

OPTIMIZING THE IMPERFECT OXIDATION PERFORMANCE OF IRON ALUMINIDES

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ABSTRACT

Iron aluminides (Fe_3Al -based) are attractive corrosion-resistant, high temperature materials due to their excellent sulfidation resistance and large Al reservoir. However, at high temperatures ($>1000^\circ\text{C}$) iron aluminides show excessive scale spallation compared to doped FeCrAl. This behavior is attributed to the inherently high coefficient of thermal expansion of these materials which results in higher cooling strains in the alumina scale. Although this problem cannot be corrected by minor alloying additions or impurity control, composition optimization can still be used to maximize performance. A multi-year effort has examined various reactive element additions and shown that optimized Hf doping (0.05 at.% Hf) provides the best observed oxidation performance at $1100\text{-}1200^\circ\text{C}$. Hafnium lowers the scale growth rate by an order of magnitude compared to undoped Fe_3Al , but does not improve the resistance to scale spallation. Possible mechanisms for the role of Hf on the scale growth rate are discussed.

1. INTRODUCTION

The good high temperature oxidation and sulfidation resistance of iron aluminides has been widely documented over the past decade, e.g. Refs.1-3. However, in recent years it has been found that, relative to other alumina-forming alloys, the external alumina scale spalls more readily on iron aluminides[4,5], even with reactive element (RE) additions of Zr, Y or Y_2O_3 which are known to improve scale adhesion[6,7]. Numerous attempts have been made to understand the nature of this greater spallation susceptibility and improve the performance of iron aluminides by micro-alloying additions and oxide dispersions. It has been concluded that the fundamental difference between iron aluminides and, for example, FeCrAl, is a higher thermal expansion coefficient. This difference is not corrected by RE doping. However, optimizing the performance of iron aluminides is still possible. Among all of the ingot-processed (IP) and oxide-dispersion strengthened (ODS) alloys evaluated, the best performance was found with a 0.05 at.% addition of Hf.

2. EXPERIMENTAL PROCEDURE

Ingot-processed alloys were fabricated by vacuum induction melting and solidified in a water-chilled Cu mold. Standard powder metallurgy techniques were used to fabricate the ODS Fe_3Al alloy[8]. Chemical compositions were measured by inductively coupled plasma analysis and combustion analysis on as-cast material[5]. Compositions are listed in atomic percent. The base iron aluminide is Fe-28Al-2Cr (designated as FAS). All IP alloys were annealed for 4h at 1300°C in quartz ampules. Oxidation coupons (1-1.5mm thick, 15mm diameter) were polished to $0.3\mu\text{m}$ alumina

and cleaned in acetone and methanol prior to oxidation. Isothermal exposures were performed in dry, flowing O_2 at $1200^\circ C$ and mass gain was measured using a Cahn Instruments model 1000 microbalance. Cyclic testing was performed in two ways[9]. Long-term cycles (100-500h) were performed in air at 1000° - $1300^\circ C$ with specimens in pre-annealed alumina crucibles. Short-term (1-10h) cycles were performed in dry, flowing O_2 with specimens attached to alumina rods with Pt-Rh wires. Specimen mass changes were measured using a Mettler model AG245 balance.

After oxidation, specimens were characterized by field emission gun, scanning electron microscopy (FEG-SEM) equipped with energy dispersive x-ray analysis (EDX). Specimens were Cu-coated and sectioned for metallography. Scanning transmission electron microscopy (STEM) equipped with EDX was used to analyze cross-sectional specimens fabricated by focused ion beam milling (FIB)[10]. Thermal expansion measurements were performed on specimens (3mm diameter, 1cm or 2.5cm long) of several alloys up to $1200^\circ C$ on a Theta Industries dual push rod differential dilatometer.

3. RESULTS

3.1. THERMAL EXPANSION MEASUREMENTS

Coefficient of thermal expansion (CTE) results for several IP and ODS Fe-base alloys are given in Fig. 1. The much higher expansion for the DO_3 -phase, iron aluminides: FAS+0.05Hf, FAL (Fe-28Al-5Cr-0.1Zr) and yttria-dispersed Fe-28Al-2Cr, PMFAS, is clearly apparent when compared to FeCrAl-based ferritic materials: Inco alloy MA956HT (ODS FeCrAl) and FeCrAlY(Fe-20Cr-10Al-0.1Y). The two kinks in the iron aluminide curves are from phase transformation from DO_3 to B2 at $550^\circ C$ and then from B2 to γ -Fe at $850^\circ C$ [8]. This high CTE has resulted in measured compressive stresses of $>9GPa$ in the scale on PMFAS after oxidation for 20h at $1200^\circ C$ [11]. The high CTE for the B2 phase suggests that higher Al contents (i.e. FeAl-base) also will suffer from a similar problem.

