High-Temperature Corrosion and Applications of Nickel and Iron Aluminides in Coal-Conversion Power Systems

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Abstract

Nickel and iron aluminide intermetallics are being developed for use as structural materials and/or as cladding for conventional engineering alloys. In addition to strength advantages, these materials exhibit excellent resistance to corrosion in single- and multioxidant environments at elevated temperatures by the formation of slow-growing, adherent alumina scales. Corrosion resistance in a given environment is strongly dependent on the composition of the alloy and on the nature of the corrosive species prevalent in the service environment. This paper presents a comprehensive review of the current status of the corrosion performance of these intermetallics in oxidizing, sulfidizing, and multicomponent gas environments of typical coal-conversion systems. Mechanisms of scale development/breakdown, performance envelopes for long-term usage of these materials, approaches to modifying the surfaces of engineering alloys by cladding or coating them with intermetallics, and in-service experience with these materials are emphasized.

Introduction

New structural materials based on Ni-Al and Fe-Al intermetallic alloys are being developed for application in process industries and power generation systems. In the Ni-Al system (see Fig. 1), the alloys of interest are Ni$_3$Al and NiAl; in the Fe-Al system (see Fig. 2), they are Fe$_3$Al and FeAl. Relevant properties of these alloys are listed in Table 1.

In general, other elements are added to these alloys to improve their mechanical and/or corrosion properties in differing environments. For example, Ni$_3$Al exhibits superior strength properties for application at elevated temperatures but, in polycrystalline forms, it exhibits low ductility and brittle fracture.

![Ni-Al phase diagram](image1)

![Fe-Al phase diagram](image2)
Table 1. Properties of Ni-Al and Fe-Al intermetallics

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal structure</th>
<th>Melting point (°C)</th>
<th>Density (g cm⁻³)</th>
<th>Young's modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃Al</td>
<td>L₁₂</td>
<td>1380</td>
<td>7.50</td>
<td>178.5</td>
</tr>
<tr>
<td>NiAl</td>
<td>B₂</td>
<td>1640</td>
<td>5.86</td>
<td>294.2</td>
</tr>
<tr>
<td>Fe₃Al</td>
<td>DO₃, B₂</td>
<td>1520</td>
<td>6.72</td>
<td>140.6</td>
</tr>
<tr>
<td>FeAl</td>
<td>B₂</td>
<td>1250</td>
<td>5.56</td>
<td>260.4</td>
</tr>
</tbody>
</table>

White and Stein⁶ attributed the brittleness of polycrystalline Ni₃Al to segregation of S at the grain boundaries. Aoki and Izumi⁷ and Liu et al.⁸-¹⁰ used microalloying processes to add small concentrations of dopants, such as B, C, Ti, Ce, etc. to Ni₃Al, and thereby controlled the chemistry and cohesion of the grain boundaries in the material. Boron was identified as the most effective dopant for improving the tensile ductility of the alloys at room temperature.⁷,⁸ Liu et al.¹⁰ studied, in detail, the effects of B concentration, alloy stoichiometry, and microstructure on the strength and ductility properties of Ni₃Al. The melting temperature of the B₂ nickel aluminate, Ni₃Al, is high and its density is low; these properties enhance its potential for structural applications at elevated temperatures. It has been reported that Ni₃Al alloy exhibits some tensile ductility at room temperature if the composition is nearly stoichiometric but seems to be brittle when the composition is on either side of the stoichiometry.¹¹

Iron aluminides have been of interest primarily because of their much lower costs than those of Ni aluminides, their density, which is lower than that of stainless steels (with, potentially, their better strength-to-weight ratio), and their high-temperature corrosion resistance. However, limited ductility at ambient temperatures and a sharp drop in strength above 600°C have been major deterrents in the use of these aluminides as structural materials.¹²-¹⁵ More recent studies have demonstrated that adequate engineering ductility in the range of 10-15% can be achieved in Fe₃Al-based alloys by adding various alloying elements and controlling the microstructure by thermal treatment.

The purpose of this present paper is to examine the oxidation performance of the Ni and Fe aluminide alloys in single- and multioxidant environments and further assess their corrosion behavior in environments typical of coal-conversion systems.

Behavior in Single-Oxidant Environments

Corrosion resistance is generally imparted to structural alloys by in-situ development of chromia, alumina, or silica scales on the alloy surface. The slower the growth rate of the oxide, the better the oxidation resistance of the alloy. In this vein, alumina scales, with inherently slower growth rates, can offer substantial advantage over chromia scales, especially in single-oxidant environments. The oxide scales also act as barriers to the transport of corrosion-accelerating reactants such as S, Cl, and alkalis, and they retard the scaling kinetics of the underlying substrate alloys when they are exposed to multioxidant environments.

