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## Behavior of Iron Aluminides in Oxidizing and Sulfidizing Environments

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### Introduction

To date, use of iron aluminides based on  $Fe_3Al$  ( $\leq 30$  at. % Al) or  $FeAl$  (30-50 at. % Al) for structural applications has been limited by their low ductility and poor fracture toughness at room temperature and inadequate strength above 600°C. However, in recent years, a renewed effort has been devoted to the development of ductile iron aluminides with increased strength (see, for example, refs. 1-3), particularly in view of their good potential for use in hostile environments.<sup>3-5</sup> While it is expected that such aluminides will be able to form oxide scales for corrosion protection in oxidizing high temperature environments,<sup>3</sup> resistance to degradation in oxidizing salt or oxidizing/sulfidizing gas environments has not been adequately addressed as a function of compositional and microstructural changes.

This paper reviews and extends results for iron aluminides exposed to an oxidizing/sulfidizing gas and presents the first data for corrosion of this class of materials by an aggressive oxidizing molten nitrate salt.

### Experimental Procedures

The iron aluminides used in these experiments were produced<sup>3</sup> at the Oak Ridge National Laboratory. High purity metals were arc melted under argon, drop cast, and hot rolled. Compositional ranges were: 28-40 Al, 0-10 Cr, and 0-0.2 B. (Unless otherwise indicated, all alloy concentrations are in at. %.)

The molten salt corrosion experiments were conducted in alumina crucibles containing a nitrate salt. The baseline salt composition was 48.5NaNO<sub>3</sub>-50.5KNO<sub>3</sub>-1Na<sub>2</sub>O<sub>2</sub> (mol %) which was used for all but a few of the experiments. During exposure of specimens in the salt, dry air was bubbled continuously through the melt, which was held at 650°C. At this temperature, the salt composition results in a highly aggressive oxidizing environment.<sup>5-7</sup> After exposure, the residual salt on a specimen was removed by rinsing in warm water and weight changes were recorded. In certain cases, the salt was allowed to remain on the specimen, which was then carefully prepared for metallographic examination. The procedures for the salt experiments are described in detail elsewhere.<sup>5</sup>

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The corrosion of iron aluminides exposed to an oxidizing/sulfidizing gas was determined by thermogravimetric analysis using a Cahn 1000 continuously recording microbalance. An  $H_2 + H_2S$  gas mixture in argon was fed to a constant temperature water bath to set the  $H_2O$  level. The oxygen activity in the resultant mixture was controlled by the water bath temperature and was measured at the exposure temperature ( $800^\circ C$ ) by use of a  $Y_2O_3$ -stabilized  $ZrO_2$  solid-state electrochemical cell. The gas mixture was fed directly from the oxygen cell to the specimen and then to a gas disposal system. The partial pressure of sulfur at  $800^\circ C$  was calculated from the known  $H_2:H_2S$  ratio assuming chemical equilibrium of the gas mixture. For the present experiments,  $\log P_{S_2} = -6.0$  and  $\log P_{O_2} = -22$ .

## Results

### Oxidizing Molten Nitrate Salt Environment

The initial experiments with iron aluminides were part of a larger set of exposures that investigated the corrosion of different classes of materials by molten nitrate salt.<sup>5</sup> The observed response of metallic materials, using weight change as a figure of merit, could be broadly classified as being one of four types: catastrophic degradation by solution and/or rapid oxidation of the solid (for example, Ti, Co); severe corrosion; moderate to low rates of reaction (as typified by Ni-50Al, iron aluminides, and Zr); and excellent resistance (Hf). Figure 1 contains representative results for the latter three categories and shows the relatively good performance of Fe-35Al. Such data prompted more extensive investigation of the corrosion of iron aluminides in this salt environment.

Weight losses were measured for iron aluminides containing 26-40 at. % Al. The average weight change as a function of aluminium concentration is shown in Fig. 2, which shows that weight loss decreased with increasing aluminum content up to approximately 35%. (Typically, standard deviations were 10-50% of the averages for the molten salt exposures.<sup>5</sup>) For a constant aluminum content (35%), weight loss behavior was not monotonic with exposure time (Fig. 3). The weight losses after 24 h were essentially constant - they fell within the experimental data scatter. Examination of selected specimens failed to reveal the presence of a complete oxide scale (see, for example, Fig. 4) even when care was taken not to remove residual salt from the specimen. However, energy dispersive x-ray (EDX) analysis showed the presence of aluminum enrichment along much of the surface consistent with the formation of alumina or aluminate (see Discussion). While

there were some indications that the addition of chromium to iron aluminide decreased weight losses in  $\text{NaNO}_3\text{-KNO}_3\text{-Na}_2\text{O}_2$  (see bottom curve of Fig. 5), there was no observed effect of chromium on the corrosion of another iron aluminide in a more aggressive nitrate salt (upper curve, Fig. 5).