3.2. OXIDATION BEHAVIOR

Previous work indicated that RE alloy additions (Zr, Y, Hf) to the FAS base alloy all had a similar beneficial effect on the oxidation behavior when added at the level of approximately 0.1at.%. [5] However, based on the superior performance of a 0.05% Hf addition to NiAl[12] and the significant

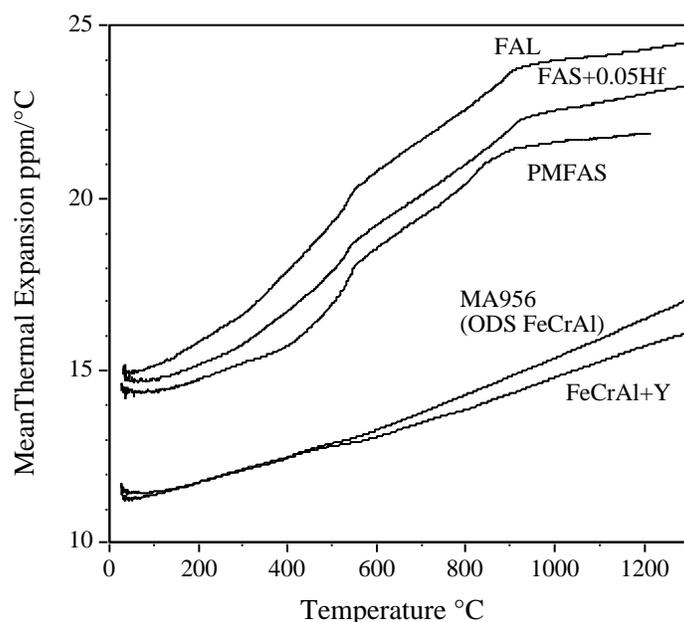


Figure 1. Thermal expansion as a function of temperature for several iron-base alloys. Iron aluminides have a significantly higher thermal expansion coefficient than FeCrAl-base materials.

