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INTERIM REPORT
THE INFLUENCE OF COMPOSITION ON ENVIRONMENTAL
EMBRITTLEMENT OF IRON ALUMINIDES

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Report Prepared by
D. A. Alven and N. S. Stoloff
Rensselaer Polytechnic Institute
Materials Science and Engineering Department
Troy, NY 12180-3590
under
Subcontract No. 19x-SF521C

for

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. Department of Energy
under Contract No. DE-AC05-84OR21-400

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ABSTRACT

The effects of water vapor in air and hydrogen gas on the tensile and fatigue crack growth behavior of Fe_3Al alloys have been studied at room temperature. Fe-28a%Al-5a%Cr alloys to which either Zr alone or Zr and C have been added have been tested in controlled humidity air environments as well as in 1.3 atm hydrogen or oxygen gas and in vacuum. As with other Fe_3Al alloys, oxygen produces the lowest crack growth rates as well as the highest critical stress intensities and tensile ductility in each of the alloys tested. However, while Zr lowers crack growth rates in the Paris regime, there is no apparent beneficial effect on crack growth thresholds. Hydrogen gas also produces unusual results. While crack growth rates are very high in hydrogen in the Paris regime for all alloys, hydrogen only lowers the crack growth threshold relative to air in ternary Fe-28Al-5Cr; it does not lower the threshold in the Zr-containing alloys. It was found that decreased test frequency leads to increased crack growth rates in a Zr-containing alloy which points to a moisture-induced embrittlement mechanism responsible for the higher crack growth rates in air. Fracture path tends to be insensitive to environment for each alloy.

1 INTRODUCTION

Iron aluminides are currently being considered for use in applications where excellent corrosion resistance, moderate strength at temperatures up to 500°C, and low cost are desired. Binary iron aluminides do not possess high ductility at room temperature in air; however, when tested in vacuum or gaseous oxygen environments iron

aluminides have demonstrated ductility of greater than 10% (1, 2, 3). This indicates that Fe_3Al is an inherently ductile material and the low ductility in air is due to an environmental interaction.

The purpose of this research was to examine the changes in mechanical properties of several $\text{Fe}_3\text{Al,Cr}$ intermetallic alloys in various environments. The tensile behavior and fatigue crack growth resistance were examined and the resulting data will be discussed in the light of the role of hydrogen in embrittlement of the iron-aluminum alloys.

2 EXPERIMENTAL PROCEDURE

2.1 Alloy Composition and Heat Treatment

Four alloys were used in this study, an Fe-28%al-5%Cr alloy designated ternary, an Fe-28%al-5%Cr-1%Zr alloy designated 1%ZrC, and two Fe-28%Al-5%Cr-0.5%Zr alloys, one with carbon and one without, designated 0.5%ZrC and 0.5%Zr, respectively. All the alloys are ordered Fe_3Al type intermetallics. The compositions of these alloys are shown in Table 1. All alloys were fabricated at Oak Ridge National Laboratory (ORNL) by vacuum induction melting, extrusion to 1.27 cm square bar, and hot rolling to the final thickness. The plate thickness of 1%Zr used in compact tension specimens was 4.0 mm, while the final plate thickness for the other alloys was 4.75 mm. For tensile test the material was extruded to a 1.08 cm diameter bar.

Due to the texture imparted by the rolling process the terms longitudinal, short transverse, and long transverse will be used to indicate the three perpendicular planes relative to the rolling direction. These planes are illustrated in Fig. 2.1, where the longitudinal plane is the rolling direction, and the short and long transverse planes are the remaining planes.

All alloys used in this study had the same B2 order. The annealing parameters for the B2 order consisted of a 700°C anneal for 1 hour with a mineral oil quench which was then repeated.

