CORROSION PERFORMANCE OF STRUCTURAL ALLOYS*

by

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ABSTRACT

Component reliability and long-term trouble-free performance of structural materials are essential in power-generating and gasification processes that utilize coal as a feedstock. During combustion and conversion of coal, the environments encompass a wide range of oxygen partial pressures, from excess-air conditions in conventional boilers to air-deficient conditions in low-NOx and gasification systems. Apart from the environmental aspects of the effluent from coal combustion and conversion, one concern from the systems standpoint is the aggressiveness of the gaseous/deposit environment toward structural components such as waterwall tubes, steam superheaters, syngas coolers, and hot-gas filters. The corrosion tests in the program described in this paper address the individual and combined effects of oxygen, sulfur, and chlorine on the corrosion response of several ASME-coded and noncoded structural alloys that were exposed to air-deficient and excess-air environments typical of coal-combustion and gasification processes. Data in this paper address the effects of preoxidation on the subsequent corrosion performance of structural materials such as 9Cr-1Mo ferritic steel, Type 347 austenitic stainless steel, Alloys 800, 825, 625, 214, Hastelloy X, and iron aluminide when exposed at 650°C to various mixed-gas environments with and without HCl. Results are presented for scaling kinetics, microstructural characteristics of corrosion products, detailed evaluations of near-surface regions of the exposed specimens, gains in our mechanistic understanding of the roles of S and Cl in the corrosion process, and the effect of preoxidation on subsequent corrosion.

INTRODUCTION

In general, coal-conversion processes generate a complex, multicomponent, and multiphase mixture of combustion products, the composition of which depends on such factors as reaction conditions, type of coal feedstock, coal pretreatment, heat supply, reactor configuration, and gas purification. Furthermore, the conversion of coal releases a wide variety of contaminants from coal feedstock, char, ash, and sulfur/chlorine/alkali-containing species. Contaminants such as alkali, Cl, and S vaporize during the conversion process and eventually condense on metal surfaces, removing the protective layer from those surfaces by chemical reactions, fluxing, or fracturing. This type of material degradation can occur in conventional pulverized-coal-fired boilers, where combustion temperatures generally range from 1300 to 1600°C, and in advanced combustion systems such as the High Performance Power System, in which metallic heat exchangers will be used downstream of the ceramic heat transfer surfaces in the high-temperature furnace. The high temperatures and excess air needed for complete combustion in a coal-fired boiler generate significant amounts of SO2, SO3, and HCl, in addition to alkali and alkali-chloride vapors. On the other hand, in low-NOx and gasification systems the environments are low in O partial pressure (pO2) and S is present as H2S, and Cl is present as HCl. Because of the diverse processing conditions (temperature, pressure, air/fuel ratio, etc.) in the conversion of coal to gas, a thorough understanding of the influence of various gaseous species on material degradation is needed to enable selection of materials for a reliable system.

In a previous paper, thermodynamic calculations were reported on the gas chemistries that arise during combustion of coal under excess-air and air-deficient conditions. Laboratory corrosion experiments were conducted at 650°C under simulated combustion gas chemistries that included SO2
and HCl. Results indicated that in the presence of HCl, the scale is more prone to cracking and spallation, and eventually, accelerated metal wastage, especially in Fe-based alloys such as austenitic stainless steel and Alloy 800. The results also indicated that high-Ni alloys are more resistant to corrosion in Cl-containing combustion environments, primarily because of the formation of solid NiCl₂ corrosion product. However, pull-test results indicate that scales that developed on high-Ni alloys were more susceptible to spallation or erosion-induced loss when exposed in combustion environments without Cl₂ or HCl.

