

THE EFFECT OF VARIOUS OXIDE DISPERSIONS
ON THE OXIDATION RESISTANCE OF Fe_3Al

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ABSTRACT

Oxide-dispersed Fe -28at.% Al -2% Cr alloys were produced by a powder metallurgy technique followed by hot extrusion. Yttria and ceria were added to the base alloy to assess the effect of these dopants on the oxidation behavior. The amount of dopant was varied from 0.05-0.5 at.% Y in a series of Y_2O_3 -dispersed alloys. Isothermal and cyclic oxidation testing was conducted at temperatures from 800° to 1300°C. A CeO_2 addition was detrimental to the oxidation behavior. The Y_2O_3 improved the α - Al_2O_3 scale adhesion relative to an undoped alloy, but was not as effective as similar additions to an oxide-dispersed $FeCrAl$ alloy.

INTRODUCTION

Aluminides based on Fe_3Al and $FeAl$ are being investigated because of several potential advantages: (1) lower density relative to typical structural alloys, (2) minimal use of strategic and/or expensive alloying elements, and (3) exceptional high-temperature corrosion resistance in oxidizing, oxidizing/sulfidizing, sulfidizing, and oxidizing/chlorinating environments.¹⁻⁵ At present, the environmental resistance of iron aluminides containing > 20 at.% Al is maintained at temperatures (800°-1200°C) that are well above those at which these alloys have adequate mechanical strength. One possibility for improving the high temperature strength of the alloy while still maintaining the oxidation resistance is by oxide dispersion strengthening (ODS). By using a "reactive" element (RE) oxide dispersion, it might also be possible to further improve the adhesion of α - Al_2O_3 scales on iron aluminides. Use of RE oxide dispersions have improved the oxidation resistance of various Al_2O_3 -forming alloys such as $FeCrAl$,⁶⁻⁸ $NiCrAl$,^{9,10} and $NiAl$.^{11,12} The present paper examines the effects of certain RE oxide additions (Y_2O_3 and CeO_2) on the oxidation behavior of an Fe_3Al alloy. A parallel study is being conducted on the mechanical properties of these same ODS alloys.

EXPERIMENTAL PROCEDURES

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Gas-atomized Fe -28 at.% Al -2% Cr (FAS) powder and sub-micron oxide powder (Y_2O_3 , CeO_2) were mechanically blended in a flowing Ar atmosphere using a high-speed attritor and stainless steel balls. Yttria additions of 0.05, 0.1, 0.2, 0.3 and 0.5 at.% Y and a CeO_2 addition of 0.2 at.% Ce were made. The blended powder was canned, degassed, and extruded at 1100°C. For comparison, a FAS powder extrusion without an oxide addition, wrought Fe -28% Al -5% Cr -0.1% Zr (FAL) and Ni -10% Cr -19% Al ($NiCrAl$) alloys, and a commercial ZrO_2 -dispersed (0.06% Zr) Fe -20% Cr -10% Al alloy (Kanthal alloy APM) were also tested. Oxidation coupons (\approx 15 mm diameter \times 1 mm thick) were polished to 0.3 μm alumina and ultrasonically cleaned in acetone and methanol prior to oxidation. Isothermal oxidation experiments were conducted in dry, flowing air with weight gains measured by a Cahn model 1000 microbalance. Cyclic oxidation experiments were conducted at 1200°C in air and in dry flowing O_2 . In short-term cyclic testing (2 hr cycles), specimens were hung in a furnace and weight changes were measured continuously using a Cahn model 1000 microbalance to check for any indication of isothermal spallation. (In these tests, spallation was only observed upon pre-cooling.) In long-term testing (100 hr cycles), specimens were placed in the furnace in pre-cooling.)

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annealed alumina crucibles so that spalled oxide could be collected and weighed. In both types of cyclic tests, the specimen weight changes were measured before and after oxidation using a Mettler model AE240 balance. After oxidation, specimens were examined using scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDXA).

