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**EVALUATION OF THE INTRINSIC AND EXTRINSIC FRACTURE
BEHAVIOR OF IRON ALUMINIDES**

July 27, 1998

Report Prepared by

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P.O. Box 6315

Morgantown, WV 26506-6315

under

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OAK RIDGE NATIONAL LABORATORY

Oak Ridge, Tennessee 37831

Managed by

LOCKHEED MARTIN ENERGY RESEARCH CORP.

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WVU-2, Evaluation of The Intrinsic and Extrinsic Fracture Behavior of Iron Aluminides

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FINAL REPORT

ABSTRACT

Iron aluminides have excellent corrosion resistance in high-temperature oxidizing-sulfidizing environments; however, there are problems at room and medium temperatures with hydrogen embrittlement as related to exposure to moisture. In this research, a coordinated computational modeling/experimental study of mechanisms related to environmental-assisted fracture behavior of selected iron aluminides has been undertaken. The modeling and the experimental work connect at the level of coordinated understanding of the mechanisms for hydrogen penetration and for loss of strength and susceptibility to fracture.

The focus of the modeling component has been on the challenging question of accurately predicting the iron vacancy formation energy in Fe_3Al and the subsequent tendency, if present, for vacancy clustering. We have successfully performed, on an *ab initio* basis, the first calculation of the vacancy formation energy in Fe_3Al . These calculations include lattice relaxation effects which are quite large for one of the two types of iron sites. This has significant implications for vacancy clustering effects with consequences for hydrogen diffusion. Indeed, our *ab-initio-based* estimate of the divacancy binding energy indicates a likely tendency toward such clustering for iron vacancies on the sites with large lattice relaxation.

The experimental work has focused on the relationship of the choice and concentration of additives to the improvement of resistance to hydrogen embrittlement and hence to the fracture behavior. For this reason, environmental assisted fracture behavior of three iron aluminides (designated as FA-186, FA-187, and FA-189, with and without various alloy additives such as

Zr, C, or B) were investigated to study the effect of alloy additives on fracture behavior, in particular, the improvement of resistance to moisture-induced hydrogen embrittlement. Our test results indicate that the susceptibility to hydrogen embrittlement may be related to grain size. While the Zr, C, or B additions can improve GB cohesive strength and GB-dislocation interaction (the ability to absorb and emit dislocations more effectively); the problem appears to be that, the smaller grain size also enhances moisture assisted intergranular cracking due to high stress concentration at the crack tip. Based on the results from this research, we point out that better grain boundary design and control is needed for iron aluminides. In particular, larger grain sizes of FA-187 and FA-189 may improve their resistance to environmental embrittlement. This can be achieved through refined fabricating processes and heat treatment to produce larger grain sizes for FA-187 and FA-189.

WVU-2, Evaluation of The Intrinsic and Extrinsic Fracture Behavior of Iron Aluminides

FINAL REPORT

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WVU-2, Evaluation of The Intrinsic and Extrinsic Fracture Behavior of Iron Aluminides

I. INTRODUCTION AND SUMMARY

Iron aluminide has excellent corrosion resistance in high-temperature oxidizing-sulfidizing environments; however, there are problems at room and medium temperature with hydrogen embrittlement as related to exposure to moisture. In this research, a coordinated computational modeling/experimental study of mechanisms related to environmental-assisted fracture behavior of selected iron aluminides has been undertaken. The modeling and the experimental work connect at the level of coordinated understanding of the mechanisms for hydrogen penetration and for loss of strength and susceptibility to fracture.

The focus of the modeling component has been on the challenging question of accurately predicting the iron vacancy formation energy in Fe_3Al and the subsequent tendency, if present, for vacancy clustering. Atomistic computational modeling was undertaken to find the preferred geometries and the formation energies of iron vacancies and vacancy pairs (Fe-Fe) for FeAl and Fe_3Al . An indication of vacancy clustering in Fe_3Al , with consequences for dislocation behavior, may be important for understanding the role of dislocation-assisted diffusion in the hydrogen embrittlement mechanism. We have successfully performed, on an *ab initio* basis, the first calculation of the vacancy formation energy in Fe_3Al . These calculations include lattice relaxation effects which are quite large for one of the two types of iron sites. This has significant implications for vacancy clustering effects with consequences for hydrogen diffusion. Indeed, our *ab-initio-based* estimate of the divacancy binding energy indicates a likely tendency toward such clustering for iron vacancies on the sites with large lattice relaxation.

