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Diffusion Coatings for Corrosion Resistant Components in Coal Gasification Systems

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DISCLAIMER

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 focused on getting a bench-scale test system to expose alloy coupons to simulated gasifier environment. The test facility was designed to allow about 20 specimen coupons to be exposed simultaneously for an extend period to a simulated coal gas stream at temperatures up to 1000°C. The simulated gas stream contained about 26%H_2, 39%CO, 17%CO_2, 1.4% H_2S and balance steam.

We successfully ran a 100+h test with coated and uncoated stainless steel coupons. The tested alloys include SS304, SS316, SS405, SS409, SS410, and IN800. The main finding is that Ti/Ta coating provides excellent protection to SS405 under conditions where uncoated austenitic and ferritic stainless steel alloy coupons are badly corroded. Cr coatings also appear to afford some protection against corrosion.

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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 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.

Wabash River Energy Laboratory (WREL), a subsidiary of Conoco/Phillips operates an IGCC system at Terre Haute, IN. 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..

Previously, we coated coupons of selected alloy steels with diffusion coatings of Cr and Al, as well as with titanium and tantalum nitrides. Several coated and uncoated samples were sent to Wabash River Energy Laboratory to place the coupons in the stream of an operating gasifier. These specimens will not be available for several months and hence, we proceeded to test the coated and uncoated alloys in our laboratory.

A test reactor was designed and installed to expose about 20 different coupons to simulated gasifier environment at high temperatures. About 10 coated and uncoated coupons were exposed to a simulated coal gas mixture containing 26%H_2, 39%CO, 17%CO_2, 17%H_2O, and 1.4H_2S at 900°C for about 120 h. The tested alloys include SS304, SS316, SS405, SS409, SS410, and IN800. The main finding is that Ti/Ta coating provides excellent protection to SS405 alloy. Cr-coatings also appear to afford some protection to these alloys against sulfidation attack. Under the test conditions, uncoated austenitic and ferritic stainless steel alloy coupons were badly corroded.

INTRODUCTION

Heat-exchangers, filters, turbines, and other components in coal-fired power plants 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 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 operated by Wabash River Energy Laboratory (WREL) in Terre Haute, IN. 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

During this reporting period, we assembled a test facility to expose coupons to simulated gasifier environments. The test facility consists of a 9.0-cm OD by 90-cm long electrically-heated tube furnace. The furnace is long enough to easily accommodate over 20 coupons. The ends of the tube furnace are capped with steel flanges with ports to admit and/or vent gases.

The gas stream at the WREL plant consists mostly of H_2, CO, and CO_2 in roughly 30:36:15%. The balance is steam and about 2% H_2S. To achieve some degree of flexibility in metering in different amounts of H_2, CO and CO_2, and H_2S, we opted in favor of using two mixed-gas cylinders. One cylinder contained H_2, CO, and CO_2 in a 19:57:24 ratio. The other cylinder contained 10% H_2S in H_2. Mass flow controllers metered these mixtures to blend a simulated coal gas stream of desired composition. A heated evaporator was used to produce steam with controlled rate of injection of liquid water by a syringe pump. The tube carrying steam and other gases were heated to prevent further condensation. H_2S/H_2 was added near the inlet of the reactor to prevent corrosion of metal tubing. The final gas composition was 25.7% H_2, 38.9% CO, 17.3% CO_2, 1.4% H_2S and balance steam. The total flow rate of the gas stream was about 120 sccm. A schematic diagram of the test system is shown in Figure 1.

