

SRI International

Technical Progress Report • June 2006

Diffusion Coatings for Corrosion-Resistant Components in Coal Gasification Systems

Quarterly Technical Progress Report 10

Covering the period October 1, 2005 through December 31, 2005

SRI Project P13063

Contract No.: **DE-FC26-03NT41616**

Prepared by:

Gopala N. Krishnan, Ripudaman Malhotra, Esperanza Alvarez,
Kai-Hung Lau, and Angel Sanjurjo
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Prepared for:

U.S. Department of Energy
National Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

Attention: Dr. Richard Read

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Heat-exchangers, particle filters, turbines, and other components in integrated coal gasification combined cycle system must withstand the highly sulfiding conditions of the high-temperature coal gas over an extended period of time. The performance of components degrades significantly with time unless expensive high alloy materials are used. Deposition of a suitable coating on a low-cost alloy may improve its resistance to such sulfidation attack, and decrease capital and operating costs. The alloys used in the gasifier service include austenitic and ferritic stainless steels, nickel-chromium-iron alloys, and expensive nickel-cobalt alloys.

In previous tests, we had frequently encountered problems with our steam generator that were exacerbated by the very low flow rates that we needed. During this period we installed a new computer-controlled system for injecting water into the steam generator that eliminated this problem. We also tested alloy coupons coated by using the improved procedures described in our last quarterly report. Most of these coatings were nitrided Ti and Ta coatings, either by themselves, or sometimes with barrier layers of Al and Si nitrides. The samples were tested for 300 h at 900°C in a gas stream designed to mimic the environment in the high temperature heat recovery unit (HTHRU). Three samples that showed least corrosion were exposed for an additional 100 h.

TABLE OF CONTENTS

Disclaimer	2
Abstract	3
List of Tables	5
List of Figures	5
Executive Summary	6
Introduction	7
Work Performed.....	7
Exposure to High Temperature Simulated Coal Gas: Test #9	8
Conclusions and Future Work	10

LIST OF TABLES

Table 1. Samples Tested and Results Test 9.....	8
---	---

LIST OF FIGURES

Figure 1. Samples before and after exposure for 306 h at 900°C in simulated gasifier Test 9a....	8
Figure 2. Samples before and after exposure for 100 h at 900°C in simulated gasifier Test 9b. ..	9

EXECUTIVE SUMMARY

Advanced coal gasification systems such as integrated coal gasification combined cycle (IGCC) processes offer many advantages over conventional pulverized coal combustors. Heat-exchangers, filters, turbines, and other components in IGCC plants often must withstand the highly sulfiding conditions at high temperatures. In collaboration with U.S. Department of Energy and ConocoPhillips, we are developing corrosion-resistant coatings for high-temperature components in IGCC systems.

SG Solution's coal gasification power plant in Terre Haute, IN, uses ConocoPhillips' E-Gas technology. The need for corrosion-resistant coatings exists in two areas: (1) the tube sheet of a heat exchanger at $\sim 1000^{\circ}\text{C}$ that is immediately downstream of the gasifier, and (2) porous metal particulate filter at 370°C , which is downstream of the heat exchanger. These components operate at gas streams containing as much as 2% H_2S . A protective metal or ceramic coating that can resist sulfidation corrosion will extend the life-time of these components and reduce maintenance.

In previous tests, we had frequently encountered problems with our steam generator that were exacerbated by the very low flow rates that we needed. During this period we installed a new computer-controlled system for injecting water into the steam generator that eliminated this problem. We also tested alloy coupons coated by using the improved procedures described in our last quarterly report. Most of these coatings were nitrided Ti and Ta coatings, either by themselves, or sometimes with barrier layers of Al and Si nitrides. The samples were tested for 360°C at 900°C in a gas stream designed to mimic the environment in the high temperature heat recovery unit (HTHRU).