Oxidation of Nickel Aluminides

Several studies have been conducted to evaluate the oxidation behavior of Ni aluminide alloys as a function of temperature, oxygen partial pressure (pO₂), and exposure time. In addition, the effects of alloying additions and thermal cycling on the oxidation process have been studied. Kuenzly and Douglass¹⁶ studied the isothermal oxidation behavior of Ni₃Al with and without addition of 0.5 wt.% Y over a temperature range of 900-1200°C in air. They concluded that the scaling in either alloy followed a strict parabolic time dependence and that the addition of Y did not alter the steady-state scaling rate of Ni₃Al. The scales on Ni₃Al that were oxidized in air generally consisted of an outer layer of NiO, an intermediate layer of NiAl₂O₄, and an inner layer of Al₂O₃. Scale spallation was reported at all temperatures, especially on cooling the sample from the test temperature. The spallation of the scales on Ni₃Al was attributed to numerous voids at the alloy/scale interface. Based on a comparative analysis of the microstructures of scales developed on Ni₃Al with and without Y, a vacancy sink mechanism (rather than a "pegging effect" or increased Al₂O₃ plasticity) was identified as the dominant mechanism for increased scale adherence to a Y-containing alloy.

Tsipas¹⁷ studied the effect of Hf additions on the cyclic oxidation behavior of Ni₃Al in an air environment and concluded that the stoichiometric and Al-rich Ni₃Al suffered severe spallation, whereas the alloys with 2 at.% Hf resisted spallation. NiO was identified as the predominant oxide phase on both the retained and spalled scales in all the alloys studied. NiAl₂O₄, Al₂O₃, and HfO₂ were reported to be present in the Hf-containing alloys. HfO₂ protrusions from the scale into the alloy substrate of the Hf-containing alloys were attributed to enhanced adhesion of the scale to the substrate. In addition, lack of spalling, buckling, ridging, or scale detachment, noted in the alloys to which Hf was added, was attributed to a reduction in the void formation at the alloy substrate, possibly due to elimination of vacancies from the alloy/scale interface to preferential sites such as HfO₂.
Taniguchi and Shibata examined the cyclic oxidation behavior of Ni3Al with and without B, but with additions of Ti, Zr, and Hf. The tests, conducted in an O2 environment at a peak temperature of 1027°C, showed that addition of B at a level of 0.09 wt.% to Ni3Al had no beneficial effect on the spalling resistance of the scale. When Ti was added together with B, an improvement in scale adherence was reported, but, when Ti was added alone, the scale was found to be only partly adherent to the alloy. The addition of Zr to Ni3Al and Ni3Al-0.1B increased the rate of alumina formation followed by a decrease in the rate during subsequent cycles because of the growth of ZrO2 particles that formed ahead of the alumina. Improved adherence in Zr-containing Ni3Al was explained in terms of pegging of the alloy substrate by extensive penetration of Al2O3 and possible increase in oxide/alloy bond strength. The vacancy-sink mechanism was ruled out because significant number of voids was noted in both alloys (with and without Zr) after the oxidation process. The results of this study also indicated that Hf addition (≈1.9 wt.%) exerted the greatest effect, because the oxidation rate was greatly decreased and scale adherence was improved significantly. The authors suggested enhanced plasticity of Al2O3 scales (in the presence of Hf) as the major reason (rather than "pegging" or vacancy-sink mechanism) for the improved scale adherence.

Natesan studied the oxidation behavior of Hf-containing Ni3Al in air and in low-pO2 environments and concluded that, in air, the alloy develops a scale of NiO, accompanied by internal precipitates of HfO2 particles, whereas, in a low-pO2 environment, the same alloy develops α-Al2O3 scale along with HfO2 particles. The oxidation rate constant in a low-pO2 atmosphere was about one order of magnitude lower than in air and was dependent on the exposure temperature and pO2. Natesan also compared the rates of oxidation of Ni3Al with those of Ni-Al alloys with Al concentrations in the range of 11.8-15 wt.%. The results, shown in Fig. 3, indicate that an Al level in excess of 12 wt.% is needed to obtain slow-growing alumina scale and to minimize NiO and NiAl2O4 spinel formation at elevated temperatures. Based on a detailed thermodynamic analysis of the oxidation of Ni-Al binary alloys at temperatures between 900 and 1300°C in air, it can be concluded that alloys with >12 wt.% Al will develop predominantly α-Al2O3 scale but scale breakdown can occur if the depletion of Al in the matrix stabilizes the NiAl2O4 phase, which generally degrades the spalling resistance. However, in low-pO2 environments, the alumina scale seems to stabilize, indicating that the scaling process may be dictated by the transport of Al outwards rather than by transport of O inward through the scale.

Natesan also compared the oxidation behavior of Ni3Al with that of Alloy 800 (a chromia former), an oxide-dispersion-strengthened alloy, MA 956 (an alumina former), and Ti3Al in a test in which the specimen temperature was cycled between 1000°C and room temperature every 24 h (see Fig. 4). The results showed adherence of scales to Ni3Al was excellent and that the oxidation rate for this alloy was even superior to that of the more expensive alloy MA 956.

At high Al concentrations typical of NiAl alloy, the scale is primarily α-Al2O3 in air and low-pO2 environments. However, the scale is susceptible to cracking and spallation during thermal cycling, due to the difference in thermal expansion between the alloy and the oxide. Addition of 0.1 wt.% Zr seems to improve the adhesion of the alumina scale. Nesbitt et al. modeled the oxidation of Zr-containing NiAl alloys to correlate the stability of alumina scale and formation of spinel phase with Al depletion in the alloy, and thereby, established the maximum use temperature for the alloy as a function of specimen thickness and lifetime before spallation occurs.

