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Diffusion Coatings for Corrosion-Resistant Components in Coal Gasification Systems

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ABSTRACT

Heat exchangers, particle filters, turbines, and other components in an 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 a simulated gasifier test primarily with TiN-coated steel samples. Although the test showed these coatings to offer significant protection against corrosion, they also revealed a lack of uniformity in the coatings. We spent a considerable amount of effort improving our coatings procedure as well as the fluidized bed reactor and its heater. Based on the results collected thus far, we selected 12 samples and sent them to ConocoPhillips for testing in their gasifier at the Wabash River Energy plant.

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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 ~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_2S. 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 a simulated gasifier test primarily with TiN-coated steel samples. Although the testing showed that these coatings offered significant protection against corrosion, it also revealed a lack of uniformity in the coatings. We spent a considerable amount of effort improving our coatings procedure, as well as the fluidized bed reactor and its heater. Based on the results collected thus far, we selected 12 samples and sent them to ConocoPhillips for testing in their gasifier at the Wabash River Energy plant.

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 at SG Solution's facility 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 situations in other coal-fired power plants.

WORK PERFORMED

During this reporting period, we conducted a simulated gasifier test primarily with TiN-coated steel samples. Although the test showed these coatings to offer significant protection against corrosion, they also revealed a lack of uniformity in the coatings. We spent a considerable amount of effort improving our coatings procedure, as well as the fluidized bed reactor and its heater. Based on the results collected thus far, we selected 12 samples and sent them to ConocoPhillips for testing in their gasifier at the Wabash River Energy plant.

A review of the literature showed that addition of Ti and Si to the alloy steels can be beneficial in improving their sulfidation resistance.[1] Formation of a compact, protective oxide layer that resists the ingress of S into the alloy is likely to be the cause of the improved sulfidation resistance. The Ni-Co-based alloy HR-160 contains Si as an additive and it has high sulfidation resistance. TiN coatings are used in the semiconductor resistance as diffusion barrier coatings. Based on these factors, we decided to investigate the use of TiN coatings.

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[1] K. Natesan, "Corrosion Resistance of Iron Aluminides." Report by Argonne National Laboratory under Contract No. W31-109-Eng-38, 2001.

EXPOSURE TO SIMULATED COAL GAS: TEST 7

The samples used in Test 7 and the results of exposure are listed in Table 1. We focused on samples coated with Ti nitride from several deposition runs with an attempt to get uniform coatings. To see the effect of surface morphology, we sand-blasted a sample of SS409 coupon (#14) and coated it alongside another coupon that was not sand-blasted (#14). Also included was a porous SS316 sample coated with (Ti/Ta) nitride to see if this coating would fare better than the previous attempts with Ti/T nitride (Exposure Test 4) or the oxidized Cr/Al-Al coating (Exposure Test 6). Figure 1 shows the picture of the coated samples before they were exposed to simulated gasifier conditions at 900°C. The test was conducted for 96 h, after which the reactive gases were turned off and the furnace cooled to retrieve the samples for examination. Figure 2 is a photograph of the samples after exposure.

Table 1. Samples Tested and Results Test 7a, 96 h (April 21, 2005)

Sample No.	Material	Coating/ Run	Appearance
1	HR160 – 08	TiN/64	Some discoloration
2	Porous SS 360	(Ti/Ta)N/62	Badly corroded
3	SS410 – 06	TiN/65	Pinhole corrosion or bubbles from adjacent sample
4	SS409 – 12	Ox-Cr/Al-Al/ 59	No apparent degradation
5	SS409 – 13	TiN/63	Some corrosion, reverse side looks good
6	SS409 – 14	TiN/63	Some corrosion, reverse side looks good

Figure 1. Samples from Exposure Test 7a before and after exposure to simulated gasifier environment for 96 h.

We noticed that some of the samples in the run had different degrees of corrosion on the top and bottom surfaces although most of them seemed to have survived well. We decided to continue exposing them to gasification environment after flipping them over. Also, we removed the SS409-12 sample (coated with Cr/Al-Al, oxidized) that had survived over 500 h under the gasifier conditions with no signs of corrosion. We added a sample of TiN-coated SS405 that was recently prepared (run 66). Table 2 lists the samples that were exposed in the continuation of this run (Test 7b).

Table 2. Samples Tested and Results Test 7b, 240 h (April 27, 2005)

Sample No.	Material	Coating/ Run	Appearance
1	HR160 – 08	TiN/64	Survived. Minimal corrosion at edges.
2	SS409 – 13	TiN/63	Lots of signs of corrosion.
3	SS409 – 14	TiN/63	Only edges corroded.
4	SS410 – 06	TiN/65	Only edges show corrosion.
5	SS405 – 17	TiN/66	Badly corroded.

By and large, these samples seemed to have fared well. The HR160 sample had minimal corrosion. The pair of SS409 samples show the effect of sand-blasting. The fact that corrosion was often limited to the edges and that sand-blasting also helped suggests that morphological stresses may be a contributing factor in corrosion. The SS405 sample showed extensive signs of corrosion. We have previously noted that the presence of Ni in the alloys such as the 300 series steels interferes with the formation of the diffusion barrier coating. The result with SS405 suggests that the presence of carbon in the alloy also interferes with the coating process. Only 409 steel, which has extremely low carbon, appears to be amenable to protection by our coating process.