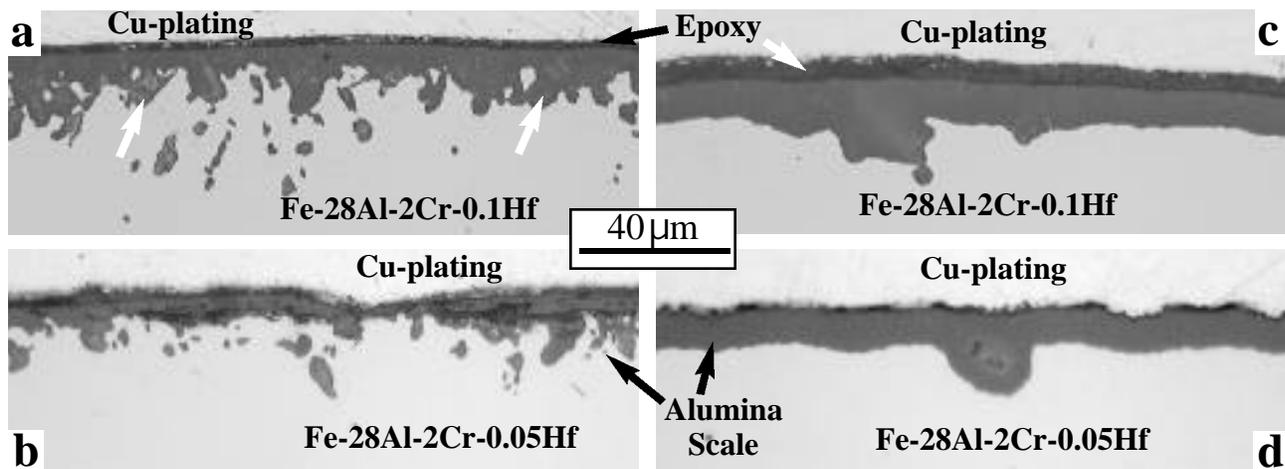


Figure 2. Copper-plated metallographic cross-sections of the scale formed after 10x500h at 1000°C in laboratory air on (a) FAS+0.1%Hf and (b) FAS+0.05%Hf and after 100h at 1300°C (isothermal) on (c) FAS+0.1%Hf and (d) FAS+0.05%Hf. Under these conditions, changing the Hf content of the alloy had little effect. At 1000°C, little spallation was observed but more oxide penetrations (pegs) consisting of alumina-encapsulated Hf-rich oxide (arrows) were observed with the higher Hf content. At 1300°C, there were fewer pegs and little difference between the two materials.

internal oxidation observed for FAS+0.1%Hf (Fig. 2a), a lower Hf content was investigated. The oxidation performance of FAS+0.05Hf (Fe-28.1Al-2.0Cr-0.05Hf-0.004B-0.04C-31ppma S) was found to be superior to any previously studied IP or ODS iron aluminide. The lower Hf content reduced the extensive internal oxidation observed for the higher (0.1%) Hf content (Fig. 2), which resulted in excessive mass gains at 1000°C (Fig. 3). However, at 1000°C the benefit of 0.05%Hf was not observed relative to the more-common IP iron aluminide composition, FAL, or the ODS alloy, PMFAS. All of these alloys began to exhibit scale spallation by 5000h (Fig. 3b). The difference was more distinct at 1100°C, where FAS+0.05Hf showed a lower total mass gain (specimen + spalled oxide) compared to FAS+0.1Hf, FAL or PMFAS (Fig. 4). The specimen mass

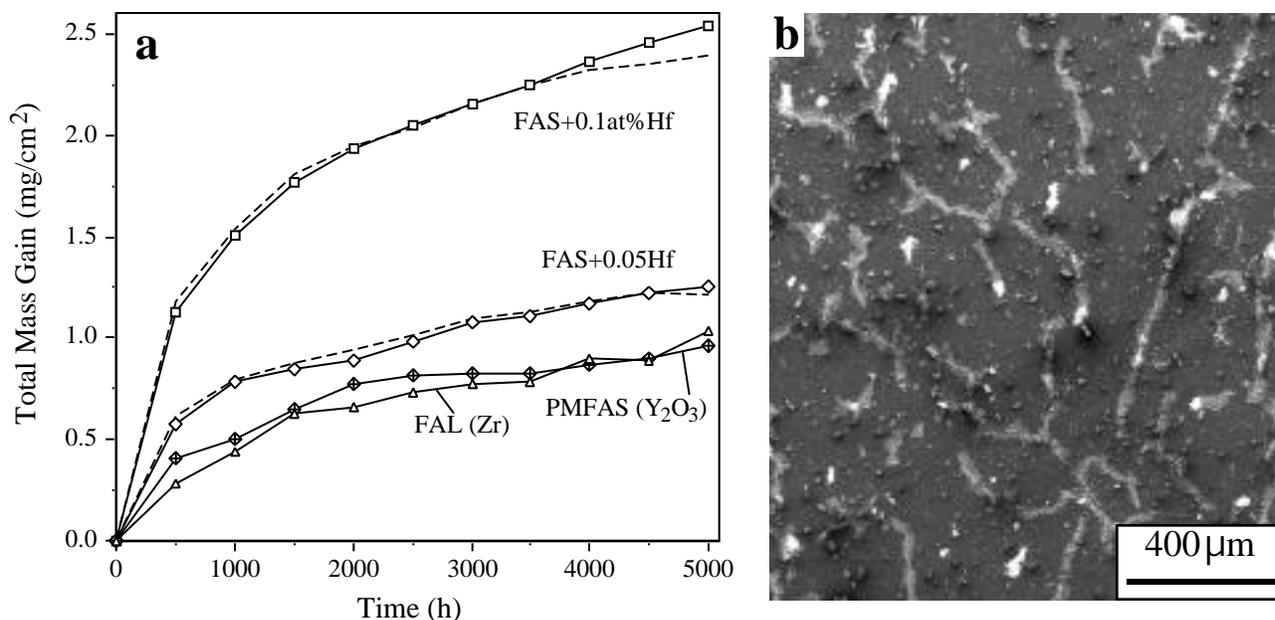


Figure 3. (a) Dashed lines show specimen mass gain and solid lines show total mass gain (specimen + spalled oxide) for several iron aluminides during 500h cycles at 1000°C in laboratory air. A 0.1%Hf addition resulted in higher mass gains than 0.05Hf, not due to spallation, but due to excessive internal oxidation. (b) FEG-SEM secondary electron plan-view image of spalled oxide formed on FAS+0.05Hf after 5000h at 1000°C.

