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SURFACE MODIFICATION FOR CORROSION RESISTANCE*

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INTRODUCTION

Coal gasification technologies emphasize production of intermediate-Btu syngas by using oxygen and steam to gasify coal; the syngas is used as a feedstock for chemical production or is burned to provide industrial process heat, steam, and/or electricity. Three different types of gasifiers—fixed-bed, fluidized-bed, and entrained slagging-bed—are being considered. In dry-ash gasifiers, metallic alloys with lifetimes of at least 20,000 h are required for use in gasifier internal components. In the case of slagging gasifiers, no metallic internals will be used because gasification occurs at much higher temperature, but metallic cyclones and heat-recovery systems are needed outside the gasifier vessel.

Apart from the enormous size of the heat-recovery units, the selected material must withstand a hostile environment that contains low-partial-pressure oxygen (pO_2) and moderate-to-high-partial-pressure sulfur (pS_2), and coal slag condensates.^{1,2} In addition, with a viable hot-gas clean up system, the hot cleaned gas is expected to drive a gas turbine in integrated gasification combined-cycle (IGCC) plants. Several modes of material degradation have been identified including, oxidation, sulfidation, hot corrosion, deposit-induced corrosion, and erosion. Furthermore, the classes of materials used for different components in these systems are also wide-ranging. For example, relatively inexpensive carbon steel and low-alloy steels are used for waterwalls, economizers, and evaporators; austenitic alloys are used for steam superheaters and reheaters; high-chromium/aluminum iron-base alloys are used for sulfidizing conditions; and nickel- and cobalt-base alloys are used for hot corrosion environments. As a result, the modification of surfaces for corrosion minimization in these systems must focus on a given application. Figure 1 shows the stability of different metals as a function of pO_2 , pS_2 , and pCl_2 calculated for a metal temperature of 650°C. Also shown in the figure are the regions of excess-air and air-deficient combustion (the latter is typical of gasification),

Figure 1. Oxygen/sulfur and oxygen/chlorine thermochemical diagrams for several metals, calculated for temperature of 650°C. Also shown are regions of excess-air (A) and oxygen-deficient (B) combustion conditions

which depict the chemistry in conversion of Illinois #6 coal. To minimize corrosion wastage of materials in these applications, two approaches have been attempted: alteration of the bulk alloy chemistry, and/or modification of the chemistry of surface regions of structural materials through different coating techniques. The decision to use a coating is based on several technical and economic factors, some of which are listed in Table 1.

BULK ALLOYING

The formation and maintenance of protective surface oxide scales is essential in preventing rapid degradation of structural alloys used in oxygen/sulfur mixed-gas environments. In principle, one of the three oxides, Cr_2O_3 , Al_2O_3 , or SiO_2 , will constitute the major component of a thermally formed surface scale, especially at elevated temperatures. However, at the low temperatures of interest in waterwalls and evaporators, the scaling kinetics will be slow and a number of transient oxides will be present for a long periods of exposure, and thermodynamically stable oxides (such as Cr_2O_3 and Al_2O_3) may never form a continuous layer to protect against sulfidation attack. The alloying elements Mn and Si, which form oxides more stable than Cr_2O_3 , have a tendency to migrate from the bulk of the alloy to the scale/substrate interface. In the oxide mode of interaction, Mn preferentially segregates in the scale and has an adverse effect on the scale spallation, leading to enhanced corrosion rates. At high Mn concentrations, formation of brittle MnS is a distinct possibility. Si content

Table 1 Technical/Economic Factors in Coating Application

Cost comparison with monolithic but expensive material
Cost comparison with cladding and/or coextruded materials
Chemical compatibility with environment
Chemical compatibility with substrate
Coating/substrate interactions over time
Ease of application/coating integrity/reproducibility
Joining of coated components
Thermal compatibility with substrate
Feasibility of repair/recoat in field
Replacement cost and down-time expense
Initial cost outlay

up to 4 wt.% has been found to be beneficial for the formation of protective layers in oxidation studies involving a single oxidant. Since the mobility of Si is much lower than that of Fe, Cr, and Mn, the Si-containing alloys rarely develop external silica scales when exposed to oxygen/sulfur environments, especially at temperatures of interest in heat-recovery systems.

