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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 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 is 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.

A review of the literature indicated that the Fe- and Ni-based high-temperature alloys are susceptible to sulfidation attack unless they are fortified with high levels of Cr, Al, and Si. To impart corrosion resistance, these elements need not be in the bulk of the alloy and need only be present at the surface layers. We selected diffusion coatings of Cr and Al, and surface coatings of Si and Ti for the preliminary testing. These coatings will be applied using the fluidized bed chemical vapor deposition technique developed at SRI which is rapid and relatively inexpensive. We have procured coupons of typical alloys used in a gasifier. These coupons will be coated with Cr, Al, Si, and Ti. The samples will be tested in a bench-scale reactor using simulated coal gas compositions. In addition, we will be sending coated samples for insertion in the gas stream of the coal gasifier.

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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 that is immediately downstream of the gasifier, and (2) porous metal particulate filter, which is downstream of the heat exchanger. These components operate at gas streams containing as much as 2% H_2S. The temperatures of the heat exchanger and the metal filters are about 1000° and 370°C, respectively. A protective metal or ceramic coating that can resist sulfidation corrosion will extend the life-time of these components and reduce maintenance.

Although the specifications of the material components used in the gasifier system are proprietary, alloys used in the gasifier service include austenitic stainless steels such as 304 alloy, ferritic stainless steels such as 405 and 410 alloys, nickel-based alloys such as Incoloy 800, and nickel-cobalt alloys such as HR160.

Based on a brief review of the published literature reported earlier, we selected the following coating compositions: (1) Cr diffusion coatings with a surface concentration of about 50 wt%, (2) aluminum diffusion coatings with surface concentration of about 15 wt%, (3) silicon diffusion coating of about 10 wt%, and (4) titanium coatings either nitrided or in combination with silicon coatings.

We have developed a fluidized-bed chemical vapor deposition technique to coat several metal and ceramic compositions on powders, tubes, and sheets. This technique is more rapid than pack cementation used for chromizing and aluminizing metal parts. It is relatively low in cost in comparison with conventional chemical vapor deposition technique as the precursors are generated in the fluidized bed reactor. Because of excellent mass and heat transfer characteristics of the fluidized bed, the rate of coating is rapid. The technique can be used to coat complex shapes because the chemical vapor deposition technique is not limited to line-of-sight.

We have procured coupons of HR 160, Incoloy 800, stainless steel 304 and alloy steel 410. In the next quarter, we will be coating them with Cr, Al, Si, and Ti. The samples will be tested in a bench-scale reactor using simulated coal gas compositions. In addition, we will be sending coated samples to WREL for insertion in the gas stream of the coal gasifier. A window of opportunity exists in May 2004 for coupon exposure to an actual coal gas atmosphere when the gasifier will be undergoing maintenance.

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 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.

To help select the appropriate substrate and coating materials, we conducted a brief review of the different environments that the components may be exposed to, the substrate materials that are commonly used, and the coating technologies. Based on the information available in the literature the corrosion reaction is the competition between oxidation and sulfidation reactions. The Fe- and Ni-based high-temperature alloys are susceptible to sulfidation attack unless they are fortified with high levels of Cr, Al, and Si. To impart corrosion resistance, these elements need not be in the bulk of the alloy and need only be present at the surface layers.

Discussions with Dr. Albert Tsang of Conoco/Phillips revealed two main areas of concern: 1) heat exchanger, which is a separate chamber immediately downstream of the gasifier, and 2) porous metal filter, which is downstream of the heat exchanger. The specific conditions of these problem areas are discussed below:

1. The heat recovery unit is a single pass tubes in shell design (Figure 1). The hot gases pass through the tubes, and the steam is in the shell. Hot gases enter the exchanger from top at 1800-1900°F (982° to 1038°C) and 400 psig and contain between 1.0 and 1.5% H_2S. Most of the gas is CO, H_2, and CO_2. In addition, ash and other particulate matter are also present. They exit from the bottom at 700°F (370°C), with no significant drop in pressure or change in composition. Condensate is brought in near the bottom, and steam

1500 psi (saturated at about 600°F or 315°C) exits near the top. The tube sheets have to withstand about 1100 psi of pressure differential at about 1900°F (1000°C). The upper tube sheet is where most of the material problems occur.