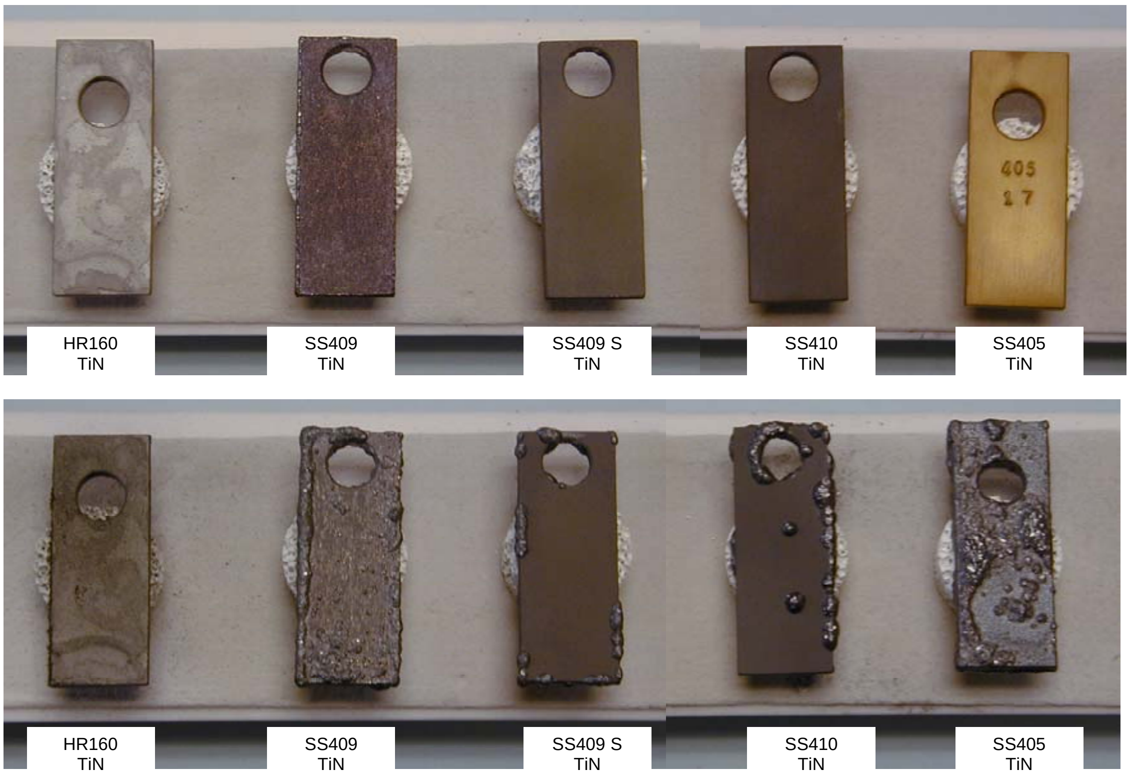

Figure 2. Test 7b samples, before and after 240 h exposure.

IMPROVEMENTS TO THE COATING PROCEDURE

Fluidized beds generally provide uniform heat and mass transfer and, hence, we chose it for the coating step with the expectation that the coatings would be uniform. However, we observed that many of the coupons showed non-uniform coatings. Careful examination of the apparatus showed two major shortcomings. First, when we use many coupons in the same run, the fluidizing between the coupons is sometimes adversely affected. Second, portions of some of the coupons were outside the optimal heating zone of the RF heater. This Quarter, we began to address these deficiencies. We decided to use fewer coupons in the future runs and also increase the spacing between them. We also modified the heater coil to ensure that the coupons were completely within the RF heating zone. Details of the final coating procedure and surface analysis of the coated samples are presented in the next Quarterly Report.

SAMPLES FOR EXPOSURE IN CONOCO PHILLIPS GASIFIER

We had previously (June 2004) sent samples to ConocoPhillips for placement in their gasifier. However, because of certain difficulties with the run, the samples were never exposed to coal gas. Those samples were exposed to about 100 h of start-up attempts with natural gas.

Subsequent plant shutdown and labor disputes delayed the start of the next run. In July 2005, the plant was to be restarted, and that presented another opportunity to test samples in a real gasifier. Over the past year, we had improved our coating procedures and also observed that oxidized Cr/Al-Al and TiN coatings seemed to be quite effective. We chose samples of coated and uncoated alloys (listed in Table 2) for the test, and sent them to ConocoPhillips. These samples will likely be retrieved when the plant is next shut down for scheduled maintenance.

CONCLUSIONS AND FUTURE WORK

Both TiN and oxidized Cr/Al-Al coatings seem to offer protection against corrosion when the substrate does not contain Ni or carbon. We noticed that surface roughness impairs the quality of coating, and that sand blasting the sample prior to coating leads to better results. We also observed that the protection is least effective at the edges. These two observations may be linked, and point to some geometric factors that may cause a variation in local temperature.

Table 3. Samples for Gasifier Exposure Tests (April 29, 2005)

Coupon	Alloy	Marking	Coating	RUN NO.	Size (mm)
1	HR160	05	None	-	41.7x19.6x3.2
2	I 800	08	None	-	51.2x19.4x3.7
3	SS 410	05	None	-	51.2x19.6x3.0
4	SS 304 L	02	None	-	51.2x19.5x3.0
5	SS 409	12	Cr-Al/Al/Ox	59	51.5x19.5x3.9
6	SS 409	16	Cr-Al/Al/Ox	70	51.3x19.5x3.8
7	SS 409	17	Cr-Al/Al/Ox	70	51.4x19.5x3.8
8	SS 405	15	TiN	66	51.2x19.6x3.6
9	SS 405	16	TiN	66	51.2x19.5x3.4
10	SS 409	18	TiN	68	51.5x19.5x3.8
11	SS 409	20	TiN	68	51.4x19.5x3.9
12	SS 316 porous	-	TiN	62	52.8x24.8x3.3

1. Sample 5 has already survived 500+ hours in simulated gasifier environment in the lab.
2. Sample 12 will not survive the high-temperature conditions. It is to be exposed to only colder gases after the HTRU, perhaps in a slip stream.