Oxidation of Iron Aluminides

The oxidation resistance of iron aluminides depends on the formation of a chemically stable Al2O3 surface.

Fig. 3. Oxidation rate data from various sources for Ni-Al alloys and Ni3Al as a function of temperature.
layer upon exposure to an oxidizing environment. Studies of the phase stabilities in the Fe-Al-O system demonstrate that Al2O3 will form on the Fe aluminide class of alloys even at relatively low pO2. The Al levels present in Fe aluminides are well in excess of the critical concentration needed for the formation of a continuous alumina scale on the surface. However, at lower temperatures, transient Fe oxides will be present and the thermodynamically stable alumina can develop a continuous scale only over long exposure times.

Figure 5 (left panel) shows a series of Raman spectroscopy data obtained from the binary Fe3Al alloy.25 The top spectrum, obtained at room temperature before oxidation, is featureless because the underlying metal provides no Raman sensitivity in this spectral range. Beginning at 300°C, the samples were oxidized for 1 h, and a Raman spectrum was taken at room temperature. One-hour oxidation treatments, followed by room-temperature measurements, were repeated at 100°C intervals to a final temperature of 1200°C. The data in Fig. 5 indicate that, by 500°C, Fe2O3 appears prominently in the scale and is replaced by Al2O3 at T > 1000°C. Shown in the right panel of Fig. 5 are room-temperature "ruby line" fluorescence measurements from the scales that developed after 1 h of exposure, beginning at 750°C, with sequential oxidation at 50°C intervals. The fluorescence signal first appears at T of ~750°C and grows rapidly in intensity with the peak position displaying a red shift when samples are oxidized at increasingly elevated temperatures. This shift indicates an increasing compressive strain in the scale. Strain relief (at room temperature) clearly occurs when reaction temperatures exceed ~950°C, probably because of crack formation in the scales, thus signaling the onset of spallation. The 1050°C spectrum in Fig. 5 is that of natural, unstrained ruby; apparently this spectrum identifies scale delamination.

Stress determination in thermally grown alumina scales by ruby luminescence has been recently addressed.26,27 The technique has shown potential to elucidate our understanding of the strains that develop in thermally grown scales. The basic premise is that one can quantitatively assess the shift in the peaks of a relatively sharp fluorescence doublet obtained from the alumina scale, and, assuming a plane strain condition, calculate the strain in the scale. It is difficult to assess the importance of the measured strain values in scale fracture because little or no quantitative data are available in the literature for films of alumina. Nonetheless, the technique can be used to compare the strain values for specimens that have received differing treatment or to compare the values obtained for various alloy specimens that have been oxidized under the same conditions. The trends identified in such an approach can shed light on the important variables that are responsible for the observed microstructure, alloying-element effect, adhesion, and time-dependent variations in the scale and at the scale/metal interface.

Making use of the known piezospectroscopic coefficients and elastic constants for Al2O3, Natesan et al.28 translated the observed shifts to compressive strain in the scales developed on several Fe aluminide alloys. Alloy FA 186 is a ternary alloy that contains Fe,
Cr, and Al and is considered a base alloy. Alloy FA 129 is designed to exhibit high ductility at room temperature while retaining its strength at high temperatures, whereas FAL is designed for improved oxidation resistance through addition of Zr. Alloy FAS is designed to resist sulfidation, and FAX is designed for improved resistance in aqueous environments by deliberate addition of Mo.

Figure 6 shows the in-plane strain, calculated from the peak shifts, for Alloys FA 186, FA 129, FAS, FAL, and FAX oxidized for 100 h at 800, 1000, and 1200°C. The results show that the strain values ranged between 0.007 and 0.012 for specimens oxidized at 800°C. Generally, the scatter in the data is fairly small among the three sets of measurements made on each of the specimens. The results for specimens oxidized at 1000°C show low strain values for FA 186 and FAS, indicating significant spallation of the scale. The in-plane strain values for FA 129, FAL, and FAX are consistently high, and indicate that the scales developed in these alloys can accommodate the deformation, as evidenced by the lack of spalling in the oxidized alloys. The results for specimens oxidized at 1200°C indicate low strain values for all of the specimens with the exception of FAL, which exhibited strain values in the range of 0.01-0.016. The higher strain values in FAL seems to correlate with the lack of convoluted scale and absence of substrate deformation in this alloy when compared with the others.

To examine the adhesion of thermally grown scales to the substrate, Natesan et al.28 applied a tensile pull to separate the scale from the substrate. The technique they used involves attaching an epoxy-coated pin to the scale surface at a temperature sufficient to cure the epoxy. The pin is subsequently separated from the sample at room temperature by applying a tensile load. The surfaces of pulled pins are subsequently examined to assess whether the debonding occurred in the scale itself or at the scale/metal interface. The strength of the epoxy, and hence the maximum strength measurable by this procedure, was 71 MPa. If the applied load and pin area of contact are known, the stresses needed to pull the scale from the substrate can be calculated. The results obtained indicate a substantial scatter in the data from oxidized specimens. It is believed that, for many samples (especially for those prone to oxide spallation), voids or variations in the topography of the oxide layer result in an incomplete bond between the oxide and the epoxy-coated pin. Furthermore, in some of the samples, the separation between the pin and the oxide occurred in the oxide itself rather than at the oxide/substrate interface.