INTRODUCTION

Heat-exchangers, filters, turbines, and other components in coal-fired power plants must withstand demanding conditions of high temperatures and pressure differentials. Further, the components are exposed to corrosive gases and particulates that can erode the material and degrade their performance. In collaboration with U.S. Department of Energy and ConocoPhillips, SRI International recently embarked on a project to develop corrosion-resistant coatings for coal-fired power plant applications. Specifically, we are seeking to develop coatings that would prevent the corrosion in the tube-sheet of the high-temperature heat recovery unit of a coal gasification power plant of SG Solution's plant in Terre Haute, IN, which uses ConocoPhillips' E-Gas technology. This corrosion is the leading cause of the unscheduled downtime at the plant and hence success in this project will directly impact the plant availability and its operating costs. Coatings that are successfully developed for this application will find use in similar situation in other coal-fired power plants.

WORK PERFORMED

In many previous runs, we had encountered difficulties with our syringe pump used to inject water for generating steam. At the very slow linear velocities that we were using, the pump would often fail to inject water at appropriate quantities into the steam generator; most likely because of the high static friction. During this period we installed a new computer-controlled system for the syringe pump. With this system, we were able to use a smaller diameter syringe that would allow a larger linear displacement, and having a computer control meant that the system could automatically refill itself periodically. The refilling requires a one-minute interruption in the flow, but in view of about 8-h residence time for the gas in the reactor, the interruption is insignificant. Shakedown tests, with this system showed that it worked to our complete satisfaction.

In the next hot run we exposed nine coupons to a simulated coal-derived gas of composition: 25.7% H₂, 38.9% CO, 17.3% CO₂, 1.4% H₂S, and 16.7% H₂O. The samples were coated by using the improved procedures described in our last quarterly report. Most of these coatings were nitrided Ti and Ta layers, either by themselves, or sometimes with barrier layers of Al and Si nitrides. After about 300 h on stream, the samples were retrieved and the three that appeared to have survived well were exposed for an additional 100 h.

EXPOSURE TO HIGH TEMPERATURE SIMULATED COAL GAS: TEST #9

The top panel of Figure 1 shows the picture of the coated samples before they were exposed to simulated gasifier conditions at 900°C. The bottom panel is a photograph of the samples after exposure after 306 h. Table 1 lists the samples, the specific coatings, and some general observations.



Figure 1. Samples before and after exposure for 306 h at 900°C in simulated gasifier Test 9a.

**Table 1. Samples Tested and Results Test 9
300 h (Dec 14, 2005)**

Sample No.	Material	Coating	Run	Appearance	% Wt. Gain
1	HR160	(Ti/Ta)N,	64	No significant attack	-1.12%
2	HR160	TiN,	64	No significant attack	-0.31%
3	SS410	(Ti,Al)N,	79	Severe attack, sulfide deposit	34.05%
4	SS405	(Ti,Al)N,	80	Severe attack, sulfide deposit	30.12%
5	SS409	(Ti/Ta)N,	81	Severe attack, sulfide deposit	34.20%
6	SS409	(Ti,Al,Ta)N,	82	Severe attack, sulfide deposit	8.39%
7	SS410	(Ti,Si)N,	84	Severe attack, sulfide deposit	44.72%
8	SS410	(Ti,Si)N,	89	No significant attack	0.73%
9	SS410	TiN,	90	Severe attack at the edges	13.33%

As is evident from Figure 1, most of the samples gained in weight substantially and showed signs of significant sulfidation attack; only the two HR 160 coated samples, and a 410 steel that was coated with (TiSi)N appeared to survive well. These three samples were put back into the furnace and exposed to simulated gasifier environment for an additional 100 h. Figure 2 shows their picture before and after this second round of exposure.