The experimental work has focused on the relationship of the choice and concentration of additives to the improvement of resistance to hydrogen embrittlement and hence to the fracture behavior. For this reason, environmental assisted fracture behavior of three iron aluminides (designated as FA-186, FA-187, and FA-189, with and without various alloy additives such as Zr, C, or B) were investigated to study the effect of alloy additives on fracture behavior, in particular, the improvement of resistance to moisture-induced hydrogen embrittlement. Comparative delayed crack growth tests (i.e. under constant load) on FA-186, FA-187, and FA-189 iron aluminide samples provided by ORNL, were conducted under air, oxygen, or water

environments. All alloys had the same basic composition of Fe-28Al-5Cr at %; FA-186 is the ternary alloy, while FA-187 is micro-alloyed with additives of Zr (0.5%) and C (0.05%), and FA-189 is micro-alloyed with additives of Zr (0.5%), C (0.05%) and B (0.005%). The purpose of micro-alloying was to improve low temperature ductility and better resistance to hydrogen embrittlement. Zr, C, or B additions to the ternary alloy alter grain boundary (GB) chemistry and structure, and yield smaller GB size and better GB cohesive strength. Accordingly, the mechanical properties, especially ductility and fracture resistance to hydrogen embrittlement, should be improved. However, our test results showed that all the alloys tested were still susceptible to room temperature hydrogen embrittlement in both B₂ and DO₃ conditions. Furthermore, FA-189 and FA-187 were more susceptible to environmental hydrogen embrittlement. Our test results indicate that the susceptibility to hydrogen embrittlement may be related to grain size. While the Zr, C, or B additions can improve GB cohesive strength and better GB-dislocation interaction (to absorb and emit dislocations more effectively); the problem appears to be that, the smaller grain size also enhances moisture assisted intergranular cracking due to high stress concentration at the crack tip. Based on the results from this research, we point out that better grain boundary design and control is needed for iron aluminides. In particular, larger grain sizes of FA-187 and FA-189 may improve their resistance to environmental embrittlement. This can be achieved through refined fabricating processes and heat treatment to produce larger grain sizes for FA-187 and FA-189.

II. COMPUTATIONAL MODELING

A. Summary of Calculations and Results

A fully quantum mechanical full-potential LMTO technique, including force calculations, was applied to find the formation energies of iron vacancies and vacancy pairs (Fe-Fe) in FeAl and Fe₃Al. The method used was our well established fully quantum mechanical full-potential linear-combination-of-muffin-tin-orbitals (LMTO) [1,2] technique. This is an *ab initio* all-electron technique with full relativistic corrections included. To assure high accuracy we have implemented [2,3] an augmented basis through use of multiple κ 's and energy windows. Initially we have found the preferred unrelaxed geometry through use of total energy minimization. To treat relaxation effects for this transition metal system, we have implemented a force methodology based on our full-potential LMT total energy technique and have applied this to

vacancy formation energies in both FeAl and Fe_3Al . We next calculated the divacancy binding energy.

The vacancy energy is obtained by first calculating the total energy of the initial perfect (without vacancy) supercell. We then subtract from that the energy the sum of the total energy of the supercell with a vacancy plus the energy contribution of the removed atom. The atomic energy contribution is taken from the bulk energy of the element (iron) scaled to reproduce the total energy of the intermetallic compound.

In Fe_3Al there are two types of iron sites (see Fig. 1). Type A has eight iron nearest neighbors at a distance of $\sqrt{3}a/4$; while type B has four iron and four aluminum nearest neighbors. This then leads to there being two types of vacancies and the possibility of three types of divacancies (AA, AB, BB). We have carefully examined the density of states for the two types of iron site, and they are quite different (see Fig. 2).

In order to have sufficient degrees of freedom to fully investigate the effects of lattice relaxation, we have used a 32-atom supercell (eight formula units of Fe_3Al). For the type A iron sites. The unrelaxed vacancy formation energy is 2.47 eV, and there is an energy lowering of 0.65 eV caused by lattice relaxation. This gives a net vacancy formation energy of 1.82 eV. Interestingly, the changes in bond lengths are quite large, between 5 and 6% of the nearest neighbor distance. For the type B sites, the unrelaxed vacancy formation energy is 3.66 eV, and there is an energy lowering of 0.1 or 0.2 eV associated with lattice relaxation. For B sites, this gives a net vacancy formation energy of 3.56 eV. The changes in bond lengths are much smaller than for the A sites.