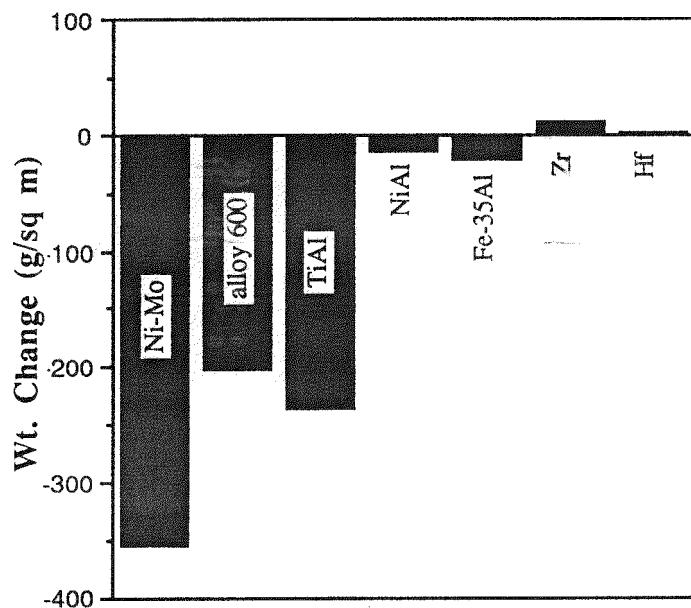


Fig. 1. Average weight change for different materials exposed to  $\text{NaNO}_3\text{-KNO}_3\text{-Na}_2\text{O}_2$  at  $650^\circ\text{C}$  for approximately 24 h.

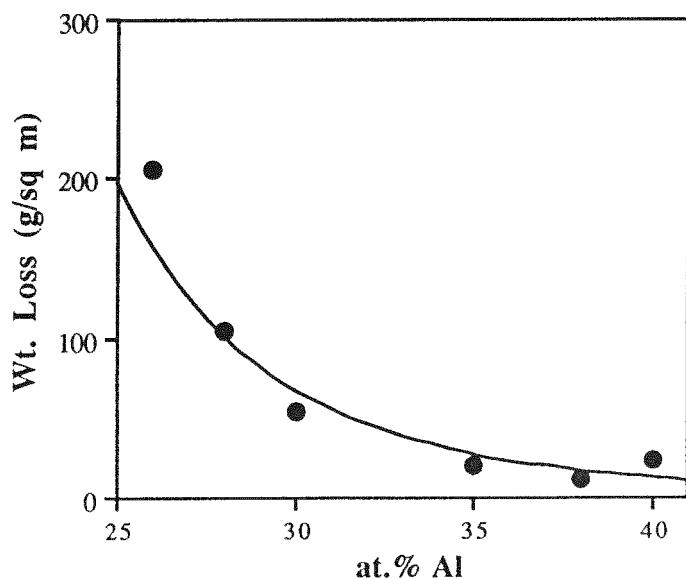


Fig. 2. Average weight loss for iron aluminides exposed to  $\text{NaNO}_3\text{-KNO}_3\text{-Na}_2\text{O}_2$  at  $650^\circ\text{C}$  for approximately 24 h.

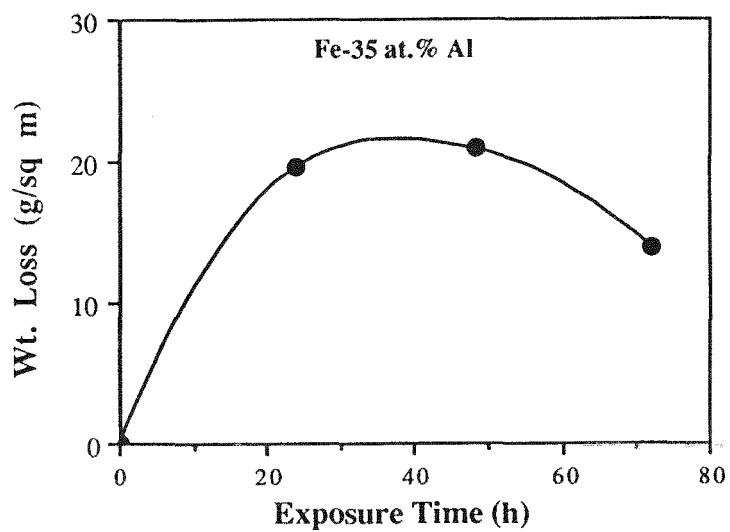


Fig. 3. Average weight loss as a function of time for Fe-35 at. % Al exposed to  $\text{NaNO}_3\text{-KNO}_3\text{-Na}_2\text{O}_2$  at  $650^\circ\text{C}$  for approximately 24 h.