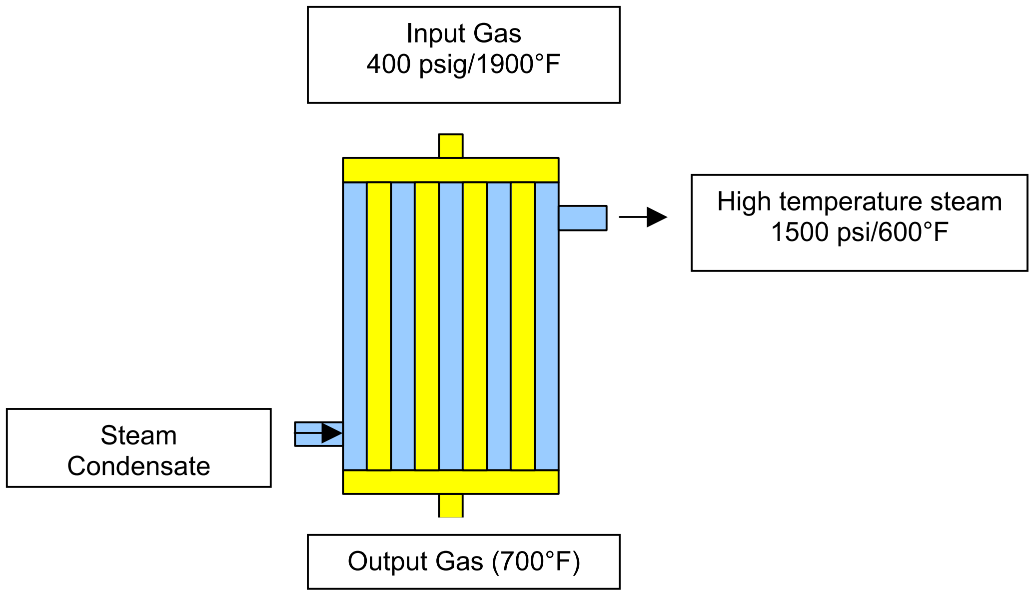

Figure 1. Schematic of high-temperature heat-recovery unit (HTHRU) at WREL

2. A second problem is with the porous metal filters they use to trap the particulates. The metal sees the gases exiting from the heat exchanger at 700°F (370°C). No significant pressure differential exists between the inlet and the outlet of the filter, but the material must stand up to the corrosion due to H_2S. The ceramic filters that were tested broke too readily. A protective metal or ceramic coating on the porous metal surfaces that can resist sulfidation corrosion without blocking the pores will extend the life-time of the metal filters.

COMPONENT MATERIALS

Both iron-based and nickel-based alloys are used in the heat exchanger and metal filter applications. Because of the proprietary nature, the exact composition of the alloys cannot be disclosed publicly. However, Table 1 describes the composition of typical alloys used in these high temperature applications

Table 1

COMPOSITION OF ALLOY STEELS USED IN THE COAL GASIFIER SYSTEMS

Alloy[1]/Element	HR160, N12160	Incoloy800, N0880	SS304, S30400	SS405, S40500	SS410, S41000, Tempered	SS410, S41000, Annealed
Aluminum		0.15-0.6		0.2		0.2
Carbon	0.05	<0.1	0.015	<0.08	<0.15	<0.08
Chromium	28	19-23	19	13	13	13
Cobalt	30					
Copper		<0.75				
Iron	<3.5	>39.5	69	85	85	85
Manganese	0.5	<1.5	1	<1	<1	<1
Molybdenum	<1					
Nickel	37	30-35	10			
Niobium	<1					
Phosphorus			0.23		<0.04	<0.04
Silicon	2.75	<1	0.5	<1		<1
Sulfur		<0.015	0.015		<0.03	<0.03
Titanium	0.5	0.15-0.6				
Tungsten	<1					

[1] The composition of the elements is in weight percent. Alloys are designated both in common nomenclature and unified numbering system