Figure 7 shows the maximum stress endured by the scales on the alloys oxidized at 800, 1000, and 1200°C. The results show a peak in maximum stress value for specimens of FAS, FA 186, and FA 129 exposed at 1000°C. On the other hand, maximum stress values for FAL and FAX specimens are almost independent of exposure temperature. The adhesion test results from FAL and FAX also indicate that, even with a wide variation in the oxide layer thickness (resulting from oxidation for 100 h at 800-1200°C), the tensile stress needed to pull the sample from the substrate is fairly independent of oxide thickness. The difference in the stress values for FAL and FAX must be due to differences in the chemistry in the scales and in the scale/substrate interface, which are directly influenced by the initial composition of the substrate alloy. The results also show that Zr (in FAL) and Nb (in FA 129) additions have a similar effect at 1000 and 1200°C, where α-Al₂O₃ will be the stable oxide in the scale. A comparison of the results obtained from these two alloys after 800°C oxidation indicates that Zr, rather than Nb, addition may
stabilize the alumina scale (i.e., minimize the transient oxides) on the alloy surface.

Behavior in Multioxidant Environments

Protection of Ni and Fe aluminides from corrosion and environmental effects that arise from reaction with multicomponent gases and condensed products is best afforded either by formation of stable surface oxides (in this case alumina) that are slow growing, sound, and adherent to the substrate, or by deposition of coatings that contain or develop oxides with similar characteristics. This is especially true for application of the intermetallics in integrated combined-cycle coal-gasification, low-NOx systems, pulverized-coal-fired and fluidized-bed combustion systems, and in gas turbine environments that are of interest in the development of fossil energy systems (see Fig. 8).

In coal-gasification and low-NOX systems, and in the first stage of magetohydrodynamic systems, the gas environment is characterized by low pO2 and moderate-to-high S partial pressure (pS2), and the S is present as H2S, as depicted by region B in Fig. 8. In combustion atmospheres and gas turbine environments, pO2 is generally high and pS2 is low, and the sulfur is present as SO2 as depicted by region A in Fig. 8. However, if combustion occurs near metal surfaces, e.g., in a bubbling fluidized bed, the local environment can be reducing and is dictated by the S sorbent equilibria, which are determined by stability fields of the CaO/CaSO4-phase equilibrium. The effect of the gas chemistries on the corrosion of structural materials can be examined with a pO2-pS2 and pO2-PCl2 thermochemical diagram, shown in Fig. 8 for a metal temperature of 650°C.

Oxidation/Sulfidation of Nickel Aluminides

The kinetic behavior of Ni3Al and NiAl over the temperature range of 600-800°C in S vapor at 10⁻² atm is generally parabolic over test times of 25 h.29 The rate constants are in the range of 0.036-3.6 mg²·cm⁻⁴·h⁻¹, and are slightly lower for the alloy that contains a higher concentration of AI. Both alloys develop duplex scales that consist of an outer layer of Ni3S2 and an inner layer of Al2S3. In a H2-H2S-H2O gas mixture at 600-800°C, with pO2 in a range of 10⁻¹⁰-10⁻¹³ atm and pS2 in a range of 10⁻⁶-10⁻⁸ atm, parabolic rate constants for the same two Ni-Al alloys are slightly lower than the corresponding rates in S vapor (without O2) and showed a much smaller temperature dependence.30 Scales that formed on Ni3Al and, initially, on NiAl are essentially the same as those formed in S vapor except for the presence of Al2O3 particles in the inner Al2S3 scale. However, in the case of NiAl, a continuous Al2O3 inner layer forms after 35 h at 700 and 800°C. The kinetics of sulfidation of Ni3Al at 875°C were also determined in several H2-H2S gas mixtures (see Table 2).19 At H2S concentration <0.5 vol.%, the weight change kinetics are of the same order as in air exposure. When the H2S level is 0.75 vol.%, the kinetics are significantly faster than in air, but they are parabolic. When the H2S level >1.5 vol.%, the alloy exhibits accelerated corrosion. It is significant that a Ni3S2 layer forms in most of these sulfidizing environments, even at an Al concentration of 50 at.%. Accordingly, the use of Ni aluminides in high-S/low-O environments does not appear practical at temperatures above the Ni-Ni3S2 eutectic (=635°C), where one of the corrosion products becomes liquid and leads to rapid oxidation of the material.

Table 2. Sulfidation kinetics of Ni3Al in H2-H2S atmospheres at 875°C

<table>
<thead>
<tr>
<th>H2S content in H2-H2S mixture (vol.%)</th>
<th>Sulfur partial pressure (atm)</th>
<th>Rate constant (mg²·cm⁻⁴·h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16</td>
<td>2.2 x 10⁻⁹</td>
<td>8 x 10⁻⁴</td>
</tr>
<tr>
<td>0.38</td>
<td>1.2 x 10⁻⁸</td>
<td>1 x 10⁻³</td>
</tr>
<tr>
<td>0.75</td>
<td>4.8 x 10⁻⁸</td>
<td>4 x 10⁻²</td>
</tr>
<tr>
<td>1.50</td>
<td>2.0 x 10⁻⁷</td>
<td>7 x 10⁻²</td>
</tr>
<tr>
<td>4.70</td>
<td>2.1 x 10⁻⁶</td>
<td>3</td>
</tr>
</tbody>
</table>

