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APPLICATIONS OF COATINGS IN COAL-FIRED ENERGY SYSTEMS*

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APPLICATIONS OF COATINGS IN COAL-FIRED ENERGY SYSTEMS*

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Abstract

Corrosion and erosion of metallic structural materials at elevated temperatures in complex multicomponent gas environments that include particulates are potential problems in many fossil energy systems, especially those using coal as a feedstock. The use of appropriate corrosion-resistant coatings on metallic components offers an avenue to minimize material degradation and extend component life. The purpose of this paper is to review the current status of coating performance in environments typical of pulverized-coal-fired boilers, coal gasification, fluidized-bed combustion, and gas turbines. The paper discusses the complexity of environments in different systems and the coating requirements for acceptable performance. Examples illustrate the morphology and corrosion/erosion performance of coating/structural alloy combinations exposed in some of these systems. In addition, future research and development needs are discussed for coating applications in several coal-fired systems.

Introduction

A number of advanced technologies that convert coal to clean fuels for use as a feedstock in chemical plants and for generation of electric power are being developed.¹ In general, coal conversion processes result in a complex, multicomponent, multiphase mixture, the composition of which depends on a number of factors (e.g., reaction conditions, type of coal feedstock, coal pretreatment, heat supply, reactor configuration, and gas purification). Further, conversion of coal releases a wide variety of contaminants from coal feedstock, char, ash, and sulfur/chlorine/alkali-containing species. The manner in which these contaminants are released, transported in the gas phase, and subsequently deposited on relatively cooler metallic surfaces can significantly affect the

performance of several functional components.

The use of different coals under a variety of combustion conditions, ranging from widely varying combustion gas chemistry to widely varying nucleation, growth, and condensation of particulates, can have a direct effect on material degradation in these systems. Contaminants such as alkali, chlorine, and sulfur vaporize during gasification and combustion and eventually condense on metal surfaces, removing the protective layer from those surfaces by chemical reactions, fluxing, or fracturing. Because of diverse processing conditions (temperature, pressure, air/fuel ratio, etc.) involved in the conversion of coal to gas, a thorough understanding of the influence of various gaseous species and particulates on material degradation is needed to enable selection of adequate materials and coatings for a reliable system.

Coal-Fired Systems

The coal-fired systems of interest for energy production are listed in Table 1. In conventional pulverized-coal-fired (PC) boilers, combustion temperatures are generally in the range of 1300–1600°C (2370–2910°F). These high temperatures and the excess air needed for complete combustion in a coal-fired boiler result in the generation of significant amounts of SO₂, SO₃, and HCl, in addition to alkali-sulfate and alkali-chloride vapors. The condensation of these volatilized constituents and deposition of ash constituents lead to fouling, corrosion, and erosion of evaporators and steam superheaters. In addition, the waterwalls of combustion chambers are subject to attack by a mixture of coal ash and alkali compounds. While the current superheater systems operate at steam temperatures in the range of 538–566°C (1000–1050°F) and pressure of 16.55 MPa (2400 psi), efforts are underway in the United States and other countries to develop advanced steam cycles that operate at steam a temperature of 650°C (1200°F) and

pressure of 34.5 MPa (5000 psi). Recently, the U.S. Department of Energy has proposed to develop a high-performance power system (HIPPS) in which a very-high-temperature furnace will be used for combustion of coal and the heat of combustion will be transferred to a working fluid (air) via heat exchangers.² The high-temperature air, with auxiliary heat input, is expected to reach 1370°C (2500°F) at the inlet to a gas turbine. Another proposal is to develop a low-emission boiler system (LEBS) that will use current boiler technology for combustion of coal but will incorporate new technologies for environmental control in combustion and heat transfer to reduce SO_x, NO_x, and particulate emissions.² The basic difference between combustion in a conventional PC boiler and in a LEBS is in the air-to-coal stoichiometric ratio. A PC boiler is operated under excess-air conditions, which lead to an oxidizing environment that includes SO₂ and alkali sulfate deposits, whereas a LEBS is operated under reducing conditions with sulfur present as H₂S and deposits of sulfides.