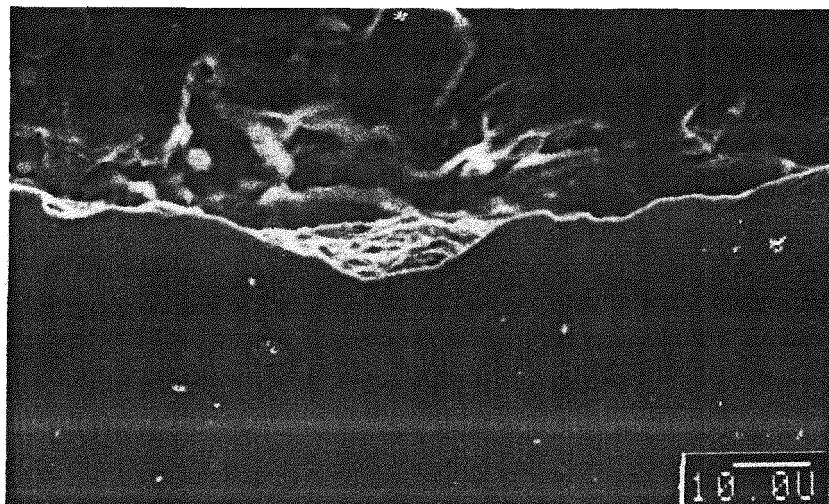


Fig. 4. Polished cross section of uncleaned Fe-35 at. % Al after exposure to  $\text{NaNO}_3\text{-KNO}_3\text{-Na}_2\text{O}_2$  at  $650^\circ\text{C}$  for approximately 24 h.

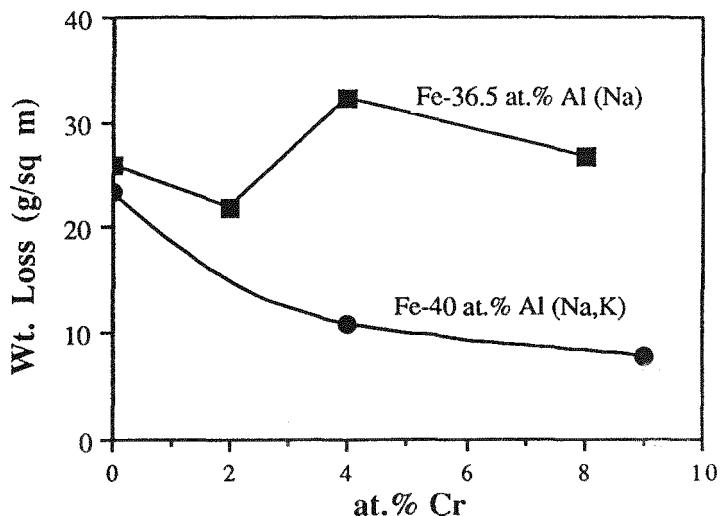


Fig. 5. Weight loss for iron aluminides exposed to  $\text{NaNO}_3\text{-KNO}_3\text{-Na}_2\text{O}_2$  (40 at. % Al) and  $\text{NaNO}_3\text{-Na}_2\text{O}_2$  (36.5 at. % Al) at 650°C for approximately 24 h

#### Oxidizing/Sulfidizing Gaseous Environment

The thermogravimetric results for corrosion of Fe-28Al and Fe-35Al in  $\text{H}_2\text{S}\text{-H}_2\text{-H}_2\text{O}$  at 800°C are shown in Fig. 6, which also contains data for alloys of Fe-Cr-Ni and Fe-Cr-Al. Weight changes were much less for the iron aluminide binary alloys. Figure 7 shows some of the scale that formed on the Fe-28Al. Much of it spalled from the surface on cooling to room temperature. Examination of areas where spalling occurred revealed little corrosion of the underlying metal substrate. EDX analysis of the scale showed aluminum was the principal species and the x-ray diffraction pattern of the scale matched that of  $\gamma$ -alumina.

