WELDABILITY OF POLYCRYSTALLINE ALUMINIDES
Final Report

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A. A. Fasching, R. P. Burt, G. R. Edwards and S. A. David

July, 1996

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CENTER FOR WELDING, JOINING, AND COATINGS RESEARCH
Colorado School of Mines
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Abstract

When gas-tungsten arc welded, iron aluminides form a coarse fusion zone microstructure which is susceptible to hydrogen cracking. Magnetic arc oscillation and weld pool inoculation were implemented to refine the fusion zone microstructure in iron aluminide alloy FA-129 weldments. Magnetic arc oscillation effectively refined the fusion zone microstructure, and slow strain rate tensile tests showed fine-grained microstructures to be less susceptible to hydrogen cracking. However, magnetic arc oscillation was found to be suitable only for well-controlled fabrication environments. Weld pool inoculation offers a potentially more robust refinement method. Titanium inoculation was also shown to effectively refined the fusion zone microstructure, but weldment properties were not improved using this refinement method. The effect of titanium on the size, shape and distribution of the second phase particles in the fusion zone appears to be the cause of the observed decrease in weldment properties.

Introduction

Interest in developing polycrystalline, long-range ordered iron aluminide alloys for high-temperature applications is great because of unique properties such as superior resistance to oxidation and sulfidation in gaseous environments.

Iron aluminides produced by conventional ingot metallurgy have typically manifested low ambient temperature ductilities. Efforts to understand and improve their ductility through control of grain structure, alloying additions and material processing have shown that room temperature ductility can be increased significantly by chromium additions up to 6 atomic percent. The chromium additions improved the ductility by providing a protective oxide layer that minimized environmental embrittlement, thus increasing the cleavage strength and lowering the antiphase boundary (APB) energy [1]. Partially recrystallized microstructures have also demonstrated increased ductilities in moisture-free environments [2].

Recent research on iron aluminide weldability has revealed that the mechanical behavior of weldments is sensitive to both composition and the welding process. Preliminary tests on binary alloys containing 1.0 weight percent TiB_2 and welded by the gas-tungsten arc (GTA) process showed liquation or hot cracking in the fusion zone. This was attributed to the dissolution of TiB_2 in the fusion zone and re-precipitation at the dendrite boundaries [3]. Alloys not containing TiB_2 showed evidence of cold cracking during or after welding by the GTA process. The cold cracking problem has been attributed to diffusible hydrogen reduced from the moisture in the air, and subsequently incorporated into the molten weld pool. Delayed cracking of the fusion zone was frequently observed. If these alloys are to find practical applications, the cold cracking mechanism must be better understood.

The mechanism of hydrogen embrittlement in iron aluminides has been explained [4] as a reaction between aluminum and water vapor at the solid-vapor interface. The chemical reaction responsible for the liberation of hydrogen in the presence of iron aluminide is:

Although Al_2O_3 is a product of this reaction, the film is assumed to be porous and nonprotective. Thus, atomic hydrogen can interact directly with the intermetallic compound.

The weakening of bonds in iron aluminides (decohesion mechanism) has been proposed to explain hydrogen effects in intermetallics; however, direct experimental measurements are lacking. Evidence for decohesion in iron aluminides is largely based upon the fracture appearance of hydrogen-induced and moisture-induced cracks [4]. Li and Liu [5] have suggested that the Cottrell mechanism for the formation of an edge $\langle 100 \rangle$ crack nucleus for two mixed $\langle 111 \rangle$ dislocations can be enhanced by hydrogen, thus causing $\langle 100 \rangle$ cleavage of ferritic steels. A similar mechanism may operate in B2 intermetallics such as FeAl, thereby leading to $\langle 100 \rangle$ cracks in the presence of hydrogen. However, it is also clear that hydrogen can cause intergranular fracture under certain conditions in both FeAl and Fe_3Al . Hydride formation also is a mechanism of hydrogen embrittlement in intermetallics. Hydrides have been identified in embrittled Ti_3Al and TiAl [6]. There is no evidence, however, for hydride formation in iron aluminides.

The overall mechanical properties of a weldment are determined by the characteristic properties of the individual microconstituents present in the fusion zone and the heat-affected zone (HAZ). The microstructures produced during welding are a function of the welding parameters such as: current, voltage, travel speed, thickness of material, material composition and shielding gas.

The grain size of a polycrystalline material plays an important role in the mechanical properties observed for the material. The Hall-Petch equation was the first to relate grain size to flow stress and fracture stress. This model was based on dislocations piling up at grain boundaries, and quantified how yield stress increased with decreasing grain size [7]. Other mechanical properties, such as fracture toughness, are also affected by grain size. Hence, grain refinement is often important in improving the ductility of a material. Welding of iron aluminides results in a coarse fusion zone grain structure which is susceptible to environmental embrittlement. Refining the fusion zone grain structure should lessen the susceptibility of the material to environmental embrittlement.

The columnar grains in the fusion zone usually grow epitaxially from grains in the HAZ, and retain the same orientation and similar size. Nucleation of grains in the fusion zone

can also occur by other means such as dendrite fragmentation, grain detachment, heterogeneous nucleation or surface nucleation. Dendrite fragmentation occurs when dendrites in the mushy region of the fusion zone are broken off by convective forces and are carried into the weld pool. In the weld pool they may act as nuclei for new grains. Grain detachment is similar, in that partially melted grains from the HAZ immediately adjacent to the weld pool are also broken off by the convective forces. In the weld pool, they do not melt back, but rather continue to grow, acting as grain nuclei. Heterogeneous nucleation occurs when the weld pool is inoculated with particles that remain solid at very high temperatures. These solid particles act as sites for heterogeneous nucleation. Finally, surface nucleation can occur if the weld pool surface is supercooled by a stream of cooling gas. Solid nuclei form at the surface of the weld pool.

There are several mechanical methods available for fusion zone grain refinement. Inoculation is a technique that promotes heterogeneous nucleation by adding nucleating agents to the liquid metal. Typically, the inoculants have a high melting point, with a crystal structure and lattice parameter similar to that of the weld metal. Weld pool stirring, arc oscillation, and arc pulsation result in dendrite fragmentation or grain detachment. Weld pool stirring results when the weldment is vibrated during welding. Magnetically oscillating the arc column using a single- or multi-pole magnetic probe, mechanically vibrating the welding torch, or pulsing the welding current can perturb the solidification in the weld pool and refine the fusion zone.

