



## HIGH TEMPERATURE SULFIDATION BEHAVIOR OF LOW Al IRON-ALUMINUM COMPOSITIONS

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### Introduction

Iron-aluminum weld overlay coatings are currently being considered for enhanced sulfidation resistance. The performance of these alloys in reducing atmospheres far exceeds other conventional materials presently used (1–8). However, the application of iron-aluminum alloys is currently limited due to hydrogen cracking susceptibility subsequent to welding (9–11). A direct correlation between the severity of embrittlement and the amount of aluminum in the alloy has been observed (12–14), specifically when the composition resides in the ordered region of the Fe-Al phase diagram (above 10 wt% Al). Higher Al overlays have been deposited (9, 15), but only with extensive pre-heat and post-weld heat treatments which are not always feasible. In addition to the welding problem, detailed corrosion studies indicating the sulfidation behavior of these binary alloys has not been fully conducted. Previous research (1–8, 16–22) has utilized gas compositions and temperatures which would be considered very aggressive (temperatures above 700°C and  $P_{S_2} \geq 10^{-7}$  atm), especially when compared to industrial boiler environments (23–25). Less assaulting conditions could not be found in the open literature. Therefore, research has been initiated to evaluate the sulfidation behavior of weldable iron-aluminum compositions, in the range of 5–10 wt% Al, in moderately reducing environments.

### Experimental Procedure

Cast Fe-Al alloys, with 5, 7.5, and 10 wt% aluminum, were produced by arc-melting high purity components under argon and drop casting into a water cooled copper mold. Obtaining bulk specimens eliminated the timely task of removing samples from the weld material, as well as eliminating the aluminum-poor region near the substrate that could negatively influence the corrosion behavior (6). High temperature sulfidation corrosion behavior was characterized by use of a Netsch STA 409 high temperature thermogravimetric balance which measured weight gain as a function of time. The cast samples were ground to 600 grit with silicon carbide papers, ultrasonically cleaned, and weighed to the nearest mg before being placed in the balance. Samples were heated at a rate of 50°C/min and isothermally held at 600°C for 50 hr in a mixed gas consisting of 0.1% H<sub>2</sub>S-3.0% H<sub>2</sub>-bal Ar (by volume). This H<sub>2</sub>S content is similar to that recently measured in coal fired power plants operating with low NO<sub>x</sub> burners (23–25). The oxygen partial pressure, as determined by a solid-state oxygen cell, was 10<sup>-28</sup> atm and the sulfur partial pressure was calculated to be 10<sup>-9</sup> atm. After exposure, samples were

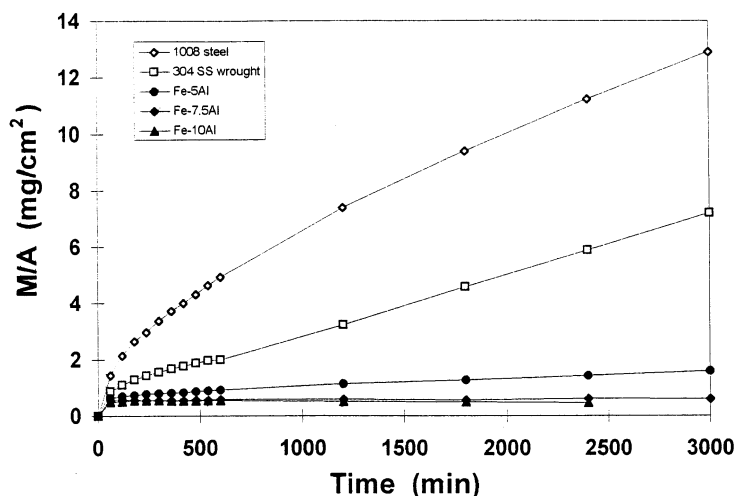


Figure 1. Weight change versus time for commercial and cast Fe-Al alloys exposed to 0.1% $H_2S$ -3.0% $H_2$ -bal Ar at 600°C for 50 hr.

cooled to room temperature at a rate of 20°C/min. Microstructural characterization was performed using light optical microscopy (LOM), scanning-electron microscopy (SEM), and energy dispersive spectroscopy (EDS).

### Results and Discussion

Fe-Al alloys were cast to produce nominal aluminum contents of 5, 7.5, and 10 wt% for testing in moderately reducing environments. From the work of Tortorelli et al. (6, 7), it was shown that the oxidation/sulfidation resistance of iron aluminide weld overlay coatings could be explained on the basis of what was known from previous studies of bulk samples of similar compositions. In addition, by using the cast alloys, the aluminum-poor region near the coating-substrate interface of the weldment was eliminated. Prior research (6) demonstrated that the corrosion products more readily form on the surface closer to the substrate of the weld overlay corrosion samples due to the inhomogeneous composition in this area. If this Al depleted region is not thoroughly removed, the corrosion behavior may be negatively influenced. In addition, the corrosion environment chosen for this study was generally *less aggressive* than those presently found in the literature, in terms of gas composition and temperature, so as to be more representative of boiler conditions. Previous work (2) on binary Fe-Al alloys showed that up to  $\sim 750^\circ\text{C}$ , at least 10 wt% ( $\geq 18$  at%) is needed for good sulfidation resistance.