Fig. 8. Oxygen/sulfur and oxygen/chlorine thermochemical diagrams for several metals, calculated for a metal temperature of 650°C.
The corrosion of Ni₃Al in atmospheres that contain SO₂ is generally more rapid than in environments that contain only O₂ and results in scales that contain mixtures of oxides and sulfides. In cyclic tests on Ni₃Al in N₂-10 vol.% SO₂ at 750°C, an incubation period of several hundred hours was sometimes observed before severe attack occurred, but in all cases, the weight gain after 1000 h is relatively high (≥20 mg/cm²). The scale consists of discontinuous layers of Al₂O₃ and Ni₃S₂, with no evidence of the formation of the Ni-Ni₃S₂ eutectic. Significantly lower corrosion rates (0.5, 2.8, and 3.7 mg/cm² at 600, 700, and 800°C, respectively) are measured for Ni₃Al exposed to a simulated combustion gas (N₂-1 vol.% O₂-0.5 vol.% SO₂). Similarly, low corrosion rates are measured in circulating He that contains atm O₂ and SO₂ with an activity of S₂ of atm. After ~170 h, the corrosion rates of NiAl and Ni₃Al-based alloys are 0.01-0.06 mg/cm² at 650°C, 0.06-0.16 mg/cm² at 750°C, and 0.2-0.75 mg/cm² at 871°C. However, the associated corrosion product layer, which is 0.2-0.4 μm thick and consists mainly of Al₂O₃, spalled when cooled to room temperature. Thus, the properties of the oxide that formed in the presence of even this small amount of SO₂ differs from that observed in air exposures, where no spallation tendency is observed at intermediate temperatures.

**Oxidation/Sulfidation of Iron Aluminides**

Extensive studies have been conducted on the corrosion performance of Fe₃Al-based alloys in O/S mixed-gas environments. Figure 9 shows thermogravimetric analysis (TGA) data for two heats of Fe₃Al alloys that were tested in an ~1.35 vol.% H₂S-H₂ gas mixture at 875°C. The sulfidation rates, which were fairly low when compared with those for chromia-forming alloys, were similar for both heats. The dew point of the gas mixture used in these experiments was such that enough water vapor was present in the exposure environment for the alloys to develop thin alumina scales, even in sulfidation tests.

Weight change data from TGA of several Fe-Al binary alloys and Fe₃Al tested in an O/S mixed-gas environment at 875°C are shown in Fig. 10. The results indicate significant corrosion of alloys with 8 and 10 wt.% Al, whereas the alloy with 12 wt.% Al and Fe₃Al (with 13.9 wt.% Al) exhibited negligible corrosion under the same conditions. Figure 11 shows scanning electron microscopy (SEM) photomicrographs of cross sections of Fe₃Al binary alloys and Fe₃Al after exposure to a mixed-gas environment. Energy-dispersive x-ray analysis showed that the alloys with 8 and 10 wt.% Al developed predominantly Fe sulfide scale, whereas the other two alloys developed Al oxide scale. The 8 wt.% Al alloy was tested for only 1.75 h, whereas the 10 wt.% Al alloy was tested for 5.5 h; as a result, the absolute values of the scale thicknesses should not be compared. However, both alloys appear to undergo catastrophic sulfidation in the O/S mixed gas with S levels that are anticipated in gasification systems that use high-S coal as feedstock. Figure 11 also shows that the 12 wt.% Al and Fe₃Al alloys develop extremely thin scales after ~90 h of exposure to the mixed-gas environment.

Figure 12 shows TGA weight change data for several high-purity Fe-Cr, Fe-Cr-Ni, Fe-Al, and Fe-Cr-Al alloys and Fe₃Al after exposure to an O/S mixed-gas environment at 875°C. Data for the Fe-Cr binary alloy show that Cr concentration at the high level of 25 wt.% does not improve the sulfidation resistance of the alloy, which develops a scale (consisting of a mixture of Fe
Weight change data for several Al-containing specimens. SEM photomicrographs of cross sections of (a) Fe-12% Al, (b) Fe-12% Al and Cr steel, after exposure to O2 environment with \( P_{O_2} = 9.4 \times 10^{-7} \).
corrosion rate. Detailed microprobe examination of as-coated specimens showed that the coating was substantially diluted and the coated surface contained an average Al concentration of ≈6-8 wt.%. As a result, the corrosion performance of the coated specimen is similar to that of Fe-Al binary alloys that contain 8 and 10 wt.% Al. At present, coatings are being developed with FeAl filler wire, rather than Fe3Al, so that even with dilution, the Al content in the coated region will exceed 12 wt.%. The alloys GE 1541 and RV 8413 are Fe-based alloys with moderate Cr content and 4-6 wt.% Al. Corrosion performance of these alloys is not adequate for service in coal-gasifier environments.