Magnetic arc oscillation was the method chosen for grain refinement of iron aluminide alloy FA-129 during GTA welding in Fasching's study. Arc oscillation has been used previously to solve solidification cracking problems in weldments. Kou et al. [8,9] employed magnetic arc oscillation to reduce weld solidification cracking in aluminum alloys. Transverse and circular oscillation proved the most effective in reducing solidification cracking, a result attributed to significant grain refinement in the fusion zone. Longitudinal oscillation did not result in any grain refinement in the fusion zone [8]. Intermediate frequencies and low amplitudes did not result in any grain refinement in 5052 and 2014 aluminum weldments [9]. Tseng and Savage [10] found similar results for employing magnetic arc oscillation to reduce hot cracking in HY-80 steel.

Fasching was able to achieve significant fusion zone refinement utilizing magnetic arc oscillation. This study showed that the refined fusion zone was less susceptible to hydrogen cracking and more tolerant of high hydrogen concentration environments. However, the magnetic arc oscillation process was found to be sensitive to changes in the welding environment. Unique oscillation parameters were required for each welding environment experienced.

Given the improved weldability resulting from the fusion zone refinement, Burt studied weld pool inoculation as a method to refine the fusion zone microstructure. Inoculation was speculated to be less sensitive to changes in the welding environment. Weld pool inoculation has been employed as a method to reduce hot cracking susceptibility by other researchers. Masuda et al. [11] added zirconium to aluminum welds and reduced hot cracking susceptibility due to the refined microstructure. Similarly, Nordin et al. [12] added yttria to titanium welds, resulting in a refined fusion zone microstructure and reduced susceptibility to hot cracking. A refined microstructure improves the weldability of materials, and ultimately should improve the mechanical properties of the weldment.

Experimental Procedure

Material Processing

The material for this investigation was vacuum arc remelted ingots provided by Oak Ridge National Laboratory. The nominal composition of alloy FA-129 is shown in Table 1. The ingots were extruded and hot rolled at a temperature of 900°C to a thickness of 3.2 millimeters and then warm rolled at 650°C to a nominal thickness of 0.76 millimeters. Welding samples were sheared to 50mm x 76mm coupons. Metallographic samples were sheared to 50mm x 50mm coupons. All samples were annealed at 650°C for two hours prior to welding. The final microstructure consisted of recovered and unrecrystallized grains.

Table 1. Iron aluminide alloy FA-129 composition.

	Fe	Al	Cr	Nb	C
wt. pct.	66.3	28.0	5.00	0.50	0.20
at. pct.	77.7	15.9	5.45	0.97	0.05

The hot-rolling oxide on the surface of the as-received material was removed using a solution of 10 parts water, 1 part nitric acid and ½ part hydrofluoric acid. After pickling, samples were cleaned with methanol.

Magnetic Arc Oscillation

An experiment was developed to test the resilience of the refined fusion zone microstructures to hydrogen embrittlement in water vapor atmospheres. Weldments were fabricated in pure argon, then tensile tested at a slow strain rate in argon containing varying levels of water vapor. Four different weldments were produced using the welding and oscillation parameters in Table 2. Different heat inputs and oscillation parameters were used to produce four unique microstructures, which were then evaluated regarding their resistance to hydrogen embrittlement.

Table 2. Welding Parameters Used to Produce Fusion Zones of Differing Grain Sizes.

Microstructure Type	Current (amps)	Arc Gap (mm)	Heat Input (J/mm)	Oscillation Frequency (Hz)	Oscillation Amplitude Setting	Oscillation Orientation to Welding Direction
Microstructure A	38	1.5	81	--	--	--
Microstructure B	31	1.5	73	--	--	--
Microstructure C	31	1.5	73	10.0	250	90°
Microstructure D	31	1.5	73	10.0	250	45°

A PowCon two-pole magnetic arc oscillator was used to deflect the arc. Individual controls independently adjusted the frequency and amplitude of the wave. Both the arc position and dwell controls were set at a neutral position (along the centerline) for these experiments. The frequency to amplitude ratio was determined from the waveform, and the amplitude setting was converted to distance of deflection using travel speed and the relation to frequency. The correlation between amplitude setting and arc deflection is known to vary, depending on the power supply, oscillation head, and the welding substrate.

Weld Pool Inoculation

For the inoculation study, a groove was machined into the coupons using a band saw with no lubrication. The coupons were given a final cleaning with methanol, and titanium powder (99.5%, <44 μ m) was then deposited into the groove. A thin 0.43mm strip of alloy FA-129 was used to encapsulate the powder-filled groove. The final sample configuration is shown in Figure 1.

As in the magnetic arc oscillation study, GTA welding was performed in a pure argon environment to produce samples for slow strain rate tensile testing in environments of varying water vapor concentrations. Initial work centered on quantifying the effects of welding parameters and titanium concentration on the fusion zone microstructure. Table 3 summarizes the matrix used. From the initial microstructural characterization, welding parameters and titanium concentrations were chosen to produce three unique fusion zone microstructures for slow strain rate tensile testing.

Table 3. Range of Test Variables.

	Low	High
Heat Input (J/mm)	118	142
Titanium Addition (mg/10mm)	2	6

Figure 1. Schematic diagram of welding coupon used for inoculation study.

Slow Strain Rate Tensile Testing

The weldments were loaded in uniaxial tension transverse to the welding direction at a strain rate of 2.8×10^{-6} /s. Iron aluminides are embrittled when tested at strain rates slower than 10^{-3} /s. The slowest reasonable strain rate was selected to maximize the time for hydrogen diffusion.

The slow strain rate tensile tests were performed with an MTS 810 Material Test operating in strain control (a one-in. extensometer with a $\pm 1.5\%$ range card monitored displacement). The specimen geometry used for the magnetic arc oscillation study is shown in Figure 2a. A reduced section was not necessary for these specimens because the fusion and heat-affected zones were consistently weaker than the base material. However, a different specimen configuration was required for the inoculation study. In initial tests, fracture did not consistently occur within the fusion zone, so it was necessary to grind the fusion zone flat as well as to grind a reduced section into the specimen at the fusion zone (Figure 2b). Epoxy beads were added to both samples in order to prevent slipping of the extensometer blades. Because a precise water vapor concentration could not be repeated, duplicate tests occurred within water vapor concentration ranges of ± 1000 ppm. At the higher levels of water vapor, control of the atmosphere was limited to ± 500 ppm. Load and strain at fracture were recorded for each sample.

Tensile testing was conducted in an environmental chamber designed specifically for the MTS system. For the lowest water vapor concentration tests, the chamber was purged with grade 5 (99.999%) argon until less than 200ppm moisture was present, and argon was continuously passed through the chamber during the test. A Nyad Series 300 moisture/oxygen analyzer was used to measure moisture content. For tests in water vapor environments, argon was bubbled through distilled water and routed through the chamber until the desired water vapor concentration was achieved. The chamber was then allowed to equilibrate prior to testing.