As shown in Fig. 8, chromium additions above 2% adversely affected the corrosion resistance of Fe-28Al, but with higher concentrations of Al (40%), the deleterious effect of 4% chromium was effectively offset.<sup>4</sup> The corrosion product scales formed on the Fe-28Al-4 and -10Cr alloys were thicker than on the Fe-28Al and Fe-28Al-2Cr alloys (Fig. 9). EDX analysis of the reaction products at the scale-gas interface showed them to be mixtures of iron and chromium, while the underlying scale contained predominantly

aluminum and sulfur. X-ray diffraction patterns showed the presence of both  $\text{Cr}_2\text{S}_3$  and  $\text{Al}_2\text{S}_3$ . No alumina was detected and it was thus concluded that it must comprise less than 10% of the scale mass. The scale that formed on the Fe-40Al-4Cr alloy was typical of that formed on the Fe-28Al without chromium additions.

A limited number of air exposures of iron aluminides were conducted at 800°C and the weight change results are shown in Fig. 10. Corrosion rates were lower than corresponding rates in  $\text{H}_2\text{S}$ - $\text{H}_2$ - $\text{H}_2\text{O}$ . Overall weight gains in air were quite low for all the alloys, but were slightly higher for the chromium-containing alloys than for the binary compositions.

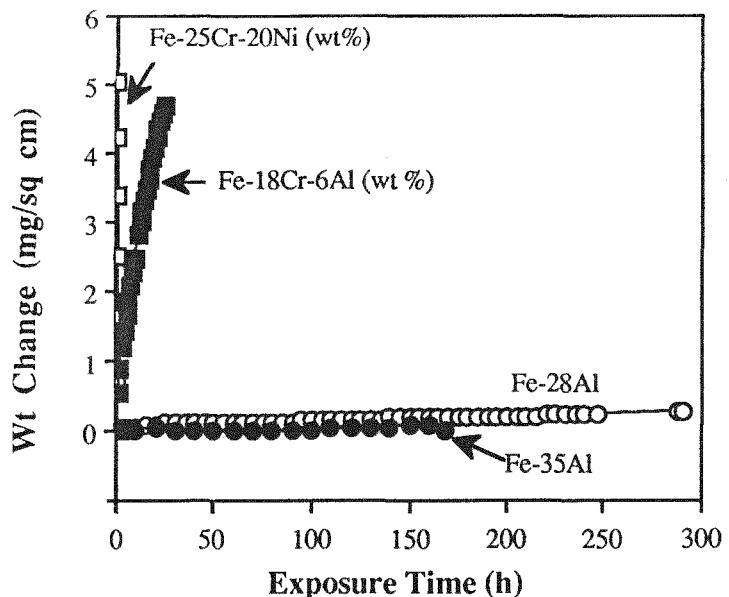


Fig. 6. Weight changes versus time for exposure to  $\text{H}_2\text{S}$ - $\text{H}_2$ - $\text{H}_2\text{O}$  ( $\text{P}_{\text{O}_2} = 10^{-22}$  atm and  $\text{P}_{\text{S}_2} = 10^{-6}$  atm) at 800°C.

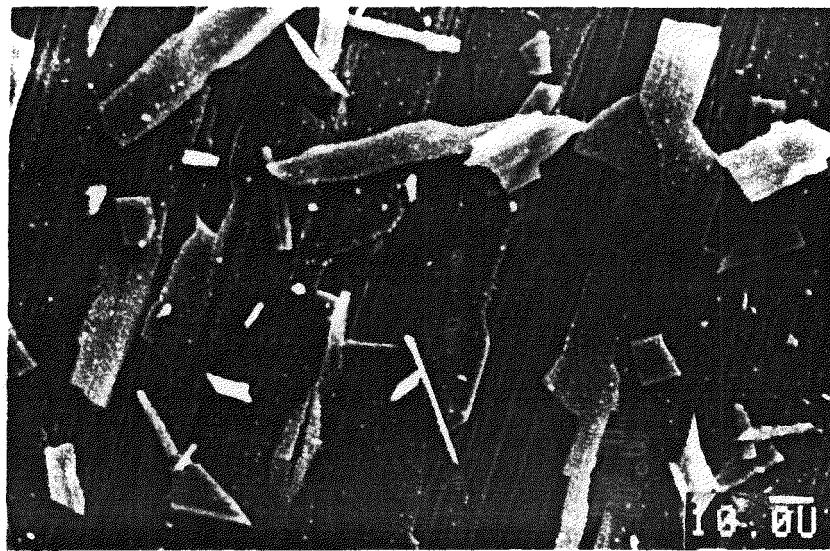


Fig. 7. Corrosion product scale formed on Fe-28 at. % Al after exposure to  $\text{H}_2\text{S}-\text{H}_2-\text{H}_2\text{O}$  ( $\text{PO}_2 = 10^{-22}$  atm and  $\text{PS}_2 = 10^{-6}$  atm) at  $800^\circ\text{C}$  for 248 h.