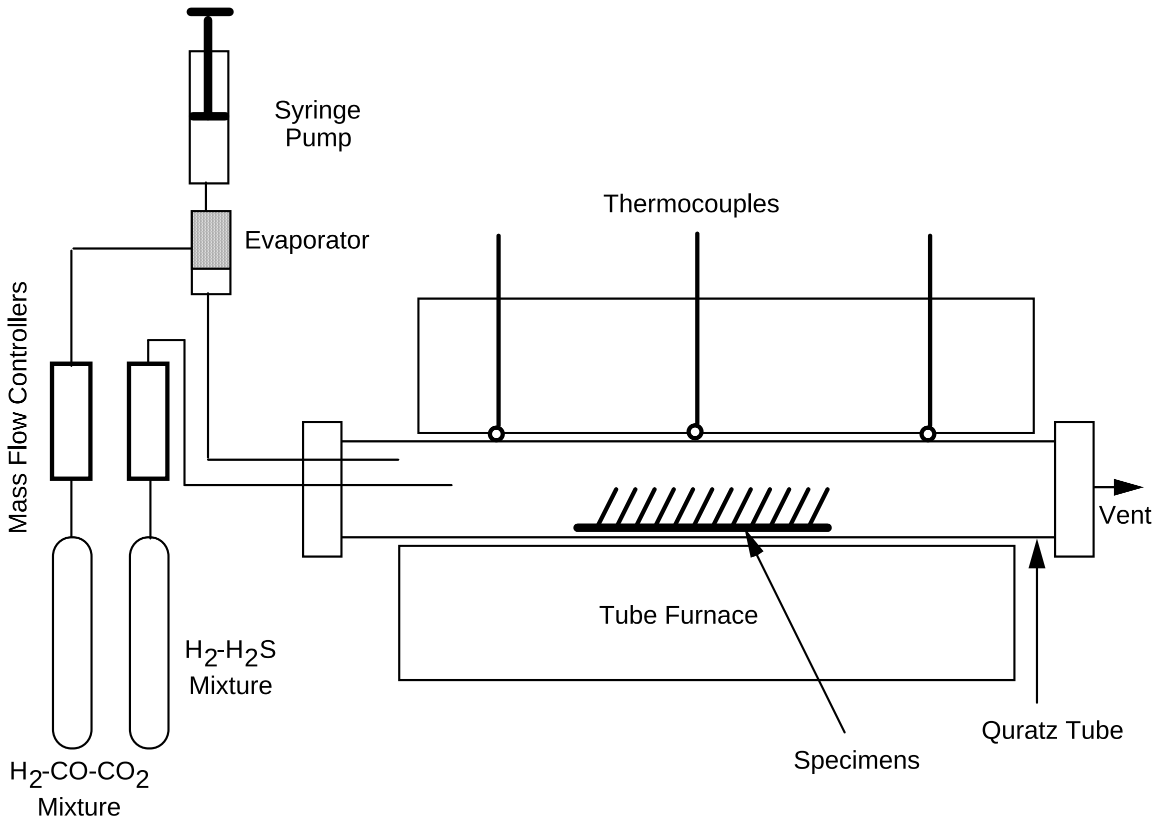

Figure 1. Schematic diagram of the bench-scale exposure test system.

The furnace has three heating zones, each of which can be independently controlled. After a few adjustments to the power supply, we were able to achieve a uniform temperature profile across most of the central portion of the furnace as shown in Figure 2. The temperature inside the furnace was 900°± 5°C through the central 50 cm length. About 20 sample coupons can be placed inside the furnace using a notched-sample holder made of quartz. This arrangement allowed all samples to be exposed to the coal gas uniformly. Both coated and uncoated specimen coupons were tested for their resistance to sulfidation.

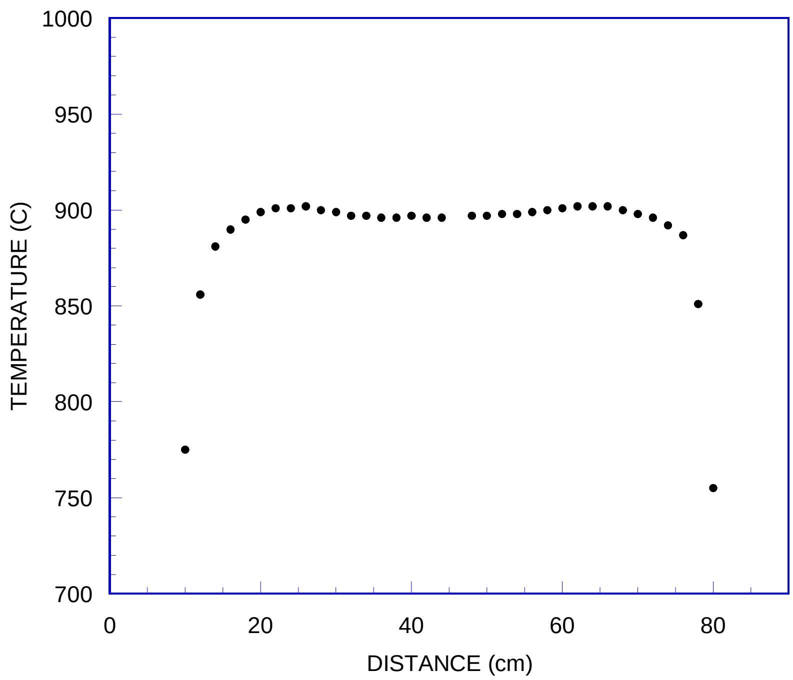

Figure 2. Temperature profile across the length of the furnace.