Significantly for the possibility of vacancy clustering, our calculations in the 32-atom supercell in comparison with those for a 16-atom supercell indicate an interaction between nearest-neighbor vacancies in type A sites of about 0.1 eV. However, based on our systematic study of the individual vacancy formation energies, we do not view these results as a completely reliable measure of the isolated divacancy binding energy. The reason for this is that the use of a periodically repeated 32-atom cell is not large enough to isolate a divacancy from its periodically-repeated identical neighboring divacancies. However, this probably does give an indication of vacancy clustering, ie. whether for a divacancy or for a substantially larger cluster. Clearly the next step is to extract and use atomistic potentials to predict the energetics of

divacancy formation and vacancy clustering. Therefore we have initiated that calculation. Such atomistic potentials will also be useful in the proposed research dealing with oxide scale spallation.

B. Details of Computational Modeling and Results

1. Vacancy formation energy.

There is a well recognized problem associated with vacancy formation energy calculations. Even at zero temperature, evaluation of vacancy formation energy E_{vac} requires a knowledge of three energies -- internal energy E_N of the initial supercell with N atoms, internal energy E_{N-1} of the supercell with one vacancy, and molecular potential μ of the atom at the site on which the vacancy was created. Knowing those energies, vacancy formation energy can be found as:

$$E_{vac} = E_N - E_{N-1} - \mu \quad (1)$$

For a material with one atom per unit cell (elements), the chemical potential can be easily determined from the same calculations, at zero temperature the chemical potential is just equal to the internal energy per atom in the bulk:

$$\mu = \frac{E_N}{N} \quad (2)$$

The problem is significantly more complicated for compound or alloy materials. For example, consider a binary alloy -- AB. If chemical potentials μ_v^{AB} (where v symbolizes element A or B, and superscript AB emphasize that this is chemical potential for alloy AB) are known, then the vacancy formation energies are:

$$E_{vac}^v = E_N - E_{N-1}^v - \mu_v \quad (3)$$

where E_{N-1}^v is the energy of the supercell with vacancy on the site of element v (A or B). However, we cannot directly determine chemical potentials μ_A and μ_B ; instead, calculation gives us only a chemical potential μ_{AB} of the AB pair (or a chemical potential of an elementary unit cell, in the general case).

There are two solutions to this problem:

In the simplest case, it might be hypothesized that an atom adjusts any local environment to achieve optimum electron density; and therefore, the atomic energy is approximately the same

for different equilibrium environments. Therefore, as the first approximation we can use chemical potentials of corresponding elements. Then, recalling the fact that the chemical potential of the unit cell is equal to the sum of chemical potentials of all composing elements:

$$\mu_{AB} = \mu_A^{AB} + \mu_B^{AB}, \quad (4)$$

we can introduce a coefficient β :

$$\beta = \frac{\mu_{AB}}{\mu_A + \mu_B} \quad (5)$$

which can be used as a correction coefficient to the first approximation:

$$\mu_A^{AB} \approx \beta \mu_A; \quad \mu_B^{AB} \approx \beta \mu_B; \quad (6)$$

With this, the requirement (4) is automatically satisfied. Accuracy of this approximation can be judged by the deviation of β from unity. In our case, $\beta - 1 \cong 10^{-4}$.

The second, more rigorous, approach was developed by M.Fähle and coworkers in several publications [see Ref. 4 and earlier citations therein]. Their thermodynamic approach is based on conservation of atoms. From the usual statistical consideration we can write:

$$C_V^\alpha = C_A^\alpha \exp \left[-\frac{E_N - E_{N-1}^A + \mu_A}{KT} \right] \quad (7)$$

$$C_V^\beta = C_B^\beta \exp \left[-\frac{E_N - E_{N-1}^B + \mu_B}{KT} \right] \quad (8)$$

$$C_B^\alpha = C_A^\alpha \exp \left[-\frac{E_N^{A \leftrightarrow B} + \mu_A - \mu_B}{KT} \right] \quad (9)$$

$$C_A^\beta = C_B^\beta \exp \left[-\frac{E_N^{B \leftrightarrow A} + \mu_B - \mu_A}{KT} \right] \quad (10)$$

where C_V^α and C_V^β are the concentration of vacancies on sites for atoms A (these sites form lattice α) and on sites for atoms B (denoted by β), respectively; C_B^α and C_A^β are the concentrations of type B atoms on sites for atoms A and type A on sites for atoms B, respectively and; $E_N^{A \leftrightarrow B}$ ($E_N^{B \leftrightarrow A}$) are energies of supercells where the atom of type A(B) is replaced by an atom of type B (A).