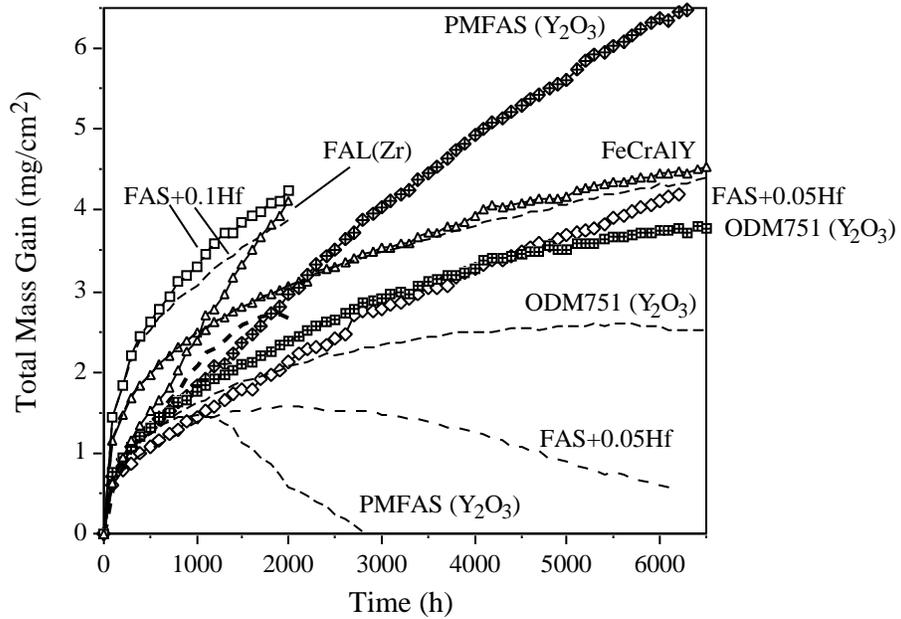


Figure 4. Dashed lines show specimen mass gain and solid lines show total mass gain (specimen + spalled oxide) for several iron aluminides during 100h cycles in alumina crucibles at 1100°C in laboratory air. FAS+0.05Hf shows a lower total weight gain than other IP Fe₃Al compositions. All of the specimens spalled except for FeCrAlY.

gain curves (dashed lines) also are plotted in Fig. 4 which indicate that the 0.05Hf addition did not eliminate scale spallation but rather reduced the scale growth rate. All of the alloys spalled at 1100°C except for FeCrAlY, where the specimen and total mass gains were equal. Thus the total mass gain of FAS+0.05Hf eventually exceeded that for ODM751 (ODS FeCrAl) and will eventually exceed that of FeCrAlY due to scale spallation (provided that the same rate of growth and spallation continues). Initially, the mass gain rate of FeCrAlY was much higher due to internal oxidation of Y.

Similar results were observed for cyclic testing at 1200°C. However, the optimized effect of Hf is

