

---

Technical Progress Report • March 2005

# Diffusion Coatings for Corrosion Resistant Components in Coal Gasification Systems

Quarterly Technical Progress Report 6  
Covering the period October 1, 2004 through December 30, 2004

SRI Project PYU-13063

Project Identification 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: Mr. 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.

During this reporting period we conducted two exposure tests with coated and uncoated coupons. The first one was aborted after a short period, because of a leak in the pressure regulator of a CO/CO<sub>2</sub>/H<sub>2</sub> gas mixture gas cylinder that was used to prepare the simulated coal gas stream. Nevertheless, this run was very instructive as it showed that during the brief exposure when the concentration of H<sub>2</sub>S increased to 8.6%, even specialty alloys such as HR160 and I800 were badly corroded, yet the sample of a SS405-steel that was coated with Ti/Ta showed no signs of corrosion.

After replacing the pressure regulator, a second run was conducted with a fresh set of coated and uncoated samples. The Ti/Ta-coated on to SS405 steel from the earlier runs was also exposed in this test. The run proceeded smoothly, and at the end of test the uncoated steels were badly damaged, some evidence of corrosion was found on coupons of HR160 and I800 alloys and the Cr-coated steels, but again, the Ti/Ta-coated sample appeared unaffected.

## TABLE OF CONTENTS

DISCLAIMER .....	2
ABSTRACT .....	3
EXECUTIVE SUMMARY .....	6
INTRODUCTION .....	7
WORK PERFORMED .....	7
CONCLUSIONS AND FUTURE WORK .....	12

## LIST OF TABLES

1. Samples tested and the result from Test 2.....	8
2. Samples and their weight changes during Test 3 .....	10

## LIST OF FIGURES

1. Samples after brief exposure to gasifier environment with 8.6% $H_2S$ (Test 2) .....	9
2. Steel samples after brief exposure to gasifier environment in Test 3.....	11
3. Steel samples after exposure to gasifier environment in Test 3 .....	11

## 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 are often must withstand the highly sulfiding conditions at high temperatures. In collaboration with U.S. Department of Energy and Conoco/ Phillips, 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 ~1000°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<sub>2</sub>S. A protective metal or ceramic coating that can resist sulfidation corrosion will extend the life-time of these components and reduce maintenance.

During this reporting period we conducted two exposure tests with coated and uncoated coupons. The first one was aborted after a short period, because of a leak in the pressure regulator that unexpectedly exhausted the CO/CO<sub>2</sub>/H<sub>2</sub> gas mixture. Nevertheless, this run was very instructive as it showed that during the brief exposure when the concentration of H<sub>2</sub>S increased to 8.6%, even specialty alloys such as HR160 and I800 were badly corroded, yet the sample of SS405 steel that was coated with a Ti/Ta compound showed no signs of corrosion. Incidentally, this was the same sample that was previously exposed for 100 hours in the simulated gasifier stream.

After replacing the pressure regulator, a second run was conducted with a fresh set of coated and uncoated samples. The Ti/Ta-coated SS405 steel sample from the earlier runs was also exposed in this test. The run proceeded smoothly, and at the end of test the uncoated steels were badly damaged, some evidence of corrosion was found on coupons of HR160 and I800 alloys and the Cr-coated steels, but again, the Ti/Ta-coated sample appeared unaffected.

## **INTRODUCTION**

Heat-exchangers, filters, turbines, and other components in coal-fired power plants are often have to 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 Conoco/Phillips, 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**

We conducted two exposure tests during this with coated and uncoated coupons as well as tie rods that were received from WREL. Both tests were designed to expose samples to a simulated gasifier environment at 900°C. The gas composition was set at 30.8% H<sub>2</sub>, 46.7% CO, 20.8% CO<sub>2</sub>, 1.7% H<sub>2</sub>S and balance (20%) steam. The gas mixture was generated by blending steam with (1) a gas mixture of 57% CO, 24% CO<sub>2</sub>, and 19% H<sub>2</sub> and (2) a gas mixture of 10% H<sub>2</sub>S and 90% H<sub>2</sub> in appropriate quantities. The total gas flow was set at 120 standard cm<sup>3</sup> per min (sccm).

### **Exposure to Simulated Coal Gas: Test 2**

The samples used in Test 2 and the results of exposure are listed in Table 1. This test was aborted after 20 h, because of a leak in the pressure regulator of a CO/CO<sub>2</sub>/H<sub>2</sub> mixture gas cylinder. Overnight, this cylinder emptied and the samples were exposed to a much higher concentration of H<sub>2</sub>S (8.6%) because only the gas mixture from H<sub>2</sub>S /H<sub>2</sub> gas cylinder and steam were flowing. Some of the uncoated samples were badly corroded, and the sulfide layer buildup was severe enough to cause the quartz sample holder to break. Figure 1 is a photograph of the samples as retrieved from the aborted run. It is noteworthy that during the brief exposure when the concentration of H<sub>2</sub>S increased to 8.6%, even specialty alloys such as HR160 and I800 were badly corroded.

