset Strip-Fin Counter Flow Heat Exchanger Module

Conclusions

- Tensile properties of Alloy C-22, C-276, and Waspaloy were determined in temperatures up to 600°C in the presence of nitrogen. Waspaloy outperformed the other candidates in these tests.
- CFD modeling for pressure drop and thermal performance was completed for a baseline ceramic compact off-set strip fin heat exchanger. Results indicate that satisfactory performance is expected.
- Twenty-two coupons from four classes of materials (refractory and reactive metals, superalloys, and ceramics) were screened for 100 hours or more each in liquid HIx. Suitable candidates for the HI decomposition heat exchanger include Nb-1Zr, Ta-7.5Nb, and SiC.
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FY 2005 Publications/Presentations

1. A. Kaiparambil and R. Santhanakrishnan, "Corrosion Behavior of Candidate Materials for Hydrogen Generation," ANS Student Conference, April 2005, Columbus, OH.
2. A. K. Roy, R Karamcheti, L. Savalia and N. Kothapalli, "Metallurgical Stability and Corrosion Behavior of Structural Materials for Hydrogen Generation," *ASTM Conference*, Reno, NV, May 2005.
3. A. K. Roy, R Karamcheti, L. Savalia and N. Kothapalli, "Tensile Properties and Corrosion Characteristics of Heat-Exchanger Materials," *SAMPE*, May 2005, Long Beach, CA
4. A. K. Roy, N. Kothapalli, R Karamcheti and L. Savalia, "Mechanical Properties and Cracking of High-Temperature Heat-Exchanger Materials," *TMS Conference*, February 2005, San Francisco, CA
5. A. K. Roy, L. Savalia, N. Kothapalli and R. Karamcheti, "High-Temperature Properties and Corrosion Behavior of Nickel-Base Alloys," *Corrosion/2005, NACE International,* Paper No. 05430, Houston, TX, April 2005.
6. A. K. Roy, L. Savalia, N. Kothapalli and R. Karamcheti, "High Temperature Properties of Structural Material for Hydrogen Generation," *INMM*, July 2004, Orlando, FL.
7. A. K. Roy, L. Savalia, N. Kothapalli and R. Karamcheti, "Mechanical Properties and Cracking Behavior of High-Temperature Heat-Exchanger Materials," *ASME PVP-2005*, July 2005, Denver, CO.
8. L. Savalia, N. Kothapalli and R. Karamcheti, "Corrosion and Metallurgical Behavior of Ni-Base Alloys for Heat-Exchanger Application," *ANS Student Conference*, April 2005, Columbus, OH
9. S. Subramanian, R. Akberov, Y. Chen, and A.E. Hechanova, "Development of an Advanced High Temperature Heat Exchanger Design for Hydrogen Production," IMECE2004-59623, Proceedings of IMECE2004 ASME International Mechanical Engineering Congress, Anaheim, CA, November 13–19, 2004.
10. B. Wong, L. Brown, R. Buckingham, A. Kaiparambil, R. Santhanakrishnan, B. Russ, A. Roy, and G. Besenbruch, "Construction Material Development in Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Production," AIChE, 2005 Spring National Meeting, Hyatt Regency, Atlanta, GA, April 10-14, 2005.
11. B. Wong, R. Buckingham, L. Brown, J. Gomez, B. Russ and G. Besenbruch, "Materials Challenges in Sulfur-Iodine Thermochemical Water Splitting process for Hydrogen Production" by ASM Conference, Columbus, OH, October 20, 2004.
12. B. Wong, R. Buckingham, L. Brown, B. Russ, G. Besenbruch, A. Kaiparambil, R. Santhanakrishnan and A. Roy, "Construction Materials Development in Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Generation," *AIChE*, September 2005, Pittsburgh, PA