Metallography

Metallography was performed on all alloys to examine the grain structure. Samples from the plates were sectioned using a cut-off wheel in the longitudinal, short and long transverse directions and then mounted in epoxy molds. Polishing was

TABLE 1
Composition and Grain Size of Iron -Aluminide Alloys

	Atomic %			
	Ternary	1%Zr	0.5%ZrC	0.5%Zr
Fe	67	65.95	66.45	66.5
Al	28	28	28	28
Cr	5	5	5	5
Zr		1	0.5	0.5
C		0.05	0.05	
Grain Size	180μm	partially recrystallized	partially recrystallized	partially recrystallized

Fig. 2.1 Directional planes of a rolled plate.

performed by first lapping the samples on a Lapmaster then on a water lubricated polishing wheel with 600 grit paper. They were then polished on cloth covered wheels containing 15 μ m and 9 μ m diamond paste and finished on a felt covered wheel with 0.3 μ m alumina slurry with 10% oxalic acid. The metallographic specimens were then etched in glycerigia (30 ml glycerin, 30 ml HCl, 10 ml HNO₃) until the grain structure became visible. All photomicrographs were produced on a polarizing metallograph using Polaroid type 55 film.

2.2 Tensile Test

Tensile tests were performed on the ternary and 0.5%ZrC alloys in laboratory air, oxygen and hydrogen and on the 0.5%Zr and 1%ZrC alloys in laboratory air. Tensile specimens were machined from rods with a diameter of 1.12 cm, or from plate material with a thickness of 0.5 mm with the specimen geometry shown in Fig. 2.2. The tension specimens were polished to a 0.3 μ m finish and ultra-sonically cleansed in acetone prior to testing.

The rod specimens were tested in a servo-hydraulic MTS machine fitted with a vacuum chamber, which allowed for testing in air vacuum or any inert gas. The samples were gripped using a split-type wedge grip shown in Fig. 2.3. The strain rate used in all test was 3x10⁻⁴/sec. All test were conducted at room temperature. One specimen was tested for each environment due to the limited availability of material. The plate specimens were tested on a screw driven Instron 4200 at the same strain rate.

When testing in oxygen or hydrogen gas, the environmental chamber was first evacuated to < 6.6 x 10⁻⁴ Pa using a diffusion pump fitted with a liquid nitrogen cold trap. The appropriate gas was then admitted to the chamber at a pressure of 2300 Pa over atmospheric pressure for 1 hour prior to testing. All gases used were of Ultra-High Purity Grade, with a maximum water vapor concentration of 3 ppm.

(a)

(b)

Fig. 2.2 Tensile specimen geometry for (a) the ternary and 0.5%ZrC, (b) the 0.5%Zr and 1%ZrC alloys.

Fig. 2.3. Wedge grip used in tensile testing.

2.3 Fatigue Crack Growth Tests

Fatigue crack growth test were performed on the ternary, 0.5%ZrC, 0.5%Zr, and 1%ZrC alloys in the B2 ordered state. All alloys were tested at room temperature in 1.3 atm hydrogen gas and 1.3 atm oxygen gas. The ternary alloy was tested in laboratory air while all other alloys were tested in constant humidity environments of 21%, 48%, and 81% relative humidity (rH).

When testing in a gaseous environment the procedure previously described in section 2.2, for tensile tests, was used. For testing in vacuum the chamber was evacuated to $< 8 \times 10^{-7}$ Pa. For constant humidity tests compressed air was bubbled through a closed beaker containing an aqueous solution of potassium acetate, potassium thiocyanate, or ammonium chloride which produced 21%rH, 48%rH and 81%rH, respectively.

Compact tension specimens were used for all fatigue tests. The specimens were cut by electro discharge machining such that the crack growth direction was perpendicular to the rolling direction. Fig. 2.4 shows the specimen geometry. All specimens were polished to a $0.3 \mu\text{m}$ finish and ultra-sonically cleansed in acetone prior to testing.

Crack length was monitored using the d.c. potential drop method. A Hewlett Packard power supply supplied a 10 amp current to the specimen via two current leads positioned 11.5 mm on either side of the machined notch. The current was monitored by an IBM PC computer through a Metrabyte 12 bit analog to digital converter via a resistive shunt. The potential across the unbroken ligament was measured by two voltage probes located 2.5 mm on either side of the notch. The leads were connected to the compact tension specimen brazing them into short holes drilled into the front face.

Calibration curves were created to relate the crack length to the potential drop by optically measuring the crack length with a traveling microscope. The system was able to resolve changes in the crack length of $40 \mu\text{m}$.