Yet the sample of SS405 steel coated with Ti/Ta nitrides showed no signs of corrosion. Incidentally, this was the same sample that was previously exposed for 100 hours in the simulated gasifier stream.

**Table 1**  
**SAMPLES TESTED AND THE RESULT FROM TEST 2**

<b>Sample No.</b>	<b>Material</b>	<b>Coating Run</b>	<b>Coating (Surface Conc.)</b>	<b>Appearance</b>
1	I800; tie rod	uncoated	-	Corroded; broken
2	HR160, tie rod	uncoated	-	Badly corroded
3	HR160	uncoated	-	Badly corroded
4	SS405	uncoated	-	Thick scale
5	I800	uncoated	-	Badly corroded
6	SS410	R40	Cr (60%)	Black coating
7	SS405	R46	Cr (20%)	Minor scaling
8	SS410	R39	Cr (77%)	Black coating
9	I800	R44	Cr-Al	Some pyrite beads
10	SS405	R47	Ti-Ta	Unaffected



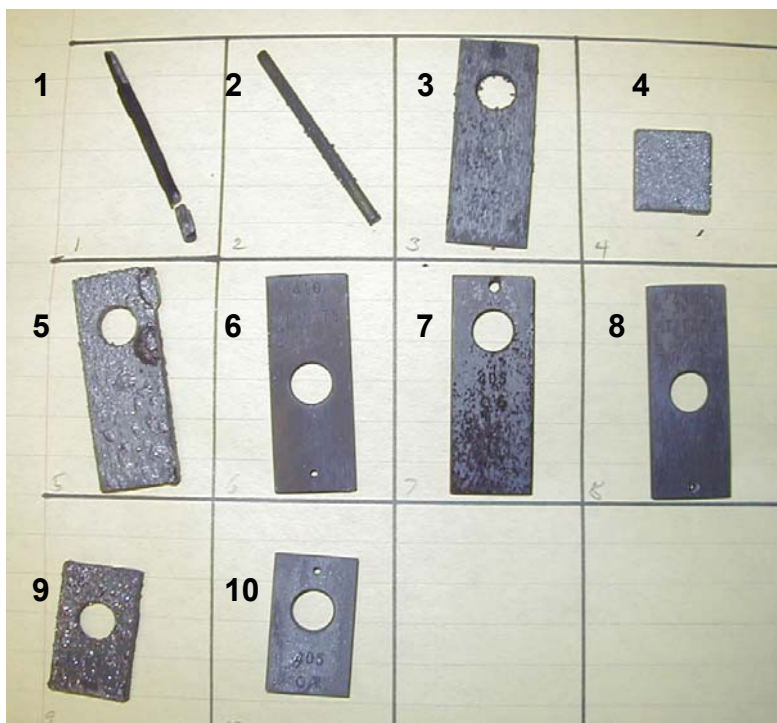


Figure 1. Samples after brief exposure to gasifier environment with 8.6% $H_2S$  (Test 2).

### Exposure to Simulated Coal Gas: Test 3

After replacing the pressure regulator, another run was conducted with a fresh set of coated and uncoated samples. The Ti-Ta-coated sample of SS 405 steel from the previous run was also exposed in this test. The exposure temperature and gas composition were the same as before, and this run test proceeded smoothly for 100 h at which point the run was terminated and the samples retrieved for examination.

The samples and their fate are listed in Table 2, and Figure 2 is a photograph of all the samples after exposure. Sample #4, the uncoated SS405 coupon, developed a thick sulfide layer and broke the quartz sample holder from the resulting expansion. This sample, along with the other steel samples used in this run, is shown in Figure 3. Samples #6 and #8 are both SS410 coupons coated with Cr. They developed a black coating and show a small weight gain (ca. 1%). Sample #7, SS405, had a lower surface concentration of Cr. It developed some scales and had a slightly larger weight gain of 1.6%. The Ti-Ta coated SS405 sample was unaffected.

**Table 2****SAMPLES AND THEIR WEIGHT CHANGES DURING TEST 3**

<b>Slot No.</b>	<b>Material</b>	<b>Coating Run</b>	<b>Coating (Surface Conc.)</b>	<b>Appearance</b>	<b>Weight Change<sup>1</sup> (%)</b>
1	I800 tie rod	uncoated	-	Corroded	N.D.
2	HR160 tie rod	uncoated	-	Corroded;	N.D.
3	HR160	uncoated	-	Some beads	N.D.
4	SS405	uncoated	-	Thick scale	N.D.
5	I800	uncoated	-	Badly corroded	N.D.
6	SS410	R40	Cr (60%)	Black coating	0.91
7	SS405	R46	Cr (20%)	Minor scaling	1.63
8	SS410	R39	Cr (77%)	Black coating	1.20
9	I800	R44	Cr-Al	Pyrite beads	-4.78
10	SS405	R47	Ti-Ta	Unaffected	0.03

N.D.: Not determined due to severe corrosion of the samples and loss of corroded layers.