As seen from Table 1, significant composition differences exist between the alloys. The HR160 nickel based super alloy that contain significant fractions of Cr, Co, and Si. The cost of HR 160 is significantly more than that of 304 stainless steel. The Incoloy 800 is also nickel-based alloy used as heat exchanger material in nuclear reactors and it contains about equal fractions of Fe and Ni and about 20% Cr. Its mechanical properties at high temperatures are not as good as HR 160. SS 304 is the well-known austenitic stainless steel containing 18% Cr and 10% Ni. Its corrosion resistance at moderate temperature is good but at high temperatures it is prone to both oxidation and sulfidation at high temperatures. The SS 400 series is less expensive than other alloys listed and they are more benefited by corrosion resistant coatings. The fraction of carbon in these alloys is very low. High levels of carbon lead to the formation of chromium carbides during chromium coating deposition.

COATING COMPOSITION

As stated in the last quarterly report, a minimum Cr concentration of 25 wt% or an Al concentration of 15 wt% is required to achieve adequate sulfidation resistance at about 650°C. Addition of V to the Cr layer minimized the formation of chromium carbides at the grain boundaries. Increasing both Cr and Al levels in the alloy is beneficial in resisting sulfidation attack, but the benefit of the coating is strongly depends on the adhesion of the coating to the substrate. Thin layers of Si or SiO_2 deposited on an Fe-Cr alloy improved corrosion resistance against sulfidation at about 700°C, due to the presence of a SiO_2 layer at the alloy surface that acts a barrier to the migration of sulfur inward and cation transport outward.

Based on the above discussion, we selected the following coating compositions:

Chromium – diffusion coating with surface concentration of about 50 wt%

Aluminum – diffusion coating with surface concentration of about 15 wt%

Silicon – diffusion coating with surface concentration of about 10 wt%

Titanium – coating

In addition to the above components, we may also coat with other elements such as vanadium and tungsten which has shown to be beneficial in some cases. Further, the metal coatings may be nitrided to prevent inter-diffusion between different coating layers. Titanium nitride is used as a diffusion barrier in the manufacture of integrated circuits.

COATING METHOD

SRI International's fluidized-bed CVD technique can be used to coat fibers, particles, powders, and fabricated parts. Briefly, in this technique, a source metal powder bed (e.g., Si) is fluidized with a carrier gas (e.g., Ar) and reacted with HCl and H_2. When the reactor is operated at an appropriate temperature and conditions for the coating metal, volatile metal halides (e.g., $SiHCl_3$, SiH_2Cl_2, $SiCl_2$) are formed *in situ* that decompose on the substrate (e.g., steel) to form a metallic coating. The substrates act as a sink because the activity of coating metal (e.g., Si) in them is typically very low (<1%) while the gas is saturated. In many cases, such coatings are deposited on substrate materials at much lower temperatures than are possible with other coating techniques. In the initial stages, deposition and diffusion are very fast for steel substrates above 550°C. Because the CVD process is not a line-of-sight coating technique, it can be applied uniformly on complex geometric shapes. The technique may also be used to coat porous materials such as metal particulate filter.

Simplified schematic diagram of a fluidized bed reactor is shown in Figure 2. The reactor is a cylindrical vessel incorporating a porous plate that serves the dual function of supporting the bed of granular or powdered material and distributing the flow of gas uniformly over the cross-sectional area of the bed. The velocity of gas necessary to levitate the particles in the bed is a function of the particle diameter, shape, and the density of the bed material. When fluidization takes place, the bed of particles expands and acts like a liquid in that it seeks its own level and assumes the shape of the containing vessel. Furthermore, during fluidization, the flow of gas through the bed is locally turbulent, favoring high rates of heat and mass transfer that result in very low thermal and concentration gradients within the bed. Figure 3 illustrates the results from a chromium coating on 409 stainless steel specimen in which the surface concentration of Cr is increased from about 12 to 27 wt%.