RESULTS AND DISCUSSION

We exposed 11 coated and uncoated samples as listed in Table 1. After loading the samples, the air inside the quartz tube was removed by purging with nitrogen overnight. The furnace was heated in N_2 and in about 2 h all three segments of the furnace were above 700°C. The reactive gases were then turned on, as was the steam generator and the temperature was increased to 900°C. During the initial run, we passed the H_2, CO, CO_2, and H_2S mixture through the steam generator. This practice resulted in the steam generator being fouled by the presence of H_2S after about 5 h. Hence, the H_2S/H_2 was allowed to bypass the steam generator and enter the reactor directly, as shown in Figure 1. Since there was only a small amount of scaling on some of the samples, we cleaned all the samples with a wire brush, reweighed them, and continued with the exposure test. The run proceeded smoothly for 117 h at which point it was terminated. After cooling the samples were retrieved and examined.

Table 1 also lists the weight changes in the samples resulting from the exposure, before and after exposure. It also includes comments on the appearance of the samples at the end of the test. Figure 3 is a picture of the samples after the 117-h exposure.

Table 1

SAMPLES AND THEIR WEIGHT CHANGES DURING EXPOSURE TO SIMULATED COAL GAS AT 900°C

Slot No.	Material	Coating Run	Coating Comp.	%Wt. Change(g)	
1	IN800	uncoated	-	0.28	Adherent deposit on the surface
2	SS410	uncoated	-	1.95	Adherent deposit on the surface
3	SS409	uncoated	-	0.72	Adherent deposit on the surface
4	SS304L	uncoated	-	24.56	Extensive attack. Sample crumpled
5	SS405	R46	Cr	0.16	Minimal adherent deposit on the surface
6	SS405	R47	Ti/Ta	0.58	Minimal adherent deposit on the surface
7	SS410	R39	Cr	0.10	Minimal adherent deposit on the surface
8	SS410	R40	Cr	0.04	Minimal adherent deposit on the surface
9	SS316	R41	Cr[1]	35.93	Extensive attack
10	SS405	R46	Cr	0.06	Minimal adherent deposit on the surface
11	SS316	uncoated	[1]	28.61	Extensive attack. Sample crumpled

[1] Porous sample.

The weight gain data shown in Table 1 should be viewed with caution. At 900°C, in the presence of H_2S and steam, sulfides of Fe and Ni are formed along the oxides of Cr, resulting in a weight gain. However, if the reaction products do not adhere well to the substrate, they can fall out, resulting in a weight loss. In some cases, the attack by H_2S was so severe (for example: sample #4, Figure 3), liquid metal sulfide dripped out the surface of the coupon. We attempted to determine the weight change as precisely as possible. The uncoated SS316 porous metal filter coupon (sample #11, Figure 3) crumpled when a slight pressure was applied.