All dimensions in centimeters

Fig. 2.4. Geometry of the compact tension specimens.

Fig. 2.5. Calibration curve relating the resistance to the crack length in 0.5%ZrC.

The optical microscope, which had an accuracy of 20 μm , determined the accuracy of the crack measurements. An example of a calibration curve obtained for the 0.5%ZrC alloy is shown in Fig. 2.5.

The load frame used was an MTS servo-hydraulic machine with a 22205 N load cell. Tests were run in load control utilizing a sawtooth waveform at a frequency of 20Hz and an R ratio ($\sigma_{\min}/\sigma_{\max}$) of 0.5. The effect of frequency was investigated by fatiguing 0.5%ZrC at 20Hz, 2Hz, 0.2Hz and 0.08Hz.

Software written for a PC allowed a fully automated test procedure. The PC recorded load applied to the specimen, current, and voltage then calculated crack length, crack growth rate (da/dN), and stress intensity range (ΔK). The calculated values were then used to produce the appropriate waveform. This digital waveform was then converted to analog and sent to the MTS as the load control input for the hydraulic system.

All parameters of the fatigue crack growth test followed ASTM E-647 (4) procedures. The fatigue crack growth testing procedure was as follows:

- 1) Precracking of the CT specimen by fatiguing in 20000 cycle increments at stress intensity levels increasing by 0.5 $\text{MPa}\sqrt{\text{m}}$ until crack initiation was observed.

- 2) A ΔK -increasing procedure was employed until the crack had grown 1.0 mm from the 5.5 mm machined notch before data collection began.

- 3) A load shedding routine was then used to reduce the da/dN values back down to approximately 5×10^{-9} m/cycle to measure crack growth rates in the threshold region. This was the lowest growth rates that could be accurately and conveniently measured.

- 4) The ΔK -increasing routine was then continued until failure. Throughout the testing procedure the R-ratio was held at 0.5 and total crack lengths were measured at crack growth intervals of 0.05 mm.

In accordance with ASTM E-647, the following equation for calculating stress intensity range, ΔK , was used:

$$\Delta K = \frac{\Delta P}{B\sqrt{W}} (0.886 + 4.64\alpha - 13.32 \alpha^2 + 14.72\alpha^3 - 5.64\alpha^4) \quad \text{Eq. 1}$$

In Eq. 1, ΔP is the cyclic load range, B is the specimen thickness, W is the specimen length from the edge to the center of the load-pin holes, and α is the ratio of crack length to W . The crack length is always measured from the center of the load-pin holes to the crack tip.

2.4 Microscopy

2.4.1 Scanning Electron Microscopy

All specimen fracture surfaces were examined in a JOEL-840 scanning electron microscope (SEM) after failure. The fracture mode (cleavage, intergranular, dimpled, etc.) was noted. The specimens were mounted in a brass specimen holder using carbon tape to ensure electrical conductivity. Chemical analysis was performed using the EDX system attached to the microscope. The SEM was used with a working distance of 39 mm and an accelerating voltage of 20 kV. All SEM micrographs were taken with Polaroid no. 55 film.

2.4.2 Transmission Electron Microscopy

All alloys tested were analyzed by transmission electron microscopy (TEM) to determine the dislocation structure and the precipitates present. Chemical analysis of the precipitates was performed by an EDS system. TEM foils were taken from the fatigued regions of the specimens that were tested in air.

The foils were prepared by cutting off a thin section (2 mm) of the fracture surface on a slow speed diamond-blade cutoff wheel. The fracture surfaces were then carefully ground with 240 grit paper on a slow speed wheel as far as required to create a smooth surface and a total thickness of 0.15 mm. Circular foils of 0.3 mm diameter were then produced by cutting with a slurry disk drill. The disks were then ground on both sides with 320 and 600 grit paper to a thickness of 90 μm . Electropolishing was then

performed on the disks to perforation in a Ficshone jet-polisher with an electrolytic solution consisting of 20% nitric acid in methanol. The parameters for jet-polishing were: 18mA, -30°C temperature, and 10 minuets of polishing time.