The objectives of the present work are to characterize the gas and deposit environments that arise from combustion of coals (that contain various Cl and S levels) as a function of excess air level, temperature, and pressure; conduct bench-scale laboratory corrosion tests on pertinent boiler materials and coatings in gas environments that include SO₂ or H₂S and Cl species, and simulate calculated gas chemistries; and evaluate the role of alkali chlorides and HCl in the corrosion process. Bench-scale corrosion studies are continued on a various boiler materials at metal temperatures typical of evaporator and waterwall boiler tubes and steam superheaters. Data in this paper address the effect of preoxidation on the corrosion behavior of structural materials such as Fe-9Cr-1Mo ferritic steel, Type 347 austenitic stainless steel, Alloys 800, 825, 625, 214, Hastelloy X, and Fe aluminide overlay when exposed at 650°C to excess-air combustion and gasification conditions with and without HCl. Results are presented on scaling kinetics, microstructural characteristics of corrosion products, composition details of near-surface regions of the exposed specimen, and gains in our mechanistic understanding of the roles of S and Cl in the corrosion process.

EXPERIMENTAL PROCEDURE

Several alloys, both ASME coded and uncoded, were selected for corrosion evaluation; however, only eight of the alloys were included in this paper. Their compositions are listed in Table 1. Among those selected, Fe-9Cr-1Mo steel is a ferritic alloy with moderate Cr content, whereas Alloys 825, 625 and X are Ni-based with a Cr concentration of 21.5 wt.%. Alloy 800 and Type 347 stainless steel are Fe-based with Cr content of 20.1 and 17.7 wt.%, respectively. Alloy 214 is Ni-based, with 16 wt.% Cr but also 4.5 wt.% Al, which makes it an alumina-forming alloy, whereas the others are chromia-forming alloys. Furthermore, Fe aluminide-coated Fe-9Cr-1Mo steel was included to assess the corrosion resistance of preformed alumina.

Multiple specimen exposures to determine the kinetics of corrosion were conducted in a three-zone resistance-heated furnace in quartz tubes that were closed at the bottom. The specimens were attached to a 5-mm-OD thermocouple well in the center of the reaction tube. The multicomponent gas mixture entered through a 5-mm-OD quartz tube attached to the inside of the reaction tube, passed through the sample section, and exited at the top. Experiments were conducted at 650°C, and temperature near the samples was controlled to within ±5°C. The dimensions and weights of the test specimens were determined before and after exposure to the gas environments. Intermediate weights of the exposed specimens were used to assess the corrosion kinetics of various alloys.

Table 1. Nominal composition (wt.%) of alloys selected for corrosion tests

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>Al</th>
<th>Fe</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-9Cr-1Mo</td>
<td>0.08</td>
<td>8.6</td>
<td>0.1</td>
<td>0.5</td>
<td>0.4</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>Bal⁴ N 0.05</td>
</tr>
<tr>
<td>347</td>
<td>0.08</td>
<td>17.7</td>
<td>12.4</td>
<td>1.8</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>Bal Nb 0.7</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>0.08</td>
<td>20.1</td>
<td>31.7</td>
<td>1.0</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>Bal Ti 0.3</td>
<td></td>
</tr>
<tr>
<td>825</td>
<td>0.04</td>
<td>21.5</td>
<td>Bal</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>-</td>
<td>30.0 Ti 1.0</td>
<td></td>
</tr>
<tr>
<td>625</td>
<td>0.05</td>
<td>21.5</td>
<td>Bal</td>
<td>0.3</td>
<td>0.3</td>
<td>9.0</td>
<td>0.2</td>
<td>2.5 Nb 3.7, Ti 0.2</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>0.1</td>
<td>21.5</td>
<td>Bal</td>
<td>0.5</td>
<td>0.5</td>
<td>9.0</td>
<td>-</td>
<td>18.5 Co 1.5, W 0.6</td>
<td></td>
</tr>
<tr>
<td>214</td>
<td>-</td>
<td>16.0</td>
<td>Bal</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>4.5</td>
<td>2.5 Co 2.0, W 0.5</td>
<td></td>
</tr>
<tr>
<td>Fe aluminide</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15.9</td>
<td>Bal</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

