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Effect of environment on the oxidation of ingot-processed iron aluminides

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Abstract

The oxidation behavior of iron aluminides was investigated in various environments at 900 to 1200 °C. The effect of water vapor on total specimen mass gain was minimal. At 1000 and 1100 °C, the mass gain of Fe–28at.%Al–5Cr without Zr was a factor of 2 or more higher in air than in oxygen or Ar–20%O_2. Nitride formation beneath the external Al_2O_3 layer was observed in air. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: A. Iron aluminides; B. Oxidation; Nitridation; High temperature; Al_2O_3; Zr effect

1. Introduction

For the high-temperature oxidation of alumina-forming alloys, differences between air versus oxygen environments or the influence of oxygen partial pressure often are not considered because minimal effects have been reported in the literature [1–3]. A notable exception is the substantial effect of nitrogen on the oxidation behavior of Ti–Al alloys [4–5]. In general however, little effect of nitrogen has been observed for commercially-used alumina-formers such as FeCrAl, NiAl and NiCrAl.

Iron aluminides based on Fe_3Al have been less widely studied than other alumina-formers but have received attention recently because of their excellent combination of sulfidation and oxidation resistance [6–10]. As more detailed experimental work has been performed on Fe_3Al, some abnormalities have been noted in oxide morphology, scale thickness and mass gains depending on test conditions [11–13]. In order to examine environmental effects in more detail, a set of screening tests was performed at 900–1200 °C in air and oxygen, with and without water vapor additions. Results based on specimen mass changes and selective microstructural characterization indicated that the strongest environmental effect was that of nitrogen on the oxidation of undoped (no Zr) Fe_3Al. Higher mass gains were found in air and were accompanied by the formation of aluminum nitride. However, exposure of a second heat of undoped Fe_3Al did not reproduce the same increase in mass, suggesting the phenomenon is not fully understood and may be related to impurity levels in the alloy.

2. Experimental procedure

The two compositions studied were Fe–28Al–5Cr (in at.%) with (ORNL designation: FAL) and without (ORNL designation: FA186) a Zr addition. Both alloys were vacuum induction melted and cast in a water-chilled copper mold. Ingots were then hot rolled to 0.75–1.5 mm thick sheet, cut into rectangular coupons (typically 1–1.5 cm on a side) and polished to a 0.3 μm finish using an alumina slurry. The chemical compositions of the alloys after rolling are given in Table 1. A different heat of undoped Fe_3Al was used in the second round of tests. Specimens were ultrasonically cleaned in acetone and methanol prior to oxidation.

Oxidation experiments were conducted in a horizontal alumina tube with air-cooled endcaps. The gas (O_2, air or Ar–20vol.%O_2) flowed through a $CaSO_4$ drying tube ("dry" gas) or a water bubbler at ≈25 °C ("wet" gas) prior

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Table 1
Chemical composition in atomic percent of the as-rolled Fe_3Al alloys obtained by inductively coupled plasma analysis and combustion analysis

Alloys	Undoped Fe_3Al (first heat)	Undoped Fe_3Al (second heat)	Fe_3Al+Zr
Fe	67.45	67.73	67.26
Al	27.70	27.36	27.72
Cr	4.80	4.83	4.79
Ni	<0.01	<0.01	0.09
Si	0.03	0.02	<0.01
Ti	<0.01	<0.01	<0.01
Y	<0.001	<0.01	<0.001
Zr	<0.01	<0.01	0.08
B	0.002	<0.004	0.05
C	<0.04	0.047	<0.04
O	0.004	0.005	0.006
N	0.001	0.001	0.001
P	0.006	0.011	<0.003
S	0.0037	0.0024	0.0030

to entering the reaction tube at a flow rate of ≈70 ml/min. The specimens were placed in separate pre-annealed alumina crucibles without lids to catch possible spalled oxide but still allow interaction with the environment. Crucibles and specimens were weighed before and after exposure in a Mettler model AG245 balance. After oxidation, selected specimens were examined using a field-emission gun, scanning electron microscope with energy dispersive X-ray analysis (SEM/EDX).