The TEM work was carried out on a Phillips CM-12 120 kV TEM. All TEM photographs were taken using Kodak Ectar high density electron microscope film.

3 RESULTS

3.1 Grain Structure

The 1 hour 700°C anneal resulted in a partially recrystallized structure for all the Zr-containing alloys. The grain structure is left partially recrystallized as it has been found by researchers at ORNL to result in the highest ductility (5). Figure 3.1(a) shows the as-received 0.5%ZrC while Fig. 3.1(b) shows the B2 ordered 0.5%ZrC. Figs. 3.2 (a) and 3.2(b) show the as received and B2 ordered 0.5%Zr while Figs. 3.3(a) and 3.3(b) show the as received and B2 ordered 1%ZrC. Round precipitates were found in all Zr-containing alloys as seen in Fig. 3.4a. Electron Dispersive X-Ray analysis (EDX) was performed in the Joel 840 SEM on the precipitates and they were found to be Zr-rich (Fig. 3.4b). They were found to be non-homogeneously scattered throughout the material.

In the case of the ternary alloy the 700°C anneal resulted in near fully recrystallized structure with a grain size of 180 μm . The ternary grain structure is shown in Figs. 3.5(a) as received and (b) B2 ordered. Notice that the ternary alloy does not have the strong directional aspect to the structure as does the Zr-containing alloys.

3.2 Tensile Experiments

Tensile data for the iron aluminides examined are listed in Table 2. Alloy 0.5%ZrC had the highest ductility and UTS of all alloys tested. Oxygen provided the

(a)

(b)

Fig. 3.1. Grain structure of the 0.5%ZrC alloy in the as received structure (a) and B2 ordered (b).

(a)

(b)

Fig. 3.2. Grain structure of the 0.5%Zr alloy in the as received structure (a) and B2 ordered (b).

(a)

(b)

Fig. 3.3. Grain structure of the 1%ZrC alloy in the as received structure (a) and B2 ordered (b).

(a)

(b)

Fig. 3.4. Round precipitate found in Zr-containing alloys (a) EDX spectrum showing the composition of the precipitate

(a)

(b)

Fig. 3.5. Grain structure of the Ternary alloy in the as received structure (a) and B2 ordered (b).

highest ductility and UTS for the Ternary alloy while 0.5%ZrC had the same values of ductility and UTS in air and oxygen. Increasing the amount of Zr to 1a% resulted in a decrease of both the ductility and UTS, while the removal of C also decreased the ductility and UTS, but not as severely.

Figs. 3.6(a) - 3.6(d) show the fracture surfaces of all the alloys tested in air. Fractographic features were found to be insensitive to environment in both the ternary and the 0.5%ZrC alloys. The fracture mode was observed to be mixed transgranular cleavage and intergranular fracture in the ternary alloy with a switch to transgranular cleavage and dimpled rupture in the 0.5%ZrC and 0.5%Zr alloys. The fracture mode reverted back to mixed transgranular cleavage and intergranular fracture in the 1%ZrC alloy.

3.3 Fatigue Crack Growth Experiments

3.3.1 Effect of Composition

Fatigue crack growth curves are shown in Figs. 3.7 - 3.10 for the iron aluminides studied. Table 3 lists the threshold and critical stress intensities, as well as the stress intensity necessary to produce a crack growth rate of 10^{-7} m/cycle. The slope in the Paris regime is not reported since a linear region in the da/dN vs. ΔK curves could not always be defined.

TABLE 2.
Tensile Properties of B2 Iron Aluminides

Alloy	YS (MPa)	Air UTS (MPa)	Ductility (%)	YS (MPa)	O ₂ UTS (MPa)	Ductility (%)	YS (MPa)	H ₂ UTS (MPa)	Ductility (%)
Ternary	500	980	10.2	510	1180	12.8	500	740	4.2
0.5%ZrC	690	1460	13.8	680	1460	13.1	680	1200	6.1
0.5%Zr *	670	1000	8.2	-	-	-	-	-	-
1%ZrC *	510	880	5.3	-	-	-	-	-	-

* Average of three tests

(a)

(b)

(c)

(d)