Refractory metals such as Ti, Zr, Nb, V, and Ta can form oxides and sulfides that exhibit greater thermodynamic stability than Cr_2O_3 and CrS . Figure 2 shows thermogravimetric test data for several refractory metals/alloys relative to data for conventional alloys exposed to an oxygen/sulfur mixed-gas atmosphere with $p\text{O}_2 = 4.1 \times 10^{-18}$ and $p\text{S}_2$ of 9.4×10^{-7} atm at 871°C .³ The morphology of exposed specimens showed catastrophic sulfidation attack in Type 310 stainless steel and Alloy 800, nonprotective oxidation in Ta, and somewhat protective oxidation in Nb and V. Vanadium developed a subscale of sulfide indicative of the less-protective nature of vanadium oxide. Molybdenum and TZM developed very thin, adherent sulfide scales. Even though the refractory metals and alloys exhibit low corrosion rates when exposed to oxygen/sulfur mixed gas,

Figure 2. Comparison of thermogravimetric test data for several refractory metals/alloys with those for conventional alloys exposed to oxygen/sulfur mixed-gas atmospheres

application of these materials as structural materials in coal-gasification systems is not feasible because of the difficulty in fabrication, inadequate mechanical properties, and cost. To find an alternative approach, studies have been conducted to evaluate the benefits of adding reactive, stable-oxide-forming elements such as Nb, Zr, and Ti to model commercial alloys.^{4,5} Even though these elements do not directly participate in scale development, the beneficial effects on corrosion resistance are derived from refinement of grain size of the alloy, increases in the effective chromium content of the alloy matrix, minimization of transient oxides, and formation of a barrier layer of refractory metal oxide at the interface between the outer scale of chromia and the alloy substrate. However, the beneficial effects of refractory metal additions to the bulk alloy have been observed at elevated temperatures in the range 875 to 1000°C, and the exposure times needed to achieve similar benefits at lower temperatures (500 to 700°C) may be substantial.

SURFACE MODIFICATION BY COATING TECHNIQUES

We are examining several approaches to the modification of surface regions (broadly termed "coatings" in the remainder of this paper) of structural alloys in order to improve the corrosion resistance of the materials in environments typical of those prevalent in coal-gasification processes. In general, coating systems can be classified as either diffusion or overlay type, which are distinguished principally by the method of deposition and the structure of the resultant coating-substrate bond. The coating techniques examined are pack cementation, electrospark deposition, physical and chemical vapor deposition, plasma spray, and ion implantation.

Pack-Cementation Coatings

In this process, the component to be coated is fully immersed in a powder mixture of a coating element, an activator, and an inert material. The pack with the component is heated to temperatures between 750 and 1100°C for 4-24 hr in a protective atmosphere. This coating process is fairly simple and inexpensive, and large components can be coated with relative ease. However, the pack process lends itself to only simple coating compositions (generally of a single element) primarily because of the thermodynamic limitations on transfer of different elements under the same temperature/activator conditions. Furthermore, during the coating process, the component to be coated is exposed to temperatures much higher than the service temperature and this can alter the microstructural and mechanical properties of the component material.

Substantial work has been conducted to evaluate the corrosion behavior of aluminized, chromized, simultaneously aluminized and chromized, sequentially aluminized/chromized, and siliconized coatings exposed to simulated oxygen/sulfur environments.⁶⁻⁸ Coatings were applied on low-alloy (1.25 and 2.25 wt.%Cr) and 9 wt.%Cr ferritic steels and austenitic alloys, such as Type 304 stainless steel and Alloy 800. Corrosion experiments conducted with Fe-Al binary alloys and Fe₃Al materials showed that a minimum Al content of 12 wt.% is needed for adequate corrosion resistance in oxygen/sulfur mixed-gas atmospheres (see Fig. 3).