Metallography

Specimens were prepared for metallographic observation using standard metallographic techniques. For microstructural observation, samples were etched in a

(a)

(b)

Figure 2. Sample geometry for slow strain rate tensile tests. a) Magnetic arc oscillation study. b) Weld pool inoculation study.

solution of 60ml methanol, 20ml hydrochloric acid, and 40ml nitric acid. The average fusion zone grain size was determined using a Leco image analysis system to measure the length, width, and thickness of the fusion zone grains. The average grain size reported is the average of the three measurements.

For inclusion analysis, an etchant of 96ml water, 2ml nitric acid, and 2ml hydrofluoric acid was used to darken the second phase particles. Using a scanning electron microscope, micrographs were taken from several locations in the fusion zone and point counting was performed to determine the fraction of inclusions in the fusion zone. Inclusions were classified as either being located in the matrix or at a grain boundary.

Results and Discussion

Magnetic Arc Oscillation

The weld microstructures developed in this study are shown in Figure 3. The welds of the unoscillated, high heat input microstructure shown in Figure 3a consisted of large columnar grains. The second unoscillated microstructure, shown in Figure 3b, also exhibited a columnar grain structure. In this lower heat input weld, however, the grains were not as large. The elongated grains in this transversely oscillated fusion zone in Figure 3c appeared similar to those of the unoscillated fusion zone in Figure 3b, but no clear centerline was visible. Oscillating the arc at 45 degrees to the welding direction resulted in a nearly equiaxed, fine-grained fusion zone (Figure 3d) that also did not show a clear centerline or fusion line.

Fractographs for weldments tested in ~6000ppm water vapor are shown in Figure 4. The fracture surfaces were either transgranular cleavage or a mixed mode of intergranular and transgranular cleavage. No variation in fracture morphology was seen between samples tested in pure argon versus those tested in water vapor at any level, as shown in Figure 5.

Fracture strength versus moisture content was plotted for welds representing each fusion zone grain structure, as shown in Figure 6. Well-defined regimes based on fusion zone grain size were evident. Data regression showed a linear relationship between a decreasing fracture stress and an increasing water vapor concentration. The values of the correlation coefficients (R) ranged from 0.78 to 0.99. The percent strain at fracture versus the moisture

Figure 3. Weldment microstructures from magnetic arc oscillation study used in slow strain rate tensile testing. a) Microstructure A (H.I. = 81 J/mm), b) Microstructure B (H.I. = 73 J/mm), c) Microstructure C (H.I. = 73 J/mm, 90 degrees at Freq = 10Hz, Amp. = 0.8mm), and Microstructure D (H.I. = 73 J/mm, 45 degrees at Freq.=10Hz , Amp.=0.8mm).

(a)

(b)

(c)

(d)

Figure 4. Fracture surfaces for welds tested in ~6000 ppm water vapor for a) Microstructure A, b) Microstructure B, c) Microstructure C, and d) Microstructure D.

(a)

(b)

(c)

(d)

Figure 5. Fracture surfaces for Microstructures B exhibiting cleavage tested in atmospheres containing a) pure argon, b) 1350 ppm H_2O , c) 3200 ppm H_2O , and d) 5770 ppm H_2O .

Figure 6. Fracture strength versus water vapor content in the atmosphere showing the effect of fusion zone grain size on the mechanical properties of the weldment.

content in the atmosphere was also plotted, as shown in Figure 7. These plots were less definitive than the fracture strength data, but ductility was observed to decrease with increasing water vapor concentration. The most refined fusion zone showed the highest elongation at fracture.

Slow strain rate tensile testing revealed that welds containing fine-grained fusion zones resisted hydrogen embrittlement in the presence of water vapor better than welds with coarse-grained fusion zones. Microstructure D, the smallest and most equiaxed fusion zone, exhibited the highest fracture strength and the most ductility at fracture.

Taking constant water vapor concentrations from the linear fits in Figure 6, the fracture strength was plotted as a function of the inverse square root of fusion zone grain size, as shown in Figure 8, for four water vapor levels. A first order polynomial equation was fit to the data for each water vapor concentration, and the correlation coefficient (R) is shown. The data for the coarsest fusion zone, Microstructure A, fall below the linear regression line. Microstructure A had a very large aspect ratio and an obvious centerline. The effect of the directional grains and the centerline was lessened by averaging the grain size from three orthogonal dimensions. The data for Microstructure C ($172\text{ }\mu\text{m}$) also fall below the linear regression line. In this case, failure occurred in the HAZ, causing the measured fracture strength to be less than that of the actual weldment.

The slopes of these lines in Figure 8 increased with water vapor concentration, suggesting that k_F , the slope in the Hall-Petch plot, was a function of water vapor concentration. The slope varied from $77\text{ MPa}\cdot\text{mm}^{1/2}$ in pure argon to $97\text{ MPa}\cdot\text{mm}^{1/2}$ in argon containing 10,000ppm water vapor. However, this small change in slope is not significant relative to the experimental variance of the data.

The y-intercept decreased as water vapor concentration increased, indicating that the friction stress, σ_0 , was also a function of water vapor concentration. The friction stress ranged from 448 MPa in pure argon to 327 MPa in argon containing 10,000ppm water vapor. Figure 9 shows that σ_0 was a stronger function of water vapor concentration than k_F . The decrease in friction stress was sufficiently large that the change could not be attributed to the experimental error.

Figure 7 Percent elongation at fracture for weldments of different fusion zone grain size tested in atmospheres of varying levels of water vapor.

Figure 8. Hall-Petch plot for iron aluminide alloy FA-129 weldments tested in varying water vapor atmospheres.

Figure 9. k_F and σ_o as a function of water vapor concentration for iron aluminide alloy FA-129 weldments.

The basic form of the Hall-Petch equation for brittle fracture is:

$$\sigma_F = \sigma_o + k_F d^{-1/2} \quad (2)$$

where σ_F is the fracture stress, d is the grain size, σ_o is the sum of contributions to the fracture stress other than grain boundary barriers, and k_F is the slope of the straight line obtained when σ_o is plotted against $d^{-1/2}$. The value k_F has been called the locking parameter, which measures the relative hardening contribution of the grain boundaries. When considering microcrack nucleation at dislocation pile-ups, the physical meaning for k_F has been stated to be [51]:

$$k_F = (\pi\mu\gamma_B)^{1/2} \quad (3)$$

where μ is the shear modulus and γ_B is the surface energy. Using the values for σ_o and k_F determined experimentally in the slow strain rate tests, the Hall-Petch equation becomes:

$$\sigma_F = (473 - 15M^{1/2}) + (70 + 0.25M^{1/2})d^{-1/2} \quad (4)$$

where M is the water vapor concentration of the atmosphere in parts per million (ppm). The results of the slow strain rate tests showed that fracture strength depended not only on grain size, d , but also on water vapor concentration in the testing atmosphere.