The weight changes for the alloys tested are shown in Figure 1. The 5 wt% alloy was the only one to display a significant weight gain among the Fe-Al alloys, which nearly tripled that of the other two tested. The linear kinetic rate constant for this alloy ( $k_f = 3.2 \times 10^{-4} \text{ mg cm}^{-2} \text{ min}^{-1}$ ) was less than those previously reported (19) for similar alloys in more aggressive conditions ( $k_f = 7.1 \times 10^{-2} \text{ mg cm}^{-2} \text{ min}^{-1}$ ). The 7.5 and 10 wt% alloys had negligible weight gain, especially when compared to Type 304 stainless steel and Type 1008 carbon steel. The weight gain measurements of the Fe-Al alloys can be correlated with SEM micrographs of the sample surfaces, Figure 2. The decrease in amount of corrosion product can be seen as the aluminum content increases in the alloy. The 5 wt% sample has a scale that completely covered the surface and EDS techniques detected iron and sulfur, Figure 3a. The scale morphology, consistent with previous research (19, 20), in addition to the EDS spectra, suggests an iron sulfide scale is present. An aluminum peak was not present in the spectra indicating that the iron

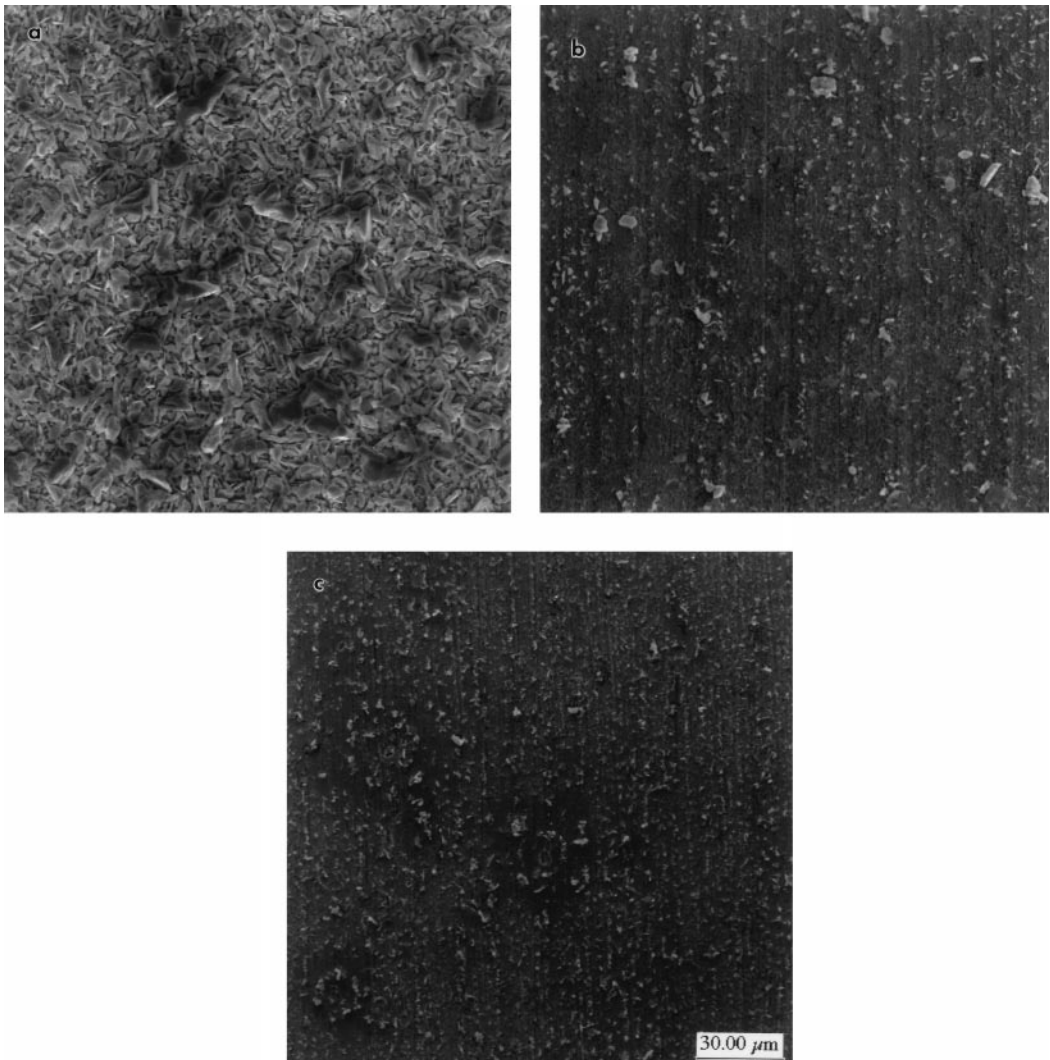


Figure 2. SEM micrographs showing the corroded surface of a) the 5 wt% Al alloy, b) the 7.5 wt% Al alloy, and c) the 10 wt% Al alloy.

sulfide scale is either a few microns thick, since the interaction volume is  $\sim 1 \mu\text{m}$  with these SEM parameters (22), or very little aluminum is present in the reaction product. The 7.5 wt% alloy had few, large iron sulfide particles on the surface (Figure 2b), with the presence of iron and sulfur in the EDS spectra, Figure 3b. The 10 wt% alloy was devoid of any large particles (Figure 2c) and Figure 3c shows the spectra containing all three peaks (Fe, Al, and S). Due to limitations of the EDS system, oxygen could not be detected to determine if the formation of any oxides occurred.