Corrosion in Chlorine-Containing Environments

Fe3Al-based alloys that contain alloying elements, such as Cr, B, Nb, C, Mo, and Zr, were tested for 48 h at a flow rate of 110 ml/min in a 1 vol.% HCl-N2 gas mixture at 650°C. Figure 14 illustrates weight change of the alloy specimens during the corrosion tests. The figure clearly shows that, depending on Cr content, the alloys either lose or gain weight under the same experimental conditions. A comparison of the weight changes of the binary alloy Fe3Al and the Cr-containing Fe3Al alloy shows that the latter loses less weight than the former during the exposure time used in the study.

Furthermore, alloys that contain 5.5 wt.% Cr show positive weight change during the tests. Therefore, it can be concluded that a critical concentration of Cr may control the general corrosion behavior of Fe3Al-based alloys in HCl-containing environments. For application in coal-gasification and -combustion environments,
Fig. 15. SEM photomicrograph of cross sections of Fe₃Al specimens after exposure in gas mixtures: (a) air-SO₂, (b) air-HCl, and (c) air-SO₂-HCl at 875°F.

**Behavior in Multioxidant Gas and in Presence of Deposits**

The effect of three types of deposits, namely, Na₂SO₄ salt with and without NaCl, CaSO₄, and coal ash on the corrosion performance of aluminides is of interest for application in fossil systems. The effect of S on the corrosion of Ni₃Al can be significantly increased by the presence of salt deposits that contain K or Na. This form of attack, referred to as hot corrosion, is commonly associated with the presence or formation of alkali sulfates. Exposure of Ni₃Al that contained small additions of Ti, Zr, and B at 600-800°C in a simulated combustion gas with Na₂SO₄-NaCl deposits resulted in significantly greater weight gains than in the absence of the salt mixture. Duplex scales, composed of NiO and unreacted salt, in the outer layer and Al₂O₃ and Al₂S₃ in the inner region form at 600°C. Scales that are a result of exposures at 700 and 800°C exhibit a complex corrosion product zone against the alloy, an Al-depleted zone with “TIS” precipitates near the surface, and, at 800°C, an outer layer that contains similar amounts of Ni and Al.

The presence of molten alkali sulfate salts significantly increases the corrosion of Fe aluminides in SO₂-containing environments. A coating of Na₂SO₄-Li₂SO₄ salt on Fe aluminides exposed in an oxidizing/sulfidizing gaseous environment (1% SO₂ in air) at 605 and 800°C leads to corrosion rates that are at least a factor of 10 higher than rates measured in the absence of the sulfate product. In contrast to the sulfidation results discussed above, increased Cr concentrations (from 2 to 5 at.%) somewhat mitigated the degradation by the molten sulfate, as did a higher concentration of Cr (36 versus 28 at.%). The relative resistance of Types 310 and 321 stainless steel was significantly better than that of the Fe aluminides.

In another study, Fe₃Al (27Al-2.2Cr-0.1B) and FeAl (40Al-0.05Zr-0.06B-0.08SiC) were coated with Na₂SO₄-containing salts and exposed to a simulated combustion gas that contained 1% O₂, 0.5% SO₂, balance N₂ (vol. %) at 600°C. Three coating compositions were tested: Na₂SO₄ with 10 wt. % NaCl, Na₂SO₄ with 15 wt. % V₂O₅, and pure Na₂SO₄. Mass gains after 96 h were 8 and 14 mg/cm², respectively, for the FeAl and Fe₃Al alloys coated with the V-containing salt and between 4 and 5 mg/cm² for both alloys coated with the other two salts. The scales showed two main layers: an outer layer that contained mainly Fe oxides and an inner layer that contained Al₂O₃ and Al₂S₃ with some Fe. Because the scales...
showed extensive cracking and spalling during cooling, it was predicted that the alloys would corrode more heavily under thermal cycling conditions.\textsuperscript{41} The short-term (8-10 h) mass gains of FeAl (40% Al) under hot-corrosion conditions (67% Na\textsubscript{2}SO\textsubscript{4}-33% K\textsubscript{2}SO\textsubscript{4} [mol. %] salt coating in a gas atmosphere of O\textsubscript{2} with 0.5% SO\textsubscript{2}) are smaller at 800 and 870°C than at temperatures below 800°C, and the oxide scales formed at 700°C and above are more compact than at lower temperatures and less subject to spallation on cooling.\textsuperscript{42} The greatest mass gain (1.8 mg/cm\textsuperscript{2}) is at 800°C; it is reached in 10 h. Additions of 4% Si or 1% B to the FeAl alloy led to higher mass gains at 650°C.\textsuperscript{42} Addition of 25 mol. % NaCl to the (Na,K)\textsubscript{2}SO\textsubscript{4} salt also increased the mass gain of FeAl at 800°C.

Under conditions that simulate air heating tubes in a fluidized bed-coal combustor, specimens of Ni\textsubscript{3}Al were coated with reagent-grade CaSO\textsubscript{4} or ash from a circulating fluid bed system and exposed to a gas mixture composed of (in vol.%) 0.4 CO, 79.7 CO\textsubscript{2}, 0.2 SO\textsubscript{2}, and 19.7 N\textsubscript{2} at 635 and 871°C. After 500-2000 h of exposure, the Ni\textsubscript{3}Al specimens developed massive Ni\textsubscript{3}S\textsubscript{2} scales; the attack was more severe in the presence of CaSO\textsubscript{4} than in the presence of ash.\textsuperscript{43} Preoxidation inhibits attack of ash-covered specimens, but not of specimens covered with CaSO\textsubscript{4}. Experiments in which the Ni\textsubscript{3}Al alloys were enclosed in sealed quartz capsules that contained CaSO\textsubscript{4} show much greater attack at 871°C than at 635°C, and there is evidence for the formation of the Ni-Ni\textsubscript{3}S\textsubscript{2} eutectic.