A number of investigations of the effects of grain size on mechanical properties of ordered alloys have shown that most obey the Hall-Petch relation for yielding and flow. Schulson and Barker [13] demonstrated that the tensile ductility of brittle NiAl polycrystals was improved by refining the grains to sizes smaller than a critical value. This improvement in tensile ductility was explained on the basis that the stress required to nucleate microcracks was sufficient to cause unstable crack propagation in the coarse-grained materials, but not in the fine-grained materials. Unstable crack propagation occurred in the fine-grained material only after plastic deformation elevated the flow stress to exceed a critical value. As a result, tensile ductility increased with decreasing grain size below a critical value. Despite the

ductility enhancement, grain size was found to have little effect on the fracture mode in NiAl. Both the coarse-grained and fine-grained materials were observed to exhibit a mixture of intergranular fracture and transgranular cleavage. This led Schulson and Barker [13] to conclude that the observed ductility enhancement was primarily related to microcrack nucleation and propagation. Chan [14] conducted an investigation to validate the theory that tensile ductility of brittle intermetallic alloys can be enhanced by reducing the critical crack size through grain refinement. The existence of a critical grain size below which NiAl exhibited improved tensile ductility was confirmed. Studies on the fracture behavior of TiAl have shown that this alloy also exhibits improved mechanical properties with a decrease in the material grain size [15].

In FeAl alloys, Baker et al. [16] measured k_F as a function of Fe:Al ratio and found a maximum at the stoichiometric composition. The k_F value showed a sharp initial decrease with increasing iron concentration to a maximum at Fe-45Al, after which k_F increased slightly again. The friction stress, σ_o , showed a similar trend. In their studies, no segregation of either element to the grain boundaries was observed [17] and, thus, the similar trends observed for k_F and σ_o were explained by invoking a dislocation pile-up model [16]. Other researchers [18,19] also measured k_F and σ_o for Fe-40Al; Gaydosh et al. [18] obtained values of 342 MPa and 462 MPa·mm^{1/2} for σ_o and k_F respectively, compared to values of 199 MPa and 720 MPa·mm^{1/2} obtained by Baker et al. [16]. These differences probably reflect differences in heat-treatment, because the concentration of retained vacancies is known to have a great effect on the mechanical properties of FeAl [20]. A comparison of the results of Baker et al. [16] and Gaydosh et al. [18] suggest that an increased vacancy concentration decreases the value of k_F , possibly because the lattice resistance of fine-grained material is less affected by retained vacancies. In the fine-grained material, a greater density of vacancy sinks exists [20]. The results of Baker et al. [16] and Gaydosh et al. [18] also compare well with the data from this study where, in a dry atmosphere, σ_o and k_F were found to be 473 MPa and 70 MPa·mm^{1/2}, respectively.

The mechanism of brittle fracture is usually regarded as a simple elastic extension of atomic bonds up to the point of final separation. A good summary of early thinking by

Griffith and Orowan on this subject has been given by Reed-Hill [21]. The ideal fracture strength may then be determined by considering the force needed to separate two atoms. If a sine function is used to approximate the energy of interaction of two atoms as a function of distance, the theoretical fracture stress derived is:

$$\sigma_{th} = \sqrt{\frac{E\gamma}{a}} \quad (5)$$

where E is Young's modulus, γ is the surface energy, and a is the mean interatomic distance across the fracture plane at zero stress.

Griffith explained why crystalline materials fail at stresses much less than the theoretical strength of the material by assuming that the theoretical stress was reached at the crack tip even though the average stress was still far below the theoretical strength. Griffith found evidence for his theories in testing of glass fibers. Orowan used the same theory as Griffith for his experiments on fracture in mica sheets. To calculate the stress at fracture, Orowan assumed a flat plate containing an elliptical crack. The length of the crack shown is 2c and the applied stress, σ , is perpendicular to the major axis of the ellipse. The calculated tensile stress at the end of the crack, σ_e is given by:

$$\sigma_e = 2\sigma \left(\frac{c}{\rho} \right)^{\frac{1}{2}} \quad (6)$$

If $\sigma_e = \sigma_{th}$, then substituting equation 5 into equation 6:

$$2\sigma \left(\frac{c}{\rho} \right)^{\frac{1}{2}} = \left(\frac{\gamma E}{a} \right)^{\frac{1}{2}} \quad (7)$$

and solving for stress:

$$\sigma_f = \left[\frac{\gamma E}{4c} \left(\frac{\rho}{a} \right) \right]^{\frac{1}{2}} \quad (8)$$

where σ_f is the average applied stress at which the crack will grow, $2c$ is the crack length, and r is the radius of curvature at the end of the crack. This relation is Orowan's version of the Griffith criterion for brittle fracture, and it shows that as the crack length increases, the stress to keep it moving decreases.

The critical stress concentration necessary to nucleate a microcrack is inversely proportional to the square root of grain size in the fusion zone. For a given applied stress, a dislocation pile up will create a lower stress concentration in a fine-grained material than in a coarse-grained material. Hence, under the same loading conditions, a coarse-grained material, such as Microstructure A, will reach a critical stress concentration and nucleate a microcrack sooner than a fine-grained material such as Microstructure D. This theoretical analysis was confirmed experimentally.

Water vapor concentrations, which embrittled the weldments of this study, further complicated the Hall-Petch model. Figure 10 shows how hydrogen is expected to affect the fracture behavior. The bold lines indicate when fracture should occur. Two lines are shown to reflect the mechanical behavior of a given material. A line for flow stress, σ_{Flow} , indicates the applied stress required at a given grain size to initiate plastic flow. In a hydrogen-free atmosphere, a brittle coarse-grained material will fracture at the flow stress because a microcrack will propagate unstably to fracture as soon as it is nucleated. As the microstructure is refined, the flow stress increases. Below a critical grain size, the material no longer fractures at the yield stress. In this case, the microcrack nucleates at the flow stress, but does not grow unstably. The microcrack grows slowly with additional strain until it reaches a critical length for unstable propagation. For this case, fracture occurs at the brittle fracture line, which passes through zero and is dotted for large grain sizes. This line corresponds to the Griffith equation (Equation 8). When hydrogen is added, the behavior is

Figure 10. Schematic of Hall-Petch plot showing the effect of hydrogen on the flow stress (σ_0) and the fracture stress (σ_F).

more complicated. Figure 10 suggests that σ_0 is decreased while the slope of the line (k_F) remains nearly constant with increasing hydrogen concentration. The Griffith line also shows a decreased slope with hydrogen concentration, corresponding to a reduction in the surface energy γ , in the Griffith equation as hydrogen concentration is increased. Hydrogen is hypothesized to reduce the surface energy of the crack by lowering the cohesive strength of the atomic bonds at the crack tip. The change in the value of σ_0 and the slope of the σ_F lines suggests that additional grain refinement is necessary to achieve the mechanical properties observed in hydrogen-free environments when water vapor is present.