3. Results and discussion

Total mass gain results after 96 h in the first set of experiments at four temperatures and five gas environments are shown in Table 2. Total mass gain was determined by the mass change of the sample plus the alumina crucible in order to include any spalled oxide. However, one source of error is that, without a lid, any violently spalled oxide may not have been captured in the crucible. In most cases this loss was minimal. Specimen mass gains are not included in Table 2. In general, the specimen mass changes only reflected an improvement in scale adhesion with the addition of Zr, which is a widely recognized reactive element (RE) effect [8,11,12,14–16].

At 900 °C, the data indicate a minimal effect of water vapor, nitrogen and Zr on oxidation behavior. Mass gains were slightly lower in air for undoped Fe_3Al but not for Fe_3Al+Zr. Variations may have been due to the θ–α Al_2O_3 phase transformation which occurs in this time and temperature regime. The transient, metastable θ-Al_2O_3 phase is known to grow at a faster rate than α (Ref. [17]) and this may have a large effect on the total mass gain and account for some of the scatter in the data. Both Zr (Ref. [18]) and water vapor [19] are known to inhibit the θ to α phase transformation as well.

At 1000 and 1100 °C, little or no transient alumina phases would be expected to form and there were much clearer effects of environment. The addition of Zr clearly reduced the total mass gain relative to undoped Fe_3Al. This effect was independent of environment. It is attributed to two factors: (1) the more convoluted scale typical of undoped Fe_3Al [12,13,20] results in more oxide formation than the flat scale that forms on Fe_3Al+Zr; and (2) the segregation of Zr to the α-Al_2O_3 grain boundaries [12] and the suppression of the outward transport of Al through the scale [16,21]. This type of RE effect has been observed for a wide range of alumina-formers [11,16,20,22–25].

At 1000 and 1100 °C, the most noticeable effect was the factor of two or more increase in the mass gain for undoped Fe_3Al in air compared to O_2 or Ar–O_2. This difference was due to the formation of aluminum nitride in air. After oxidation, SEM/EDX observations indicated the formation of aluminum nitrides beneath the Al_2O_3 scale on undoped Fe_3Al (Figs. 1 and 2).

Based on these results, a specimen of Fe–28Al–2Cr which showed high mass gains in air during 10 and 100 h cycles at 1200 °C in a previous study [11] was sectioned and examined by electron probe microanalysis (EPMA). Fig. 3 shows X-ray maps from the cross-section, indicating the AlN area beneath the Al_2O_3. This sub-scale structure is similar to that observed in Fig. 2 and several other undoped Fe_3Al specimens.

Thermodynamically, nitridation should be unlikely due to the lower free energy of formation of Al_2O_3

Table 2
Total mass gain per unit area (mg/cm^2) of Fe–28at.%Al–5Cr with Zr and without (undoped) after 96 h at specified temperature and gas environment. The total mass gain includes any spalled oxide. All samples polished to 0.3 μm

	900 °C		1000 °C		1100 °C		1200 °C	
Gas	Undoped	+Zr	Undoped	+Zr	Undoped	+Zr	Undoped	+Zr
Dry air	0.29	0.41	**1.03**	0.35	**4.56**	0.34	2.92	1.47
Wet air	0.33	0.36	1.12	0.34	4.50	0.32	2.40	1.35
Dry O_2	0.41	0.45	**0.55**[a]	0.27[a]	**1.63**[a]	0.39[a]	3.33[a]	1.07[a]
Wet O_2	0.43	0.25	0.53	0.30	2.08	0.40	3.11	1.25
Ar–20%O_2	0.41	0.34	0.47	0.22	1.25	0.39	11.50	0.96

[a] Average of two experiments.

