Metal Dusting Progress Report – Final Report

Dates	Reporting Period: 04/01/2004 to 03/31/2007 Report Date: May 6, 2008
Award #	DE-FC36-04GO14039
Project Title	Development of Materials Resistant to Metal Dusting Degradation
Project Period	04/01/2004 to 03/31/2007
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Overall Project Objectives	The overall objective of this project is to develop a database on the metal dusting performance of metallic structural alloys, surface engineered materials, and weldments and to ultimately mitigate this type of degradation. The materials included several commercial and experimental Fe- and Ni-base alloys selected in concert with the suggestions of the industrial partners.

Background

Degradation of metallic structural components by metal dusting is of concern in several industries. It is a major issue in plants used in the production of hydrogen, ammonia-synthesis processes, methanol-reformer systems, and syngas (H_2/CO mixtures) systems that are pertinent to the chemical and petrochemical industries. Metal dusting is also observed at high temperatures in oxidizing-carburizing environments that are prevalent in the heat-treating industry. Metal dusting is also a problem in direct reduction processes in the production of iron.

Industry as a whole had significant uncertainty in the mechanism that led to metal dusting in their systems and they could not and did develop an approach to combat this attack. Research conducted over the years only showed that the materials can undergo metal dusting in the laboratory but the laboratory simulation of actual process environments was difficult and was not attempted, especially since the processes operate at high pressures while the laboratory tests are performed at 1 atm pressure.

The industry as a whole tried to mitigate metal dusting attack on their metallic components by designing around the conditions where the attack is prevalent, but this approach results in a significant penalty in terms of lower efficiency, wastage of energy, a decrease in product yield and increased levels of uncertainty in operation of the plant.

During the past several years, the work performed at Argonne National Laboratory has clearly established the role of carbon deposition in the mechanism leading to initiation and propagation of metal dusting attack. The laboratory work was conducted at both atmospheric and high pressures and simulated the gas chemistry (including the high steam content) prevalent in reformer environments. The development of materials that are resistant to metal dusting (as proposed in this project) can potentially lead to a complete redesign of reformers with improved efficiency, increased product yield, and decreased energy consumption.

The development of laboratory data on the initiation and the rate of metal dusting that simulates commercial practice are valuable in the operation of industrial processes and the design of new plants and the repair of existing plants.

Executive Summary

The purpose of this work was to develop a fundamental understanding of metal dusting and to develop ways to mitigate metal dusting. Metal dusting is corrosion process that leads to catastrophic destruction of equipment in certain industrial processes in the chemical industry and the refining industry. The project successfully identified and quantified the mechanism of metal dusting. A potential solution, a new alloy, was identified to this costly problem. A partner in the project funded a project to scale up the alloy to a semi-commercial level. Several alternate solutions to mitigate metal dusting were identified and are under going further development.

Key Project Summary Results

New alloy identified and scaled to semi-commercial level. Samples of the alloy are available for testing by MTI members in industrial processes experiencing metal dusting.

Industrial steering team formed and guided the project. The team met 13 times during the project.

A new technique was developed at Argonne to measure metal dusting pit initiation and pit growth.

Argonne filed for a patent on the alloy identified by Argonne that resists metal dusting.

There are nineteen publications from this work. They are available in the public technical literature. (List is shown at the end of this report.)

All the research results from Argonne were made available to MTI members on the MTI website. The MTI website has 700 plus users.

MTI is continuing funding of metal dusting studies to promote commercialization of the technology.

Technical Progress Report from Argonne and MTI Related Projects

Summary of Argonne Results

The main results of the Argonne work are summarized below. The detailed technical report documenting the work at Argonne is available at: http://www.mti-global.org.

Summary of Results from the Argonne Technical Report

The deposition of carbon from carbonaceous gaseous environments is a problem in many chemical and petrochemical processes, such as reforming systems and syngas production systems, iron ore reduction plants, heat treatment, and others. One of the major consequences of carbon deposition is the degradation of structural materials by a phenomenon known as "metal dusting." In recent years, an extensive program has been conducted at Argonne National Laboratory to establish the mechanisms for metal dusting degradation in metallic materials exposed to carbon-bearing gaseous environments, to identify the key parameters that influence the onset of metal dusting and propagation of degradation, to establish the metal wastage under a variety of exposure conditions, to characterize the morphology of degradation using a wide variety of analytical techniques, and to assess the effect of alloy chemistry, carbon activity, and system pressure on the extent of metal dusting.