Furthermore, we can use the thermodynamic relation:

$$\frac{2E_N}{N} = \mu_A + \mu_B - KT \ln(4C_A^\alpha C_B^\beta) \quad (11)$$

(where we are considering the binary alloy AB at stoichiometry (say 50% of each constituent)).

Finally, since the total number of atoms A (B) does not change:

$$C_A^\alpha + = \frac{1}{2} - C_B^\alpha - C_V^\alpha \quad (12)$$

$$C_B^\beta + = \frac{1}{2} - C_A^\beta - C_V^\beta \quad (13)$$

$$1 = \frac{N_A}{N_B} = \frac{(C_A^\alpha + C_A^\beta)}{(C_B^\alpha + C_B^\beta)} \quad (14)$$

Therefore, we have eight equations for eight variables. Although at the first glance this approach looks much more solidly-based and accurate, in reality it might have several flaws.

- a) It requires significantly more calculations (all vacancy + antisite energies).
- b) Concentrations are found as a solution to a nonlinear system of equations. This system involves all energies; and therefore, a single error in calculations affects all results.
- c) The initial assumption about conservation of total number of atoms is not always correct.

Consider the following example. For simplicity, let us consider that the antisite energies are extremely high. Therefore, concentrations of antisite defects (Eqs. (9) and (10)) are equal to zero. In this case, according to (14), the number of vacancies on the α sites is equal to the number of vacancies on the β sites, even if internal energies are significantly different (chemical potentials would compensate for changes in internal energy). For a real material, such a situation would result in a formation of precipitates of the material with the lowest vacancy formation energy, or a segregation of this material toward surfaces or grain boundaries.

2. Current situation for our calculations:

1.) Initially all our Fe_3Al calculations were conducted at the experimental value of the lattice constant. This was incorrect for this type of calculation because it causes an extra artificial stress since the system will tend to relax to the predicted calculated lattice constant. This stress can change a relaxation process and vacancy formation energies. Therefore we performed

calculations using the calculated lattice constant instead. The current results for iron vacancies using the first method (see above) are:

16 atoms:

Unrelaxed type A 1.06 eV

Relaxed type A 0.77 eV

Relaxation energy 0.3eV

Unrelaxed type B 1.87 eV

Relaxed type B 1.87 eV (no relaxation, probably because of very high symmetry since there was only one type of motion available).

32 atoms:

Unrelaxed type A 2.47 eV

Relaxed type A 1.82 eV

Relaxation energy 0.65 eV

Unrelaxed B 3.66 eV

Relaxed B 3.56 eV

Relaxation energy <0.2eV

The differences in results for 16 and 32 atom cells suggest that our cells are too small to consider an "isolated" vacancy. Computer limitations restrict us to cells smaller than 64 atoms. Judging from the difference between 16 and 32 atom supercells we can estimate that the interaction between two vacancies at type A sites is about 0.1 eV $\{(1.82-0.77)/12 \text{ neighbors}\}$. This is a reasonable estimate.

Since increasing the size of supercells does not look promising, further accuracy requires employment of accurate interatomic potentials. In our established procedure for extracting interatomic potentials we first extract potentials for pure elements, and then use them to extract cross-type atomic potentials. Fe_3Al has DO_3 structure which is an "ordered BCC" structure, therefore we anticipate that we need 3-body potentials to model it.

At present, we have extracted consistent 3-body atomic potentials for iron using results of non-spin polarized calculations. This procedure involved building a database of internal energies (LMTO calculations) of various deformations of a 4-atom unit cell of iron. The extracted atomic potentials closely reproduced the entire database. We are in the process of extracting potentials based on spin-polarized calculations. We are conducting molecular dynamics (MD) tests of the interatomic potentials we have at present, especially considering their ability to reproduce physical and mechanical properties of iron.