⁴Indicates balance.
Table 2. Calculated partial pressures (in atm) of gas mixtures used in experiments at 650°C

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>Air+SO₂</th>
<th>Air+Low HCl</th>
<th>Air+High HCl</th>
<th>Air+SO₂+HCl</th>
<th>Low-pO₂+H₂S</th>
<th>Low-pO₂+H₂S+HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>0.23</td>
<td>0.14</td>
<td>-</td>
<td>0.15</td>
<td>1.5 x 10⁻²³</td>
<td>1.2 x 10⁻²³</td>
</tr>
<tr>
<td>S₂</td>
<td>&lt;10⁻⁴⁰</td>
<td>-</td>
<td>-</td>
<td>&lt;10⁻⁴⁰</td>
<td>5.6 x 10⁻¹⁰</td>
<td>5.2 x 10⁻¹⁰</td>
</tr>
<tr>
<td>SO₂</td>
<td>3.0 x 10⁻³</td>
<td>-</td>
<td>-</td>
<td>2.3 x 10⁻³</td>
<td>1.3 x 10⁻¹¹</td>
<td>9.1 x 10⁻¹²</td>
</tr>
<tr>
<td>SO₃</td>
<td>7.0 x 10⁻³</td>
<td>-</td>
<td>-</td>
<td>4.4 x 10⁻³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl₂</td>
<td>-</td>
<td>8.0 x 10⁻⁴</td>
<td>1.6 x 10⁻³</td>
<td>8.1 x 10⁻⁴</td>
<td>-</td>
<td>1.5 x 10⁻²³</td>
</tr>
<tr>
<td>H₂</td>
<td>-</td>
<td>1.6 x 10⁻¹⁴</td>
<td>5.3 x 10⁻¹⁴</td>
<td>1.5 x 10⁻¹⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>-</td>
<td>8.0 x 10⁻⁴</td>
<td>1.6 x 10⁻³</td>
<td>8.1 x 10⁻⁴</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.7 x 10⁻³⁰</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HCl</td>
<td>-</td>
<td>1.7 x 10⁻³</td>
<td>4.4 x 10⁻³</td>
<td>1.7 x 10⁻³</td>
<td>-</td>
<td>2.1 x 10⁻³</td>
</tr>
</tbody>
</table>

From the materials-corrosion standpoint, the major important gas species are O, S, and Cl. Oxygen partial pressure in a given gas mixture is established by the relative amounts of CO, CO₂, H₂, and H₂O. The dominant S-containing species in the experiments that simulate combustion is SO₂. The dominant S-containing species in the experiments that simulate gasification is H₂S. Desired gas chemistries for various experiments were obtained by adjusting the relative flow rates of mixed gases such as air or CO/CO₂/CH₄, SO₂/N₂ or H₂/W/H₂, HCl/N₂, and pure N₂. Table 2 lists the calculated values for the partial pressures of various gas species in several of the exposure environments.

Upon completion of the experiments to determine corrosion kinetics, the specimens were examined by optical metallography and a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyzer. Optical examination of cross sections of exposed specimens, and analyses with the SEM, were used to identify the types and locations of various phases in the specimen scales and corrosion penetration depths.

RESULTS AND DISCUSSION

Thermodynamic calculations of multicomponent gas chemistries showed that the environment under excess-air combustion can be characterized by high pO₂, moderate-to-high pCl₂, and low pS₂; that under air-deficient conditions, it is characterized by low pO₂, low pCl₂, and moderate-to-high pS₂ (see Fig.1). The implications of the gas chemistries on the corrosion of structural materials were examined with pO₂-pS₂ and pO₂-pCl₂ thermochemical diagrams for 650°C.¹ Also, information on the morphological developments of corrosion-product layers was used to establish the mechanism for scale breakdown and accelerated corrosion. In this paper, the effect of preoxidation of these alloys in air at 650°C on their subsequent corrosion performance in complex gas environments is compared with data developed earlier on alloys that were not preoxidized.

