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ABSTRACT

Iron aluminide intermetallics are being developed for use as structural materials and/or as cladding for conventional engineering alloys. In addition to their strength advantages, these materials exhibit excellent resistance to corrosion in single- and multioxidant environments at elevated temperatures through the formation of slow-growing, adherent alumina scales. Even though these intermetallics develop protective oxide scales in single-oxidant environments, the simultaneous presence of several reactants in the environment (typical of practical systems) can lead to development of oxide scales that are nonprotective and that undergo breakaway corrosion, or to nonoxide scales that are detrimental to the performance of the underlying alloy. This paper describes the corrosion performance of Fe-Al intermetallics in environments that contain sulfur, carbon, chlorine, and oxygen and that are typical of fossil energy systems. Emphasis is on mechanisms of scale development and breakdown, performance envelopes for long-term usage of these materials, and approaches to modifying the surfaces of engineering alloys by cladding or coating them with intermetallics to improve their corrosion resistance.

INTRODUCTION

New structural materials that are based on Fe-Al intermetallic alloys are being developed for application in process industries and power-generating systems. In the Fe-Al system, the alloys of interest are Fe$_3$Al and FeAl. In general, other elements are added to these alloys to improve their mechanical and/or corrosion properties in differing 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 (which have inherently slower growth rates) can offer substantial advantages 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.

The oxidation resistance of iron aluminides depends on the formation of a chemically stable Al$_2$O$_3$ surface layer upon exposure to an oxidizing environment. Studies of the phase stability in the Fe-Al-O system demonstrate that Al$_2$O$_3$ will form on the Fe aluminide class of alloys even at relatively low oxygen partial pressure (pO$_2$). The Al levels present in Fe aluminides (15.9 and 20-30 wt.% in Fe$_3$Al and FeAl, respectively) 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. The purposes of this paper are to examine the oxidation/corrosion performance of bulk Fe aluminide alloys and electrospark-deposited layers of Fe aluminides in single- and multioxidant environments, evaluate the chemical and mechanical stability of the scales in such environments, and compare
their performance in environments that simulate those in coal gasification and coal combustion systems.

**EXPERIMENTAL PROCEDURE**

The experimental study focused on oxidation and sulfidation of binary Fe-Al and ternary Fe-Cr-Al intermetallic alloys, sheets of which were procured from Oak Ridge National Laboratory. The composition of the binary and ternary alloys was Fe-15.9 wt.% (28 at.%) Al and Fe-15.9 wt.% Al-5.0 wt.% Cr, respectively; FAL is a modification of the ternary alloy, with additions of 0.1 wt.% Zr and 0.05 wt.% B. The sheet materials were subjected to either a single annealing treatment at 750°C for 1 h followed by oil quenching or a dual annealing treatment for 1 h at 850°C and 7 days at 500°C.

Oxidation of these alloys was conducted in a thermogravimetric apparatus (TGA) in high-purity air environment at temperatures between 650 and 1200°C. The oxidized specimens were analyzed extensively by Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and the ruby fluorescence technique. Auger data were collected by point analysis, with the electron beam at 5 kV, 100 nA. All of the samples were run at a 60° tilt. The ion beam used for sputtering was Ar+, 3 kV, 50 μA/cm². Sampling frequency for depth profiles was 0.5 or 1.0 min/cycle (depending on the oxide thickness), but the sputter rate was maintained the same. The beam size was =0.3 μm and raw data of peak-to-peak counts were used to compare data obtained from various samples.

In addition, claddings of high Al content were produced by the electrospark-deposition (ESD) technique. ESD is a microwelding technique wherein short-duration, high-current electrical pulses are used to deposit an electrode material on a metallic substrate. Several specimens with Al-enriched surfaces, applied by the ESD with Fe₃Al and FeAl weld rods on Type 316 stainless steel and on Alloy 800, were tested in simulated gasification and combustion environments that contained H₂S or SO₂ with or without HCl. In the first experiment, performance of the ESD coatings (which included Fe₃Al or FeAl with differing bond coats of refractory metals and/or noble metals) was compared with that of uncoated austenitic alloys. The chemistry of the gas mixtures at 650°C led to pO₂ = 1.2 x 10⁻²³, pS₂ = 5.2 x 10⁻¹⁰, pCl₂ = 9.4 x 10⁻¹⁷, and pHCl = 2.1 x 10⁻³ atm, which is typical of coal gasification, low-NOₓ, and air-deficient combustion systems. Similar specimens with Al-enriched surfaces, applied on a Type 316 stainless steel substrate alloy by ESD, were also tested in simulated combustion environments that contained SO₂ with or without HCl. Specimens were tested for ≈900 h at 650°C in gas mixtures with pO₂ = 6.7 x 10⁻³, pS₂ = 1.5 x 10⁻³⁵, pCl₂ = 3.6 x 10⁻⁴, and pHCl = 1.7 x 10⁻³ atm.