III. EXPERIMENTAL COMPONENT

A. Summary

In this research, environmental assisted fracture behavior of three iron aluminides (designated as FA-186, FA-187, and FA-189, with and without various alloy additives such as Zr, C, or B) were investigated to study the effect of alloy additives to fracture behavior, in particular, the improvement of resistance to moisture-induced hydrogen embrittlement. Crack growth tests of the iron aluminides subjected to constant tensile loading in moist air, oxygen or water environment were conducted. Moire interferometry was applied to obtain full-field crack-tip displacements, from which crack extension, crack growth rate, and stress intensity factor were evaluated. Evidence of moisture embrittlement for the three iron aluminides was observed. We found that the presence of a small amount of moisture is sufficient to cause embrittlement. The comparative tests also showed that specimens in B₂ condition have slightly better crack resistance than those in DO₃ condition. Test results indicated that FA-187 and FA-189 are extrinsically more brittle than FA-186 in both B₂ and DO₃ conditions. SEM fractographic and optical microstructural analyses relevant to failure analysis of the iron aluminides are also discussed below. Based on our findings, we suggest that increasing the grain size of FA-187 and FA-189 should increase their resistance to hydrogen embrittlement.

B. Materials

Alloys used in this study were fabricated at Oak Ridge National Laboratory (ORNL) by vacuum induction melting and casting into graphite molds. The ingots were then hot forged (two passes, 25% per pass) at 1000°C followed by hot rolling at 800°C for seven passes (15% per pass) to produce a finished plate thickness of 6.35 mm. The finished plates were either heat

treated at 900°C for one hour then air quenched to produce partially ordered B2 structure or heat treated at 900°C for one hour followed by 550°C for 72 hours then air quenched to produce DO₃ structure. Table 1 shows the alloy composition of FA-186, FA-187 and FA-189, and Figure 3 shows typical microstructures of the alloys. The grain sizes of FA-186, FA-187 and FA-187 are 193μm, 72μm, and 75μm, respectively. They were measured using the linear intercept method.

Singe-edge-notched (SEN) specimens were cut from the plates using an EDM machine and specimen surfaces were hand-polished with fine grid sandpapers followed by thorough solution cleaning. Figure 4 shows the test specimen geometry. The notch of each specimen was cut using 0.1 mm diameter EDM wire with notch direction parallel to the rolling direction.

C. Test Apparatus

An environmental materials testing chamber was constructed to conduct crack growth tests of iron aluminides using moire interferometry and under controlled gas content (air, argon, hydrogen gas or dry oxygen) environments. The chamber can also be filled with water to conduct crack growth tests in water. Figure 5 shows a schematic drawing of the environmental test chamber. For crack growth tests under oxygen environment, the chamber was first pumped down to about 10⁻¹ torr, and oxygen with research purity of 99.999% was used to fill the chamber at a pressure of 1.2 atm. The pumping and filling cycle was done 4 or 5 times before the crack growth test. Additionally, a moisture trap with absorption capacity of 25 grams H₂O was put inside the chamber to reduce the residual moisture in the test environment. It should be noted that unless the chamber is pumped down to a high vacuum state (say 10⁻⁶ torr), some amount of residual moisture is still present in the chamber, particularly, near the EDM-cut crack tip region. We did a preliminary residual gas measurement of the chamber under the above mentioned "oxygen" environment using RGA and estimate that the partial pressure of residual moisture and hydrogen is about 0.25-0.04 and 0.06-0.05 times that of the atmospheric air, respectively.

Moire interferometry is capable of high sensitivity full-field surface deformation measurement [5] (typical measurement sensitivity can range from 0.1 μm/fringe to 1.6 μm/fringe). For a moire interferometry test, a specimen grating is bounded onto the specimen surface to assume the same surface deformation of the specimen. Two collimated laser lights are then directed to shine on the specimen grating, and the reflected laser wavefronts generate the

moire fringes which represent in-plane surface deformation contours and can be evaluated through $u=N_x/2f$ and $v=N_y/2f$ where u and v are the in-plane surface displacements, N_x and N_y are the moire fringe orders along x - and y -direction, respectively, and f is the specimen grating frequency. Recently, we have demonstrated [6,7] that moire interferometry can be applied to study environmental assisted cracking problems. Figure 6 shows a schematic drawing of the optical setup for moire interferometry test with the environmental chamber mounted on the optical bench.