The kinetics of hydrogen transport as well as the mechanisms of failure must be considered when evaluating the effect of hydrogen on fracture strength. In general, both internal (solute) hydrogen and external (atmospheric) hydrogen may contribute to fracture [22].

Internal hydrogen reaches the failure location by diffusion and/or dislocation sweeping. Hydrogen transport is characterized by high diffusivities and low activation energies. Hydrogen has been shown to migrate to stress concentrations such as cracks [23]. In addition to transport of hydrogen by diffusion in response to stress gradients, it has been suggested that moving dislocations can transport hydrogen as solute atmospheres [22]. This mechanism, based on a hypothesis by Cottrell [24], requires a large binding energy between the hydrogen solute and the dislocation traps. Experimental evidence for deformation-enhanced mobility has been obtained during studies of the effects of plastic strains on hydrogen evolution. These results suggest that at low strain rates, the range of dislocation transport can exceed that due to diffusion by a factor of 10^4 [22].

In the case of external hydrogen environments, hydrogen may be produced at the crack tip either by adsorption and dissociation of H_2O molecules or by the release of hydrogen from a chemical reaction. For the case of iron aluminides embrittled by water vapor in the atmosphere, the hydrogen is thought to enter through cracks in the oxide layer at the surface and then move internally to the stress concentrations. However, hydrogen entry at points of stress concentration is not a limiting factor in the observation of hydrogen

embrittlement [22]. The mechanism by which fracture occurs is independent of the hydrogen source.

For the hydrogen embrittlement seen in iron aluminide alloy FA-129 weldments, two types of mechanisms of fracture can be argued. Hydrogen embrittlement may occur by the decohesion mechanism. This mechanism postulates that brittle fracture occurs when the local stress exceeds the atomic bond strength and that the presence of hydrogen decreases the atomic bond strength [22]. The energy required to break the atomic bonds across an atomic plane while maintaining all other atom spacings at their equilibrium values is the thermodynamic surface energy, γ . Adsorption of hydrogen decreases this surface energy. The decohesion mechanism postulates that hydrogen produces a decrease in the maximum bonding force between atoms across an atomic plane as they are being separated. Brittle fracture is assumed to occur at a critical bond distance where the local applied stress exceeds the cohesive stress; it is assumed that the cohesive stress decreases as the local hydrogen concentration is increased [22].

An alternate (and most widely accepted) hydrogen embrittlement mechanism concludes that hydrogen changes the plastic deformation characteristics of a material. Bond et al. [25] studied hydrogen embrittlement mechanisms in Ni_3Al alloys and found that transgranular crack growth by hydrogen resulted from enhanced dislocation mobility. These results were consistent with the "hydrogen-enhanced localized plasticity" mechanism [26,27], in which hydrogen enters the material near the crack tip through the surfaces produced by slip. This results in a reduction of the flow stress which, in turn, leads to a highly localized transgranular failure by ductile processes. Because of this localization, the resulting fracture surface will appear to be macroscopically brittle. As discussed previously, these tests found that the friction stress, σ_0 , decreased as hydrogen content increased and that the locking parameter, k_F , increased with hydrogen content. These results are consistent with Bernstein [28] who made Hall-Petch measurements at room temperature on zone-refined iron under dynamic charging conditions. Bernstein found a lower friction stress and increased Hall-Petch slope with increasing hydrogen concentration. Beachem [29] torsion tested hydrogen-charged 1020 steel and found a reduction in the yield and flow stress compared to uncharged

material. However, Adair [30] precharged zone-refined iron specimens of various grain sizes and tested them at 242°K. An analysis of fracture stress versus inverse square root of grain size indicated an increased friction stress and a decreased k_F value slope for charged specimens. These results indicate that more than one hydrogen mechanism may be operating simultaneously.

The softening behavior, evidenced by the decreasing friction stress, is associated with enhanced motion of dislocations and possibly with enhanced injection of dislocations at free surfaces [23]. A number of possible explanations have been proposed for the solid solution softening. The first is a reduction in the magnitude of the Peierls-Nabarro stress field by the solute [31]. The second theory suggests that hydrogen increases the mobility of screw dislocations by enhancing the rate of double kink nucleation [32]. Finally, softening has been said to be a result of a reduction in the effectiveness of solutes as dislocation pinning points resulting from the formation of solute clusters [33,34].

The hardening behavior, indicated by an increasing Hall-Petch slope, is more difficult to explain. In steel, increases in k_F have been related to carbon and nitrogen strengthening the grain boundaries. Bernstein [28] suggested that hydrogen might play a role similar to carbon and nitrogen at the grain boundaries. He compared the relative strengthening effect of carbon and hydrogen and found them to be comparable, although the hydrogen value was low. Interactions between dissolved hydrogen and grain boundary solutes such as oxygen and sulfur were suggested to result in further strengthening. A slightly strengthened grain boundary would provide resistance to microcrack nucleation.

The final stage of the magnetic arc oscillation study was to characterize the hydrogen cold cracking behavior of refined fusion zone microstructures with water vapor present in the shielding gas. Welds were performed using a shielding gas of pure argon and with argon containing either 93 ppm or 560 ppm water vapor. The resulting microstructures of the welds made with 93 ppm water vapor are shown in Figure 11. With water vapor present in the shielding gas and without arc oscillation, the microstructure was characterized by large columnar grains (Fig. 11a), consistent with the results obtained when welding in pure argon. When the arc was oscillated, using the parameters shown previously to result in an equiaxed

(a)

(b)

Figure 11. Fusion zone microstructures of weldments welded with water vapor present in the shielding gas. a) Unoscillated b) Oscillated

microstructure, no significant grain refinement was observed in the water vapor containing environment (Fig. 11b).

When the coupons welded in the presence of water vapor were tensile tested, the fracture strength of the unoscillated and oscillated welds were not significantly different. In other words, magnetic arc oscillation did not improve the properties of weldments fabricated in an environment containing water vapor. This result was not unexpected given the lack of refinement in the fusion zone.

Further testing indicated that the arc oscillation parameters which resulted in microstructural refinement were not only dependent upon the welding environment (water vapor concentration), but the material composition and heat input as well. Given the sensitivity of the process, it was concluded that microstructural refinement by arc oscillation was suitable only for well-controlled fabrication environments, and that potentially less environmentally sensitive refinement methods should be investigated.

