Integration of a Structural Water Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device

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Project ID # **PD18**

Overview

Timeline

- Start - 7/1/05
- End – 12/31/07
- 80% complete

Budget

- Total project funding
  - $500,000 DOE share
  - $125,000 Contractor share
- Funding FY06 - $250,000
- Funding FY07 - $250,000

Barriers

- Removal of water gas shift equipment capital costs for IGCC
- Hydrogen transport membrane cost

Partners

- University of Wyoming as full partner
- Project management - WRI

Objectives

2006

- **Develop a structural water gas shift catalyst capable of withstanding compressive forces.**

- **Develop vanadium alloy hydrogen separation membranes for fabrication of devices by brazing.**

2007

- **Integrate the WGS catalyst and metallic membranes into a device and test under gasifier conditions.**

Approach

- **Task 1 Water Gas Shift (85%)**
  - **Monolithic ceramic approach**
  - **Impregnated substrate approach**
- **Task 2 Brazable Vanadium membranes (100%)**
  - **Alloying element effects on brazability of vanadium**
  - **Brazing vanadium to structural alloys**
- **Task 3 Integrated Device (80%)**
  - **Design and fabrication of V + WGS device**
- **Task 4 Gasifier testing (20%)**
  - **Demonstrate catalyst and membrane operations under coal gasification conditions**

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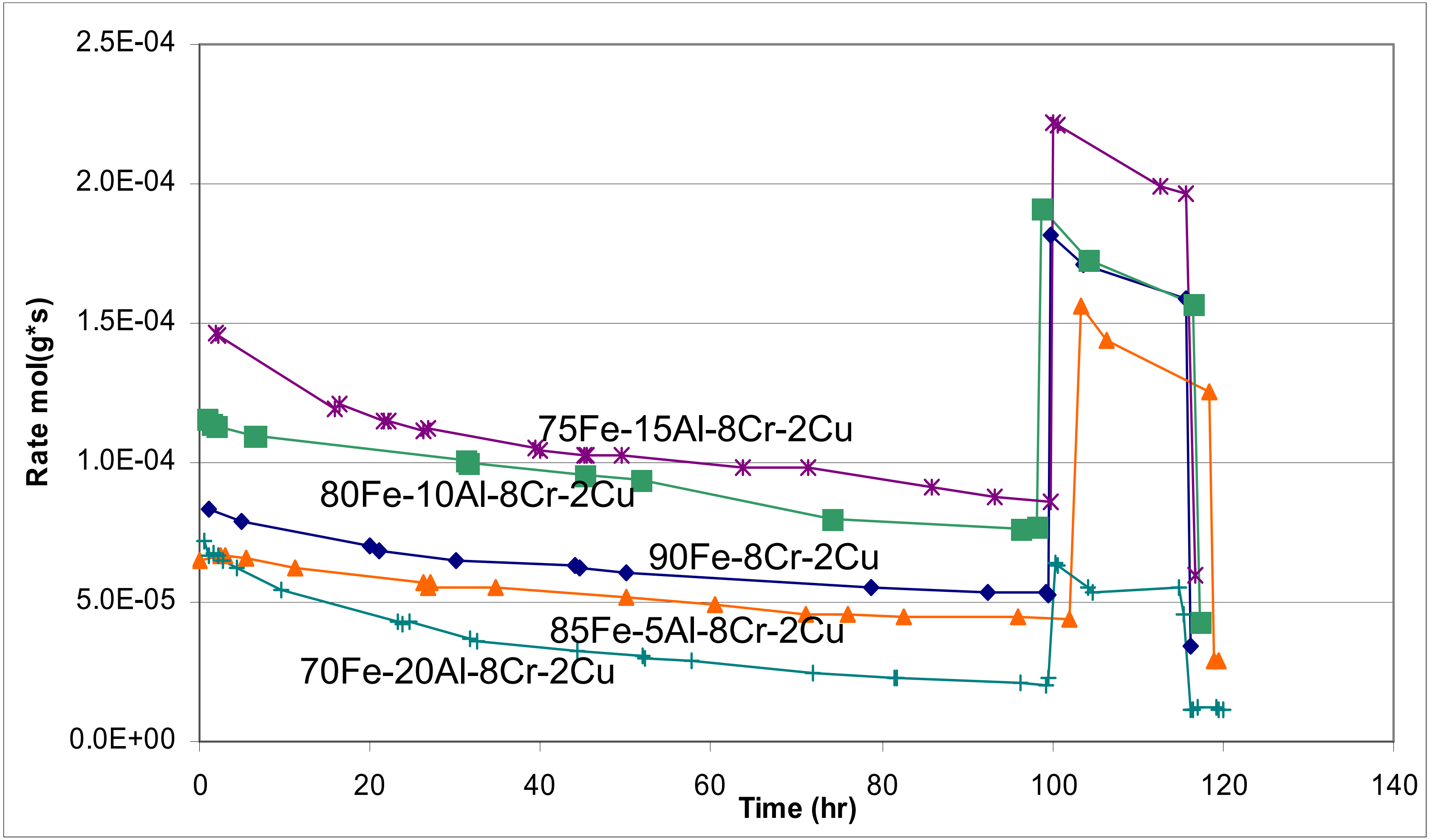
Results