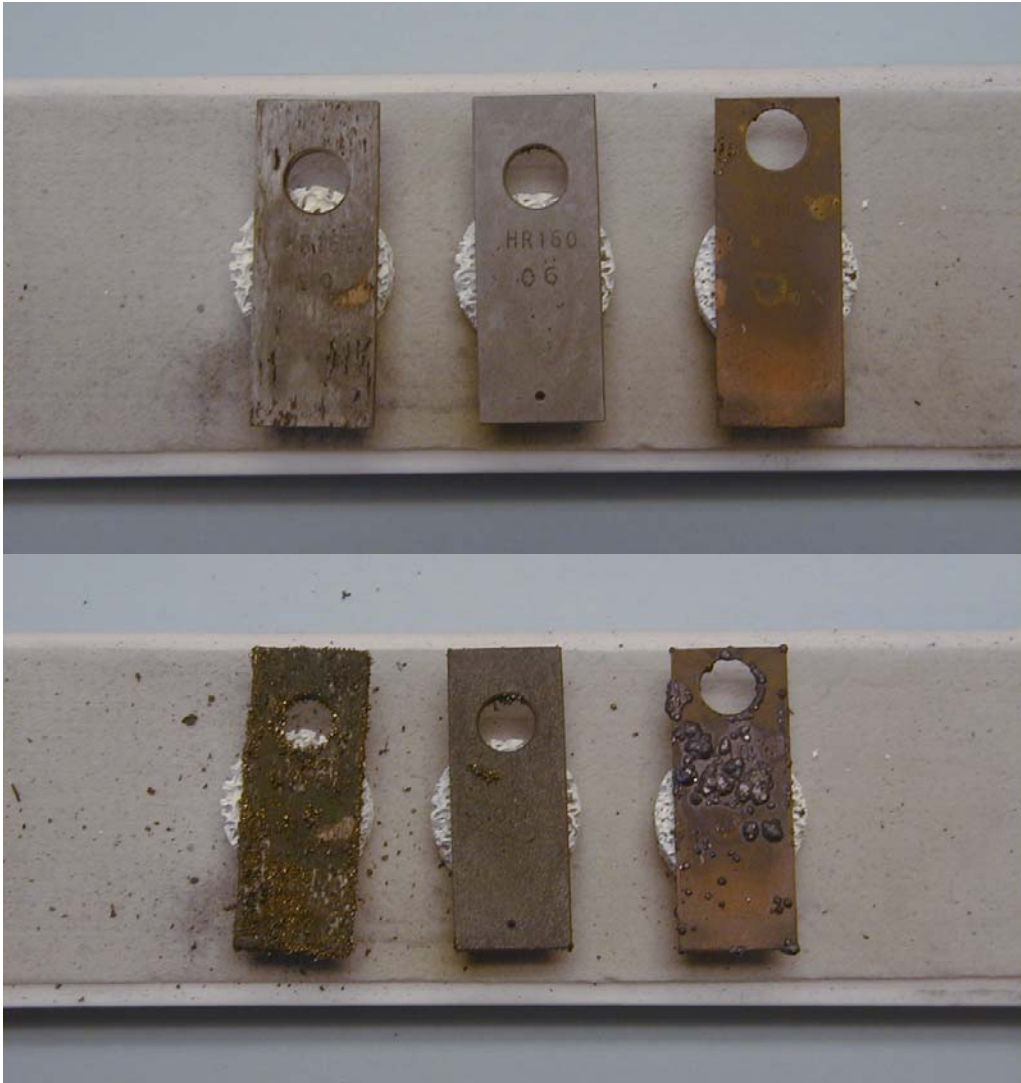


Figure 2. Samples before and after exposure for 100 h at 900°C in simulated gasifier Test 9b.

Significant amount of corrosion was evident on both HR160 alloy and the coated 410 alloy.

CONCLUSIONS AND FUTURE WORK

- Fluidized-bed chemical vapor deposition technique was used to coat low alloy 410 stainless steel coupons with titanium nitride, silicon nitride, tantalum nitride and mixtures of these nitrides. The coatings were adherent.
- The 410 alloy coupons and uncoated high alloy HR160 coupons were exposed to a simulated coal-derived gas mixture containing 1.4% H₂S at 900°C for 300 h. During this period, only the HR160 and a 410 alloy coupons coated with titanium and silicon nitrides did not exhibit sulfidation attack. Other 410 alloy coupons coated with titanium, aluminum, and tantalum nitrides showed extensive sulfidation attack.
- On continued exposure for another 100 h to the simulated coal gas mixture, all samples showed sulfidation attack, indicating that the coatings provide only a limited resistance to sulfidation at 900°C.
- Further testing of coated coupons formed with tungsten barrier layers between the TiN (or TaN) layers will be conducted in the next quarter. We also expect to receive samples that were exposed in the ConocoPhillips plant at Wabash River. Analysis of these coupons, as well as hose exposed in our laboratory is planned.