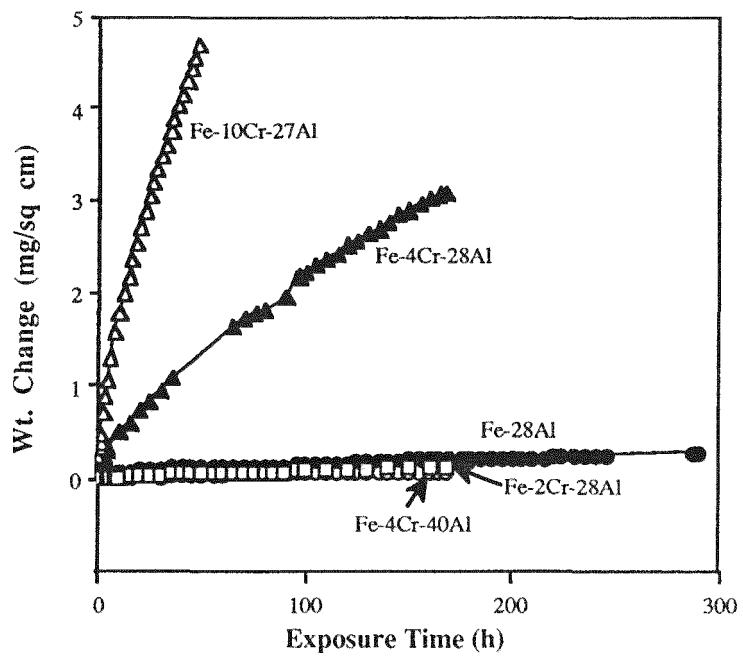


Fig. 8. Weight changes versus time for exposure to  $\text{H}_2\text{S}-\text{H}_2-\text{H}_2\text{O}$  ( $\text{PO}_2 = 10^{-22}$  atm and  $\text{PS}_2 = 10^{-6}$  atm) at  $800^\circ\text{C}$ .

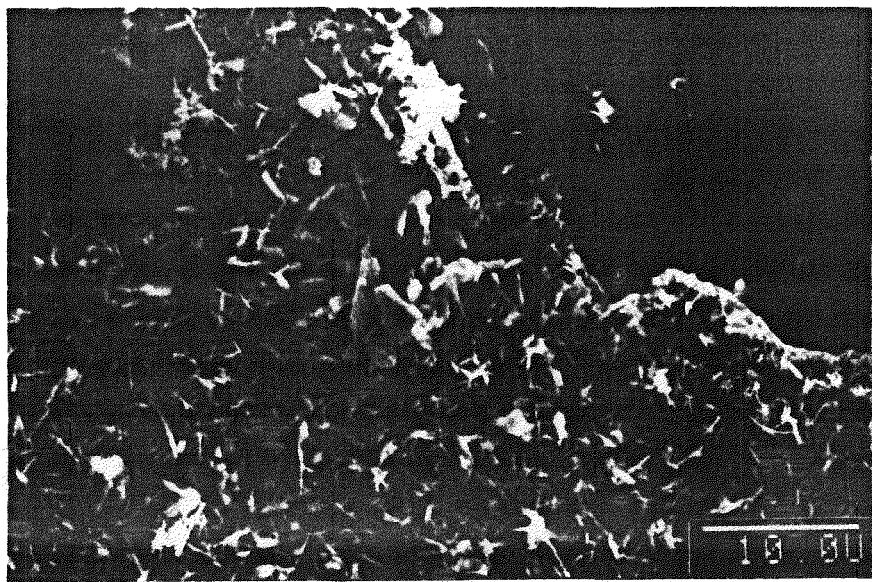


Fig. 9. Corrosion product scale formed on Fe-28Al-4Cr exposed to  $\text{H}_2\text{S}-\text{H}_2-\text{H}_2\text{O}$  ( $\text{PO}_2 = 10^{-22}$  atm and  $\text{PS}_2 = 10^{-6}$  atm) at 700°C for 20 h.