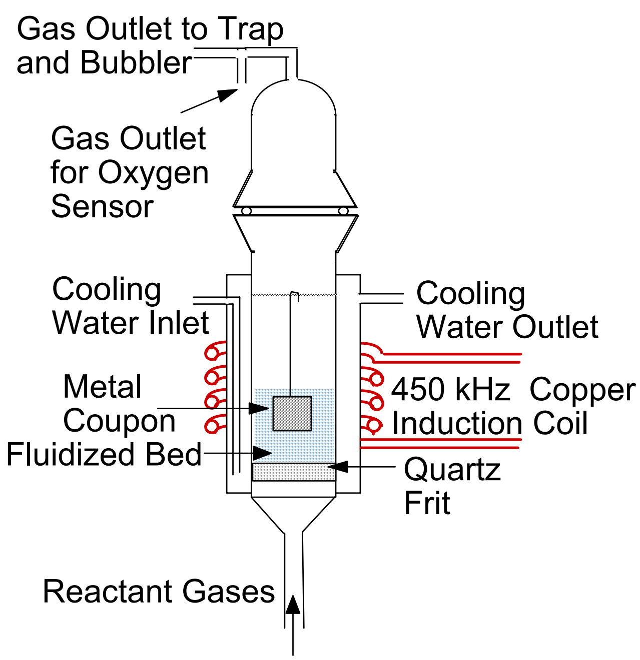

Figure 2. Simplified schematic of a fluidized bed reactor with RF heating.

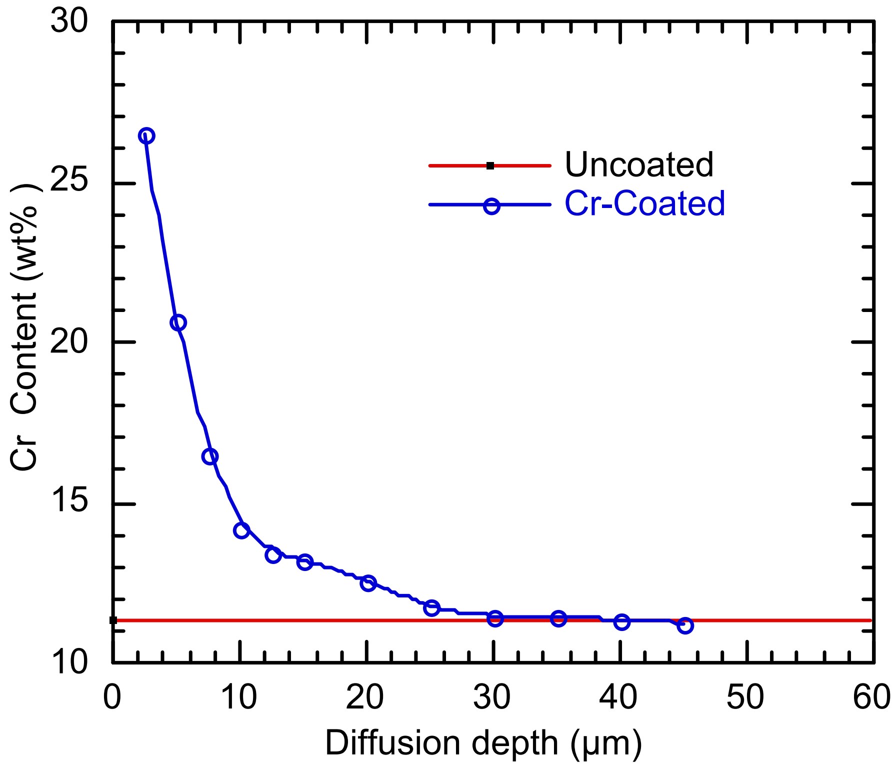

Figure 3. Concentration profile of chromium diffusion coating on 409 stainless steel.

CONCLUSIONS AND FUTURE WORK

The fluidized-bed chemical vapor deposition technique is ideally suited to deposit of coatings of Cr, Si, Al, and Ti. We have procured coupons of HR 160, Incoloy 800, stainless steel 304 and alloy steel 410. In the next quarter, we will be coating them with Cr, Al, Si, and Ti. The samples will be tested in a bench-scale reactor using simulated coal gas compositions. In addition, we will be sending coated samples to WREL for insertion in the gas stream of the coal gasifier. A window of opportunity exists in May 2004 for coupon exposure to an actual coal gas atmosphere when the gasifier will be undergoing maintenance.