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 production of chemicals or is burned to provide industrial process heat, steam, and/or electricity. Currently, the emphasis is on pressurized, entrained, slagging-type gasifiers. Because gasification occurs at a high temperature, 10-15% of the energy in the coal is converted to sensible heat in the raw gas, the recovery of which requires large heat exchangers. Figure 1 shows the relative sizes of the gasifier and syngas coolers. Apart from the size of the units, the material selected must withstand a hostile environment that contains low partial-pressure oxygen (pO₂) and moderate-to-high partial-pressure sulfur (pS₂), and coal slag condensates.

² Combustion of coal in a fluidized bed is widely considered a viable process

for producing electric power and generating industrial process steam. In power-generating applications, tubes carry a working fluid (either steam or air) that eventually drives a turbine. In steam cycles, the fireside surfaces of the superheater tubes reach 550-700°C (1020-1300°F), whereas in air cycles the tube temperatures can be as high as the bed temperature, i.e., 850-900°C (1560-1650°F). Two types of fluidized-bed combustion (FBC) systems, namely bubbling- and circulating-fluid beds (BFBs and CFBs), are being considered at present. Heat exchanger tubes in a BFB system are immersed in the bed and in the convective sections of the system, whereas in a CFB system, the heat exchanger tubes are generally situated outside the bed. As a result, tubes in the CFB system are generally exposed to a much finer particles and to an environment in which coal combustion does not occur (i.e., a more stable oxidizing atmosphere is prevalent).

System pressure is another important variable in current systems. Combustion of coal has been achieved in both atmospheric and pressurized FBC systems; the method of coal feeding and the sorbent materials in the two systems are different, but the prevalent combustion environment is similar. Figure 2 shows schematic diagrams of typical BFB and CFB systems.

Magnetohydrodynamic (MHD) generation of power is based on the direct conversion of fuel energy into electrical energy by flowing a heated, electrically conducting fluid through a magnetic field. In a coal-fired open-cycle MHD system, the working fluid is utilized on a once-through basis and consists of multiphase coal-combustion products. The overall plant consists of a topping cycle, where the electrical energy is directly produced by the MHD generator, and a steam-bottoming plant, where additional heat energy and the seed material are recovered. In the present MHD concept, the combustor walls will be exposed to a reducing environment with coal slag deposits, and the channel electrodes and

insulators will be exposed at high temperatures to an environment of ionizing gas, molten slag, and sulfated seed material. Downstream components will be exposed to deposits of K_2SO_4 and/or ash constituents and an oxidizing-gas environment.

Other systems/components of interest are direct coal-fired gas turbines and indirectly-fired turbines that use the effluents from coal gasifiers in combined-cycle plants and from FBC systems in cogeneration plants. Performance requirements for the materials in these turbines are much more demanding, life expectancy is longer, and repair/reuse/cost considerations are much more stringent than those for aviation turbines. Another important concern is the materials needs of hot-gas cleanup systems, which are mandatory in the cleanup of raw gas streams from gasifiers and FBC units before the gas enters the turbines.

Conversion of coal into clean energy in any process, either by conversion to gaseous and liquid fuels or by direct combustion, requires materials that can withstand high or reasonably high temperatures in aggressive environments. Construction materials often are the limiting factor in the design of vessels and components for containment of the processes. Table 2 lists the service conditions and modes of degradation for key components (e.g., heat exchangers and gas turbines) in several fossil systems that use coal as a feedstock. It is evident from this table that the gas environment in various systems can vary widely in terms of oxygen activity, temperature range, types of deposits and particulates, and particulate velocity range. The table also lists several modes of material degradation that include oxidation, sulfidation, hot corrosion, deposit-induced corrosion, and erosion. Further, key variables and possible rate-limiting steps for the degradation of materials in coal-fed energy-producing systems can be

identified (Table 3) . Details of the mechanisms for metal wastage exposed to environments in several coal-fired systems are discussed elsewhere.¹

As one can see from the discussion thus far, the environments that are prevalent in coal-fired systems are fairly complex, wide-ranging in terms of thermodynamic activity of the corrodants, at times particulate-laden and containing deposits of wide-ranging chemistries, and subject to a wide spectrum of system-specific operating conditions. Furthermore, the classes of materials used for construction of 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-containing iron-base alloys are used for sulfidizing conditions; and nickel- and cobalt-base alloys are used for service in hot corrosion environments. As a result, the development of coatings for use in these systems must focus on a given application and the decision to use a coating is based on several technical and economic factors, some of which are listed in Table 4.