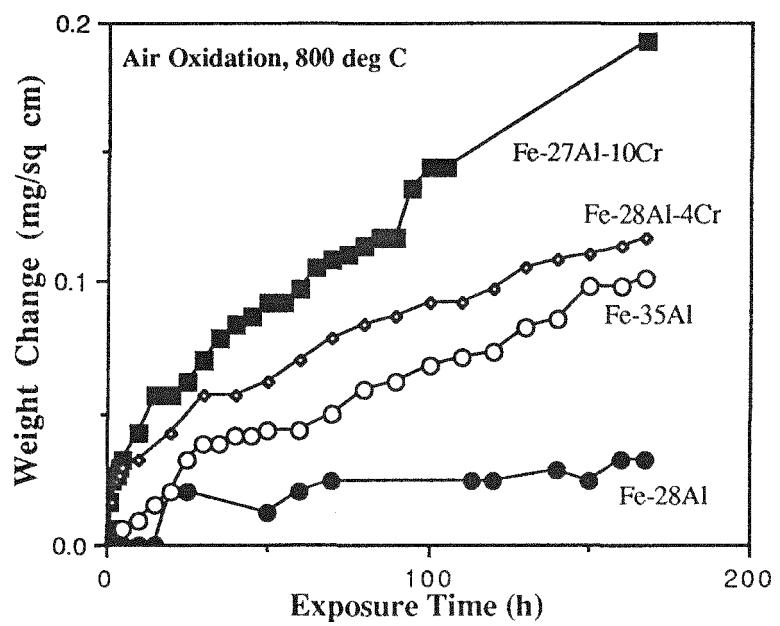


Fig. 10. Weight changes in air at 800°C.

## Discussion

### Oxidizing Molten Nitrate Salt Environment

As demonstrated previously,<sup>6-8</sup> corrosion in molten nitrate salts can result from both oxidation of the base metal and solubility-driven dissolution reactions. The relatively poor resistance of alloys with substantial concentrations of chromium (such as alloy 600) can be explained on the basis of the dissolution reaction, while the catastrophic corrosion of reactive metals like titanium and cobalt and their alloys can be ascribed to their rapid oxidation kinetics and subsequent loss of reacted metal when specimens were cleaned. On the other hand, the excellent resistance of hafnium is presumably due to the formation of a protective oxide scale that is slowly growing and adherent. Zirconium also appeared to grow an adherent scale (thus resulting in a weight gain), but at a significantly greater rate such that long-term compatibility with the salt is not assured. The behavior of the FeAl falls somewhere between the extremes of the most reactive and resistant materials: their modest weight losses (see Fig. 1) indicated iron aluminides are among the best materials that can be considered for large scale engineering uses.

With competing reactions of dissolution and corrosion product formation, the significance of weight change measurements must be considered in any analysis of results for this salt environment. For aluminides, it is expected that the aluminum will react with the salt to form stable  $\text{NaAlO}_2$  (some evidence of this has been observed<sup>5</sup>) and that iron should also form an oxide product.<sup>9,10</sup> However, solubilities in the nitrate salt should be highly dependent on salt chemistry (that is, basicity)<sup>11,12</sup> and dissolution processes cannot be completely neglected, particularly under the transient conditions prior to attainment of equilibrium conditions. Thus, the measured weight change  $w$ , can be expressed as

$$w = w_s + w_o + w_d$$

where  $w_s$  is the weight change due to dissolution of metal ions into the salt,  $w_o$  is the change due to uptake of oxygen by the specimen, and  $w_d$  is that caused by removal of any (or all) of the surface reaction product when rinsing the salt from the specimen after exposure (descaling). Because the oxides should form and the contribution of  $w_s$  should be relatively small, the observed weight losses ( $w$ ) probably are related to the amount of surface oxide formed during exposure to the salt and subsequently removed by cleaning. Such an interpretation is consistent with metallographic observations: no evidence of scales

on polished cross sections of iron aluminide specimens from which salt was removed after exposure, but some scale on specimens that were specially handled and carefully polished so as to retain as much of the overlying residual salt as possible (see Fig. 4 and ref. 5).

Decreasing weight changes with increasing aluminum concentration of the iron aluminides (Fig. 2) is indicative of the development of a protective aluminate layer during exposure to the salt. Higher aluminum concentrations can provide a greater degree of protection by decreasing the interactions with the more reactive transition metal elements (see related discussion for oxidation/sulfidation below). A similar trend has been observed for nickel aluminides,<sup>5</sup> although relatively greater aluminum concentrations (50%) were needed to impart similar protection.