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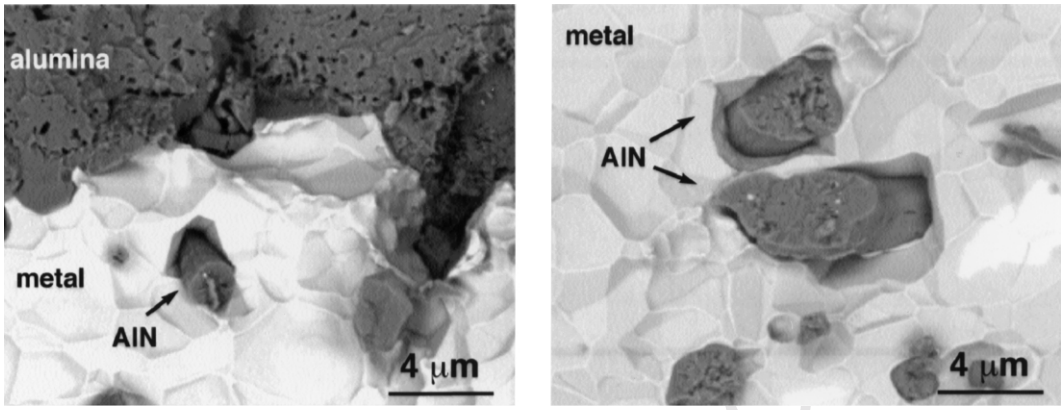

Fig. 1. SEM secondary electron plan-view images of the reaction product after 96 h at 1000 °C in dry air. Using EDX, these particles were observed to be rich in aluminum and nitrogen.

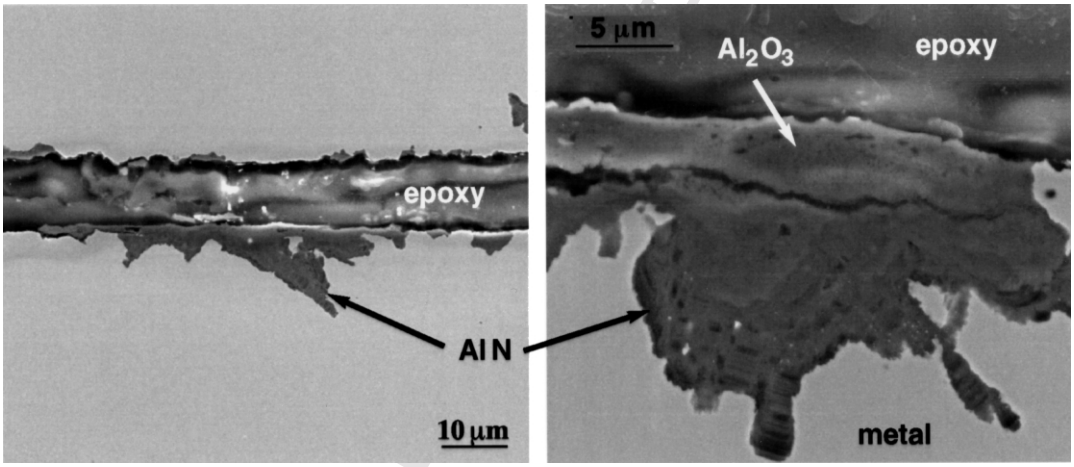

Fig. 2. SEM secondary electron images of a polished cross-section after exposure for 96 h at 1000 °C in dry air. The aluminum nitride appears to form beneath the external oxide layer (which spalls extensively on cooling) and penetrate into the metal.

relative to AlN, but the effect was evident. This nitride formation suggests two possibilities. In one case, nitridation occurs at the same time as the oxidation reaction and the AlN is converted to Al_2O_3. This would explain the oxide penetrations into the substrate with nitride at the deepest location (Figs. 2 and 3). Alternatively, nitride could form beneath the oxide because the nitrogen penetrates the already-formed Al_2O_3 scale and builds up at the metal-scale interface, where the oxygen pressure is set by the Al/Al_2O_3 equlibrium. The low O pressure combined with a high N pressure could allow nitridation.