Argonne conducted extensive studies on the coke deposit and metal-dusted alloys using Raman scattering, XRD, and SEM/EDX analysis to develop a fundamental understanding of the metal dusting process and the key variables that influence the initiation and propagation of the degradation. Based on these studies, it was concluded that there exists a strong relationship between metal dusting and degree of crystallization of the coke and proposed a mechanism for the initiation and propagation of metal dusting attack. It was found that the coke that has experienced metal dusting exhibits much better crystallinity than the coke deposits in the absence of metal dusting. Both metal dusting and carbon filament growth are related to the catalytic crystallization of carbon. Carbon does not crystallize well at low temperatures because of the strong C-C bond and its special layered structure. Carbon must dissolve and diffuse into a metal or a carbide particle. This particle acts as a catalyst to aid in the crystallization of carbon. In this catalytic crystallization process, metals are liberated as small particles which further contribute to metal dusting corrosion. The catalytic growth of carbon filaments is due to the transport of carbon from one facet of a metal or carbide particle that favors carbon deposition (but not carbon precipitation) to another facet that favors precipitation. The decrease in free energy from highly disordered carbon to well-crystallized carbon is the driving force for both catalytic growth of carbon filaments and for metal dusting.

Based on the above studies, it was concluded that the metal dusting mechanism for both iron and nickel are similar, which is due to the carbon catalytic crystallization process. The only difference is that iron carbide is thermodynamically stable and can form and can serve as a catalyst for the carbon catalytic crystallization, but nickel carbide is thermodynamically not stable. In the case of nickel, carbon dissolves and directly diffuses through nickel and uses nickel lattice as a template for its catalytic crystallization. Since the rate of the lattice mismatch of nickel and carbon is larger than that between carbon and Fe3C, the energy barrier is larger for carbon precipitating from nickel lattice than that for carbon precipitating from Fe3C lattice. Therefore, the metal dusting rate for nickel and its alloys is smaller than that of iron and its alloys.

In the current project, substantial progress was made in evaluating the performance of metallic materials subjected to simulated metal dusting environments at 1 atm and at high pressures. Surface profiler has been successfully introduced into metal dusting research for quantitative measurements on pit characteristics, in particular, pit depth. Several accomplishments can be identified from the study as:

- There are two major issues of importance in metal dusting. First is the formation of carbon/coke and subsequent deposition of carbon on metallic materials. Second is the initiation of metal dusting in the alloy and subsequent propagation of the degradation. The first is influenced by the aC in the gas mixture and the availability of the catalytic surface for carbon-producing reactions to proceed. There may be a threshold in aC (>>1) for carbon deposition. Metal dusting of the alloy in the reformer environments is determined by a competition between the oxide scale development and access to the virgin metal surface for the carbon deposit. In several long-term metal dusting experiments, we conducted extensive post-exposure analysis of the specimens to establish the time for initiation of metal dusting and propagation rates as a function of alloy chemistry, gas chemistry, and system pressure.

- By conducting long-term tests at 1 and 14.3 atm, while maintaining a carbon activity of ≈31, we established that the time for initiation of metal dusting is substantially reduced at the higher pressure, even for Ni-base alloys. Similar results were obtained when comparing the surface morphology of specimens tested at 1 and 30 atm at a carbon activity of 104.

- Surface profiler was introduced by the first time into metal dusting research to measure the depth of pits associated with metal dusting attack. We also measured the pit density in several Ni-base alloys using scanning electron microscopy. Pit density for each alloy was found to be different. The results indicated higher pit density in Alloys 601 and 45TM when compared to that in Alloys 602CA and 693.

- Based on a detailed analysis of pits (in several Ni-base alloys) as a function of exposure time, we correlated the growth in diameter of a single pit with the weight change observed for the alloys. We established that the alloys tested, except Alloy 214, lose weight by localized pitting when exposed in metal dusting environments. Alloy 214 developed numerous shallow pits leading to more uniform attack.