D. Results and Discussion

Table 2 shows the test matrix. As shown, a total of sixteen comparative crack growth tests under various environments were conducted. Figures 7 to 11 show representative moire fringe patterns of alloys FA-186 and FA-189 under air, oxygen or water environment from this research. 600 lines/mm specimen gratings were used and thus the moire fringes shown in the figures have fringe sensitivity of $0.8 \mu\text{m/fringe}$. Figure 12 shows representative SEM fractographs of alloys tested in oxygen environments. Figure 13 shows measured crack extension versus time, and Figure 14 shows measured crack growth rate versus applied stress intensity factor.

For alloy FA-186 tested in air or oxygen conditions, multiple cracks were formed as soon as the initial crack started to grow (Figures 7 and 8). The extension of these multiple microcracks formed an expanding damage zone which grew stably leading to final failure. This feature of extensive multiple microcracking was not found for alloys FA-187 and FA-189; instead, a clear single crack growth pattern was observed (e.g. Figures 9 and 10).

As shown in Table 2 and with the typical moire fringes shown in Figure 11, for alloys FA-186, FA-187 and FA-189 tested in water, an environment-accelerated effect of hydrogen embrittlement was observed and resulted in lower fracture toughness and fast fracture behavior, i.e. no slow stable crack growth was observed compared to the specimens tested in air or oxygen environment.

Test results in Table 2 also show that with the same applied stress intensity factor, specimens tested in oxygen lasted 3 to 9 times longer than those tested in air, indicating the effect of moisture embrittlement for all three iron aluminides. Also, specimens with partially ordered B2 condition have slightly better fracture resistance than those in DO_3 condition for all

three alloys. However, the susceptibility of hydrogen embrittlement varies among the test alloys. As shown in Figures 13 and 14, crack growth tests of the ternary alloy FA-186 tested in air showed a smaller amount of increased crack growth rate than those tested in oxygen; only crack growth tests in water showed a significant effect of hydrogen embrittlement for FA-186. This is not the case for alloys FA-187 and FA-189, which showed substantially faster crack growth rate in air than in oxygen.

Overall, our test results indicate that among the three alloys, the ternary alloy FA-186 has the best fracture resistance, highest fracture toughness and least sensitivity to hydrogen embrittlement (Table 2). This finding is quite surprising since the purpose of micro-alloying addition ($0.5\% \text{ Zr} + 0.05\% \text{ C}$ for FA-187) or ($0.5\% \text{ Zr} + 0.05\% \text{ C} + 0.005\% \text{ B}$ for FA-189) is to enhance its resistance to hydrogen embrittlement. (It should be noted, however, that recently Alven and Stoloff [8] conducted fatigue crack growth tests of several iron aluminides including FA-186 and FA-187 under air, vacuum or 1.3 atm hydrogen environment, and their results showed that FA-187 has lower fatigue crack growth rate than that of FA-186. Furthermore, tensile tests by Alven and Stoloff [9] also indicate that FA-186 is less sensitive to environmental embrittlement, as compared with FA-187.) It is known that hydrogen embrittlement is very complex and sensitive to many casting and metallurgical parameters, such as strain rate, grain size, notch geometry, deformation mode (static vs cyclic), etc. In order to resolve the discrepancy among the crack growth tests under static, tensile tests and fatigue tests, further research is certainly needed to evaluate the alloying effects on moisture induced environmental embrittlement in iron aluminized alloys.

Failure characteristics of the tested alloys are tabulated in Table 3. We roughly divided the fractured surface into three areas corresponding to the changes of failure mode. For alloys FA-187 and FA-189, initial crack growth always started with intergranular mode (Figure 12) then shifted to mixed intergranular/transgranular cleavage mode and finally to transgranular failure. As the moisture content was increased in the test environment (i.e. from oxygen to air to water), we observed increased intergranular failure pattern in area 2.

For ternary alloy FA-186, except for the one tested in water which showed intergranular mode in area 1, transgranular cleavage is the dominate failure mode. However, the one tested in air had rougher cleavage facets (i.e. more tilt and twist boundaries). In a hydrogen-free environment cleavage generally takes place along crystallographic planes with the lowest

packing density and thus resulted in larger cleavage facets. On the other hand, in a hydrogen-containing environment, hydrogen embrittlement has been proposed to be associated with dislocation transport of hydrogen [10], which occurs along crystallographic planes with the highest packing density, i.e. resulting in more rougher cleavage facets as we observed in the fractographic analyses (Figure 12).