**RESULTS AND DISCUSSION**

**Oxidation of Iron Aluminides**

In general, the Fe aluminides that were oxidized in air developed predominantly Al oxide at low oxidation rates. Figure 1 shows TGA data for several Fe aluminides and Type 310 stainless steel (a chromia former) exposed to an air environment at 1000 and 650°C. The observed rates for the Fe aluminides were comparable to those reported earlier for oxide-dispersion-strengthened alumina-forming Fe-based alloys and were lower than the oxidation rates of chromia-forming alloys that contained high levels of Cr. Even at the lower temperature of 650°C, Fe aluminides develop alumina scales, with the rates being 10-20% of the rate at 1000°C.
Figure 1. Thermogravimetric test data for several Fe aluminides and Type 310 stainless steel at 1000°C (left) and several Fe aluminides at 650°C (right) after exposure to air environment.

Figure 2 shows the Auger Al/O peak-to-peak ratios for the binary, ternary, and Zr-containing Fe aluminides after oxidation in air at 1000°C. The results indicate that all three alloys develop scales at least 100 Å thick within 10 min at 1000°C and that these scales grow to ~1 μm after 100 h of oxidation. The figure also shows the analysis of spalled regions after 50 h of exposure for the binary alloy and after 50 and 100 h of exposure for the ternary alloy. The values of the Al/O ratio in these specimens were high and thus indicate high Al and low O concentrations and small scale thickness. Results indicate that the reservoir of Al in the aluminide will be sufficient to re-form the alumina scale, if other competing reactions with other oxidants in the exposure environment can be avoided. No spallation was noted on the specimen that contained Zr, an observation that is indicative of better adhesion between the scale and substrate, possibly due to the “reactive element” effect. Such a beneficial effect of Zr only occurs at temperatures above ~900°C and probably is of less significance at lower temperatures, primarily because of the decreased mobility of these additives at lower temperatures. Furthermore, the alumina that forms at >1000°C is α-alumina, which is slow growing. On the other hand, at lower temperatures, other forms of alumina, such as γ, δ, and θ, prevail and these forms are generally fast growing, more voluminous, more porous, and less protective. Results of several studies indicate that the temperature stability of various aluminas follows the sequence

\[ γ \text{-alumina} \rightarrow δ \text{-alumina} \rightarrow θ \text{-alumina} \rightarrow α \text{-alumina} \]

750°C 900°C 1000°C

Even though the oxidation rates of Fe aluminides are low and the scales can re-form in single-oxidant environments, it is essential that the initially developed scale be stable for long periods of time if the alloy is to be viable for application in multioxidant environments. Two distinct modes of failure can be identified in the breakdown of alumina scales. The first is due to transport of iron outward from the substrate, through the scale, to the gas/oxide interface, a sequence of events that leads to the formation of Fe oxide nodules on the scale surface. These nodules, which eventually coalesce and cover the entire surface, form irrespective of whether the scale is α-alumina or some other low-temperature alumina. Our study indicates that, from the standpoint of additions of elements such as Zr, Nb, etc., the composition of the Fe aluminide has a negligible effect on Fe transport. Another concern at low temperatures is that the alumina scaling rate may be so low that transient oxides of Fe, Cr, and other elements may be present in the corrosion-product scale for a long period of exposure and thus the benefit of slow-growing alumina for corrosion protection may not be realized in practice.

The second mode of failure is due to mechanical separation of the scale from the substrate. The mechanical stability or the lack of it, a well-known problem associated with
alumina scales, is also an issue for Fe aluminides. Scales composed of alumina commonly exhibit mechanical instability, e.g., cracking, spallation, and delamination, which poses a serious drawback in the application of Al₂O₃-forming alloys. Several mechanisms proposed in the literature for the failure of alumina scales include generation of thermal expansion mismatch and stress during oxide growth, poor scale/substrate adhesion, impurity (e.g., sulfur) segregation at the scale/metal interface, generation of vacancies and coalescence to form voids at the interface, etc.

Natesan et al.³,¹⁰ evaluated the adhesion strength of thermally grown scales to the substrate by applying 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. Stresses needed to pull the scale from the substrate were calculated from the applied load and pin area of contact. The tests showed that Zr-containing alloys exhibited scale pull stress that was almost independent of exposure temperature in the range 800-1200°C; the values ranged between 30 and 50 MPa.