- Generally, the time for initiation of pits in Ni-base alloys is of the order of thousands of hours. However, the pit propagation rate is of major importance in assessing the viability of an alloy for any chemical process application. To expedite the initiation step and thereby emphasize pit propagation, we developed a pre-pitting approach. We used Alloy 800 and 9Cr-1Mo steel, as surrogate alloys, to develop the pre-pitting approach, since these alloys have a short initiation time for pitting. Subsequently, we applied the same approach to several Ni-base alloys. The method has led to development of multiple specimens of each alloy with pits for further study on propagation as a function of process variables such as temperature, system pressure, and gas chemistry.

- Argonne developed an approach to identify the locations of pits and potential pitting areas by an electrochemical copper deposition approach since the pit locations exhibit low resistance, leading to enhanced deposition of copper. Copper indicator experiments showed that there may be channels in the oxide scales for transfer of carbon into alloy substrates. These channels could be located because their electrical resistance is much lower than that of the oxide scale.

- Argonne tested several Ni-base alloys at a carbon activity of 104 at system pressures of 1 and 30 atm. The environment in these tests being more aggressive, the time for pit initiation is short. The emphasis in these tests is to quantify the pit propagation rates and correlate the data with alloy chemistry.

- Synchrotron X-ray nanobeam was used to analyze the thin oxide scale and oxide sub layers on the surface of alloys after exposure in simulated metal dusting environment. Results showed spinel with enhanced iron content as the major phase in the oxide scale at the metal dusting pit region. The oxidation state of Iron in spinel in the oxide scale on alloy surface is greater than +2, which diminishes the stability of oxide scale in the reducing condition prevalent in the reformer environments. Nickel metal particles were also identified in oxide scale which may join to form continuous channels for transport of carbon into the alloys.

- Increasing the Cr content (from 20 to 29 wt.%) in alloys had less effect in decreasing the pit growth rate when compared with the benefit of decreasing the Fe content in the alloy on the growth rate. The presence of Fe in the alloy leads to formation of (Fe,Cr) spinel phase in the scale. Over time, the Fe/Cr ratio in the spinel increases to essentially make it unstable in the high-carbon environments and eventual breakdown of the protective capacity of the scale. Therefore, we designed and prepared several alloys with low concentration of Fe and tested in metal dusting environments. Results showed that the ANL-developed alloys formed predominantly Cr oxide in the scale and the incubation time (for metal dusting) was extended ten times more than that of the commercial alloys with similar chromium contents.

- Argonne developed a process-control approach to mitigate metal dusting, in which the metal-dusted alloys (i.e., with pits on the surface) were given an intermediate oxidation treatment in an atmosphere without carbon. Subsequent exposure of these oxidized specimens to metal dusting environments showed substantial drop in pit-progression rate leading to possibility of extended service life for the metallic components.

- Argonne also evaluated Cu, Cu-coated, and Cu-clad materials for their susceptibility and pitting degradation in metal dusting environments. Copper and Cu-coated materials did not exhibit adequate resistance to metal dusting, especially after thousands of hours of exposure. The performance of Cu-clad alloys is dependent on the thickness and mechanical integrity of the clad layer. Additional long-term tests are needed to establish the adequacy of their performance in metal dusting environments.

- Argonne developed several Cu-Ni-Al alloys and evaluated their resistance in metal dusting environments and their tensile properties in air. Cu-Ni-Al alloys were resistant to metal dusting attack and they need to be evaluated further in a systematic manner for commercializing them for structural applications.

- Argonne evaluated weldment specimens of several Fe- and Ni-base alloys in metal dusting environments at a system pressure of 1 atm. In general, Ni-base alloy weldments exhibited superior performance than the Fe-base alloy weldments when tested in the same environment. The study focused on the relative performance of the weld metal, heat affected zone, and base metal upon exposure to metal dusting environments. The pit growth rates at the weld area are generally higher than those of the corresponding base alloys. Severe corrosion at the heat-affected zones was also observed.

- Argonne evaluated the pit progression in Alloys 602CA and 693 that were exposed at 659°C for 1.5 and 3 years in a metal dusting environment of a reformer plant. Both alloys exhibited several pits on the surface. Maximum size of the pit in Alloy 602CA was larger than that in Alloy 693. The average pit depth/diameter ratio for Alloy 693 is higher than that for Alloy 602CA. The size of pits in the bent regions (probably cold worked) of both Alloys 602CA and 693 are smaller than that in the flat regions.