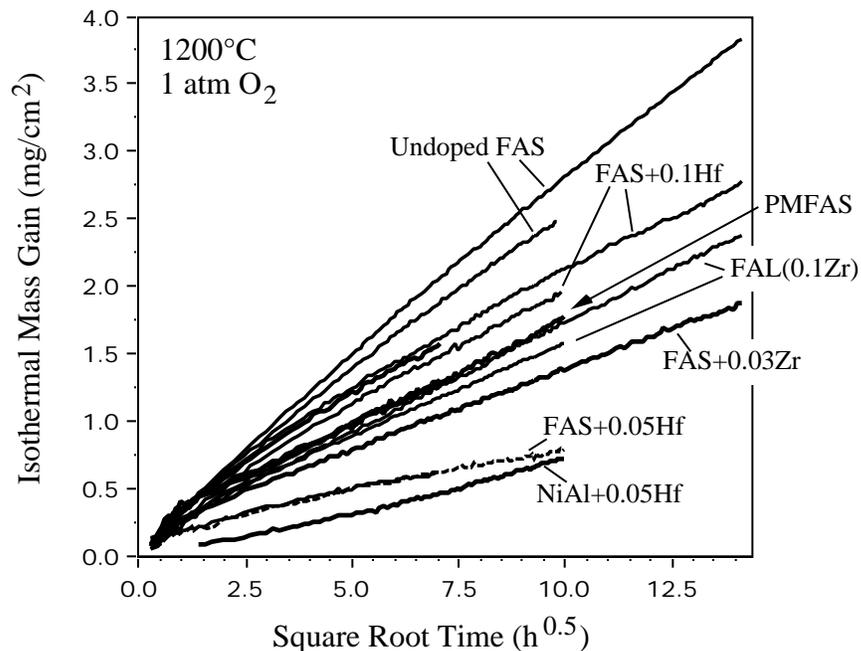


Figure 5. Isothermal specimen mass gains at 1200°C plotted versus the square root of time to illustrate the near-parabolic relationship. The addition of 0.1Hf or Zr to iron aluminide reduces the growth rate relative to undoped FAS but further reducing the Hf content to 0.05% reduces the rate nearly an order of magnitude, similar to the rate observed for Hf-doped NiAl.

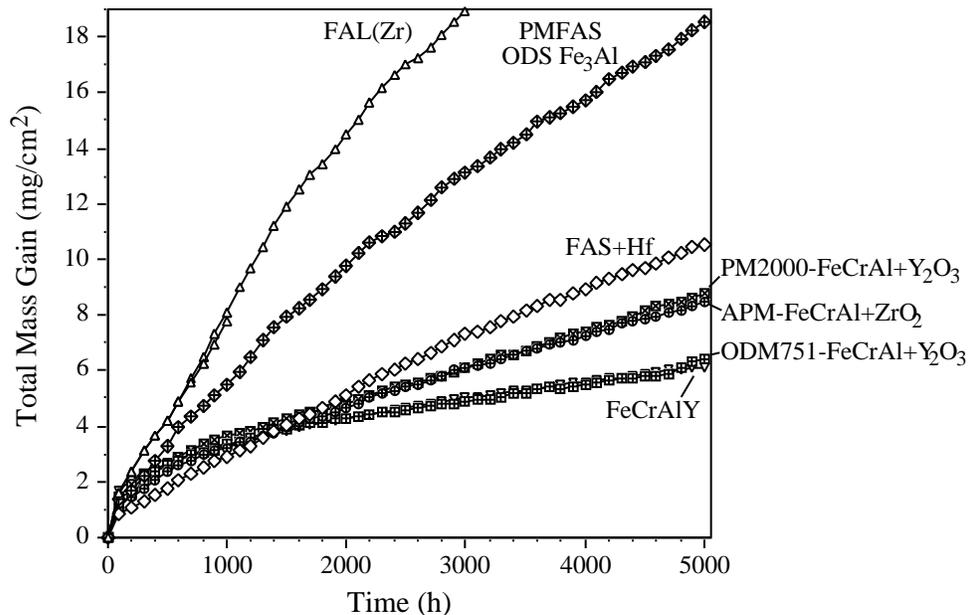


Figure 6. Total weight gain (specimen + spalled oxide) for several iron aluminides during 100h cycles in alumina crucibles at 1200°C in laboratory air. FAS+0.05Hf shows a lower initial total weight gain but, due to scale spallation, it is increasing at a linear rate. FeCrAlY and ODM751 show little spallation and have a nearly parabolic weight gain.

more clearly illustrated in isothermal tests at 1200°C (Fig. 5). Compared to undoped FAS, 0.1% additions of Hf or Zr reduced the isothermal growth rate. Multiple tests were performed to check repeatability of this result. With the addition of 0.05% Hf, the growth rate was reduced by an order of magnitude to $1.3\text{-}1.5 \times 10^{-12} \text{ g}^2/\text{cm}^4\text{s}$. Reducing the Zr content to 0.03% did not produce a similar effect (Fig.5). Thus at 1200°C, the principal benefit of optimizing the Hf content also was in minimizing the $\text{-Al}_2\text{O}_3$ scale growth rate and not in preventing scale spallation. The scale still spalled from this alloy; however, even with spallation, the scale appeared to re-grow at the slower rate, thus retaining a long-term benefit for this alloy. This was also apparent in 100h cycles at 1200°C (Fig. 6) where FAS+0.05Hf initially showed excellent performance. However, there was less scale spallation for many of the RE-doped FeCrAl substrates and, therefore, the total mass gain for FAS+0.05Hf eventually exceeded them (Fig. 6).

