ADMINISTRATIVE INFORMATION

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

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5. **Date Project Initiated:** 4-1-04

6. **Expected Completion Date:** 3-31-07

PROJECT RATIONALE AND STRATEGY

7. **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.

8. **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.

9. **Project Pathway:**

The project involves laboratory testing of the commercial alloys and new materials that are developed to establish the metal dusting rates as a function of key process variables. The project establishes procedures for surface modification of candidate alloys to develop oxide scales that resist metal dusting. With MTI and member company support, materials that are successful in the laboratory tests will be produced in different product shapes and tested in pilot and/or commercial process environments.

10. **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.
- Establish viable process fix, which when implemented can retard metal dusting degradation and extend the life of the component material.

PROJECT PLANS AND PROGRESS

11. **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 continued long-term exposures of Ni-base alloys at a carbon activity of 100 and at a system pressure of 440 psi. We have established the role of carbon activity and system pressure on the time for onset of metal dusting and evaluated the pit propagation rates.

Based on the results from our study, we have fabricated several Ni-base alloys and tested them to assess their metal dusting resistance. After 7000 h exposure, the alloys seem resistant to attack at a carbon activity of 100 and no pits were observed on the specimen surfaces.

We have also procured/fabricated weldment specimens of several Fe- and Ni-base alloys and exposed them at 593°C in a metal dusting atmosphere with a carbon activity of 100. Information on weight change and pit characteristics are being developed for the weldments and will be compared with those for the base metals.

12. **Future Plans:**

Date	Milestone/Deliverable	Partner Activities
9/06	Metal dusting rate for Ni alloys at a_C=100	-
9/06	Surface engineering of alloys	-
12/06	Correlate pitting kinetics with alloy chemistry and gas chemistry	-
12/06	Testing of weldments	

13. **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. Even though Air Products agreed to supply their high-pressure equipment to ANL, the cost of procurement of monitoring equiment, installation, and safety evaluation would cost an additional $150K, which was not available and therefore, the installation of the new high-pressure equipment was cancelled.

14. **Commercialization Potential, Plans, and Activities:**

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 since the alloys exhibit superior resistance to metal dusting and we have filed for a patent for the alloys.

15. **Patents, Publications, Presentations:**

- Development of Alloys with improved resistance to metal dusting, applied for a patent.
- Relationship between the Growth of Carbon Nanofilaments and Metal Dusting Corrosion," Z. Zeng and K. Natesan, Chem. Mater. 2005, 17, 3794-3801.
- Metal Dusting Induced Pitting in Alloy 800," Aditya Putrevu, Z. Zeng, K. Natesan, S.K. Varma, and W.G. Durrer, Ferrous Physical Metallurgy of Highly Alloyed Steels, Materials Science and Technology 2005, Edited by James P. Materkowsky, pp.47-52, 2005.
- Metal Dusting and Oxidation at 593 and 704°C," S.K. Varma, Aditya Putrevu, Maduri Pasala, Z. Zeng, and Ken Natesan. International Conference on Processing & Manufacturing of Advanced Materials, THERMEC'2006, Vancouver, Canada, July 4-8, 2006
- Initiation of Metal dusting Pits and a Method to Mitigate Metal Dusting Corrosion", Z. Zeng and K. Natesan, Oxidation of Metals, accepted for publication
- Control of Metal Dusting Corrosion in Ni-Base Alloys", Z. Zeng and K. Natesan, International Journal of Hydrogen Energy, submitted.
- Effect of Water Vapor on Metal Dusting Behavior of Ferrous Alloys," Aditya Putrevu, S.K. Varma, Z. Zeng, and K. Natesan. TMS Annual Meeting, San Antonio, March 12-16, 2006.
- Metal Dusting Research at ANL, Presented at MTI Meeting, Orlando, FL, February 20-22, 2006.
- Steering Committee Meeting, Presentation at Pittsburgh, PA, October 24, 2005.
- Metal Dusting Research, Presented at MTI Meeting, Pittsburgh, PA, October 24, 2005.
- Metal Dusting Performance of Structural Alloys, Presented at NACE Meeting, April 3-7, 2005, Houston, TX, also Paper published by NACE.