- Argonne conducted a detailed analysis of two Alloy 800HT components that failed in a hydrogen reformer service. Results showed that the oxide scale on the alloy surface was predominantly Fe1+xCr2-xO4 spinel phase with high Fe content, which has been shown to offer little resistance to metal dusting attack.

- Argonne examined a failed component made of Alloy RA333 that was exposed to a metal dusting environment in a gas boiler. The analysis showed evidence for Cr depletion in the surface region and accumulation of Fe and Ni which can act as channels for transport of carbon and continued metal dusting degradation of the substrate alloy.

Scale Up Activities on Alloy Identified by Argonne

MTI funded a project to scale up the best performing alloy identified in the Argonne Studies. MTI contracted with Special Metals to make three 50 heats of the Argonne Alloy.

Alloy composition was achieved in the heats. The alloy was successfully hot rolled into plate at 0.25 inches and cold rolled into strip at 0.125 inches. The physical properties of the alloy were determined and found to be in the expected ranged.

MTI is making the alloy available to MTI members for evaluation in their processes requiring alloys with metal dusting resistance.

MTI is developing a MTI funded project to further evaluate the alloy that was scaled up and to compare it to coatings that are reported to be resistant to metal dusting.

MTI funded a worldwide review to the available technical literature on metal dusting. The review identified Argonne as one of the leading centers of metal dusting research in the world.

Patents The legal department at Argonne has filed a patent application for the new alloys that were developed in this project.

Awards The newly developed alloys selected as a winner in the R&D 100 Award competition for 2006.

Publications and Presentations

PUBLICATIONS ON METAL DUSTING PROJECTS

Availability of The Metal Dusting Report
The final report is available, at no cost, at http://www.osti.gov/bridge. It is also available on paper to the U.S. Department of Energy and its contractors, for a processing fee, from:

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phone (865) 576-8401
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Z. Zeng, K. Natesan, and S. B. Cai, “Characterization of the Oxide Scale on Alloy 446 by X-ray Nanobeam Analysis,” Electrochem. Solid-State Letters Volume 11, Number 1, 2007.

Milestone Schedule

Task Number Per SOO	Title or Brief Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Test Ni-base alloys	9/06			100%	Completed
2	Develop alternate alloys	12/05			100%	Completed
3	Surface Eng alloys	9/06			100%	Completed
4	Mechanical tests	9/05	9/06		100%	Completed
5	Plant testing	9/06			50%	Ongoing Industry

6	Pitting kinetics	12/06			100%	Completed- New task
7	Testing weldments	6/05	12/06		100%	Completed Rev. schedule

Argonne National Laboratory Cost Information

Current Budget Period: 10/1/05 to 9/30/2007*

Current Period: 1/1/2007 to 9/30/2007

Spending Schedule

Budget Category	Project Approved Budget	Project Expenditures	
		This Period	Cumulative to Date
RECIPIENT: Wages		68018	516,655
Fringe Benefits		38322	351,892
Travel		-1005	5,195
Equipment		0	92,588
Supplies		455	45,596
Contractual		0	0
Construction		0	0
Other		0	455
Total Direct Charges		105790	1,020,376
Indirect Charges		46386	326,421
Sub-Total		152176	1,346,797
National Lab Work		152176	1,346,797
DOE Share of Budget		152176	1,346,797
***Recipient Cost Share**			
Total Project Budget			
(*Detail Cost Share Contribution on Next Schedule)			

*The project was targeted to be complete March 31 2007. Argonne received and extension until September 2007 to complete the project.

Budget and Schedule Status

The Budget Numbers for Argonne, MTI and Industrial Participants are shown in the **Table below.**

Total Budget – In Kind and DOE Funds

Participant	Source of Funds	1st Qtr 2007	Total 2004/2007
MTI	In Kind	38,832	79,952
Air Products	In Kind		351,500
Haldor Topsoe	In Kind		249,750
ConocoPhillips	In Kind		627,171
Haynes International	In Kind		18,037
Special Metals	In Kind		7840
Rolled Alloys	In Kind		NA
Thyssen Krupp	In Kind		62,400
Total In Kind Industrial Contribution			1,396,650
Argonne National Lab	DOE	61,533	1,346,797
	Total Project		2,743,447

Plans for Next Quarter Project Complete