ADMINISTRATIVE INFORMATION

1. **Project Name:** Development of Materials Resistant to Metal Dusting Degradation

2. **Lead Organization:** Argonne National Laboratory
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5. **Date Project Initiated:** 4-1-04

Expected Completion Date: 3-31-07

PROJECT RATIONALE AND STRATEGY

Project Objective:

The primary objective of the project is to mitigate metal dusting degradation of metallic structural alloys by development of alternate structural alloys with improved corrosion resistance and with adequate mechanical properties at temperatures up to 816°C (1500°F) and by surface modification of currently available structural alloys. The project will involve development of data on incubation time and propagation rate for metal dusting as a function of gas chemistry in the exposure environment, alloy chemistry, temperature, and alloy surface modification /pretreatment.

Technical Barrier(s) Being Addressed:

The production of hydrogen could be done more efficiently if the issue of metal dusting was better understood and materials were available to resist this type of degradation in the temperature range of 400-800°C. Current technology, generally, avoids the use of metals or alloys in the temperature range of 400-800°C and recovers the heat at temperatures of 400°C or lower. In effect, the “high” quality heat is used to generate steam because there are no known alloys that can reliably resist metal dusting. This excess steam represents about 125 BTU/{standard cubic foot of hydrogen (scfh)}, which could be saved if 800°C heat could be utilized directly in hydrogen plants. In the year 2000, there were about 3.8B scfh/d produced in the U.S.

Project Pathway:

The project will involve laboratory testing of the commercial alloys and new materials that will be developed to establish the metal dusting rates as a function of key process variables. The project will also establish procedures for surface modification of candidate alloys to resist metal dusting. Materials that were successful in the laboratory tests will be produced in different product shapes and tested in pilot and/or commercial process systems.

Critical Metrics:

Develop metal dusting rates based on pit size, distribution, and pit progression for Ni-base alloys over a 10,000 h exposure period.

Develop correlations that relate pit progression with weight loss measurements for several alloys as a function of exposure time.

Based on detailed analysis of metal dusting performance of commercial alloys, develop new Ni-base alloys of controlled composition with adequate strength and metal dusting resistance.

PROJECT PLANS AND PROGRESS

Past Accomplishments:

We completed exposures of Ni-base alloys in several gas mixtures with different carbon activities. A set of specimens, after 10,000 h exposure (in a gas mixture of carbon activity of 30), was analyzed for pit size, distribution, and pit progression. Pit size data were correlated with weight change measurements for several Ni-base alloys. We have established an electrochemical procedure to identify the location of pits in the early stage of degradation of an alloy. The technique is also used to assess the integrity of intermediate oxidation approaches being developed to mitigate further pitting. We have made some specimens of arc-melted buttons of alternate alloys and fabricated into sheets.

Exposures are in progress at 30 atm and 593°C (at a carbon activity ≈100) and the specimens have accumulated 2800 h. In addition, specimens are exposed at 1 atm and 593°C at carbon activities of 31 and ≈100. The specimens in these runs have accumulated 4500 and 2800 h, respectively. We have initiated exposure of specimens of newly-developed alloys to carburizing environments to evaluate their resistance to coking and to metal dusting degradation.

Future Plans:

Date	Milestone/Deliverable	Partner Activities
10/05	Metal dusting rate for Ni alloys at a_C=100	-
12/05	Intermediate oxidation procedure to mitigate metal dusting	-
3/06	Correlate pitting kinetics with alloy chemistry and gas chemistry	-
9/06	Establish rates for newly developed alloys	-

Project Changes:

We are trying to acquire another high-pressure system. Based on the deliberations on the importance of pit size measurements, we allocated the equipment dollars to obtain surface profiler with capability to measure pit depth up to 1 mm. The instrument was procured and installed at ANL and data on pit depth were obtained on several metal dusted alloys. The fabrication and/or procurement of the high-pressure unit are differed. However, Air Products agreed to supply their high-pressure equipment to ANL, but it will cost an additional $50K to procure water pumps (which won't be supplied by Air Products) and safety sensors and to get the equipment installed at ANL.

Commercialization Potential, Plans, and Activities:

The steering committee will be used by the project team to transfer the technology to industry. The materials developed under this project will have broad applications in the chemical, petrochemical, petroleum, steel, and heat-treat industry sectors of the economy. A gradual implementation of new/modified materials is envisioned in U.S. plants for hydrogen production, and ammonia and methanol reformers, and in refinery environments over the time period of 2007-2025. MTI with member affiliates and with other avenues will disseminate the information to the technical communities at large and accelerate the implementation of the results in practice. Several alloy manufacturers have shown interest in fabricating the newly developed alloys. ANL plans to pursue this approach upon satisfactory evaluation of the alloys and upon filing an application for patent.

Patents, Publications, Presentations:

Development of Alloys with improved resistance to metal dusting, Patent Application in progress.
Metal Dusting Research at ANL, Presented at AIChE Meeting, April 27, 2004, New Orleans, LA,
Metal Dusting Performance of Fe- and Ni-base Alloys, Materials Solutions Conference, ASM International, Columbus, OH, October 2004.
Metal Dusting Research at ANL, Presented at MTI Meeting, October, 18, 2004, Houston, TX.
Steering Committee Meeting at ANL, Presentation on October 18, 2004, Argonne, IL.
Metal Dusting Research at ANL, Presented at MTI Meeting, February 22, 2005, Tampa, FL.
Metal Dusting Performance of Structural Alloys, Presented at NACE Meeting, April 3-7, 2005, Houston, TX, also Paper published by NACE.