Measured weight changes as a function of time are represented by the data shown in Fig. 3. Weight losses at longer times were essentially the same as those measured after 24 h. This may be indicative of the contribution of transient dissolution during the early stages of exposure and the protective nature (decreasing corrosion rate with time) of the reaction product that forms. However, an interpretation of data like that in Fig. 3 is complicated by the fact that the salt composition is also changing (decreasing peroxide) with time. Indeed, weight losses at 48 and 72 h were much greater than those shown in Fig. 3 when the peroxide was refreshed every 24 h.<sup>5</sup> While the present data are insufficient to understand this effect, it is quite possible that such changes in salt chemistry (salt basicity) can significantly alter the solubility of the oxides in the salt<sup>11,12</sup> and affect dissolution over an extended period of time, particularly if the salt does not come to equilibrium due to periodic increases in the peroxide concentration. The use of weight losses as a figure of merit must therefore be carefully considered in terms of the dominant corrosion process and its dependence on time.

The influence of chromium on the corrosion of iron aluminides in the nitrate salt is consistent with the formation of a protective aluminum-containing scale. After exposure of chromium-bearing alloys (stainless steel, alloy 800) to nitrate salt, chromium was found to be dissolved in the salt in significant concentrations.<sup>6-8</sup> If a protective scale was not forming when iron aluminides are exposed to the nitrate salt, the presence of chromium in significant concentrations should increase measured weight losses. As shown in Fig. 5, this is not observed for iron aluminides. In the case of the baseline salt chemistry, chromium actually seems to improve corrosion resistance at a constant aluminum concentration, while, for  $\text{NaNO}_3\text{-}0.4 \text{ mol \% Na}_2\text{O}_2$ , there is little influence of chromium.

As shown by the results for these aluminides under oxidation/sulfidation conditions (see below), the presence of sufficient aluminum can protect modest amounts of chromium in the matrix from reaction with the environment. Any improvement in corrosion behavior due to the presence of chromium can probably be attributed to the reported influence of this element on more rapid development of a protective scale.<sup>13</sup> It is interesting to note, however, that this effect of chromium was not observed for Fe-28Al during air oxidation at 800°C (see Fig. 10).

#### Oxidizing/Sulfidizing Gaseous Environment

Weight change and metallographic results for binary iron aluminides with  $\geq 28$  at. % Al exposed to air and an oxidizing/sulfidizing environment show such alloys oxidize slowly and are very resistant to sulfur attack. When compared to more conventional alloys, their corrosion resistance in sulfur-containing gas is excellent, particularly when the chromium concentration of the Fe-28Al is minimized.

The Fe-28Al retained its sulfidation resistance despite an apparent susceptibility to scale spallation. (Fe-40Al alloys showed susceptibility to massive spallation after higher temperature air oxidation.<sup>14</sup>) The oxygen and sulfur activities are within the iron sulfide phase field, and if the  $\text{Al}_2\text{O}_3$  protective layer was disrupted, iron sulfide should form. However, as described in the Results section, no evidence of iron sulfide was found for the binary composition. Of course, much longer experiments, including thermal cycling effects, will be required to establish that spallation will not eventually lead to iron sulfidation. Nevertheless, in thermal cycling experiments to date, both Fe-28Al and Fe-35Al have shown no significant deterioration in corrosion performance. Figure 11 compares the weight change behavior of these materials exposed isothermally and under conditions where specimens were thermally cycled from 800°C to room temperature (in about 15 minutes with approximately same time to come back up to temperature) every 48 h. Although some scale loss may have occurred during one or two thermal cycles of the Fe-28Al, there were no large differences between isothermal and cycling conditions over a 300-h period. These results suggest that the initial growth of  $\text{Al}_2\text{O}_3$  is extremely fast compared to that of iron sulfide and that there is an adequate concentration of aluminum to maintain a protective oxide at the surface despite possible spallation. This is also consistent with the better performance of aluminides with higher aluminum concentrations: as shown in Fig. 11, the two curves for the Fe-35Al are essentially indistinguishable from one another.