Development and Application of Coatings

We are examining several approaches to the development of coatings that resist attack in coal-fired environments (see Table 3 for types of attack) and thereby minimize corrosion of underlying substrate alloys and extend the time for onset of breakaway corrosion. 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. In addition, ceramic coatings are used in some applications.

Pack-Cementation Coatings – Pack cementation is a process in which 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 (1382 and 2012°F) for time periods of 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 thermodynamic limitations on transfer of different elements under the same temperature/activator conditions. Attempts are being made to coat more than one element simultaneously, but this effort is still in early stages of investigation and the performance of these coatings in complex environments must be evaluated. 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 base 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.³⁻⁸ 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. Baxter⁴ has 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. A minimum aluminum concentration in a range of 15-20 wt.% is required for adequate corrosion resistance of aluminized coatings. Figure 3 shows the aluminum and chromium concentration-distance profiles for coated specimens

before and after exposure to a low- pO_2 and high- pS_2 atmosphere at 420°C.⁵ The two different aluminum profiles in Fig. 3 show the variability one can achieve by the pack process variables of temperature and exposure time.

Figure 4 shows cross sections of chromized 2.25 wt.%Cr-1Mo steel after exposure in a high- pS_2 atmosphere under isothermal and thermal cycling conditions.⁵ 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.⁶ Additions of vanadium to chromized coatings by co-diffusion 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. Long term testing of these coatings is required to establish the effects of exposure temperature, sulfur level in the gas, ash/slag deposit, etc. on coating performance.

Baxter⁵ also concluded that pack-diffusion aluminizing and simultaneous aluminizing/chromizing processes produce coatings on low-alloy and carbon steels with good resistance to corrosion in simulated gasification atmospheres,

but only under isothermal conditions. Sequentially chromizing/aluminizing produced coatings with physical defects, such as voids and cracks, and had poor corrosion resistance.

Three different coatings were applied to a T91 substrate by pack cementation.⁹ The coatings were then exposed for 500 h to an oxygen/sulfur mixed-gas atmospheres at 500 and 650°C. The results indicate that increased chromium and/or aluminum concentration is beneficial in resisting sulfidation attack, but that the integrity of the coating is strongly dictated by mechanical properties and by adhesion of the coating to the substrate rather than by chemical interactions with the exposure environment.

Figure 5 shows scale thickness and penetration data for the T91 alloy in uncoated condition and with different coatings after 500 h of exposure in a high- pS_2 gas environment at 650 and 500°C. For the uncoated alloy, corrosion losses (scale thickness plus penetration) at 500 and 650°C were ≈ 100 and 600 μm , respectively, which translate to ≈ 1.75 and 10.5 mm/yr, based on linear kinetics for the corrosion process. On the other hand, the chromized and chromized/aluminized coatings performed significantly better than the base alloy. Scale thicknesses were substantially lower (e.g., 40 μm , for a rate of 0.7 mm/yr at 650°C) at both exposure temperatures. The aluminized coating exhibited somewhat poorer performance in terms of void formation and cracking, which can be attributed to fabrication of the coating rather than to reactions occurring during exposure in a mixed-gas atmosphere.

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.^{7,8} Oxidation rates for these coated alloys have been lower

than for those without coatings. Sulfur resistance of these coatings is not known at present.

Chromized and aluminized coatings developed by the pack cementation process have also been examined for service in FBC environments.^{10,11} In laboratory experiments, coated samples were exposed for 3000 h to simulated combustion atmospheres in the presence of deposits of reagent-grade CaSO_4 and ash from a CFB. Coated specimens were also exposed for 1980 h in a 1.8 x 1.8-m atmospheric FBC facility in El Segundo, California.¹¹ In general, the results showed that the performance of aluminized coatings was poor. This is due more to difficulty in developing a crack-free coating than to exposure in an FBC environment. However, cracked regions, if present initially, exhibited accelerated oxidation and the coating integrity became poor.