Weld Pool Inoculation

The addition of titanium powder to FA-129 GTA weldments effectively refined the fusion zone microstructure. The degree of refinement observed was found to be dependent upon three parameters: travel speed, heat input, and titanium concentration. To be consistent with the magnetic arc oscillation study, initial welds were made using a travel speed of 4 mm/s. At this travel speed, a molten ball was observed to develop in front of the arc which was pushed ahead of the traveling torch. With a travel speed of 4 mm/s, no significant fusion zone refinement was observed over a large range of titanium additions and heat inputs. The travel speed was reduced to 2 mm/s (the welding current was reduced as well to keep the heat input constant) in an effort to avoid the development of an atypical weld pool. At the lower travel speed, the weld pool appeared more typical, no molten ball was developed, and fusion zone refinement was observed. Subsequently, the slower travel speed of 2 mm/s was used for the remainder of the study.

To characterize the effect of titanium concentration and heat input on the fusion zone microstructure, samples were welded using the conditions given in Table 3. The travel speed used was 2 mm/s, the welding voltage was 10V, and the current was adjusted to give the final

heat inputs shown in Table 3. The lowest heat input, 118 J/mm, was chosen because it was the minimum value which gave full penetration. At this heat input, fusion zone refinement was not uniform down the length of the weld and was not repeatable from weld to weld for either experimental titanium concentration. For the higher heat input welds, 142 J/mm, fusion zone refinement was both uniform down the weld length and repeatable from weld to weld. Table 4 summarizes the results of the initial refinement characterization study.

Table 4. Effect of Heat Input and Titanium Additions on the Fusion Zone Microstructure.

Heat Input (J/mm)	Ti Addition (mg/10mm)	Avg. Fusion Zone Grain Size (μm)	Aspect Ratio (length/width)	Uniform Refinement
118	2	215	2.6	No
118	6	280	2.9	No
142	2	370	3.6	Yes
142	6	70	1.6	Yes

Given the more consistent results obtained when the higher heat input of 142 J/mm was used with a travel speed of 2 mm/s, these parameters were used when welding coupons for tensile testing. Titanium additions of 2 and 6 mg/10mm were used to produce samples with very different fusion zone grain sizes for hydrogen embrittlement characterization. Using energy dispersive spectroscopy (EDS), it was determined that the titanium addition of 2 mg/10mm resulted in 0.8 weight percent titanium in the fusion zone. The fusion zone consisted of a mixture of columnar grains, located at the edge of the fusion zone, and more equiaxed grains at the centerline. The average fusion zone grain size was 370 μm . Similarly, a 6 mg/10mm titanium addition resulted in 1.2 weight percent titanium in the fusion zone. The fusion zone microstructure was uniform with fine, equiaxed grains. The average fusion zone grain size was 70 μm . Figure 12 shows the microstructures obtained using the above parameters along with the unrefined microstructure. These represent the microstructures used for slow strain rate tensile testing.

(a)

(b)

(c)

Figure 12. Weldment microstructures from titanium inoculation study used in slow strain rate tensile testing. a) 0% Ti b) 0.8% Ti c) 1.2% Ti

The presence of an equiaxed centerline and the dependence of fusion zone grain refinement on the welding parameters, can be attributed to changes in the weld pool temperature gradient. For a two-dimensional weld, the temperature gradient along the weld centerline can be approximated as [33]:

$$G_c = 2\pi\lambda\rho c\left(\frac{h}{Q}\right)^2 VT^3 \quad (9)$$

where:

- G_c = centerline temperature gradient
- λ = thermal conductivity
- ρ = density
- c = heat capacity
- h = sheet thickness
- Q = heat input per unit time
- V = travel speed
- T = temperature difference between the melting temperature and the ambient temperature

With a given travel speed, the temperature gradient determines the distance ahead of the solidification front at which new grains can nucleate. With a lower temperature gradient, grains can nucleate further ahead of the solidification front, allowing for longer growth times, and thus improving the chances of a grain impinging upon an advancing columnar grain growing epitaxially from the fusion line. In the weld pool, the temperature gradient is lowest at the weld centerline [33]. Conditions are therefore more favorable for an equiaxed microstructure within this region. In the partially refined fusion zones in this study, refinement occurred only at the center of the fusion zone, as predicted.

Equation 9 (which characterizes the effects of welding parameters on the temperature gradient) can be used to predict the formation of an equiaxed microstructure. With an increased heat input, the observed fusion zone refinement was more complete and consistent for a given travel speed in this study. Equation 9 predicts a lower temperature gradient with an increased heat input, allowing more time for nuclei to grow ahead of the solidification front. With higher heat inputs, therefore, conditions for grain refinement in the fusion zone

are improved. Ganaha et al. [33] added titanium and zirconium to aluminum GTA welds and also observed a more equiaxed structure with increased heat inputs.

Equation 9 also predicts a lower temperature gradient with increased welding speed when the heat input is fixed. Ganaha et al. [33] experimentally observed a more equiaxed microstructure with higher welding speeds, as expected, and attributed this to a shorter available time for melting potential nuclei. However, with a higher welding speed, no refinement was observed in the current study. As mentioned previously, higher welding speeds resulted in an atypical weld pool. Predicted results, therefore, cannot be expected.

As shown in Figure 12, the extent of refinement in the fusion zone was dependent upon the titanium concentration. Titanium was added with the expectation that the particles would be melted and the titanium would then precipitate out as second phase particles during solidification. Any additional titanium present was expected to contribute to constitutional supercooling.

The titanium addition refined the fusion zone microstructure by either one or both of two mechanisms. First, titanium-containing precipitates (oxides, carbides, or intermetallics) in the weld pool provided heterogeneous nucleation sites. Second phase particles were observed in the fusion zone in both the non-inoculated and inoculated welds (Figure 13). Energy dispersive spectroscopy indicated that the inclusions in the non-inoculated fusion zone were niobium-rich. Although further analysis was not performed to determine the specific phase, it was assumed that the inclusions observed were niobium carbides which precipitated out during solidification.

Both EDS and x-ray diffraction (XRD) were used in an attempt to identify the inclusions in the inoculated fusion zone. Energy dispersive spectroscopy again indicated that the precipitates were niobium-rich, but also showed that the precipitates consisted of an approximately equal percentage of titanium. X-ray diffraction analysis of the fusion zone was utilized to try to determine the specific phase, or phases, present; however, the results were inconclusive. The peaks observed corresponded to the characteristic peaks of titanium carbide, various titanium oxides, and niobium carbide as well as the iron aluminide matrix. The relative positions of the second phase peaks and their low intensities made conclusive identification of the phases difficult. Further work is required to determine the exact phases

(a)

(b)

(c)

Figure 13. Fusion zone second phase particles in FA-129 weldments. a) 0% Ti b) 0.8% Ti c) 1.2 % Ti

present in the weld pool. Identifying the phases would allow for a better understanding of the reactions which occurred in the weld pool with titanium additions.