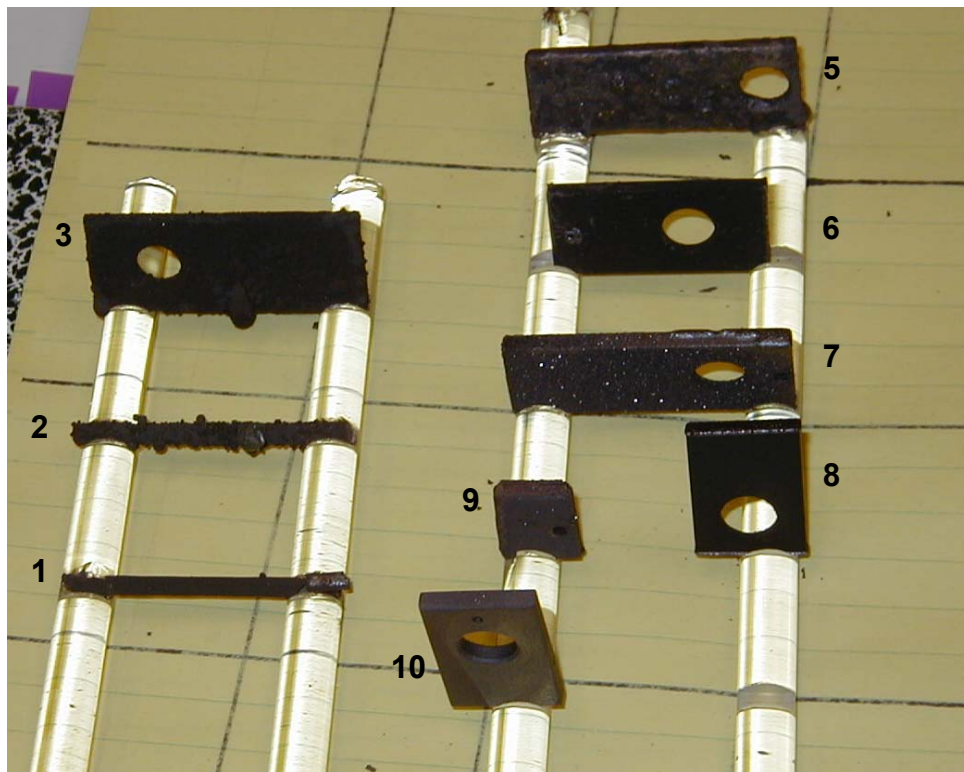


Figure 2. Steel samples after brief exposure to gasifier environment in Test 3.  
(Note: Sample 4 fell off the quartz holder)

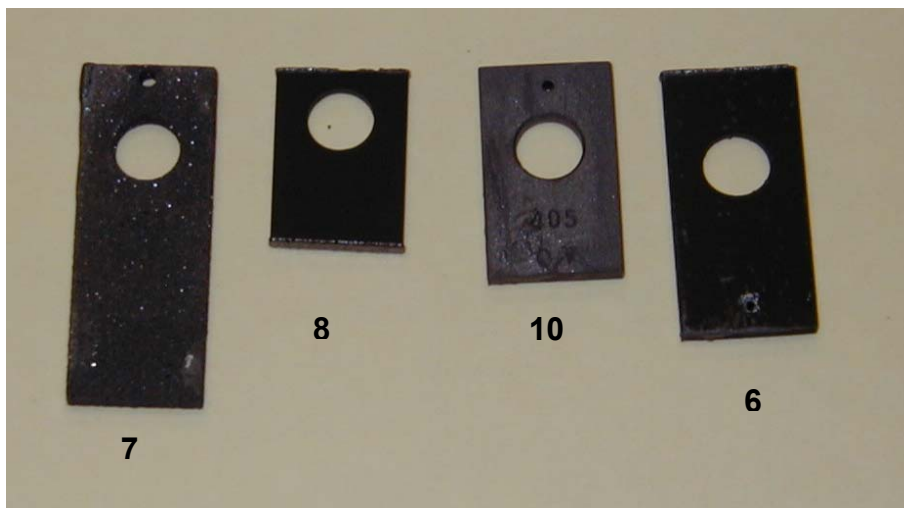


Figure 3. Steel samples after exposure to gasifier environment in Test 3.

## **CONCLUSIONS AND FUTURE WORK**

These tests show that the Cr diffusion coatings and Ti-Ta nitride coatings, both afford a certain degree of protection against corrosion. Since the Ti-Ta nitride coatings appear to fare the best, we will prepare more samples with this coating, including some porous steel samples, and expose them in longer duration tests. We will also analyze the coated samples before and after exposure to better understand the protection mechanisms of the coatings in coal gas environments.