The 600°C Fe-S-O and Al-S-O thermodynamic stability diagrams are shown superimposed on each other in Figure 4, and the partial pressures of sulfur and oxygen utilized for this research are noted in the figure. Based on these considerations, formation of iron sulfide and aluminum oxide is favored on the alloy surface. It should be noted here, however, that care should be taken when using these diagrams to predict which phases may form in the given environment. The construction of these diagrams

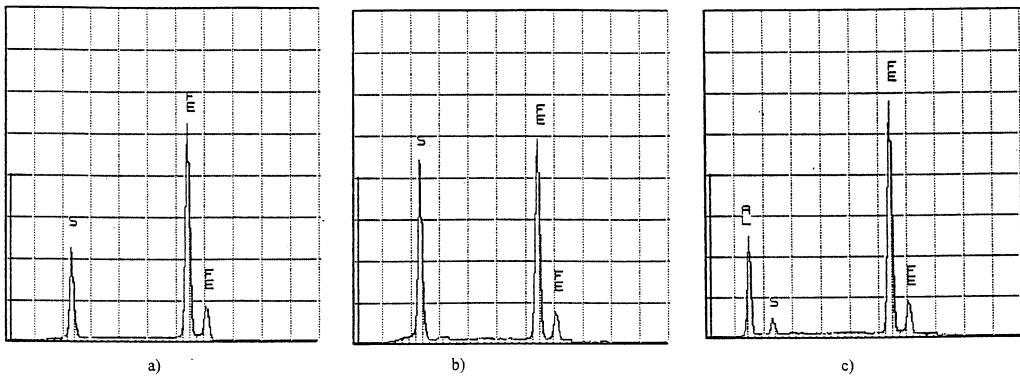


Figure 3. EDS spectra indicating elements present in surface scale of a) the 5 wt% Al alloy, b) the 7.5 wt% Al alloy, and c) the 10 wt% Al alloy.

considers only thermodynamic relationships at equilibrium and neglects the kinetic rates of the scales forming. Therefore, it is possible that a faster growing and less stable scale may prevent the formation of a continuous, protective one. This may explain the result found in this research. Although not experimentally observed, the low weight gains could be due in part to the formation of an alumina surface scale on the Fe-Al alloys. DeVan and co-workers (1–8, 26) have previously shown that the formation of this scale provided iron aluminides with excellent corrosion resistance due to its thermodynamic stability and relatively slow growth. The scales were found to be thin and adherent in isothermal conditions. This same type of scale may be present, but undetected, on the Fe-Al alloys, thus giving them their good corrosion resistance. The low corrosion rates, combined with good weldability, makes the disordered Fe-Al alloys potential candidates for corrosion protection in applications with moderately reducing environments.

### Summary

Through thermogravimetric analysis in a reducing environment, Fe-Al alloys with 5–10 wt% Al were observed to exhibit very low weight gain, indicating excellent sulfidation behavior. This is advantageous as these compositions are more easily formable and weldable. In addition, while the amount of  $H_2S$  (partial pressure of sulfur) is similar to that found for low  $NO_x$  conditions, the partial pressure of

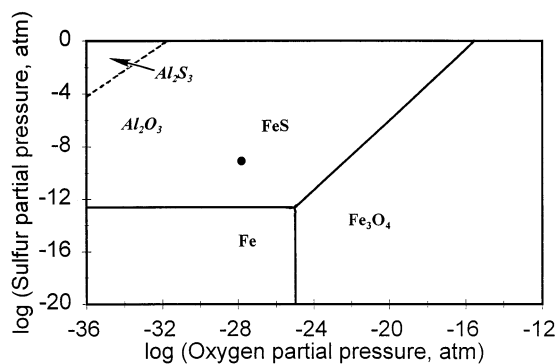


Figure 4. Thermodynamic stability diagram for Fe-O-S (solid lines) and Al-O-S (dashed line) at 600°C superimposed on each other. Conditions used in this research are marked by an ●.

oxygen used in these tests is much lower than those found in actual service conditions. Therefore, the sulfidation resistance of these alloys may increase as the formation of a protective alumina scale is further promoted thermodynamically, after being placed in service. The properties combination of formability, weldability, and sufficient high temperature sulfidation resistance, indicates good promise for the practical application of iron-aluminum weld overlays in reducing atmospheres.

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