RESULTS & DISCUSSION

Isothermal kinetic tests were conducted at 800°, 900°, 1200°, and 1300°C. The oxidation kinetics at each temperature generally followed a parabolic rate law. Rate constants are given in Table I. At the lower temperatures, the undoped alloy has a slower oxidation rate but the weight gains at these temperatures were very small and accurate measurements are difficult. The higher oxidation rate for Y-doped FAS at 900°C may be related to the formation of faster-growing, metastable aluminas (e.g. θ -Al₂O₃)¹⁴ which are stabilized by the presence of large dopant ions like yttrium^{15,16}. At the higher temperatures, the addition of Y or Zr slightly reduces the oxidation rate. This reduction was confirmed by comparing scale thicknesses after a 400 hr isothermal exposure at 1200°C. The slower oxidation rate is beneficial, but a more important factor in determining oxidative lifetime is scale adhesion. If the alumina scale spalls during cooling, aluminum depletion is greatly accelerated. Cyclic oxidation tests, where the specimen is cooled to room temperature between cycles, are better indicators of the effectiveness of the oxide dispersions.

Cyclic weight change data at 1200°C for the various alloys are shown in Figures 1 and 2. In the short-term testing (Fig. 1), the most dramatic observations were the rapid weight gains of the CeO₂-dispersed alloy and the fine powdery alumina scale grown on the undoped FAS alloy. The CeO₂-dispersed alloy test was stopped after 14 cycles when breakaway oxidation (formation of FeO_x) began at one edge. Scanning electron microscopy of the specimens after 20 cycles showed that all had some scale loss except for the ZrO₂-dispersed FeCrAl alloy and the 0.05 Y₂O₃-doped FAS which showed very little spallation (Fig. 3). Of the Y₂O₃-dispersed FAS alloys, the 0.2 Y addition had the largest amount of scale spallation (\approx 40% spalled area), in agreement with the weight change measurements. In general, spallation to bare metal was observed and voids at the metal-oxide interface were apparent. However, compared to the undoped alloy, all of the Y₂O₃ additions to FAS reduced the amount of scale spallation. Also, the Y doping produced a flatter, less convoluted scale than that observed on the undoped FAS (Fig. 4), as does the addition of Zr.

The negative effect of the CeO₂ addition on oxidation rate was noted after a single 2hr cycle at 1200°C. Rather than the flat alumina scale observed on the Y- and Zr-doped alloys, the scale on the CeO₂-dispersed alloy already showed some convolutions. Unlike the scale on the

Table I. Parabolic oxidation rate constants at several temperatures for isothermal exposures to dry, flowing air.

Temperature/ Alloy	Rate Constant (g ² /cm ⁴ s)			
	800°C	900°C	1200°C	1300°C
Undoped FAS	2.4×10^{-15}	6×10^{-15}	13×10^{-12}	4.3×10^{-11}
FAS + 0.2Y	3.8×10^{-15}	21×10^{-15}	n.d.	2.6×10^{-11}
FeCrAl + ZrO ₂	n.d.	n.d.	$3-4 \times 10^{-12}^{\dagger}$	2.8×10^{-11}

[†] from reference 13.