Corrosion Data

Weight-change data were obtained for several alloys, with and without initial preoxidation, after exposure to various gas mixtures at 650°C. The data showed that the weight losses for alloys such as Type 347 stainless steel and Alloy 800 without preoxidation, in general, are substantial when SO₂ and HCl are present simultaneously. On the other hand, alloys such as 625, X, and 214 exhibited weight loss under the same exposure conditions.
Figure 1. Partial pressures of gaseous species during combustion of Illinois #6 coal under (a) 30% excess-air and (b) 30% air-deficient conditions.

Figure 2 shows the weight change data (in μg/mm² yr, assuming parabolic kinetics) as a function of Fe, Ni, and Cr content of the alloys without and with preoxidation treatments, tested in complex gas atmospheres. The results indicate that in the absence of preoxidation (see left-hand plots in Fig. 2), alloys with a higher concentration of Fe (such as Type 347 stainless steel and Alloy 800) exhibited greater weight loss when exposed in HCl-containing environments than those in environments without HCl. Moreover, alloys with high Ni content exhibited less weight change when exposed in HCl-containing environments. Alloys with a lower Cr content exhibited more weight loss, except for Alloy 214, which contains less Cr but also 4.5 wt.% Al. The weight change in these alloys is generally not a true measure of corrosion rates, because the weight change is the net of two competing processes, namely gain in weight due to oxide/sulfide formation and loss due to escape of volatile chlorides. Furthermore, the long-term corrosion performance of the alloys will be dictated by intergranular penetration of the substrate alloys, which is not evident from the weight change data. Therefore, the scale thicknesses and penetration depths in all of the specimens were measured metallographically and plotted as a function of Fe, Ni, and Cr content of the alloys as reported earlier. The results for scale and penetration followed a relationship similar to that of the weight change data for Fe, Ni, and Cr content of the alloys, with the exception of Type 347 stainless steel and Hastelloy X exposed to an air/SO2/HCl environment. For Type 347 stainless steel, the scale plus penetration was much smaller than expected; for Alloy X, it was much larger than expected, based on weight change data for these alloys.

The effect of ~950-h preoxidation at 650°C is a substantial decrease in the weight change under all test conditions for all of the alloys, and for the examined overlay. Weight change data indicate (see right-hand plots in Fig. 2) that the rate decreased from 1600 to 220 μg/mm² yr because of preoxidation treatment of Type 347 stainless steel. Similarly, the rate for Alloy 800 decreased from ~500 to 20 μg/mm² yr because of preoxidation. Inherently resistant alloys such as 625, 825, and 214 exhibited marginal improvement in corrosion behavior. A substantial reduction in corrosion rate was observed when Fe aluminide was applied as an overlay on Fe-9Cr-1Mo steel by electrospark deposition.

Microstructural Analysis

Detailed microstructural examinations were conducted on several of the tested specimens and the observations are being correlated with the exposure environment and alloy chemistry. Effects of S and Cl on the corrosion of structural materials can be analyzed by the type of scale that develops in mixed-gas atmospheres. In the chromia-forming alloys such as Type 347 stainless steel and Alloy 800, the predominant effect of HCl in the combustion environment is to initiate pitting attack that
Figure 2. Weight change data after exposure to complex gas environments at 650°C for several alloys as a function of Fe, Ni, and Cr content without (left) and with (right) preoxidation treatment.