Figures 6 and 7 show scanning electron micrographs of cross sections of specimens of chromized Type 304H stainless steel and Alloy 800H, respectively, after a 3000-h exposure. Also shown in these figures are the elemental concentration profiles across the coating to the substrate regions of the specimens. In all four coated alloys, the coatings interacted with the deposit, and thin layers of corrosion reaction product were observed. The chromized alloys exhibited a low rate of attack in these tests. The attack-zone thicknesses, in general, were smaller than the initial coating thicknesses, indicating resistance of the coated layers to catastrophic attack. Except for the interactions in the surface regions of the coatings, the elemental concentration profiles from X-ray analyses were similar to those for as-coated specimens. In addition, chromized coatings have performed well against corrosion-erosion attack in waterwall applications and evaporator sections of AFBC and PFBC systems.^{12,13}

Chromized coatings have also been tested for their resistance to coal-ash

corrosion in superheaters and reheaters.^{14,1} Results showed pitting attack of the coating at high concentrations of SO₂ and alkali sulfate deposit. Additional tests are needed to establish the mechanisms of pitting attack and to establish performance envelopes for application of these coatings in boiler fire side environments.

Aluminide coatings developed by the pack-cementation process have been used extensively as protection against hot corrosion of nickel- and cobalt-based superalloys in gas turbine applications. Corrosion of materials in the presence of liquid sodium sulfate, either by itself or in combination with sodium chloride, has been a problem in gas turbines; this corrosion process has been termed "hot corrosion" to differentiate it from gas-phase sulfidation attack. Two types of hot corrosion have been identified: Type I, operative at 800-950°C (1470-1740°F), and Type II, operative at 600-750°C (1100-1400°F).

Type I hot corrosion can be divided into an initiation (or incubation) stage and a propagation stage. The process, in general, requires the presence of liquid sodium sulfate (melting point 884°C) on the metal surface. In the initiation stage, the protective oxide scale dissolves by a basic fluxing mechanism and the corrosion rates are generally low. In the propagation stage, with the protective oxide having been destroyed and not able to reform, the alloy is subjected to sulfidation by inward diffusion of sulfur, leading to accelerated corrosion rates. Extensive reviews of Type I hot corrosion have been published.^{16,17}

Type II hot corrosion, also known as low-temperature hot corrosion, involves the eutectics of base-metal sulfates and sodium sulfate and, therefore, occurs predominantly at lower temperatures, especially in turbines that operate in the effluent of FBCs.¹⁸ Protective coatings examined for hot-corrosion resistance are simple aluminides, precious-metal aluminides, and overlay-type

coatings. The former two are made by the pack process, whereas in the overlay process, the coating elements are applied directly onto the substrate by physical vapor deposition (PVD) or by the low-pressure plasma spray (LPPS) approach.

Figure 8 shows comparative data for corrosion of simple aluminides, aluminides with rhodium and platinum bond coats, and CoCrAlY overlay coating after exposure to a hot corrosion environment at 982°C (1800°F).¹⁹ The results show that the performance of a given coating is strongly influenced by the substrate alloy (more so in pack than in overlay coatings) and a bond coat of precious metal platinum (rather than rhodium) is beneficial in reducing corrosion in alloys such as IN 792 and IN 738. The overlay CoCrAlY coating on a cobalt-base MarM-509 alloy exhibited the best performance among all the coatings examined in this study. Extensive microstructural analyses of the tested coatings have been reported¹⁹ and qualitative inferences have been drawn from the test results but a discussion of those results are beyond the scope of this paper. Corrosion test data obtained in the effluent of a pressurized FBC system showed that both nickel- and cobalt-base alloys were equally susceptible to accelerated corrosion. This susceptibility to accelerated corrosion was attributed to the presence of potassium in the FBC effluent.¹⁸ Information on the performance of coating/substrate combinations under low-temperature hot-corrosion conditions is particularly lacking at present. Another study conducted to evaluate the performance of different coatings and coating methods on a given alloy substrate showed that the LPPS overlay of CoCrAlY, especially the high-chromium version, exhibited the longest life when compared with electron-beam overlay of CoCrAlY, precious metal aluminides, and simple aluminides (see Fig. 9).²⁰