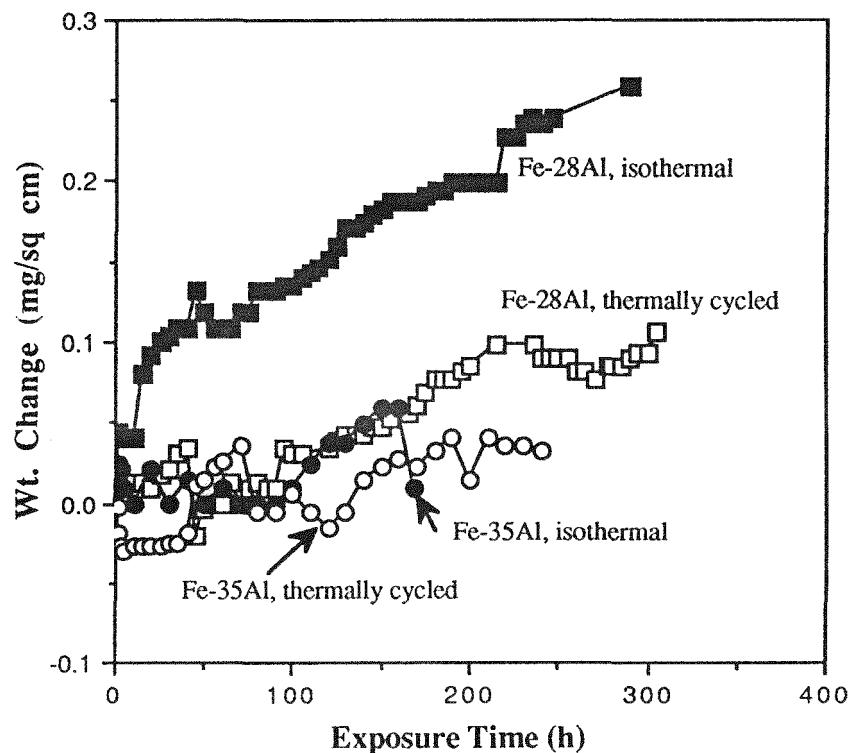


Fig. 11. Effect of thermal cycling on weight changes of Fe-28Al and Fe-35Al exposed to  $\text{H}_2\text{S}-\text{H}_2-\text{H}_2\text{O}$  ( $\text{P}_{\text{O}_2} = 10^{-22}$  atm and  $\text{P}_{\text{S}_2} = 10^{-6}$  atm) at 800°C.

Adding chromium to the Fe-28Al alloy significantly changed the morphology of the product scale and increased the corrosion rate in  $\text{H}_2\text{S}-\text{H}_2-\text{H}_2\text{O}$ . At chromium concentrations greater than 2%, the scale changes from a thin  $\text{Al}_2\text{O}_3$  to a thicker sulfide containing product comprised of  $\text{Cr}_2\text{S}_3$  platelets growing out of an  $\text{Al}_2\text{S}_3 - \text{Al}_2\text{O}_3$  layer. Results to date have not allowed determination of whether the effect of chromium is to simply increase the diffusion of sulfur by changing the defect concentration of the  $\text{Al}_2\text{O}_3$  scale or by the selective nucleation and growth of chromium sulfide nodules that cause disruption of an otherwise protective oxide scale. The observation that raising the aluminum concentration suppressed the deleterious effect of 4% Cr cannot distinguish between these two possibilities. Increased aluminum content can dilute the effect of chromium on the transport of sulfur and/or provide more complete surface coverage of protective alumina thereby blocking nucleation and growth of chromium sulfides.

As expected, the iron aluminides are resistant to isothermal air oxidation at 800°C (Fig. 10), but the integrity of the scale that forms has not been characterized. Given the differences in temperature and the type of scale formed, the present data are consistent with air oxidation results for Fe-40Al at 900°C.<sup>14</sup> In this environment, as well as in the presence of sulfur, their corrosion resistance appears to extend to service temperatures above the limits set by mechanical property considerations, thereby indicating possible use of such compositions as claddings.

#### Summary and Conclusions

Results for iron aluminides exposed to a highly oxidizing molten nitrate salt at 650°C have indicated that, at sufficiently high concentrations of aluminum (about 35 at. %), such materials can form a protective aluminum-containing layer that effectively provides corrosion resistance. Less aluminum is needed for complete protection in an oxidizing/sulfidizing gaseous environment: Fe-28 at. % Al, as well as those with higher aluminum levels, have very low reaction rates. Higher aluminum concentrations were found to offset a tendency to form relatively fast growing chromium sulfides when chromium was added to the base binary aluminides.

Further examination and better understanding of the corrosion processes and chemistry in highly aggressive molten nitrate salts are certainly required, and the effects of thermal cycling on resistance in the salt and oxidizing/sulfidizing gas need to be completely characterized. However, the results to date are indicative of good corrosion resistance in the respective environments, particularly when compared to conventional alloys based on Fe-Cr-Al and Fe-Cr-Ni. Because of their tendency to form protective surface layers, iron aluminides have the potential for development as low cost, low density materials for use in high-temperature corrosive environments.<sup>1-3</sup>

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