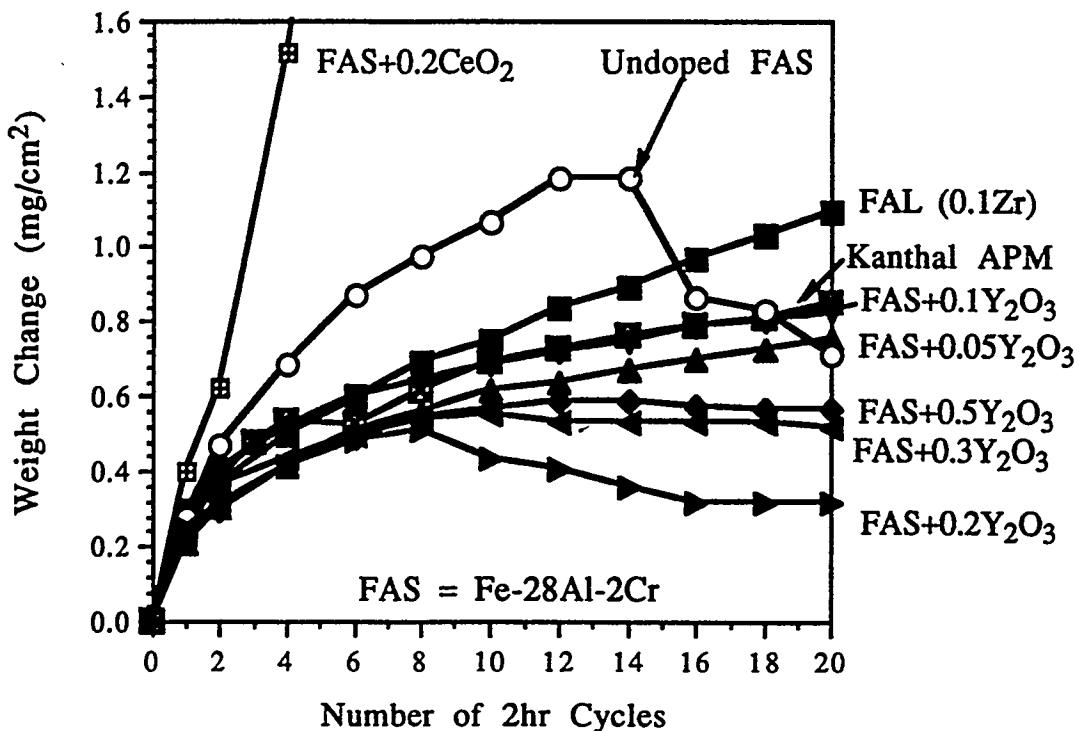


Figure 1. Short-term cyclic oxidation weight change during 20 2-hr cycles at 1200°C for various oxide dispersions in iron-base alloys.

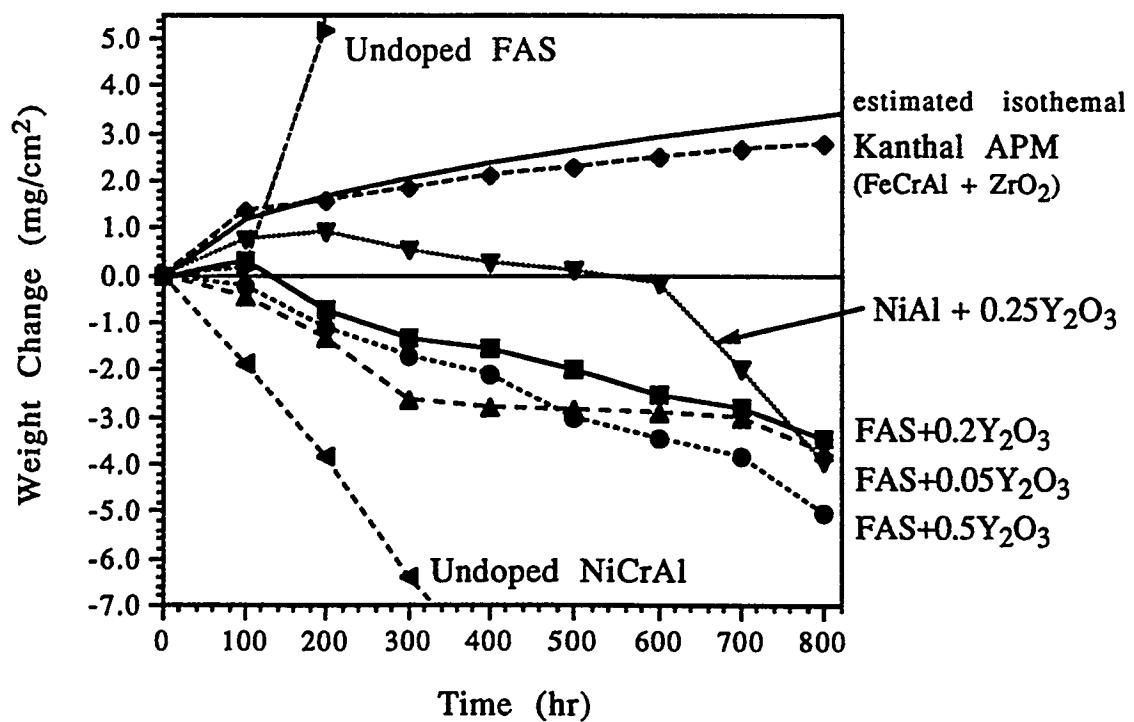


Figure 2. Long-term cyclic oxidation weight change during 100-hr cycles at 1200°C for various alloys. The Y_2O_3 additions in FAS are not as effective as a ZrO_2 addition to a FeCrAl alloy.