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.²¹ 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 (see Table 5) were applied on T22 and T91 substrate alloys by the ESD technique and tested in simulated gasification atmospheres that contained sulfur as H_2S .⁹ The performance of the ESD coatings was compared with that of coatings developed by pack cementation. Figure 10 shows scanning electron micrographs of corrosion scale morphologies observed on different coatings after exposure in a gas environment at 500°C (930°F). The Fe_3Al coating, with or without Nb-1Zr bond coat, exhibited iron sulfide scales of substantial thickness. Figure 11 shows a comparison of the corrosion-loss data obtained in the uncoated condition and for several different coatings after exposure to a high- pS_2 environment at 500 and 650°C (930 and 1200°F). The data for the Fe_3Al - and Cr-carbide/Al-coated specimens were obtained after 500 h of exposure, whereas the data for the others were obtained after 2000 h of exposure. The results showed substantial improvement for the pack cementation coatings and the ESD Cr carbide/Al coating in these reducing environments.

Plasma Spray Coatings – In a conventional plasma spray process, the coating material, in powder form, is melted in a plasma arc and propelled onto the target surface to form a coating. The method is amenable to development of coatings of complex compositions and large thicknesses but generally have some

porosity. In addition, poor adherence of the coating to the substrate alloy can lead to spalling of the coating, especially under thermal-cycling conditions. Vacuum or low-pressure plasma spray, in which high particle and gas velocities are achieved, has been used to develop low porosity coatings with better corrosion resistance than those developed by conventional plasma spray. Interaction between the coating constituents and the underlying alloy elements is generally minimal and the coating, for all practical purposes, is similar to an overlay coating. However, the size limitation on the vacuum chamber makes coating of large components using this technique virtually impossible.

The resistance to sulfidation of several coatings (applied by low-pressure plasma spray) have been evaluated for application in coal gasification atmospheres.²² Figure 12 shows cross sections of uncoated and Co-Cr-Al-Y coated IN 792 specimens after exposure in an oxygen/sulfur mixed-gas environment at 871°C (1600°F). It is evident that the uncoated specimen formed liquid nickel sulfide and exhibited catastrophic corrosion, whereas the coated specimen offered substantial resistance to corrosion by sulfidation.

Physical- and Chemical- Vapor Deposition – These techniques involve vaporization of coating constituents from a source and subsequent deposition onto a substrate alloy. Several means for vaporization, such as, electron beam, plasma, and arc, have been used in the development of coatings. Even though PVD is a viable procedure for coating applications, lack of or poor adhesion of the coating to the substrate can be detrimental to coating performance. However, a number of coatings developed by these techniques have been examined for their corrosion resistance and for protection of the underlying alloy for service in coal-fired systems.

Thin layers of silicon or silicon plus oxygen has been sputter deposited onto

iron-base alloys, which were subsequently tested at 700°C (1300°F) in mixed-gas atmospheres that contained low pO_2 and high pS_2 .²³ Thermogravimetric test data are shown in Fig. 13 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. Figure 14 shows 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- pS_2 environment. It is evident 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. Even though substantial reduction in corrosion rates is possible by this approach, these techniques can, at best, be considered as research tools for optimizing coating compositions and morphologies and establishing viable coating/substrate combinations. The same coatings must be developed by methods that are amenable to large components and at lower costs for wide-scale application in coal-fired systems.

Ion Implantation – Surface modification by ion implantation is predominantly a research tool and is used as such 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 and engineering ceramics.

Sulfidation resistance of iron-base alloys has been substantially improved by implantation of niobium on the surface.²⁴ 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 15 shows typical scanning electron micrographs obtained from two different alloys, with and without Nb implantation, after exposure to a high-sulfur mixed-gas environment at 700°C. Reactive elements, such as Y, La, and Hf, have been implanted in structural alloys to modify the surface regions in chromia- and alumina-forming alloys to improve scale integrity and scale/metal adhesion, especially under thermal-cycling conditions. Most of the studies on surface-modified alloys have been conducted to improve the high-temperature oxidation resistance, and little data are available on the performance of these "coatings" in complex environments of interest in coal-fired systems.