leads to catastrophic corrosion at 650°C. Figure 3 shows the SEM photomicrographs of Type 347 stainless steel, without and with preoxidation, after exposure to several complex gas environments at 650°C. The photographs in the right-hand pictures are magnified at least three times more than those in the left-hand pictures. The results indicate that the preoxidized layer acts as a barrier to Cl and S attack, which confirms the smaller weight change observed for these specimens. Such a beneficial effect of preoxidation is more pronounced for Alloy 800 (see Fig. 4). Figure 5 shows the SEM photomicrographs of initially preoxidized Fe-9Cr-1Mo steel specimens without and with an overlay of Fe aluminide after exposure to several complex gas environments at 650°C. The results indicate that for the steel without Fe aluminide overlay, which develops iron oxide scale, preoxidation is nonprotective in H₂S environments because the low pO₂ environment leads to reduction of Fe oxide and subsequent formation of FeS. The preoxidation of the overlay layer of Fe aluminide significantly reduced corrosion loss of the underlying steel substrate. The crack regions in the overlay layer were
Figure 3. Scanning electron photomicrographs of Type 347 stainless steel, without (left) and with (right) preoxidation treatment, after exposure to several complex gas environments at 650°C.

Figure 4. Scanning electron photomicrographs of Alloy 800, without (left) and with (right) preoxidation treatment, after exposure to several complex gas environments at 650°C.
Figure 5. Scanning electron photomicrographs of Fe-9Cr-1Mo steel, without (left) and with (right) preoxidized layer of Fe aluminide, after exposure to several complex gas environments at 650°C.

oxidized to form Al₂O₃ and neither S nor Cl attack was noted. A similar benefit of preoxidation was also observed for the Alloy 214.

Near-Surface Analysis

To examine the beneficial effect of preoxidation on corrosion of the tested structural alloys in complex gas atmospheres, depth profiles of several of the pertinent elements in the scale were obtained by Auger analysis after sputtering the surfaces for various times. Figure 6 shows concentration as a function of depth for elements in the scale layer for initially oxidized Type 347 stainless steel specimens after exposure to O₂+HCl, O₂+SO₂+HCl, and H₂S+HCl environments at 650°C. The results clearly show that the preoxidation treatment, which develops Fe-rich (Fe,Cr) oxide, offers protection against corrosion in combustion environments with and without HCl. On the other hand, the preoxidized layer is completely destroyed in H₂S-containing environments, as expected because Fe oxide will be unstable in the low-pO₂ environments used in the present study and sulfidation of the alloy will ensue. Furthermore, the specimens have been subjected to five temperature cycles (from 650°C to room temperature) during the testing and the scale seems to be adhere to the substrate.

Figure 7 shows peak-to-peak height as a function of depth (developed from an earlier study²) for various elements in the corrosion scale layer on bare (without preoxidation) Fe aluminide overlay specimens after exposure to O₂+SO₂ and O₂+SO₂+HCl environments at 650°C. The results indicate that in the presence of HCl in the exposure environment, the Al in the alloy formed volatile Al chlorides whereas, in the absence of HCl, the alloy exhibited protective alumina scale in this environment. The specimen exposed to air/SO₂ developed an alumina scale =0.4 μm thick whereas that tested in air/SO₂/HCl developed a thicker scale (>5 μm) that contained no detectable Al.
Figure 6. Auger electron spectroscopy depth profiles for preoxidized specimens of Type 347 stainless steel after exposure to O₂+HCl (top left), O₂+SO₂+HCl (top right), and H₂S+HCl (bottom) environments at 650°C.

Furthermore, the scale of the latter specimen exhibited enrichment in predominantly Ni, S, and Cl (in addition to O).

Figure 7. Auger electron spectroscopy depth profiles for Fe aluminide overlay specimens after exposure to O₂+ SO₂ (left) and O₂+SO₂+HCl (right) environments at 650°C.

Figure 8 shows concentration as a function of depth for various elements in the corrosion scale layer for preoxidized Fe aluminide overlay specimens after exposure in O₂+ HCl, O₂+SO₂+HCl, H₂S, and H₂S+HCl environments at 650°C. The results clearly indicate that the alumina scale that developed at 650°C was sufficient to substantially reduce the corrosion in S- and Cl-containing environments, typical of both coal-combustion and -conversion systems.
Figure 8. Auger electron spectroscopy depth profiles for preoxidized Fe aluminide overlay specimens after exposure to O₂+HCl (top left), O₂+SO₂+HCl (top right), H₂S (bottom left), and H₂S+HCl (bottom right) environments at 650°C.