Hallum and Baeslack [34] used titanium powder to refine the fusion zone of titanium GTA welds. The grain refinement observed was attributed to heterogeneous nucleation on partially melted titanium particles present in the fusion zone. In their study, the powder was added to the trailing edge of the weld pool, and the diameter of the powder used was approximately ten times that of the powder used in this study. With these conditions, only a fraction of the particles survived in the weld pool to act as nucleation sites. Given the smaller particle size and addition technique used in the current study, it is unlikely that the grain refinement observed can be attributed to nucleation on partially melted titanium particles. All EDS readings taken from fusion zone inclusions showed either niobium or niobium and titanium providing further evidence that the titanium melted completely and that heterogeneous nucleation occurred on liquid-state precipitates.

Titanium was not the only inoculant studied. Niobium carbide powder (97%, $<5\mu\text{m}$) was added to the weld pool, using the same method described previously, in an attempt to refine the fusion zone microstructure. Given the higher melting point of niobium carbide, 3500°C , only a small fraction of the particles should have been melted. With minimal melting, the contribution to supercooling would be minimal and refinement could be attributed only to the addition of nucleation sites. However, no grain refinement was observed using niobium carbide as an inoculant. It is reasonable, therefore, to assume that the titanium addition did more than provide heterogeneous nucleation sites to refine the fusion zone microstructure. This statement is further strengthened by the fact that as the titanium concentration was increased, the fraction of second phase particles in the fusion zone did not significantly change. For all titanium concentrations, including non-inoculated welds, inclusions constituted approximately 6 percent of the fusion zone microstructure.

The addition of titanium must have also increased the supercooling in the weld pool, giving more favorable conditions for an equiaxed microstructure. Supercooling is affected by solute segregation during solidification, fluid flow, welding parameters, and cooling rate [12, 33, 35]. During steady-state solidification, solute is rejected into the liquid ahead of the

solid-liquid interface as predicted by the Scheil equation [35]. The gradient in solute concentration in front of the solidification front creates a gradient in the liquidus temperature. If the liquidus temperature gradient is greater than the actual temperature gradient in the liquid (determined by the degree of superheating, material properties, and welding parameters [33]), then the liquid ahead of the solidification front is constitutionally supercooled. The liquid persists below the equilibrium solidification temperature because of enriched composition [36]. To determine if an alloying addition will increase constitutional supercooling, the equilibrium liquidus diagram can be referenced. For a solute to increase constitutional supercooling, the liquidus temperature must decrease with increasing solute concentration. The iron-aluminum-titanium liquidus diagram is given in Figure 14. In the region of alloy FA-129, the liquidus temperature decreases with increasing titanium concentration, indicating that titanium additions will increase constitutional supercooling.

Increased constitutional supercooling has been found to be essential in refining fusion zone microstructures. Yunjia et al. [38] found that with increasing titanium concentration, the solidification mode changed from cellular to equiaxed dendritic in aluminum welds, and a model was proposed attributing their observation to enhanced constitutional supercooling. Heintze and McPherson [39] inoculated steel with titanium and concluded that the observed grain refinement was due to the formation of titanium nitrides. However, for these particles to be effective nucleation sites, additional titanium and boron were required to increase the constitutional supercooling. Similarly, Davies and Garland [40] referenced Garland's Ph.D. dissertation, in which it was concluded that titanium additions to steel welds formed titanium carbides, which nucleated grains as long as sufficient constitutional supercooling existed.

From this discussion, the important contribution of titanium inoculation to fusion zone refinement in iron aluminide welds is not the formation of precipitates. Second phase particles exist without titanium additions, but no extensive refinement is observed. Rather, increased constitutional supercooling, which improves the effectiveness of second phase particles as nucleation sites, is the dominant contribution of titanium.

Increased constitutional supercooling would also account for the non-uniform refinement observed with the 0.8 percent titanium addition (Figure 12b). A critical degree of supercooling must be achieved before inclusions in the weld pool can be effective nucleation

Figure 14. Iron-aluminum-titanium equilibrium liquidus diagram [37].

sites. At the onset of solidification, the titanium concentration at the fusion line may not be sufficient to create the needed supercooling with only a small titanium addition. As solidification proceeds and solute is rejected towards the weld centerline, the titanium concentration may reach the required level for effective grain refinement. The result is a fusion zone microstructure, initially columnar, which transforms to an equiaxed structure towards the weld centerline, as was observed experimentally.

Misra et al. [41] approached the issue of a non-uniform microstructure in a different manner. Misra observed grain refinement only at the center of the titanium welds which were inoculated with yttrium. He explained the phenomena as being the result of the competition between the time to nucleate one grain (t_1) and the time for one grain to grow across the bead (t_o). The equations relating supercooling to the critical times were:

$$t_1 = \frac{\exp \frac{c_1'}{(\Delta T)^2}}{c_1 V} \quad (10)$$

and

$$t_o = \frac{x_o}{k \Delta T} \quad (11)$$

where: $c_1' = \text{constant}$
 $\Delta T = \text{degree of supercooling}$
 $c_1 = \text{constant}$
 $V = \text{volume}$
 $X_o = \text{distance for grain to grow}$
 $k = \text{Boltzman's constant}$

For a grain growing epitaxially from the fusion line not to grow across the fusion zone, t_1 must be less than t_o . A critical degree of supercooling (ΔT_c), therefore, must be reached where nucleation occurs rapidly, allowing for nucleating grains at the weld centerline to impinge epitaxially growing grains. If this is to occur, the supercooling associated with the welding process must be greater than ΔT_c . Minor alloying elements reduce ΔT_c . Misra

concluded that the presence of yttria changed the liquid-solid interfacial energy or the contact angle, thereby reducing ΔT_c .

Simpson [42] also observed the non-uniform fusion zone refinement described when yttrium was used to inoculate titanium welds. He found that a high concentration of yttria existed at the grain boundaries and that the yttria concentration increased from the fusion line towards the centerline. The representative micrographs in Figure 13 indicate that when titanium was added to the FA-129 fusion zones, more inclusions were formed at the grain boundaries. Quantitative metallography confirmed this observation (Table 5). In general, the fraction of inclusions increased in a direction from the fusion line towards the centerline of the fusion zone (Figure 15). Simpson concluded that as the yttria concentration at the solid-liquid interface increased with solidification, the particles pushed ahead of the interface, creating drag and reducing the rate of solidification. Given a constant cooling rate, the reduced solidification rate increased the supercooling ahead of the interface and created an increased tendency for nucleation. A similar mechanism may account for the observations in this present study.