Again as shown in Tables 2 and 3 and Figures 12 to 14, our test results indicated that FA-187 and FA-189 are extrinsically more susceptible to environmental embrittlement than FA-186. As discussed in ref. 11, the level of zirconium addition needs to be carefully controlled. Some amount of zirconium addition (say about 0.1%) is beneficial to promote scale adhesion for protection against corrosion in harsh environment. However, too much zirconium addition (such as 0.5% Zr in FA-187 and FA-189) may produce extrinsically brittle iron aluminide alloys.

E. Conclusions

Comparative crack growth tests of FA-186, FA-187 and FA-189 iron aluminides under air, oxygen or air environment were conducted, and the results showed substantial differences of crack-tip deformation profile and crack growth rate among the alloys. Test results also showed that with the same applied stress intensity factor, specimens tested in oxygen lasted 3 to 9 times longer than those tested in air, indicating the effect of moisture embrittlement for all three iron aluminides. Alloys with partially ordered B2 structure have slightly better fracture resistance than those in DO₃ structure. Our test results indicated that FA-187 and FA-189 containing Zr, C and B are extrinsically more brittle than FA-186. Larger grain sizes of FA-187 and FA-189 should increase their resistance to hydrogen embrittlement.

The purpose of adding a small amount of boron in FA-189 was to improve the strength of grain boundaries so that intergranular failure can be minimized. However, our test results indicate just the opposite. This may be related to the grain size effect. As shown in Figure 3, with microalloying of Zr, and/or B, FA-187 and FA-189 have much smaller grains. Grain boundary fragility is important in controlling the environmental embrittlement. It is well-known that grain boundaries act as the source or sink of dislocation motion. Segregation of Zr or B to grain boundaries lowers the energy barrier and reduces the distortion difference between neighboring grain boundaries, i.e. facilitating the slip transfer across the grain boundary. We suggest that the grain boundaries of FA-187 and FA-189 may be of low energy type compared

to that of FA-186 and thus intrinsically FA-187 and FA-189 should have higher fracture toughness than that of FA-186. However, our results indicate that, due to their smaller grain sizes, FA-187 and FA-189 are extrinsically much more susceptible to environmental embrittlement. Based on our finding, we suggest that ORNL should try to produce larger grain sizes of FA-187 and FA-189 to increase their resistance to hydrogen embrittlement. Further studies are needed to verify this suggestion.

IV. PUBLICATIONS AND PRESENTATIONS

1. B.S.-J. Kang, Q. Yao and B.R. Cooper, "Evaluation of the Intrinsic and Extrinsic Fracture Behavior of Iron Aluminides", Proceedings of the Tenth Annual conference On Fossil Energy Materials, pp. 405-417, Knoxville, TN, May 14-16 1996.
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Table 1 Chemical Composition of Iron Aluminides (at %)

Alloy	Fe	Al	Cr	Zr	C	B
FA-186	balance	28	5			
FA-187	balance	28	5	0.5	0.05	
FA-189	balance	28	2	0.5	0.05	0.005

Table 2 Test Matrix

Iron aluminide	Specimen	Structure Condition	Initial Crack	Environment	Initial K $MPa\sqrt{m}$	Lasting Time
FA-186	86-1	B2	FP	Air	36.9	7 min
	86-5	B2	FP	Dry Oxygen	36.8	21 min
	86-10	DO ₃	EDM	Air	25 28.3	94 min ^c 1 min
	86-9	DO ₃	EDM	Dry Oxygen	25 28.7	19 hr ^d 21 min
	86-w1	DO ₃	EDM	Water	13.35 22.12	2 hr ^d 8 second
FA-187	87-1	B2	EDM	Air	25	3.5 min
	87-5	B2	EDM	Dry Oxygen	25	15 min
	87-8	DO ₃	EDM	Air	25	2 min
	87-7	DO ₃	EDM	Dry Oxygen	25	18 min
	87-w1	DO ₃	EDM	Water	15.43	46 second
FA-189	89-2	B2	EDM	Air	17.36	7 min
	89-1	B2	EDM	Dry Oxygen	17.36	20 min
	89-7	DO ₃	EDM	Air	17.36	3 min
	89-6	DO ₃	EDM	Dry Oxygen	17.36	12 min
	89-w1	DO ₃	EDM	Water	13.1	60 second
	89-w2	DO ₃	EDM	Water	20.76	8 second

^a All tests were conducted at room temperature;

^b FP: Fatigue Pre-cracked; EDM: Electron-Discharge Machining;

^c Slow crack growth;

^d Almost no crack growth.