Fig. 3.6. Fracture Surfaces of the (a) Ternary Alloy, (b) 0.5%ZrC Alloy, (c) 0.5%Zr Alloy and (d) 1%ZrC Alloy Tested in Tension at 25°C in Air

TABLE 3.
FCG Data for the B2 Iron Aluminides

Alloy	Environment	ΔK (10^{-7}) (MPa $\sqrt{m}$)	ΔK_{TH} (MPa $\sqrt{m}$)	ΔK_C (MPa $\sqrt{m}$)	Failure Mode
Ternary	Air (30% rH)	20.3	16.9	26.4	TG , IG
Ternary	O ₂	38.4	24.2	42.4	TG, IG
Ternary	Vacuum	32.6	29.2	39.1	TG, IG
Ternary	H ₂	15.1	14.2	19.9	TG, IG
0.5%ZrC	Air (21% rH)	29.0	18.0	59.4	TG tearing
0.5%ZrC	Air (48% rH)	27.1	18.0	47.4	TG tearing
0.5%ZrC	Air (81% rH)	24.3	17.9	37.2	TG tearing
0.5%ZrC	O ₂	42.3	18.6	68.7	TG tearing
0.5%ZrC	Vacuum	29.0	23.2	38.0	TG tearing
0.5%ZrC	H ₂	21.1	19.8	42.8	TG tearing
0.5%Zr	Air (21% rH)	28.1	18.7	39.0	TG, IG
0.5%Zr	Air (48% rH)	25.2	18.9	34.3	TG, IG
0.5%Zr	Air (81% rH)	23.9	19.2	32.2	TG, IG
0.5%Zr	O ₂	43.3	20.0	48.9	TG, IG
0.5%Zr	Vacuum	32.6	32.5	46.1	TG, IG
0.5%Zr	H ₂	21.2	20.5	38.9	TG, IG
1%ZrC	Air (21% rH)	22.8	16.2	27.6	TG, tearing, some IG
1%ZrC	Air (48% rH)	21.2	16.7	27.1	TG, tearing, some IG
1%ZrC	Air (81% rH)	20.2	17.1	23.6	TG, tearing, some IG
1%ZrC	O ₂	35.9	23.0	36.8	TG, tearing
1%ZrC	Vacuum	30.4	26.9	35.1	TG, tearing
1%ZrC	H ₂	21.2	20.5	38.9	TG, tearing, some IG

Fig. 3.7. Fatigue Crack Growth Curves for the Ternary Alloy at 25°C.

Fig. 3.8. Fatigue Crack Growth Curves for the 0.5%ZrC alloy at 25°C.

Fig. 3.9. Fatigue Crack Growth Curves for the 0.5%Zr Alloy at 25°C.

Fig. 3.10. Fatigue Crack Growth Curves for the 1%ZrC Alloy at 25°C.

In all alloys tested oxygen provides the lowest crack growth rates. The 0.5%ZrC alloy has the highest critical stress intensity values in all environments, except vacuum, of the alloys studied. The addition of carbon to the 0.5%Zr alloy does not affect the crack growth rates but significantly increases the fracture toughness. The increase in Zr content to 1a% is detrimental to the crack growth resistance while increasing the threshold stress intensities in all environments except air. In all Zr-containing alloys the threshold stress intensity when tested in hydrogen gas was found to be higher than in air.

Figs. 3.11(a) - 3.11(d) show the fracture surfaces of the fatigued specimens. The fracture surfaces were found to be insensitive to environment for all alloys except for 1%ZrC. The ternary alloy exhibited mixed transgranular cleavage and intergranular fracture, while the fracture mode of the 0.5%ZrC alloy was transgranular, by what appears to be a tearing mechanism. The 0.5%Zr alloy failed by mostly transgranular tearing. The 1%ZrC alloy failed by mixed transgranular tearing with some intergranular fracture in hydrogen bearing environments, while it failed by transgranular tearing in inert environments

3.3.2 Effect of Humidity

The effect of constant humidity on the iron aluminides studied is shown in Figs. 3.12 - 3.14. Table 3 lists the threshold and critical stress intensities as well as the stress intensity necessary for a crack growth rate of 10^{-7} m/cycle.