Three mechanisms may be responsible for Cl attack on structural materials. These are direct reaction between structural metal constituents and Cl₂ or HCl, leading to formation of volatile chlorides; reaction between oxides of structural metal constituents and Cl₂ or HCl, leading to volatile chlorides; and formation of solid metal chlorides but loss of metal due to the high vapor pressure of these chlorides at the exposure temperature. Calculations were performed to evaluate the equilibrium partial pressures of various volatile chloride species that form by reaction of Al, Cr, Ni, and Fe and their oxides with Cl₂ or HCl at 650°C. Based on the HCl content that was used in the present experiments, partial pressures of various chlorides and oxychlorides were calculated and are listed below.

\[
\begin{align*}
\text{Al} + \text{Cl}_2 & \rightarrow \text{AlCl}_3 \quad 2.7 \times 10^{25} \text{ atm} \\
\text{Al} + \text{HCl} & \rightarrow \text{AlCl}_3 \quad 0.19 \text{ atm} \\
\text{Al} + \text{Cl}_2 & \rightarrow \text{Al}_2\text{Cl}_6 \quad 2.2 \times 10^{30} \text{ atm} \\
\text{Al} + \text{HCl} & \rightarrow \text{Al}_2\text{Cl}_6 \quad 3.0 \times 10^{30} \text{ atm} \\
\text{Al} + \text{Cl}_2 & \rightarrow \text{AlOCl} \quad 9.3 \times 10^{17} \text{ atm} \\
\text{Al} + \text{HCl} & \rightarrow \text{AlOCl} \quad 1.3 \times 10^{14} \text{ atm} \\
\text{Al}_2\text{O}_3 + \text{Cl}_2 & \rightarrow \text{AlCl}_3 \quad 4.0 \times 10^{13} \text{ atm} \\
\text{Al}_2\text{O}_3 + \text{HCl} & \rightarrow \text{AlCl}_3 \quad 8.6 \times 10^{10} \text{ atm} \\
\text{Cr} + \text{Cl}_2 & \rightarrow \text{CrCl}_3 \quad 7.4 \times 10^{14} \text{ atm} \\
\text{Cr} + \text{HCl} & \rightarrow \text{CrCl}_3 \quad 8.7 \times 10^{14} \text{ atm} \\
\text{Cr}_2\text{O}_3 + \text{Cl}_2 & \rightarrow \text{CrCl}_3 \quad 2.3 \times 10^{5} \text{ atm} \\
\text{Cr}_2\text{O}_3 + \text{HCl} & \rightarrow \text{CrCl}_3 \quad 1.6 \times 10^{-19} \text{ atm}
\end{align*}
\]
Ni + Cl₂ ⇒ NiCl₂ \quad \text{solid at } T<987°C
Ni + HCl ⇒ NiCl₂ \quad \text{solid at } T<987°C
NiO + Cl₂ ⇒ NiCl₂ \quad \text{solid at } T<987°C
NiO + HCl ⇒ NiCl₂ \quad \text{solid at } T<987°C

Fe + Cl₂ ⇒ FeCl₃ \quad 8.1 \times 10^{11} \text{ atm}
Fe + HCl ⇒ FeCl₃ \quad 4.0 \times 10^8 \text{ atm}
Fe₂O₃ + Cl₂ ⇒ FeCl₃ \quad 3.3 \times 10^{-7} \text{ atm}
Fe₂O₃ + HCl ⇒ FeCl₃ \quad 6.3 \times 10^{-7} \text{ atm}