Sulfidation of Iron Aluminides

Sulfidation experiments have been conducted on several heats of Fe aluminide at temperatures between 400 and 1000°C. Figure 3 shows TGA data for several heats of Fe aluminides that were tested in H₂S-H₂ mixtures with various H₂S concentrations. Figure 3 shows TGA data for ternary Fe aluminate tested in a 1.35 vol.% H₂S-H₂ mixture at 650, 875, and 1000°C. Also shown in the figure are data for 310 stainless steel oxidized in air at 1000°C and sulfidized in the 1.35 vol.% H₂S-H₂ mixture at 875°C. The morphology of the sulfides on the Fe aluminate surfaces seemed different at different temperatures, probably because the thermodynamic activity of S in the exposure environment is lowest at 1000°C and highest at
310 SS, 875°C, sulfidation
310 SS, 1000°C, oxidation
Fe-Al-Cr, 1000°C, sulfidation
Fe-Al-Cr, 650°C, sulfidation

Figure 3. Weight change of ternary Fe₃Al and Type 310 SS at several temperatures after they were oxidized in air or sulfidized in a 1.35 vol.% H₂S-H₂ mixture.

650°C (the concentration of H₂S in the gas was kept constant). The scales on Fe aluminide consisted of (Fe,Al) sulfides and Fe sulfides, the relative proportion of the former to latter decreasing with decreasing temperature. The scale on the Type 310 stainless steel sample was predominantly (Fe,Cr) sulfides, with some nodules of Fe sulfide.

**Corrosion in Multioxidant Environments**

Protection of 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 the application of 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. In coal-gasification and low-NOₓ systems, and in the first stage of magnetohydrodynamic systems, the gas environment is characterized by low pO₂ and moderate to high S partial pressure (pS₂), and S present as H₂S. In combustion atmospheres and gas turbine environments, pO₂ is generally high and pS₂ is low, and S is present as SO₂. 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 the equilibrium of the stability fields of the CaO/CaSO₄ phase.

Extensive studies have been conducted on the corrosion performance of alumina-forming alloys in O/S mixed-gas environments. The results showed that a critical Al content in excess of 12 wt.%, which is present in Fe aluminides, is needed for the formation of alumina on the alloy surface in environments that are typical of coal conversion systems. Even though the corrosion resistance of Fe-based alloys with high Al content is significant in environments that are prevalent in fossil energy systems, the use of these alloys as structural materials at elevated temperatures is very limited because they lack adequate strength and are difficult to fabricate. A promising approach for Al enrichment is the weld overlay process, in which claddings of high Al content are produced by ESD. Figure 4 shows the Auger Al/O peak-to-peak ratios for the ternary Fe-Cr-Al intermetallic alloy and for coatings of Fe aluminide on
Figure 4. Auger analysis of Al/O peak-to-peak ratio for oxide scales developed on ternary bulk alloy and several coatings of Fe aluminate after oxidation in air at 650°C.

a Type 316 stainless steel substrate after oxidation in air at 650°C. The results indicate that the coated specimens develop scales 200-600 Å thick whereas the bulk alloy developed a scale ~1 μm thick; however, SEM analysis of the surfaces of these specimens showed similar oxide morphologies in all of the specimens.

Performance in Simulated Gasification Atmospheres

Several specimens with Al-enriched surfaces, applied on Type 316 stainless steel substrate alloys by ESD, were tested in simulated gasification environments that contained H2S with or without HCl. Performance of the ESD coatings (which included Fe3Al with differing bond coats of refractory metals and/or noble metals) was compared with that of uncoated austenitic alloys. Coatings made with an FeAl welding rod contained much more Al than those made with an Fe3Al welding rod. Figure 5 shows corrosion loss data obtained for specimens tested for 728 h at 650°C in gas mixtures where pO2 = 1.2 x 10^-23, pS2 = 5.2 x 10^-10, pCl2 = 9.4 x 10^-17, and pHCl = 2.1 x 10^-3 atm. All of the Fe aluminate 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.

Performance in Simulated Combustion Atmospheres

Specimens with Al-enriched surfaces, applied on Type 316 stainless steel substrate alloys by ESD, were also tested in simulated combustion environments that contained SO2 with or without HCl. Specimens were tested for ~900 h at 650°C in gas mixtures with pO2 = 6.7 x 10^-5, pS2 = 1.5 x 10^-25, pCl2 = 3.6 x 10^-4, and pHCl = 1.7 x 10^-3 atm. Figure 6 shows weight change data for Alloy 800 and Type 316 stainless steel and for Fe3Al- or FeAl-coated Type 316 stainless steel as a function of exposure time 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. 5. However, the absolute value for weight change after 900 h of exposure was <0.02 mg/mm². The aluminate-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
Figure 5. Corrosion loss data for several Fe-Al coatings and uncoated high-Cr alloys after exposure in gas mixtures that contained H$_2$S with and without HCl. Significant weight loss was observed at 650°C. The attack was most notable in the Fe$_3$Al-coated alloy, less so in the uncoated alloys, and least notable in the FeAl-coated alloy.