Figure 3. Weight-change data for Fe-Al binary alloys and iron aluminide specimens tested in oxygen/sulfur mixed gas at 875°C

Baxter established that a minimum chromium concentration of 25 wt.% is required to achieve adequate corrosion resistance in sulfur-containing gasification atmospheres under thermal-cycling conditions.⁴

A test program was conducted to evaluate the sulfidation resistance of pack aluminized, chromized, and simultaneously aluminized/chromized coatings on two different substrates, namely, T22 and T91 (with compositions Fe-2.25 wt.%Cr-1 wt.%Mo and Fe-9 wt.%Cr-1 wt.%Mo) and to compare their corrosion resistance with those of uncoated ferritic steels and high-Cr austenitic alloys.⁹ These tests were conducted for 500-2000 h with internally air-cooled specimens at metal temperatures of 500 and 650°C and the gas was maintained at 871°C. The oxygen/sulfur mixed-gas environments in these tests had pO_2 values of 9.2×10^{-28} and 1.2×10^{-23} atm and pS_2 values of 7.7×10^{-8} and 1.0×10^{-6} atm, respectively, at temperatures of 500 and 650°C.

Figure 4 shows the corrosion loss data for several of the uncoated and coated specimens from this test program. The scales on the ferritic steels consisted predominantly of iron sulfide and (Fe,Cr) sulfide while the high-Cr alloys developed somewhat thinner (Cr,Fe) sulfide scales with intergranular penetration of sulfur into the alloy. The results showed that alloy T22 had corrosion losses of 3.3 and 11.8 mm/yr (based on linear kinetics) at 500 and 650°C, respectively. The corresponding values for T91 alloy were 1 and 3.5 mm/yr at 500 and 650°C. On the other hand, corrosion losses for high-Cr alloys ranged between 0.2 and 1.0 mm/yr (also based on linear kinetics). The chromized, aluminized, and simultaneously chromized-aluminized samples exhibited substantial decrease in sulfidation attack and metal wastage via corrosion when compared with the uncoated T22 alloy.

Figure 5 shows scanning electron microscopy (SEM) micrographs of corrosion scale morphologies observed on different coatings subsequent to exposure in mixed gas at 650°C. The specimen with a chromized coating developed a thin chromium sulfide scale and the scale thickness was only

Figure 4. Corrosion loss data for several pack-processed coatings tested in oxygen/sulfur mixed-gas atmospheres at 500°C (top) and 650°C (bottom)

about 20% of the thickness of the chromized layer. The specimen with an aluminized coating exhibited a thinner scale that contained Fe, Al, and S. The simultaneously chromized-aluminized specimen developed a thin (Fe,Cr) sulfide scale but the zone underneath the scale was enriched in Cr and Al with virtually no Fe. This zone seemed to act as a barrier to Fe transport outwards, thereby lowering susceptibility to formation of fast-growing FeS and minimizing corrosion loss.

Even though the pack-processed coatings exhibited low corrosion rates in oxygen/sulfur mixed-gas environments, the integrity of these coatings over long periods of use is questionable. For example, Figure 6 shows cross sections of chromized carbon steel (similar in behavior to other low-Cr alloy steels) after exposure in a high- pS_2 atmosphere under isothermal and

Figure 5. SEM micrographs of uncoated and coated T91 alloys after 500 h exposure to oxygen/sulfur mixed gas at 650°C.