In contrast to the results for undoped Fe_3Al, there appeared to be little effect of nitrogen on the oxidation behavior of Fe_3Al+Zr (Table 2). At 1000 °C, the mass gain was slightly higher in air than in O_2 for Fe_3Al+Zr while at 1100 °C the reverse was true. At these temperatures, the effect of water vapor appeared minimal for both alloys. One possible reason for the greater nitrogen effect on the undoped alloy is that, when Fe_3Al contains Zr, the alumina scale is essentially flat and adherent to the substrate [11,12]. Without Zr, the α-Al_2O_3 scale on undoped Fe_3Al was highly convoluted and poorly attached. It is possible that the convolutions may have cracked or otherwise allowed ingress of nitrogen. Because of the more adherent scale on Fe_3Al+Zr, nitrogen was limited to the much slower solid state diffusion through the scale.

At 1200 °C, no detrimental effect of nitrogen was evident after 96 h. Mass gains for undoped Fe_3Al were slightly higher in O_2 than in air and an unusually high oxidation rate was observed in Ar–O_2. Again, no significant effect of water vapor on total mass gain was observed. The mass gains for Fe_3Al+Zr were slightly higher in air than O_2, and overall, the beneficial effect of Zr on the growth rate was still evident as mass gains were lower by a factor of 2 to 3 compared to undoped Fe_3Al.

Because of the somewhat surprising nature of these results, the same experiments were performed at 1000 and 1100 °C on a second heat of undoped Fe_3Al. In this case, the deleterious effect of nitrogen observed in the first heat was not reproduced (Table 3). However, there was a higher mass gain observed in wet air than in dry