To examine the cause(s) for the increased corrosion of the Fe aluminide in HCl-containing environments, depth profiles for several of the pertinent elements in the scale were obtained by Auger analysis after sputtering the surfaces for various times. Figure 7 shows peak-to-peak height as a function of depth for Fe$_3$Al-coated specimens after exposure in air/SO$_2$ and air/SO$_2$/HCl environments at 650°C. The results show that the specimen exposed to air/SO$_2$ developed an alumina scale =0.4 μm thick whereas that tested in air/SO$_2$/HCl developed a much thicker scale (>5 μm) that contained virtually no detectable Al. Furthermore, the scale of the latter specimen exhibited predominantly Ni, S, and Cl enrichment (in addition to O). Similar results were obtained for FeAl-coated specimens tested at 650°C in the two environments (see Fig. 8). The thickness of the alumina scale on the FeAl-coated specimen exposed to air/SO$_2$ in the presence of HCl was ≈0.2 μm; both the Al and Fe concentrations in the scale decreased to negligible values.

When Cl is present in the exposure environment, several constituents of the coating and substrate alloy can react to form volatile chlorides an occurrence that can lead to loss of the oxide-forming elements. The thermodynamics of the reaction of metals such as Fe, Cr, Ni, and Al with either Cl$_2$ or HCl in the exposure environment at 650°C have been calculated. Similar calculations were performed to examine the reactions between oxides of these elements and either Cl$_2$ or HCl. The results showed that the driving force for the reaction between Fe and Cl$_2$ or HCl is sufficiently high in the simulated combustion environment to form volatile FeCl$_3$. Similarly, the driving force for the reaction between Al and Cl$_2$ or HCl is sufficiently high in the simulated combustion environment to form volatile AlCl$_3$, Al$_2$Cl$_6$, and AlOCl phases. On the other hand, the calculations indicate that reactions between Fe$_2$O$_3$ and Cl$_2$ or HCl and between Al$_2$O$_3$ and Cl$_2$ or HCl are not favored at 650°C in the simulated combustion gas chemistries used in the present experiments. The results also indicate that to minimize the formation and escape of volatile chlorides of oxide-forming elements, the alloys must form the stable oxides early in the oxidation process, which is difficult, especially at lower temperatures...
Figure 6. Corrosion loss data for Fe-Al coatings on Type 316 stainless steel and several uncoated high-Cr alloys after exposure in gas mixtures that contained SO₂ with and without HCl.

Figure 7. Auger peak-to-peak height data for several elements as a function of depth for scales developed on Fe₃Al-coating on Type 316 stainless steel after exposure to (left) air/SO₂ and (right) air/SO₂/HCl environments at 650°C.

Figure 8. Auger peak-to-peak height data for several elements as a function of depth for scales developed on FeAl-coating on Type 316 stainless steel after exposure to (left) air/SO₂ and (right) air/SO₂/HCl environments at 650°C.
such as 650°C. The alternative is to preoxidize the structural alloys and coatings to form the protective oxides prior to exposure to Cl-containing atmospheres; however, the integrity of preoxidized layers under thermal- and chemical-cycling conditions must be established, especially for long design life of components for service in multioxidant environments.

**SUMMARY**

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. The chemical compositions of the raw gas environments that arise from gasification and combustion of coal vary widely from the standpoint of pO₂ and pS₂. In addition, the presence of Cl in the gas as HCl, which is determined by the Cl content of the coal feedstock, can exacerbate the corrosion process. 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 re-formation characteristics are key to adequate protection in long-term service. In H₂S-containing environments, Fe aluminides offer superior corrosion resistance. Experimental data on binary Fe-Al alloys showed that a threshold Al concentration of at least 12 wt.% is needed to minimize corrosion in these environments.

Furthermore, enrichment of conventional structural alloys with Al-enriched surfaces produced by ESD improved corrosion resistance in simulated coal gasification environments that contained H₂S and/or HCl. In Cl-containing environments, pitting-type corrosion is the dominant mode of attack on Fe aluminides but, if S is present along with Cl in the gasification atmospheres, the corrosion rate seems to be determined by sulfidation rather than by Cl. On the other hand, significant corrosion of the aluminate coatings was observed in simulated combustion environments that contained SO₂ and HCl. Thermodynamic calculations showed that direct reactions between Fe and Al and Cl₂ or HCl that lead to the formation and escape of volatile species, such as FeCl₃, AlCl₃, Al₂Cl₆, and AlOCl phases, exert a stronger degrading effect on the corrosion of these materials. The results also showed that to minimize the formation and escape of volatile chlorides of oxide-forming elements and to exhibit adequate corrosion resistance, the alloys must form stable oxides early during exposure in the service environment or they must be preoxidized in the absence of Cl.

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