In all alloys tested in controlled humidity the fatigue crack growth resistance decreased with increasing humidity. The alloy with 1 a% Zr was the most resistant to humidity changes while the alloy with 0.5 a%Zr and carbon was the least. In all alloys the change in humidity had little or no affect on ΔK_{th} . The largest change was 5% for the 1% Zr alloy. The fracture mode was also found to be unchanged with humidity for each alloy tested.

(a)

(b)

(c)

(d)

Fig. 3.11. Fracture Surfaces of (a) Ternary Alloy, (b) 0.5%ZrC Alloy, (c) 0.5%Zr Alloy and (d) 1%ZrC Alloy Fatigued at 25°C in Air

Fig. 3.12. Fatigue Crack Growth Curves for the 0.5%ZrC Alloy at 25°C.

Fig. 3.13. Fatigue Crack Growth Curves for the 0.5%Zr Alloy at 25°C.

Fig. 3.14. Fatigue Crack Growth Curves for the 1%ZrC Alloy at 25°C.

3.3.3 Effect of Frequency

The effect of decreasing the fatigue crack growth frequency for the 0.5%ZrC alloy is shown in Fig. 3.15. All tests were run at a constant humidity level of 21%rH. Also shown is the fatigue test conducted in oxygen which is considered the inert environment for determining the magnitude of crack growth enhancement.

As can be seen in Fig. 3.15 the lower frequencies enhance fatigue crack growth, as well as having a significant affect on both the threshold and critical stress intensities. The lowest ΔK_{th} , 18.1 MPa√m, was found at the highest frequency 20Hz and it increased to 24.1 MPa√m at 0.08Hz. The critical stress intensity decreased as the frequency was increased. ΔK_c dropped from 59.1 MPa√m to 33.1 MPa√m between 20Hz and 0.2Hz. The increase in ΔK_c between 0.2Hz and 0.08Hz from 33.1 MPa√m to 35.8MPa√m is not significant because it is within the experimental error.

Fig. 3.15. Effect of Frequency on the 0.5%ZrC Alloy in 21%rH Air at 25°C.

3.4 Transmission Electron Microscopy

TEM foils from the fatigued region of the alloys tested in air were examined to determine the dislocation structure, as well as the precipitate morphology. The ternary alloy exhibited no precipitates while the dislocation structure was similar to that found by previous research (6, 7). The structure consist of loosely coupled single dislocations along with a cellular subgrain structure (see Fig. 3.16). The walls of the subgrain are made up of a rectangular array of dislocations.

The 0.5%Zr alloy exhibited few subgrains with small precipitates (0.3 μm diameter) located along grain boundaries (see Fig. 3.17a). The precipitates were found to be Zr-rich as EDS showed (see Fig. 3.17b). The subgrain walls are also composed of a rectangular array of dislocations.

Fig. 3.18a shows the dislocation structure and precipitates in 0.5%ZrC. The small precipitates (0.2 μm diameter) were found to be Zr-rich (see Fig. 3.18b) and to lie along

grain boundaries. 0.5%ZrC exhibited more subgrains than 0.5%Zr along with more complex dislocation arrays.

1%ZrC exhibits much larger Zr-rich precipitates (3 μm diameter) that are located along the grain boundaries (see fig. 3.19a). The precipitates sometimes form into a band along the grain boundaries, such as in Fig. 3.19b. Few subgrains were found in 1%ZrC while there were many single and some paired dislocations.

4 DISCUSSION

The increased tensile elongation of the ternary alloy in oxygen as compared to air demonstrates the embrittling effect of moisture in laboratory air, which is consistent with previous findings on $\text{Fe}_3\text{Al,Cr}$ (8, 9). The 0.5%ZrC alloy exhibits similar elongations in air and oxygen while the elongation is reduced in hydrogen. For the Zr-containing alloys the elongation is reduced when the C is removed and further reduced when the Zr content is increased to 1a% with the C content maintained at 0.05a%. This suggests that a small amount of Zr can increase the intrinsic ductility of $\text{Fe}_3\text{Al,Cr}$ alloys.