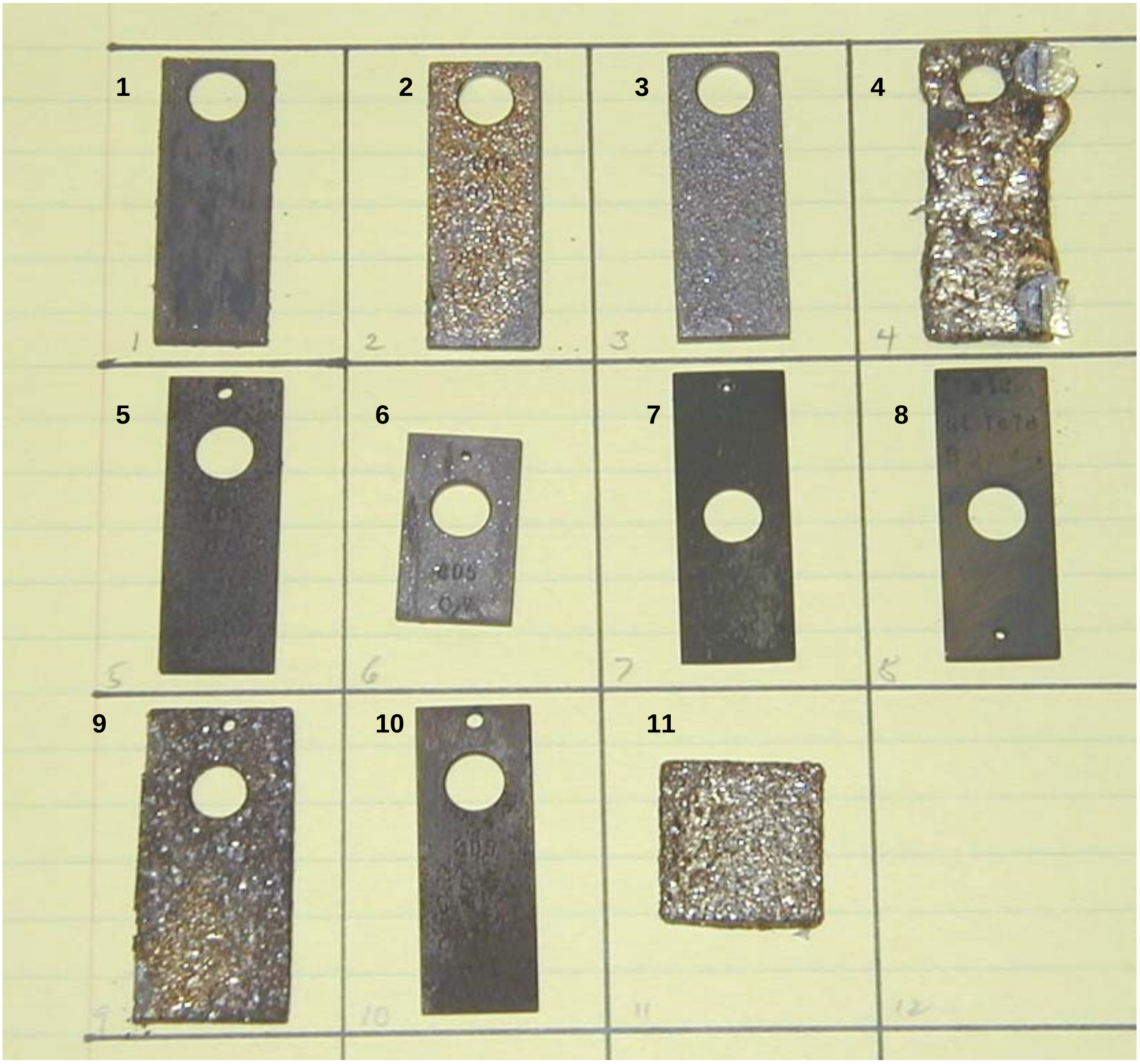

Figure 3. Samples after exposure to simulated gasifier environment for 117 h.

As expected, after the exposure to a simulated coal gas containing 1.4% H_2S at 900°C, most of the uncoated samples (Samples #1 through #4, and #11) were corroded extensively. Only the IN800 alloy showed only minor signs of corrosion, resulting in an adherent deposit. However, the deposit was not uniform, but had relative large sulfide particles embedded in the deposit.

The coated coupons (Samples #5 through #10) showed various levels of attack by H_2S. A minimum level of attack was observed on Sample #6, which is a 405 steel coated with Ti/Ta. Other coupons that were coated with chromium also had minimum weight gain, but there were visible signs of varying degrees of corrosion. Cr-coating did not prevent corrosion of the porous SS316 alloy sample, although Cr was found to have penetrated the porous interior of the sample.

CONCLUSIONS AND FUTURE WORK

Our facility for testing the durability of coupons under gasification conditions is ready. We successfully ran a 100+h test. The main finding is that Ti/Ta coating provides excellent protection to SS405 under conditions where uncoated austenitic and ferritic stainless steel alloy coupons are badly corroded. Cr-Al diffusion coatings also appear to afford protection against corrosion. Additional runs with other alloys and coated samples are planned.