The calculations showed that the direct reaction of Fe, Cr, and Al with Cl₂ or HCl will lead to significant pressures of volatile phases FeCl₃, CrCl₃, AlCl₃, Al₂Cl₆, and AlOCl at 650°C in the gas environments used in the present studies. Direct reaction between Ni and Cl₂ or HCl will produce the solid NiCl₂ phase, with a vapor pressure of 5 \times 10^{-4} \text{ atm} at 650°C. On the other hand, reaction between Fe₂O₃ and Cl₂ or HCl would produce a negligible amount of volatile FeCl₃ phase in the gas mixtures of the present studies. However, Fe can also vaporize by forming Fe₂Cl₆ and Fe oxychloride which were not included in this calculation because we lacked data. Similarly, reaction between Al₂O₃ and Cl₂ or HCl would produce negligible volatile AlCl₃ phase at 650°C. Reaction between Cr₂O₃ and Cl₂ would lead to significant pressure of the volatile CrCl₃ phase, but reaction between Cr₂O₃ and HCl is not favored in the gas environments of the present study. The reaction between NiO and Cl₂ or HCl would result in the solid NiCl₂ phase with a vapor pressure of 5 \times 10^{-4} \text{ atm} at 650°C. The calculations indicate that for the alloys to perform with good corrosion resistance, direct reaction of Fe, Cr, and Al with Cl₂ or HCl must be minimized. Furthermore, even among the oxides, Cr₂O₃ seems susceptible to attack in Cl₂ but oxides of Fe and Al help to minimize corrosion. Reactions between Ni and/or NiO and Cl₂ or HCl would form the solid NiCl₂ phase, the primary cause for Ni-containing alloys to perform better in HCl-containing environments of the present study.

Based on the experimental results and the analysis of the thermodynamics of reactions between the metal/alloy, oxides, and Cl species in the exposure environment, it can be concluded that preoxidation, even at a relatively low temperature (e.g., 650°C), can substantially improve corrosion resistance of structural alloys when exposed to the complex gaseous environments coal-fired systems.

**SUMMARY**

Corrosion performance of several metallic alloys were evaluated upon exposure to environments that are typical of coal combustion and gasification, with and without HCl. This paper addressed the effect of preformed oxide layers on the corrosion of alloys that were subsequently exposed to mixed-gas atmospheres. Several conclusions can be drawn from the study.

The presence of Cl in the environment can lead to metal chlorides of the alloy constituents, which generally exhibit high vapor pressures. Reaction of Fe, Cr, and Al with Cl₂ or HCl leads to volatile chlorides, whereas the reaction of oxides of Fe and Al can lead to chloride phases with low partial pressures. Therefore, to be corrosion-resistant to Cl, the alloys must develop oxides of Fe and Al. Reaction of chromia with Cl₂ can lead to significant corrosion, whereas chromia can offer protection against HCl corrosion. Reaction of Ni and NiO with Cl₂ or HCl will lead to solid NiCl₂ at 650°C; the vapor pressure of NiCl₂ is \approx 5 \times 10^{-4} \text{ atm}, which indicates a lower corrosion rate for alloys.
with a higher Ni content. Elemental depth profiles generated by Auger electron spectroscopy clearly showed that elements such as Fe, Cr, and Al in the alloy can volatilize as chlorides, and thus lead to catastrophic corrosion.

In general, alloys with low Ni content exhibit better corrosion resistance in O₂-SO₂ environments that contain no Cl. On the other hand, alloys that contain a higher Ni content exhibit better corrosion resistance in Cl-containing atmospheres. Preoxidation of the alloys, even at 650°C, stabilizes the chromia, Fe oxide, and alumina scales and thereby substantially reduces corrosion in S- and Cl-containing combustion environments. In H₂S-containing environments, Fe oxide is not thermodynamically stable and the alloys have a tendency to sulfidize and form FeS, whereas scales of chromia and alumina can offer substantial protection against corrosion.

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