Ceramic Coatings – These coatings have been extensively discussed in the literature but the application of these coatings in coal-fired systems is minimal. One major application for the ceramic coatings, called "thermal-barrier coatings," is in gas turbines in which a coating with a low thermal conductivity is used to thermally shield the blade material from hot gases. Several reviews on different aspects of thermal-barrier coatings are published.^{25,26} A bond coat of MCrAlY is applied onto the component by either the PVD, pack process, or plasma spray technique. Subsequently, a ceramic coating, usually Y_2O_3 -stabilized ZrO_2 , is applied onto the bond coat by the air plasma spray technique. Coating spallation is the major mode of failure of thermal barrier coatings and research to develop better adherent coatings is warranted.

Another area of application for ceramic coatings is in steam turbines. Component erosion by metallic-oxide scale in large steam turbines has led to the development of coatings that are erosion resistant at steam temperatures in the range of 538–566°C (1000–1050°F).²⁷ Tests conducted on stainless steel specimens

with iron boride, chromium-enriched iron boride, and silicon-enriched iron boride coatings at 538°C and 150 m/s for up to 100 h led to the conclusion that the enriched coatings were better than those without chromium and silicon, and the effect was attributed to an altered strain state, rather than to surface hardness, in the coating.

Summary

The materials requirements, gas, deposit, and particulate environments prevalent in several coal-fired systems are briefly reviewed. Material degradation processes operative in these systems are also reviewed. The component requirements and material selections, which are wide ranging and system specific, are discussed briefly. Requirements for viable coatings for several applications are presented and factors that influence coating selection and application are enumerated. Discussions of coating types, coating methods, and several illustrations of performance of coatings in a number of applications are presented.

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Table 1

Coal-fired systems used in production of energy

Conventional pulverized-coal-fired boilers
 High-performance power system
 Low-emission boiler system
 Coal gasification combined-cycle system
 Fluidized-bed cogeneration systems
 Gas turbines that operate on coal-derived gases and liquids
 Open-cycle MHD system
 Direct-fired turbines
 Hot-gas cleanup systems

Table 2

Service Conditions and Modes of Degradation for Component Materials in Coal-Fired Systems

Component System	Gas Env.	Gas Temp. Range (°C)	Metal Temp. Range (°C)	Deposit Type	Particulate	Mode of Degradation
Heat Exchangers						
Pulverized-Coal Boilers	Oxidizing	1,300–1,600	400–700	Alkali Sulfates Ash	Fly ash, <20 m/s	Alkali corrosion Fouling
FBC	Oxidizing, locally reducing	850	400–850	CaSO ₄ CaO Carbon Fly ash	Sorbent bed, fly ash 3–? m/s	Oxidation/sulfidation Erosion
Gasification	Reducing, moderate to high H ₂ S	900–1,100	400–650	Fly ash Alkalis Chlorides	Fly ash, <20 m/s	Sulfidation/erosion? Fouling
MHD (Secondary)	Oxidizing	1,400–1,600	400–700	K ₂ SO ₄ Fly ash/slag	Fly ash, <20 m/s Seed	Potassium corrosion Fouling
Turbines						
Combined Cycle (Gasification)	Oxidizing	850–900	850–900	Fly ash/slag Alkali	Slag, 200–500 m/s	Hot corrosion/erosion
FBC Effluent	Oxidizing	850–900	850–900	Alkali sulfates Feldspars Aluminosilicates Sorbent	Fly ash, sorbent, 200–500 m/s	Hot corrosion/erosion
Direct-Fired Turbines	Oxidizing	1,000	1,000	Alkalis Chlorides Fly ash/slag	Fly ash, 200–500 m/s	Hot corrosion/erosion

Table 3

Materials Degradation in Coal-Fired Systems

Phenomenon	Key Variables	Possible Rate-Limiting Step
Boiler-Tube Corrosion	Alkali content Chlorine level Temperature Fly ash	Alkali condensation Oxide-sulfate reaction
Substoichiometric Combustion (also Gasification)	Oxygen and sulfur partial pressures Temperature Downtime condensate Alkali/slag deposit	Fracture of oxide scale Oxidation-sulfidation Pitting and crevice formation
FBC In-Bed Corrosion/ Erosion	Bed chemistry Local particle velocity Particle size and loading	Oxidation-sulfidation of base metals Arrival rate of particles Fracture of surface scales
Low-Temperature Hot Corrosion	Temperature Salt-film thickness Temperature gradient Sulfur level Alkali level	Sulfidation of transient oxides Transport of base metals (i.e., Co, Ni)
Hot Corrosion/Erosion	Alkali level Temperature Particle size, loading, and velocity	Fracture of scale Sulfidation of transient oxides Transport of base metals