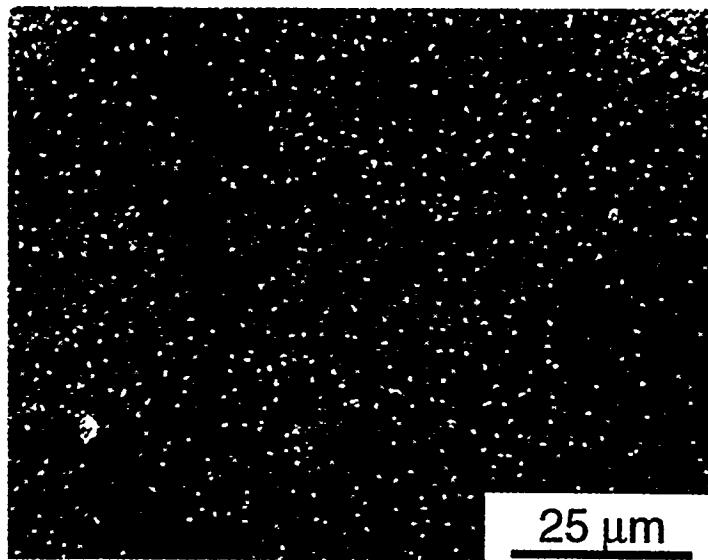


Figure 3. SEM secondary electron image of FAS + 0.05 at.%Y (as Y_2O_3) after 20 2-hr cycles at 1200°C. The $\alpha\text{-Al}_2\text{O}_3$ scale is very flat and virtually no scale spallation is observed.

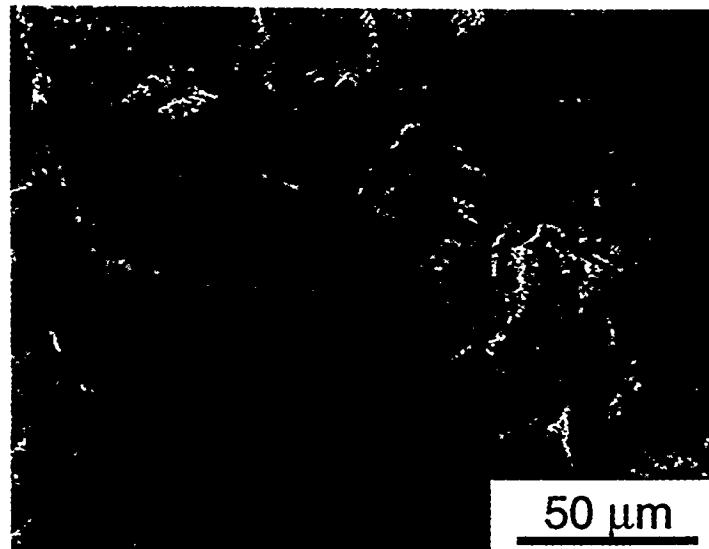


Figure 4. SEM secondary electron image of undoped Fe-28%Al-2%Cr after 20 2-hr cycles at 1200°C. The scale is cracked and very convoluted.

undoped FAS alloy, the scale on the CeO_2 -doped alloy did not appear to spall during the cyclic test. After 14 cycles, large Fe-rich nodules were observed on the sample edges. The detrimental effect of CeO_2 is comparable to that of La_2O_3 in $\beta\text{-NiAl}$.^{11,12} In both cases, these additions resulted in accelerated oxidation relative to the undoped alloy. Whether this effect is primarily in the oxide or in the alloy is unclear and is being investigated.

Exposure temperatures of 1200° and 1300°C are higher than most potential applications for iron aluminides, but were used to assess the potential lifetime of these materials. The Al consumption rate is a critical factor in predicting lifetimes and the higher Al content of iron aluminides relative to FeCrAl alloys could result in longer oxidative lifetimes. However, as illustrated in long-term cyclic testing (Fig. 2), scale spallation was more severe in the Y-doped FAS alloys than in the Zr-doped FeCrAl alloy. The FeCrAl performed almost as well as predicted by the measured isothermal rate. Based on the total weight gains (specimen + spalled oxide, Fig. 5), the aluminum consumption rate was 2 to 4 times higher on the Y-doped FAS alloys compared to the FeCrAl alloy. In previous work on ODS FeCrAl and $\beta\text{-NiAl}$ alloys,^{8,12,13} Y and Zr dopants were found to have identical beneficial effects on the oxidation behavior. Thus, it appears that the difference in oxidation behavior between the ODS FeCrAl and Fe_3Al alloys cannot be explained by the difference in their dopant oxides. Furthermore, the Zr-containing FAL suffered greater cyclic weight gains and scale spallation than the Zr-doped FeCrAl alloy (Fig. 1). In general, RE additions appear to be less effective in iron aluminides than in FeCrAl alloys. A similar result was also observed for 1300°C lifetime testing of iron aluminides and ODS FeCrAl.^{5,17} despite the lower Al content, the time to breakaway oxidation for the RE-doped FeCrAl alloy was comparable to that for wrought FAL containing 0.1% Zr. This indicates that scale spallation was greater for the FAL and resulted in a higher Al consumption rate.