The fatigue crack growth behavior of all alloys clearly show the embrittling effect of hydrogen whether it is present as hydrogen gas or water vapor in air. The lowest crack growth rates were found in oxygen for all alloys. The difference in critical stress intensity in the Zr-containing alloys between air and oxygen (about 21%) was much less than in the ternary alloy (36%) which indicates that Zr-containing alloys are less susceptible to moisture-induced embrittlement.

The increase in fatigue crack growth rate with decreased frequency further indicates the susceptibility to embrittlement. It is interesting to note that the rate decreases drastically between 20Hz and 2Hz while between 2Hz and 0.08Hz the decrease is much less drastic. The threshold stress intensity was found to increase with decreased frequency with the difference being greater between 0.08Hz and 2Hz than 2Hz and 20Hz.

The threshold stress intensities are affected by Zr additions. The addition of 1a% Zr is only beneficial in hydrogen; in all other environments there is no difference when compared to the ternary alloy. In air and in hydrogen 0.5a% Zr raises the threshold stress intensity by 6% and 28% respectively, while in oxygen it lowers the threshold stress intensity by 23% when compared to the ternary alloy.

Zr additions were found to be beneficial in reducing the susceptibility to moisture-induced embrittlement. Alloying with 1a% Zr reduced the detrimental effect of increased moisture content during testing. The stress intensity necessary to reach 10^{-7} m/cycle differed by 11% in 1%ZrC between 21%rH and 81%rH as compared to 16% for 0.5%ZrC. The addition of C had a negligible effect on the susceptibility to moisture-induced embrittlement.

An interesting effect of the addition of Zr was on the fatigue crack growth resistance in hydrogen. In all Zr-containing alloys the threshold stress intensity is higher in hydrogen gas than in air while the crack growth rate is much higher. The threshold stress intensity also exhibits no change from oxygen to hydrogen for all Zr-containing alloys.

The low crack growth rates in the 0.5%Zr alloys were the most surprising results of this investigation. An explanation by which Zr affects the crack growth rate appears to be as a grain boundary strengthener and a trap for H so that the latter cannot reach the crack-tip region. The addition of 0.5a% Zr results in a change from mixed transgranular cleavage and intergranular fracture to transgranular tearing, which points to an increase in the strength of grain boundaries. The TEM studies show that when Fe₃Al is alloyed with Zr, Zr-rich precipitates form along the grain boundaries. It was also found that as the alloying amount of Zr is increased the precipitates become larger and form bands of Zr-rich veins along the grain boundaries.

The evidence for the trapping of H by the Zr-rich precipitates is found in the 1a% Zr alloy. In the case of 1%ZrC some intergranular facets appeared only in

Fig. 3.16. Dislocation structure of the Ternary alloy fatigued in air at 25°C

(a)

(b)

Fig. 3.17. Dislocation structure of 0.5%Zr fatigued in air at 25°C (a) and EDS of precipitate(b).

(a)

(b)

Fig. 3.18. Dislocation structure of 0.5%ZrC fatigued in air at 25°C (a) and EDS of precipitate(b).

(a)

(b)

Fig. 3.19. Dislocation structure of 1%ZrC fatigued in air at 25°C (a) precipitate band along grain boundary(b).

hydrogen-containing environments while the failure mode was completely transgranular tearing in inert environments. This points to the fact that H segregates to the precipitates along the grain boundaries and when the concentration becomes great enough failure is initiated at the grain boundary as opposed to the cleavage plane.

5 CONCLUSIONS

The addition of small amounts of Zr to Fe₃Al,Cr alloys results in lower crack growth rates. The beneficial effect of Zr is limited to very low concentrations, since the addition of 1a% Zr results in higher crack growth rates, similar to those for the ternary alloy. The beneficial effect was found to be due to the formation of small Zr-rich precipitates along the grain boundaries which strengthen the grain boundaries and trap H during fatigue crack growth. The addition of C appears to only affect the fracture toughness of Fe₃Al,Cr alloys. Zr additions also result in increased threshold values in hydrogen when compared to air, while the crack growth rate at higher ΔK was higher in hydrogen.

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