The corrosion of Fe aluminides in contact with solid CaSO\textsubscript{4} surface deposits is less severe than that promoted by molten alkali sulfates. Fe\textsubscript{3}Al with 0.7% TiB\textsubscript{2} had good resistance to attack when coated with deposits of either reagent grade CaSO\textsubscript{4} or circulating-fluid-bed ash and held at 870-900°C in a relatively reducing mixed gas (pO\textsubscript{2} = 3 x 10\textsuperscript{-12}, pS\textsubscript{2} = 10\textsuperscript{-9}, pSO\textsubscript{2} = 2 x 10\textsuperscript{-3}, pSO\textsubscript{3} = 1 x 10\textsuperscript{-9}, all in atm.).\textsuperscript{43}

Laboratory corrosion studies, in which an ash deposit more typical of coal-fired boilers (Fe\textsubscript{2}O\textsubscript{3}, K\textsubscript{2}SO\textsubscript{4}, Na\textsubscript{2}SO\textsubscript{4}) was used, showed that, after 800 h at 650 and 700°C in a simulated flue gas (14% CO\textsubscript{2}, 10% H\textsubscript{2}O, 4% O\textsubscript{2}, balance N\textsubscript{2}) with 0.24 and 1% SO\textsubscript{2}, the alloy Fe\textsubscript{3}Al-2Cr was more heavily attacked than stainless steel.\textsuperscript{42} However, under the same environmental conditions, Fe\textsubscript{3}Al-5Cr exhibited the same order of weight change and thickness loss as type 347 stainless steel.\textsuperscript{44} Furthermore, results from field exposure of several conventional engineering alloys and Fe\textsubscript{3}Al-5Cr showed negligible corrosion of the intermetallic alloy after 4000 h at temperatures between 625 and 730°C.\textsuperscript{45}

**Aluminides as Overlay Claddings**

Even though the corrosion resistance of Fe aluminides is significant in environments that are prevalent in fossil energy systems, the use of these aluminides as structural materials at elevated temperatures is very limited because of their inadequate strength properties. Several approaches are being tried to apply the Fe aluminides as overlay claddings on structural alloys. The electrospark-deposition (ESD) process, which involves a short-duration microwelding technique and high-current electrical pulses to deposit an electrode material on a metallic substrate, is being used to deposit Fe aluminides. A principal advantage of the ESD process is that the overlay is 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 overlay 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, applied on Type 316 stainless steel and Alloy 800 substrate alloys by the ESD process, were tested in simulated gasification or combustion environments that contained H\textsubscript{2}S/SO\textsubscript{2} or without HCl. In the first experiment, performance of the ESD coatings (which included Fe\textsubscript{3}Al with differing bond coats of refractory metals and/or noble metals) was compared with that of uncoated austenitic alloys.\textsuperscript{46} Figure 16 shows corrosion loss data obtained for specimens tested for 1000 h at 650°C in gas mixtures where pO\textsubscript{2} = 1.2 x 10\textsuperscript{-23}, pS\textsubscript{2} = 5.2 x 10\textsuperscript{-10}, pCl\textsubscript{2} = 9.4 x 10\textsuperscript{-17}, and pHCl = 2.1 x 10\textsuperscript{-3} atm. All of the Fe aluminide coatings were resistant to sulfidation and chloride attack, whereas the base alloys were susceptible to general corrosion and pitting attack, especially in the HCl-containing environment. The weight change data and extensive microscopic analyses of tested specimens showed that the bond coats themselves do not significantly influence the corrosion process.

Further evaluation of Fe aluminide coatings was conducted with a Type 316 stainless steel substrate coated with either Fe\textsubscript{3}Al or FeAl weld rod.\textsuperscript{37} Coatings made with FeAl weld rod contained much more Al than those made with Fe\textsubscript{3}Al weld rod. The calculated chemistries of gas mixtures used in coal-conversion simulation experiments are listed in Table 4. Coated and uncoated specimens were exposed to these
The uncoated alloys exhibited some general corrosion and significant sulfidation and localized pitting corrosion. The weight gains and scaling rates were much lower for the aluminide-coated specimens than for the uncoated alloys. The figure shows two curves for Fe₃Al-coated specimens that were fabricated at different times and tested in the same environments but at different times. The weight change data for the two specimens are similar, indicating that the corrosion performance of these coated alloys is reproducible and that substantial improvement in corrosion resistance can be achieved by coating the surface of structural alloys. Figure 18 shows SEM photomicrographs of the stainless steel and Fe aluminide-coated specimens after exposure in these tests.