Figure 6. Cross sections of chromized carbon steel after exposure in (a) low- pS_2 gas under isothermal conditions, showing a breach in carbide-rich coating, (b) high- pS_2 gas under isothermal conditions, showing corrosive breakdown of carbide-rich coating, and (c) high- pS_2 gas under thermal-cycling conditions, showing severe cracking of coating

thermal cycling conditions.⁹ Although the original coating contained 23.1 wt.% chromium, the enhanced intergranular corrosion under thermal-cycling conditions was attributed to oxidation/sulfidation of chromium-rich carbides precipitated during the coating process. The attack on these carbides is especially severe when the component is cooled below the dew point of the gas, whereupon the liquid condensate containing sulfur and chlorine preferentially attacks the carbides and causes pitting and intergranular corrosion of the substrate alloy.

Studies have been conducted on minimizing the degrading effects of chromium-rich carbides on coating integrity by eliminating chromium carbide precipitation and/or adding elements to the coating that reduce pitting.⁷ Additions of vanadium to chromized coatings by codiffusion of chromium and vanadium in the pack process eliminated precipitation of chromium-rich carbides at grain boundaries, thereby reducing pitting and intergranular corrosion of the material. It was concluded that coatings containing 25–40 wt.% chromium and 4–6 wt.% vanadium on a low-alloy-steel substrate had adequate corrosion resistance, based on short-term tests.

The pack-cementation process has been used to examine codeposition of chromium/aluminum and chromium/silicon onto ferritic and austenitic alloys, and coatings with compositions of 25–35 wt.% chromium and 2–3 wt.% silicon have been reported.⁸ Oxidation rates for these coated alloys have been lower than for those without coatings. Sulfur- and chlorine-resistance of these coatings is presently being evaluated.

Electrospark Deposition (ESD) Coatings

The ESD process is a microwelding technique that uses short-duration, high-current electrical pulses to deposit an electrode material on a metallic substrate. A principal advantage of ESD is that the coatings are fused to a metal surface with a low heat input while the bulk substrate material remains at ambient temperature. This eliminates thermal distortions or changes in the metallurgical structure of the substrate. Because the coating is alloyed with the surface, i.e., metallurgically bonded, it is inherently more resistant to damage and spalling than the mechanically bonded coatings produced by most other low-heat-input processes (such as detonation-gun, plasma-spray, and electrochemical plating).

Several coatings were applied on Type 316 stainless steel and Alloy 800 substrate alloys by the ESD technique and tested in simulated gasification atmospheres that contained H₂S with or without HCl.¹⁰ The performance of the ESD coatings (which included Fe₃Al with different bond coats of refractory metals and/or overlay coatings of noble metals) was compared with that of uncoated austenitic alloys. Figure 7 shows corrosion-loss data obtained for specimens tested for 1000 h at 650°C in gas mixtures with $p_{O_2} = 1.2 \times 10^{-23}$, $p_{S_2} = 5.2 \times 10^{-10}$, $p_{Cl_2} = 9.4 \times 10^{-17}$, and $p_{HCl} = 2.1 \times 10^{-3}$ atm. All of the iron aluminide coatings were resistant to sulfidation and chloride attack, while the base alloys were susceptible to general corrosion and pitting attack, especially in the HCl-containing environment. At present, a study is being conducted to evaluate the relative performance of pack, ESD, and plasma spray coatings in oxygen/sulfur/chlorine environments.

Plasma Spray Coatings

A number of MCrAl-type coatings applied by a low-pressure plasma spray technique on a precipitation-strengthened Alloy 738 substrate have been examined for their corrosion resistance in coal gasification atmospheres.¹¹ Coating thickness was ≈ 100 – $150 \mu\text{m}$. The selected coatings (see Table 2 for composition) had Cr contents in the range 12.4–32.1 wt.%