Table 3. Failure mode and illustration of the fractured surfaces studied

Alloy	Specimen	Structure Condition	Environment	Area 1	Area 2	Area 3
FA-186	86-1	B2	Air	mixed	mixed	transgranular
	86-5	B2	Dry Oxygen	mixed	transgranular	transgranular
	86-10	DO ₃	Air	mixed	mixed	transgranular
	86-9	DO ₃	Dry Oxygen	mixed	transgranular	transgranular
	86-w1	DO ₃	Water	intergranular	mixed	transgranular
FA-187	87-1	B2	Air	intergranular	mixed	mixed
	87-5	B2	Dry Oxygen	intergranular	mixed	transgranular
	87-8	DO ₃	Air	intergranular	mixed	transgranular
	87-w1	DO ₃	water	intergranular	intergranular	mixed
	87-7	DO ₃	Dry Oxygen	intergranular	transgranular	transgranular
FA-189	89-2	B2	Air	intergranular	mixed	transgranular
	89-1	B2	Dry Oxygen	intergranular	transgranular	transgranular
	89-7	DO ₃	Air	intergranular	mixed	transgranular
	89-6	DO ₃	Dry Oxygen	intergranular	transgranular	transgranular
	89-w2	DO ₃	water	intergranular	intergranular	mixed

Fig 1. Structure of $\text{DO}_3 \text{Fe}_3\text{Al}$ indicating the two types of iron sites. A DO_3 structure may be represented as the FCC lattice with 4 atoms per unit cell – atom of aluminum at the origin, one atom of iron (type A) at $(1/2, 0, 0)$, and two crystallographically identical atoms of iron (type B) at $(1/4, 1/4, 1/4)$ and $(3/4, 1/4, 1/4)$. Iron of type A has 8 iron atoms (type B) as nearest neighbors at the distance $d = \frac{\sqrt{3}}{4}a$, while iron of type B has 4 iron atoms and 4 aluminum atoms as nearest neighbors at the same distance.

L-projected DOS

Iron Type A

Type B

Fig. 2. L-projected density of states
for the two types of iron sites.

Fig. 3 microstructure of FA-186,
FA-187 and FA-189

Fig. 4 Single-edge-notched specimen

Fig. 5 Schematic drawing of the environmental testing chamber

Fig. 6 Optical setup for moire interferometry test

Alloy FA-186
Room temp, Air $K=36.8 MPa\sqrt{m}$

Fig. 7 u- and v- displacement fields of alloy FA-186 SEN specimen tested in air

Alloy FA-186
Room Temp, oxygen $K=36.8 \text{ MPa}\sqrt{m}$

Fig. 8 u- and v- displacement fields of alloy FA-186 SEN specimen tested in dry oxygen

Alloy FA-189
Room Temp, Air $K=17.06 \text{ MPa}\sqrt{m}$

Fig. 9 u- and v- displacement fields of alloy FA-189 SEN specimen tested in air

Alloy FA-189
Room Temp, Oxygen $K=17.36 \text{ MPa}\sqrt{m}$

Fig. 10 u- and v- displacement fields of alloy FA-189 SEN specimen test in dry oxygen

V-field, $K=22.12 \text{ MPa}\sqrt{m}$

5mm

V-field $K=20.76 \text{ MPa}\sqrt{m}$

1 sec

5 sec

7 sec

FA-186(specimen 86-w1)

1 sec

3 sec

5 sec

7 sec

FA-189 (specimen 89-w2)

Fig. 11 v-displacement fields of FA-186 and FA-189 SEN specimens tested in water

(Note: as shown in Table 2, another FA-189 SEN specimen (89-w1) was tested in water under $K=13.1 \text{ MPa}\sqrt{m}$ load which caused immediate stable crack growth to failure that lasted about 60 seconds. As for the FA-186 specimen(86-w1) which was first applied $K=13.35 \text{ MPa}\sqrt{m}$ load and, after two hours, no change of crack tip displacement field and no crack growth were observed, however, the applied load was then increased to $K=22.12 \text{ MPa}\sqrt{m}$ that caused fast fracture as shown above.

Fig. 12 Representative fractographies for FA-186, FA-187 and FA-189 in Air

FA-186

FA-187

FA-189

Fig. 13 Crack Extension Versus Time

Fig. 14 Environmental crack growth rate for FA-186, FA-187 and FA-189 as a function of applied stress intensity factor, k

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