Task 1 Structural Water Gas Shift Catalyst

- Focus of the chemistry of the water gas shift catalyst has been on Fe-Al-Cr-Cu-Ce system
- Catalysts have been tested by impregnation into porous mullite substrates
- Highest activity and stability has been shown for 75Fe-15Al-8Cr-2Cu
- Small additions of CeO_2 look promising
- Producing high surface area monoliths of this catalyst series may be problematic due to sintering at higher operational temperatures

Al_2O_3 INCREASES SURFACE AREA

Reaction conditions: 0.1 g; 400 °C 100 h, 500 °C 16 h; $H_2O_{(v)}$:CO=3; H_2O+CO=$1.24 \cdot 10^{-4}$ mol/s

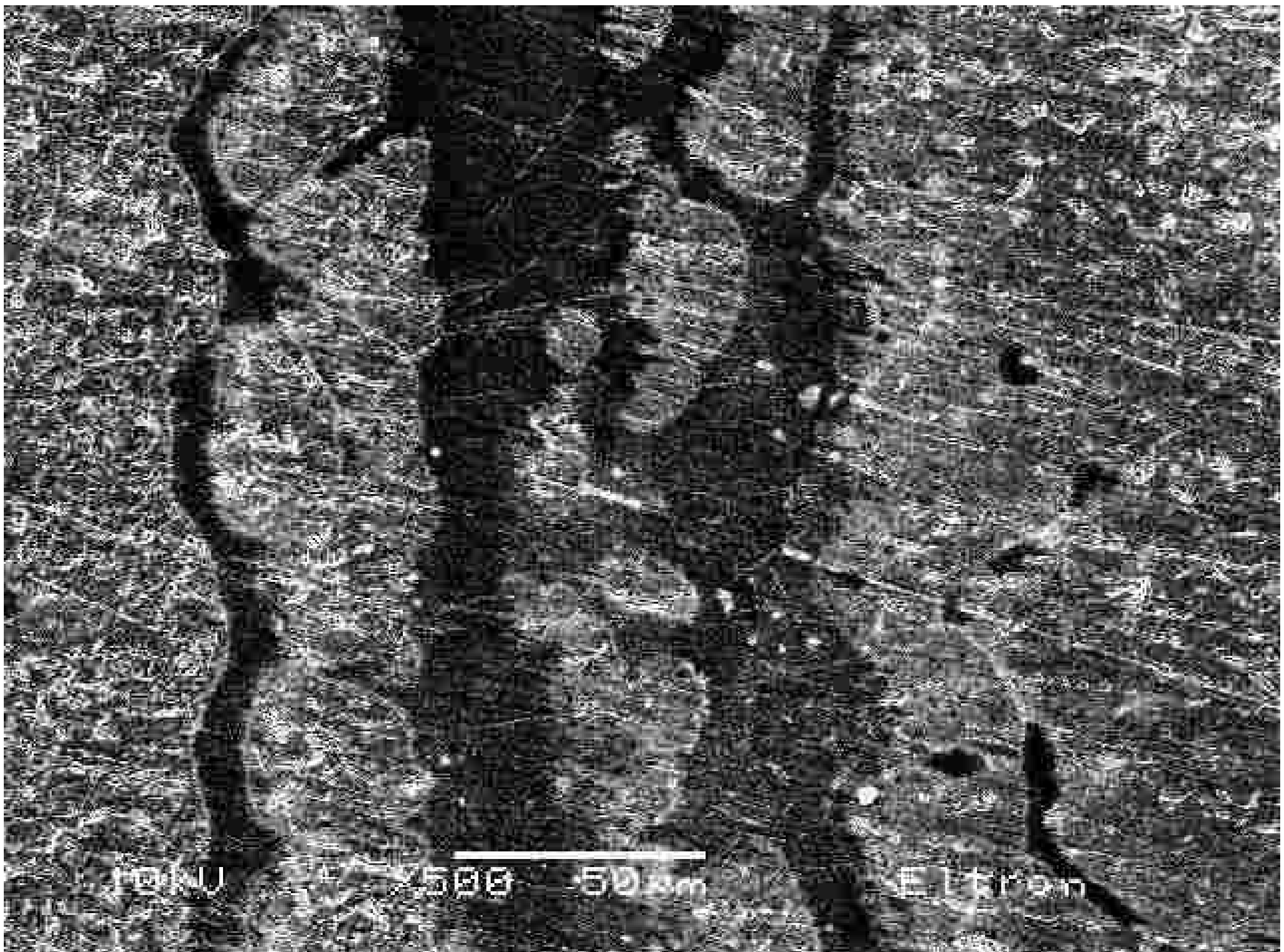


Results

Task 2 Brazing Vanadium Membranes

- Multiple vanadium alloys were obtained and tested for brazing performance with copper
- Based on the brazing tests and analysis of the literature, guidelines were developed to anticipate performance of vanadium alloys with respect to hydrogen transport and fabricability based on alloying elements.
- Elements that are potentially positive to both hydrogen transport performance and brazing performance are in alphabetical order: cerium, copper, iron, manganese, molybdenum, nickel, and zinc.
- Additional alloying elements may be sufficiently advantageous to transport characteristics to overcome their detrimental effect on brazing.