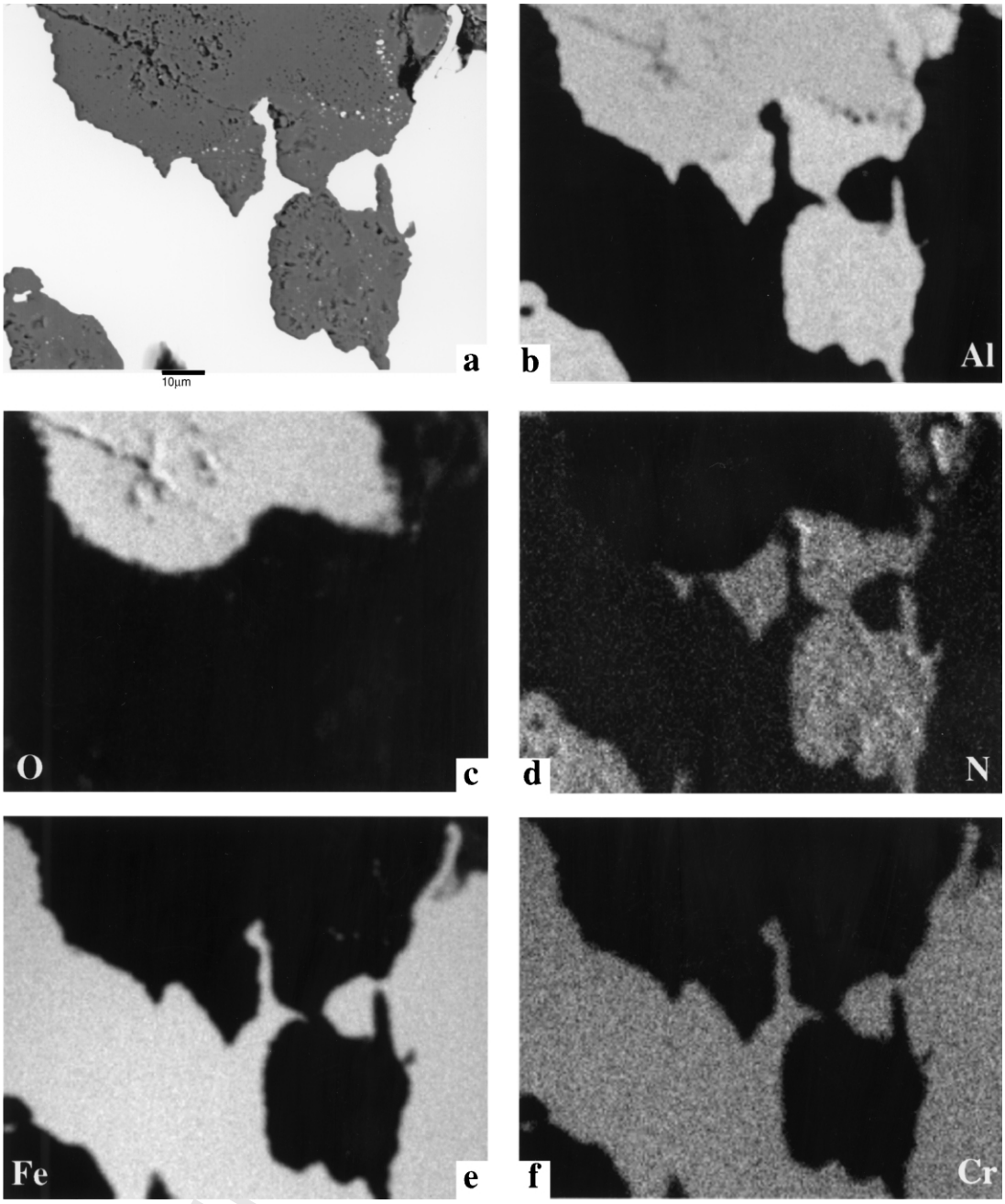

Fig. 3. EPMA back-scattered image (a) and X-ray maps of (b) Al, (c) O, (d) N, (e) Fe and (f) Cr of the reaction product formed on Fe–28Al–2Cr after 10 and 100 h cycles at 1200 °C in laboratory air.

Table 3
Total and specimen mass gains per unit area (mg/cm^2) for two heats of undoped Fe_3Al (Fe–28Al–5Cr) after 96 h in various conditions. The second heat did not show the same effect of nitrogen as the first heat (from Table 2)

	First heat		Second heat	
Environment	Total	Specimen	Total	Specimen
1000 °C, dry O_2	0.55	0.04	0.47	−0.20
Dry air	1.03	0.78	0.38	0.37
Wet air	1.12	0.82	0.94	0.70
1100 °C, dry O_2	1.63	1.14	1.20	0.64
Dry air	4.56	3.37	1.16	0.77

air or dry O_2 at 1000 °C. Overall, one reproducible result was that there was more fine spallation after exposure in O_2 than in air. However, the scale did not appear to be more adherent, it simply remained loosely attached to the substrate in larger pieces after exposure in air.

Further work is being conducted to study the effects of environment on oxidation behavior and the formation of nitrides. One possible reason for the difference in performance between the two heats of undoped Fe_3Al could be a difference in impurities. In Cr-based alloys, differences in S and O levels was observed to have an

effect on the degree of internal nitridation [26]. However, the differences in this case appear minor, Table 1. Other variables such as the alloy surface preparation and microstructure also will be evaluated.

4. Conclusions

The oxidation behavior of two iron aluminides was investigated in various environments at 900–1200 °C. The effect of water vapor on total specimen mass gain was not significant. However, a Zr addition to Fe_3Al produced a lower mass gain than measured on undoped Fe_3Al. For one heat of undoped Fe_3Al at 1000 and 1100 °C, there was a factor of 2 or more increase in mass gain in air compared to oxygen or Ar–20%O_2, but this effect was not reproduced in a second heat. Nitrogen appeared to accelerate the oxidation rate and aluminum nitrides were observed after these and other exposures.

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