Tests at 1200°C also included 1h cycles and 10h cycles in order to gauge the effect of cycle frequency on performance (Fig. 7). In shorter cycles, FAS+0.05Hf continued to perform better than FAL and a 1.5mm thick specimen has completed 3250 cycles without going into breakaway oxidation. As has been observed for other materials[9], the time to first spallation (indicated by a downturn in the specimen mass gain) decreased with increasing cycle frequency. In the first 1000h hours of testing there was little difference between 1h and 10h cycles. Unlike some other iron aluminide specimens, FAS+0.05Hf continued to lose weight throughout these tests. However, the mass loss was still not strictly linear as observed for many Ni-base alumina-formers [12]. In all of the 1200°C tests, the specimens began to macroscopically deform, reflecting the low strength of iron aluminides at this temperature.

Oxidation testing also was performed at 1300°C in order to achieve breakaway oxidation and provide data for lifetime modeling. At this temperature, the detrimental effect of 0.1Hf in FAS was not observed; thus, lowering the Hf content did not result in any lifetime improvement (Fig. 8). The scales on the 0.05 and 0.1Hf FAS alloys after 100h at 1300°C were very similar (Fig. 2).

3.3. SCALE CHARACTERIZATION

The alumina scale on FAS+0.05Hf was examined after 2h at 1200°C using TEM/EDX (Fig. 9). The

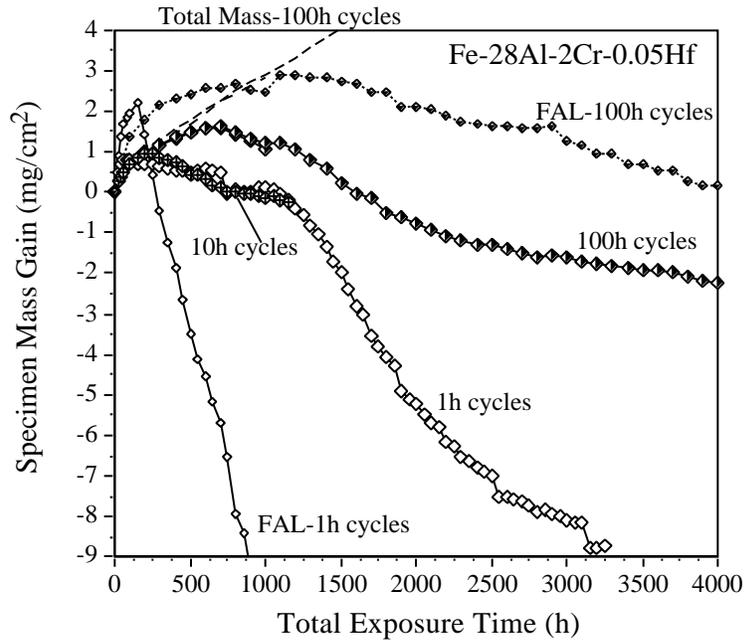


Figure 7. Specimen weight change for FAS+0.05Hf with different cycle times at 1200°C plotted versus time at temperature. Shorter cycles decreased the time to initial spallation (downturn in the mass).

scale had a columnar grain structure as has been observed on other RE-doped alumina formers [4,5,7,11,13]. Analysis of the scale grain boundaries and the metal-scale interface showed ionic Hf segregation (Fig. 9b). No Hf-rich particles were observed in the thin area of the specimen. Similar ionic segregation has been observed for all types of RE-doped alumina-formers [7,12-19]. On thicker scales, hafnia particles were observed at the scale-gas interface (Fig. 10). As has been previously reported, the particle size increased with oxidation time and temperature [7,15,19].