SEM Photo of vanadium/zirconium alloy braze



Alloying Elements

Alloying Element	Hydrogen Transport	Copper Alloy Brazing
Ag	O	+
Al	+	-
Au	O	+
Be	+	O
Ce	+	+
Co	+	-
Cr	+	-
Cu	+	+
Fe	+	+
Ga	-	+
Gd	O	+
Mn	+	+
Mo	+	+
Ni	+	+
Pd	+	-
Pt	+	-
Ru	+	-
Sn	+	-
Ta	+	-
Ti	+	-
Zn	+	+
Zr	+	-

Symbol (+) corresponds to a potential benefit

Symbol (-) corresponds to a likely detriment

Symbol (o) corresponds to no expected effect

Elements with no net benefit were left out

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Results

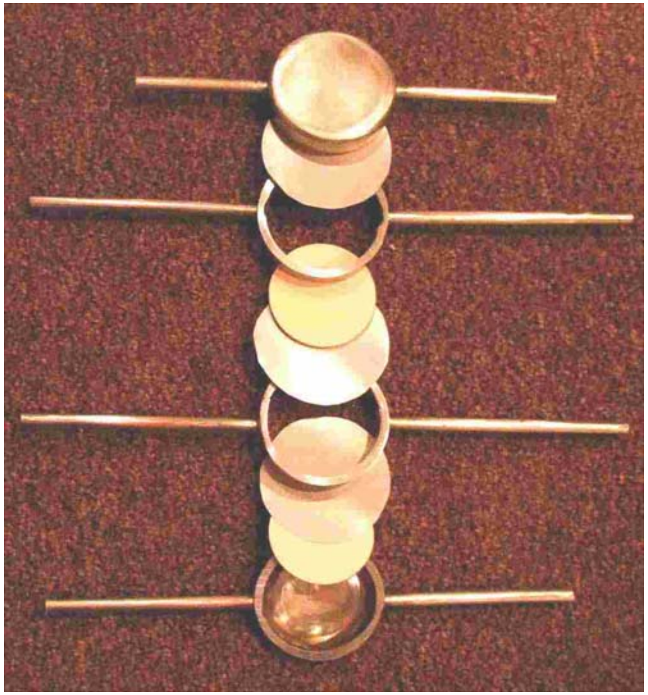
Task 3 Integrated WGS Vanadium Membrane Device

- Brazing tests were conducted between vanadium and structural alloys including mild steel, 304 stainless steel and 9Cr 1Mo steel.

- Brazing results with structural materials were generally excellent, though special attention will be necessary with respect to thermal expansion issues between large areas of vanadium foil and constrictive structural components.

- A physical model was produced with three layers of vanadium foil (2.25" diameter) and 304 SS, capable of being used as an integrated device. Testing of other geometries is planned.

Brazed Integrated Device Model with Three Membranes



Results

Task 4 Gasifier Testing of WGS – Vanadium

- WRI operates a steam/oxygen blown 7 inch fluidized bed coal gasifier using Powder River Basin coals
- Temperature control allows some hydrogen/carbon monoxide ratio adjustment (40/60 to 60/40)
- Assembled a slipstream system that can be cleaned for particulates, condensate, sulfur and mercury
- Secondary vessel is heated and compressed for testing catalysts, membranes or integrated system
- Gasifier testing on device initiated on April 12th, 2007

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Future Work

- **Task 1 Water Gas Shift Catalyst**
  - **Complete CeO_2 effect investigation on water gas shift performance**
  - **Investigate WGS monolith catalyst further**
- **Task 2 Vanadium Alloy Brazing**
  - **Mechanical testing of Cu braze strengths to compare to literature results for Au and Ag based brazes**
- **Task 3 Integrated Devices**
  - **Fabricate and braze two additional devices of alternate geometry to adjust for thermal expansion and scale-up issues**
- **Task 4 Gasifier Testing**
  - **Complete 80 hours of testing on integrated devices in coal derived syngas to examine sulfur and other contamination issues**

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Project Summary

Approach: The key to a commercially scaled device that integrates metallic hydrogen transport membranes and water gas shift catalyst will be a catalyst with high compressive strength and no friability and a practical low cost method to attach the membranes to structural alloys.

Conclusions: Impregnated porous substrates with high activities may be have more application than monolithic WGS catalysts. Brazing has been shown to be an excellent method for joining vanadium. Some alloying elements beneficial to hydrogen transport will interfere with brazing of the membranes to structural alloys. A predictive model has been generated to aid in vanadium alloy selection.

Future Work: At the completion of the project, several integrated devices of alternate geometries will have been produced that are designed towards commercially scaled integrated water gas shift/vanadium membrane assemblies.