Table 4

Technical/economic factors in the application of coatings

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
 Feasibility of repair/recoat in field
 Replacement cost and downtime expense
 Initial cost outlay

Table 5

Details on alloy/coatings used in gasification environments

Alloy/Coating	Composition	Coating Method
T22	Fe-2 1/4Cr-1Mo	-
T91	Fe-9Cr-1Mo	-
T22/Fe ₃ Al	T22/Fe-15Al	ESD
T22/Nb-1Zr/Fe ₃ Al	T22/Nb-1Zr/Fe-15Al	ESD
T22/XF2020	T22/Fe-20Mo-20Cr-10Ni	ESD
T22/KBI10/XF2020	T22/Ta-10W/XF2020	ESD
T22/KBI41/XF2020	T22/Ta-37.5Nb-2.5W/XF220	ESD
T22/C 815/Al	T22/Cr Carbide/Al	ESD
T22/Chromized	T22/Cr	Pack Cementation
T22/Aluminized	T22/Al	Pack Cementation
T22/Cr/Al	T22/Cr+Al	Pack Cementation
T91/Chromized	T91/Cr	Pack Cementation
T91/Aluminized	T91/Al	Pack Cementation
T91/Cr/Al	T91/Cr+Al	Pack Cementation

Figure 1. A schematic diagram of the entrained slagging gasifier and syngas coolers.

Figure 2. Schematic diagrams of (a) bubbling-fluidized bed (b) circulating-fluid bed systems. The abbreviation AFBAH in (a) corresponds to an atmospheric fluidized bed air heater.

Figure 3. Typical profiles for aluminum and chromium in aluminized and chromized coatings before and after exposure to mixed gas.

Figure 4. Cross sections of the chromized carbon steel after exposure in (a) a low pS_2 gas mixture under isothermal conditions, showing a breach in the carbide-rich coating, (b) high pS_2 gas mixture under isothermal conditions, showing corrosive breakdown of the carbide-rich coating, (c) high pS_2 gas under thermal cycling conditions, showing severe cracking of the coating.

Figure 5. Corrosion loss data for T91 alloy in uncoated condition and with several coatings after 500 h of exposure to a high-sulfur gas environment at 500 and 650°C.

Figure 6. Scanning electron micrographs and profiles of iron, chromium, and nickel concentration in chromized Type 304H stainless steel after a 3000-h exposure in the presence of CaSO₄ or CFB ash deposit.

Figure 7. Scanning electron micrographs and profiles of iron, chromium, and nickel concentration in chromized Alloy 800H after a 3000-h exposure in the presence of CaSO_4 or CFB ash deposit.

Figure 8. Coating life for several aluminide, precious-metal aluminide, and overlay coatings on nickel- and cobalt-base alloys exposed to hot corrosion environments.

Figure 9. A comparison of coating life for several coatings on IN 738 exposed to hot-corrosion conditions.

Figure 10. Scanning electron micrographs of T22 alloy with three different ESD coatings after 500 h of exposure to a high-sulfur gas environment.

Figure 11. Corrosion loss data for T22 alloy in uncoated condition and with several coatings after 2000-h (unless marked otherwise) exposure to a high-sulfur gas environment at 500 and 650°C.

IN 792, uncoated IN 792, Co-Cr-Al-Y coated

Figure 12. The corrosion behavior of uncoated and coated IN 792 with Co-Cr-Al-Y after exposure in an oxygen/sulfur mixed gas at 871°C.

Figure 13. Thermogravimetric test data for Fe-25 wt.% Cr alloys with and without silicon or silicon-plus-oxygen-coating after exposure to a high-sulfur environment.

Figure 14. Auger electron spectroscopy depth profiles for silicon-plus-oxygen coated Fe-25 wt.% Cr alloy exposed to a high-sulfur environment.

Figure 15. Scanning electron micrographs of cross sections of iron-base alloys with and without implanted niobium, after exposure to a high-sulfur environment at 700°C.

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