Figures 19A and B show weight change data for Type 304 and 316 stainless steel and for Fe₃Al- or FeAl-coated Type 316 stainless steel after exposure at 650°C to simulated combustion environments with or without HCl. In the absence of HCl, the uncoated alloys developed scales of (Fe, Cr) oxide or Fe oxide and tended to crack and spall, as evidenced by weight loss in Fig. 19. However, the absolute values for

Table 4. Calculated chemistries of gas mixtures used in experiments at 650°C

<table>
<thead>
<tr>
<th>Test condition</th>
<th>pO₂ (atm)</th>
<th>pS₂ (atm)</th>
<th>pCl₂ (atm)</th>
<th>pSO₂ (atm)</th>
<th>pHCl (atm)</th>
</tr>
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<tbody>
<tr>
<td>Gasification (G)</td>
<td>1.5 x 10⁻²³</td>
<td>5.6 x 10⁻¹⁰</td>
<td>-</td>
<td>1.3 x 10⁻¹¹</td>
<td>-</td>
</tr>
<tr>
<td>Combustion (C)</td>
<td>6.7 x 10⁻³</td>
<td>1.4 x 10⁻³⁵</td>
<td>-</td>
<td>1.2 x 10⁻³</td>
<td>-</td>
</tr>
<tr>
<td>(G) with HCl</td>
<td>1.2 x 10⁻²³</td>
<td>5.2 x 10⁻¹⁰</td>
<td>1.5 x 10⁻¹⁶</td>
<td>9.1 x 10⁻¹²</td>
<td>2.1 x 10⁻³</td>
</tr>
<tr>
<td>(C) with HCl</td>
<td>4.9 x 10⁻³</td>
<td>1.6 x 10⁻³⁵</td>
<td>3.6 x 10⁻⁴</td>
<td>9.1 x 10⁻⁴</td>
<td>1.7 x 10⁻³</td>
</tr>
</tbody>
</table>

Fig. 17. Weight change data for base and aluminide-coated alloys tested at 650°C in simulated gasification atmospheres: (left) without HCl and (right) with HCl.
Fig. 18. SEM photomicrographs of Type 316 stainless steel and Fe aluminate-coated specimens after exposure to simulated gasification environments with and without HCl at 650°C.

Fig. 19. Weight change data for base and aluminate-coated alloys tested at 650°C in simulated combustion atmospheres: (left) without HCl and (right) with HCl.
weight change after 900 h of exposure is small, i.e., in the range of 0.01-0.016 mg/mm². The aluminide-coated alloys showed a small weight gain due to the development of a thin adherent alumina scale. In the presence of HCl, both the uncoated and coated alloys showed substantial weight loss at 650°C. The attack was most notable in the Fe₃Al-coated alloy, less notable in the uncoated alloys, and least notable in the FeAl-coated alloy. The primary cause for the increased corrosion of Fe₃Al-coated alloys seems to be a low concentration of Al in the coating that was a result of dilution of the deposit layer with substrate constituents. Figure 20 shows SEM photomicrographs of Type 316 stainless steel and Fe aluminide-coated specimens from these tests. Even though Fe₃Al contained ~14 wt.% Al, the coated alloy contained <8 wt.% Al after fabrication. The results also indicate that the threshold Al concentration necessary to improve the corrosion resistance of structural alloys is similar for the overlay and the bulk Fe-Al alloys discussed earlier in this paper.

Iron aluminide overlays were also prepared by gas tungsten arc and gas metal arc techniques. The use of welding to produce Fe aluminide layers leads to a loss of selected elements by vaporization and significant mixing of the filler metal and substrate alloys (dilution) during deposition. Because the substrates contain essentially no Al, the concentration of this element in the overlay is generally much smaller than it is on the weld rod/wire used to produce the overlay. Several specimens of Fe aluminide overlay have been exposed to oxidizing/sulfidizing gas environments at 800°C in isothermal tests. Results...
showed that the corrosion performance of overlays that contained >21 at.% Al was superior to that of conventional Fe-Cr-Ni and Fe-Cr-Al alloys. However, a rapid degradation in corrosion resistance was observed under thermal cycling conditions when the initially grown scales spalled and the subsequent rate of reaction was not controlled by the formation of slow-growing alumina. It was concluded that Al concentrations >25 at.% are needed to ensure adequate corrosion resistance in mixed-gas environments.

Summary

Intermetallic alloys such as Ni and Fe aluminides are being developed as structural materials and as cladding/overlay for conventional engineering materials. The present paper addresses the chemical compatibility aspects of these materials in environments relevant to fossil energy systems. In single-oxidant environments, such as air and low-pO2, the oxidation rates for these alloys are significantly lower than those for chromia-forming commercial alloys. However, the mechanical integrity of the alumina scales and the reformation characteristics are key to adequate protection in long-term service. In S-containing environments, Ni aluminides can and do generally form liquid Ni sulfide corrosion products which lead to catastrophic corrosion. In similar environments, Fe aluminides offer superior corrosion resistance. Data are presented on the performance envelope for use of these materials in S-containing environments. In Cl-containing environments, Fe aluminides but, if S is present along with Cl, the corrosion rate seems to be determined by the sulfidation rather than by Cl. Limited data are available on the corrosion performance of these materials in deposits such as alkali sulfates, S sorbents, and coal ash. The results from several of these studies are discussed to explain the role of deposits in the behavior of these alloys. Finally, the paper addresses the corrosion performance of Fe aluminides as cladding or weld overlay on conventional structural alloys.

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References