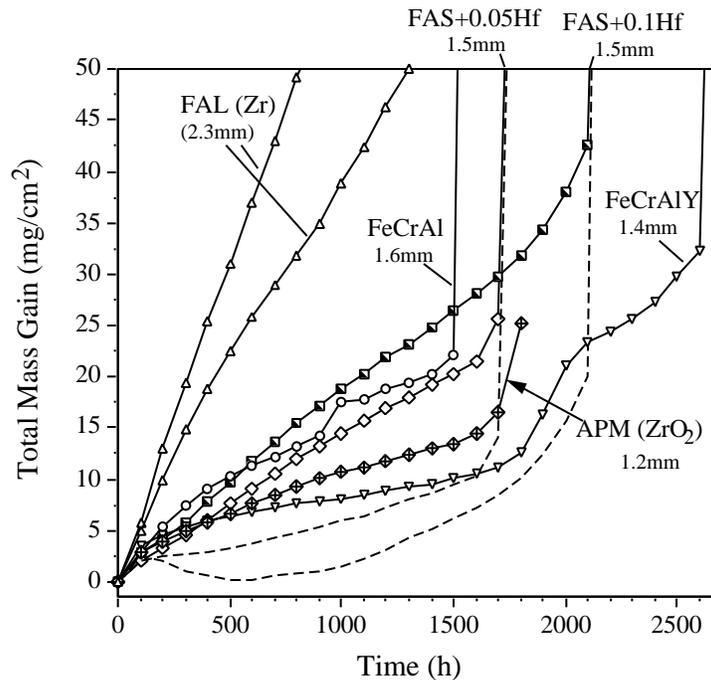


Figure 8. Dashed lines show specimen mass gain and solid lines show total mass gain (specimen + spalled oxide) for several materials during 100h cycles in alumina crucibles at 1300°C in laboratory air. Initial sample thickness is shown. FAS+0.05Hf showed no improvement over FAS+0.1Hf at this temperature. Both alloys were superior to FAL but did not perform as well as FeCrAlY or Kanthal APM.

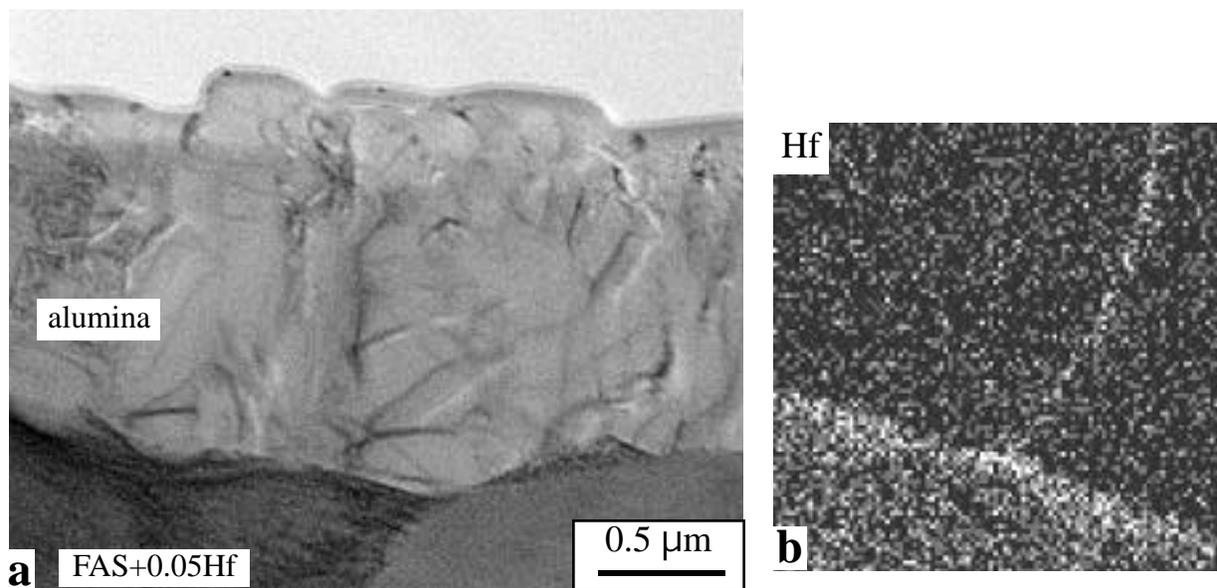


Figure 9. (a) TEM bright field image of the alumina scale formed on FAS+0.05Hf after 2h at 1200°C; (b) Hf EDS X-ray map at the interface reveals Hf ionic segregation to the metal-oxide interface and a grain boundary.