Figure 7. Corrosion loss data for several iron aluminide coatings and uncoated austenitic alloys after exposure in gas mixtures containing H₂S with and without HCl

and/or Al contents in the range 4.9–16.0 wt.%. These were higher than the concentrations of Cr and Al in Alloy 738. In addition, the coatings contained small amounts of reactive elements (Y, La) to improve scale adhesion to the substrate. The corrosion test results for these coated samples showed that the coating (34H) with an Al content of 16.1 wt.% and a Cr content of 12.5 wt.% enhanced the sulfidation resistance. Furthermore, a coating such as 36B, which contains 29.0 wt.% Cr and 4.6 wt.% Si, developed chromia scale with a subscale of SiO₂ that minimized cation transport outward from the alloy and prolonged the time to the onset of breakaway corrosion. Disappointing results were obtained for coating 34U (of composition Co–Ni–Cr–Al–Y), which showed massive (Ni,Co) sulfide formation in mixed-gas atmospheres. The test results, in general, showed that certain MCrAl-type coatings can develop adherent protective oxide scales and impart resistance to sulfidation of the substrate alloy.

Table 2. Compositions of MCrAl Coatings

Coating	Coating	Amount (wt.%) of Elements				
Number	Composition	Cr	Ni	Co	Al	Other
31A	Co–Cr–Al–Y	22.9	–	63.6	12.7	0.8Y,
36A	Ni–Cr–Al–La–Y	32.1	56.2	2.5	5.6	2.1La, 0.4Y, 0.7Ti
36B	Ni–Fe–Cr–Si–B–C	29.0	62.8	–	–	4.6Si, 3.5Fe, 0.05B
34U	Co–Ni–Cr–Al–Y	25.4	35.5	33.2	4.9	1.0Y
34H	Ni–Co–Cr–Al–Y	12.4	60.4	10.2	16.0	0.5Y, 0.5Ti

Physical- and Chemical-Vapor Deposition and Ion Implantation

Physical- and chemical-vapor deposition (PVD and CVD) techniques involve vaporization of coating constituents from a source and their subsequent deposition onto a substrate alloy. Surface modification by ion implantation is predominantly a research tool and is used to evaluate the role of variations in coating composition, coating morphologies, adhesion characteristics, substrate/coating interactions, and coating response to gas phase and deposit layer constituents in the corrosion degradation of structural alloys.

Thin (1–2 μm) layers of silicon or silicon plus oxygen were sputter-deposited onto iron-base alloys that were subsequently tested at 700°C in mixed-gas atmospheres containing low $p\text{O}_2$ and high $p\text{S}_2$.¹² Thermogravimetric test data are shown in Fig. 8 for the uncoated and Si- or Si-plus-O-coated alloys. The uncoated alloy exhibited catastrophic sulfidation corrosion, whereas the coated alloys exhibited virtually no sulfidation. Auger-electron-spectroscopy depth profiles for several of the coating/substrate constituents in an initially Si-plus-O-coated specimen after exposure to a high- $p\text{S}_2$ environment showed that enrichment of silicon and oxygen at the alloy surface acts as a barrier to migration of sulfur inward and cation transport outward of substrate, thereby minimizing sulfidation of substrate elements and reducing alloy corrosion rate. Sulfidation resistance of iron-base alloys has been substantially improved by implantation of niobium on the surface.¹³ In general, the growth rate of protective oxide scale is much higher in implanted alloys and is reflected in larger oxide grain size. Further, the presence of niobium and/or its oxide seems to act as a barrier to transport of sulfur inward and outward cation transport, thereby prolonging the time for onset of breakaway corrosion.

Figure 8. Weight-change data for iron-base alloys, showing the Si and Si+O sputter effect (left) and Nb implant effect (right) on corrosion

SUMMARY

The raw gas environments that arise from coal gasification have chemical compositions that are low in pO_2 and moderate-to-high in pS_2 . Metallic materials for service in such an environment undergo predominantly sulfidation attack at temperatures of 400 to 700°C. Modification of alloy compositions in bulk can alter the scaling processes and lead to improvements in corrosion resistance, but the benefits can only be attained at temperatures much higher than the service temperatures of the components. Modification of surfaces of structural components by several of the coating techniques examined in this study showed substantial benefit in corrosion resistance when tested in simulated coal gasification environments. The paper presents several examples of surface modification and their corrosion performance.

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