Comparing total weight gains (Figure 5), the lowest Y_2O_3 addition (0.05Y) had the worst performance in this test and 0.2Y had the best performance, the exact opposite of the short-term oxidation results. However, though not as effective as hoped, Y_2O_3 additions still outperformed the undoped FAS alloy, which went into breakaway oxidation after 3 cycles, and an undoped NiCrAl alloy, which showed massive spallation after each cycle.

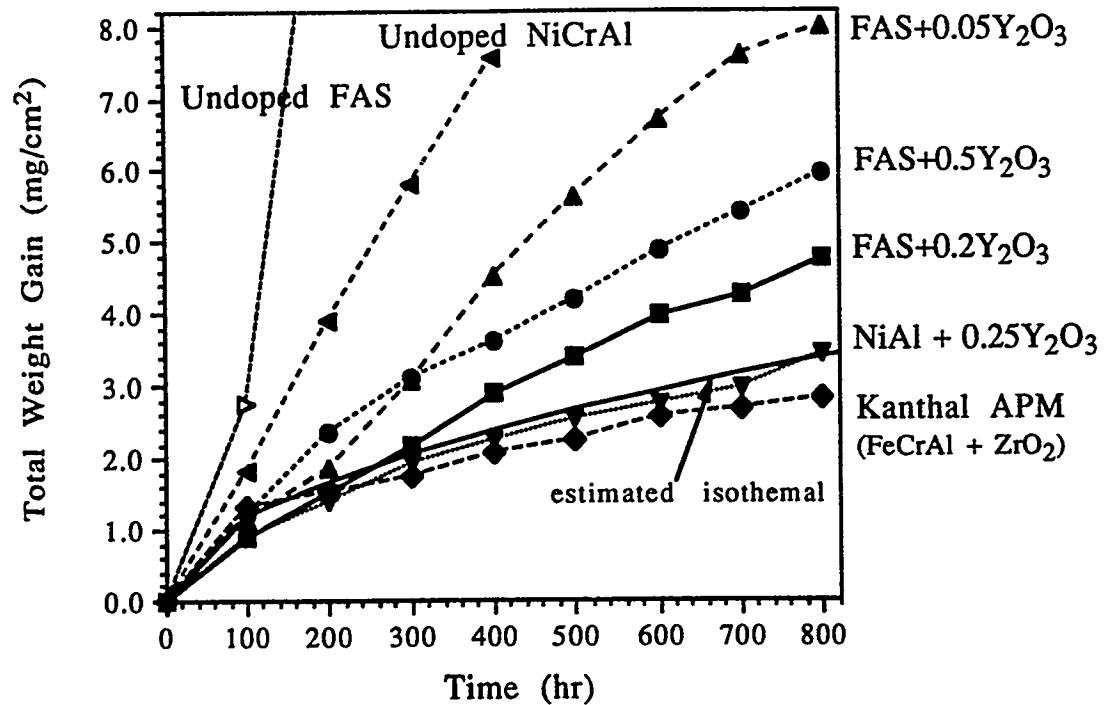


Figure 5. Total weight gain (including spalled oxide) during 100-hr cycles at 1200°C for various alloys. These measurements are proportional to the amount of Al consumption.

CONCLUSIONS

1. Yttria additions to Fe-28Al-2Cr improved oxidation resistance relative to an undoped alloy, but were not as effective when compared with ZrO_2 additions in Fe-20Cr-10Al.
2. A CeO_2 addition to Fe-28Al-2Cr was detrimental to the oxidation behavior.

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