4. DISCUSSION

The oxidation behavior of iron aluminides is dominated by their high CTE (Fig.1) and the resulting spallation problem was not corrected by RE-doping or de-sulfurization[20]. The remaining issue concerns the additional beneficial effect of Hf compared to Y or Zr additions. Such an effect was not noted in an earlier set of experiments with a 0.1Hf addition because of the excessive internal oxidation[5]. At this concentration, the presence of hafnia particles in the scale likely increased transport through the scale. With only 0.05Hf, the rate constant at 1200°C was reduced by an order of magnitude compared to undoped FAS. This was identical to the effect in NiAl[12]. The most likely explanation is that as a grain boundary segregant (Fig. 9b), Hf inhibits the Al boundary diffusion through the scale yet Y and Zr also segregate to scale grain boundaries [7,12-19]. As noted previously[5], all three dopants result in a similar columnar scale microstructure, which is indicative of growth predominantly by the inward boundary diffusion of oxygen[7]. There is no clear indication why Hf should have an additional effect. One possibility is that on an $\text{-Al}_2\text{O}_3$ grain boundary, a Hf ion has a higher effective ionic radius than predicted by standard estimates of its ion size (data collected in Ref.18). The larger ion may have an additional effect on anion or cation transport. This hypothesis can only be addressed by a combination of experimental work on RE-

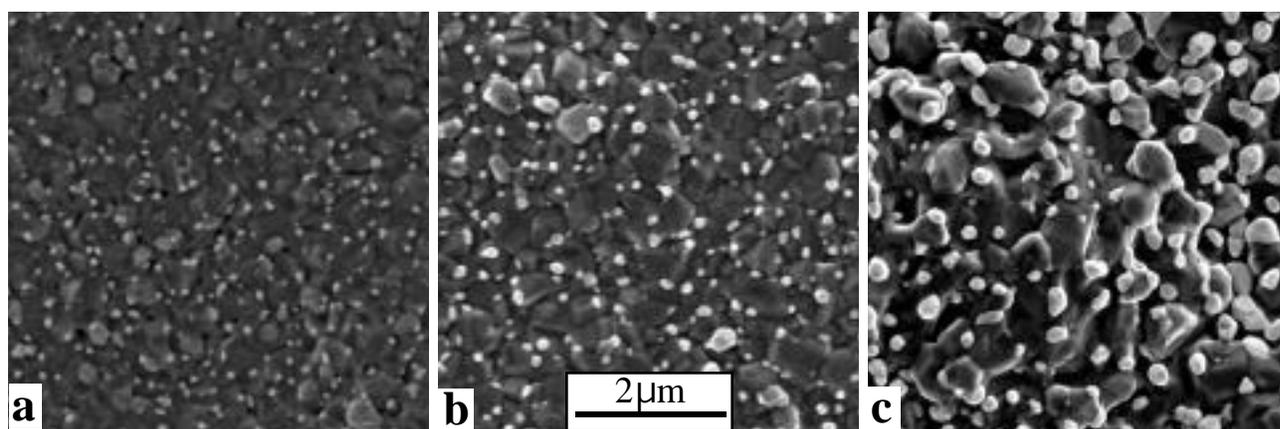


Figure 10. FEG-SEM secondary electron plan-view images of alumina scale formed on FAS+0.05Hf after (a) 200h at 1200°C, (b) 1000h at 1200°C and 100h at 1300°C. The hafnia (bright) particles at the gas interface increase with time and temperature.

doped and undoped bicrystals and atomic scale modeling.

Another curious result is that while Hf is extremely effective in Fe₃Al and NiAl, it is not as effective as Y in NiCrAl or FeCrAl.[21] This may be the result of some interaction with Cr, or be related to impurity levels. Further work is required to explore the possibilities that Hf doping may provide.

5. SUMMARY

An Fe-28Al-2Cr alloy with an optimized 0.05% Hf dopant has shown significantly better high-temperature oxidation resistance than other iron aluminide compositions. Its improved performance was mainly related to a slower isothermal γ -Al₂O₃ scale growth rate and was observed mainly at 1100°-1200°C. Scale spallation was not prevented by Hf-doping because it is attributed to the unusually high coefficient of thermal expansion of the D0₃ phase, Fe₃Al.

6. ACKNOWLEDGMENTS

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