Table 5. Effect of Titanium Concentration on Fusion Zone Inclusion Location.

Titanium Concentration	Fraction of Inclusions at Grain Boundaries
0%	15%
0.8%	43%
1.2%	50%

With the significant fusion zone refinement achieved, it was expected that slow strain rate tensile tests would show results similar to the results of the magnetic arc oscillation study. However, with increased titanium concentration (a more refined fusion zone microstructure) the fracture strength of the weldment decreased (Figure 16). Fracture strength also decreased with increasing water vapor concentration, independent of titanium concentration.

(a)

(b)

(c)

Figure 15. Second phase particle distribution and location in FA-129 fusion zone. a) 0% Ti b) 0.8% Ti c) 1.2% Ti

Figure 16. Fracture strength of inoculated FA-129 weldments slow strain rate tensile tested in various water vapor concentrations.

The first tensile tests performed were on the inoculated samples, using Fasching's data for unrefined weldments as a baseline. When the inoculated weldment fracture strengths were found to be lower than the assumed baseline, the fracture strength of unrefined weldments was verified to eliminate any compositional effects or differences due to the modified tensile sample configuration. Tests performed on the non-inoculated samples at both the high and low water vapor concentrations agreed well with Fasching's results. The decrease in fracture strength observed, therefore, cannot be attributed to differences in material composition or sample configuration. The reduced fracture strength also does not appear to be the result of a change in the fracture mode. The fracture surfaces of inoculated weldments are given in Figure 17. Fracture occurred by transgranular cleavage as observed by Fasching.

It was noted earlier that the position of inclusions in the fusion zone changed with titanium additions. With higher titanium concentrations, the fraction of inclusions located at the grain boundaries increased (Table 5). The shape, size, and distribution of carbides and other inclusions influence the fracture strength of materials.

To initiate cleavage fracture, the local stress at a defect must be large enough to overcome the cohesive strength of the material. The cohesive strength, or theoretical fracture stress, of a material is approximately equal to E/π . This value is approximately 50 times higher than the stress created ahead of a macroscopic crack [43]. Therefore, for cleavage initiation, a sharp microcrack must exist if a high enough stress level is to be reached to initiate cleavage fracture. Microcracks are formed when carbides or other second phase particles are fractured. Particles fracture because of high local stress concentration and because of the low intrinsic ductility of the particles. The particle-matrix interface can also fracture and form a microcrack.

Both fractured second phase particles and fractured particle-matrix interfaces were observed in inoculated weldments after tensile testing (Figure 18). Liu and Gurland [44] observed both fracture types in steels, and concluded that although both defect types could initiate void formation, only carbide fracture could initiate cleavage nucleation. Given the inherently brittle behavior of iron aluminides, once a microcrack is initiated at a second phase

(a)

(b)

Figure 17. Fracture surfaces of inoculated FA-129 weldments. a) 0.8% Ti b) 1.2% Ti

Figure 18. Fusion zone second phase particle associated with fracture in inoculated FA-129 weldment. a) Failed interface b) Fractured particle

particle and the Griffith crack propagation criteria is satisfied, the crack will propagate in an unstable manner. It is assumed then, that the stress required to fracture the second phase in the iron aluminide weldments controls the measured fracture strength. The reduced fracture strength in inoculated welds could be the result of a change in the location, size, distribution, or shape of the second phase particles in the fusion zone.

When spherical particles are fractured, a penny-shaped crack is formed (Figure 19a). The Griffith crack propagation criteria for a penny-shaped crack is:

$$\sigma_f = \left(\frac{\pi E \gamma_p}{2(1 - \nu^2)r} \right)^{1/2} \quad (12)$$

where: γ_p = effective surface energy
 ν = Poisson's ratio
 r = particle radius

A cracked grain boundary carbide is characterized as a through-thickness nucleus (Figure 19b). The Griffith crack criteria for a through thickness nucleus is:

$$\sigma_f = \left(\frac{2E\gamma_p}{\pi(1 - \nu^2)r} \right)^{1/2} \quad (13)$$

Note that the change from a penny-shaped nucleus to a through-thickness nucleus reduces the fracture strength by a factor of $\pi/2$. Also note, as the particle radius, r , is increased, the fracture strength decreases. Curry and Knott [45] demonstrated the dependence of the fracture strength of tool steels on carbide shape and size. Their results are summarized in Figure 20.

Characterization of the fusion zone inclusions with respect to size and shape as a function of titanium concentration will be performed to determine if the above mechanism controls fracture strength in iron aluminide weldments.

Figure 19. Schematic representation of fractured second phase particles. a) Penny-shaped (spherical inclusion) b) Through-thickness (grain boundary inclusion) [45]

Figure 20. Fracture strength as a function of second phase particle type and size [45].

The reduced fracture strength may not be due to changes in the inclusion shape and size, but rather to an increase in the probability that a critically sized carbide with the proper orientation exists at a grain boundary. The fraction of inclusions which are actually fractured is approximately 0.1 to 1 percent, with the majority being located at the grain boundaries [46]. The use of statistics to describe cleavage fracture has been used by other researchers with some degree of success [47, 48].

A model more consistent with Fasching's use of the Hall-Petch relationship to explain the effect of grain size on fracture strength has been proposed by Liu and Gurland [44]. With a reduced grain size, the length of a dislocation pile-up at a grain boundary is shorter, giving a lower stress concentration. The result is a higher fracture strength in fine-grained materials as was observed by Fasching. If dislocations are considered to pile up at second phase particles instead of grain boundaries, then the maximum slip distance is defined by the second phase particle spacing. The model proposed by Liu and Gurland for higher-carbon steels is:

$$\sigma = \sigma_o + \frac{\sigma_c}{2} \sqrt{\rho/\Lambda} \quad (14)$$

where:

- σ = applied stress
- σ_o = friction stress
- σ_c = critical fracture stress of matrix
- ρ = radius of curvature of crack tip
- Λ = available slip distance

This model then predicts that fracture strength will be reduced as the particle spacing increases. By observation, the particle spacing appears to increase with titanium additions in iron aluminide weldments (Figure 13). Future work will center on quantifying the mean particle spacing as a function of titanium addition and determining the relationship between particle spacing and fracture strength in iron aluminide weldments.

Kivineva et al. [49] viewed weld metal with second phase particles as a particulate-reinforced composite. Given that composite properties are dependent upon the volume

fraction, morphology, and distribution of the particles, their approach was to control particulate distribution to ultimately improve weldment properties. The present research suggests that the particulate distribution affects the fracture strength of the weldment, so controlling the distribution may allow for mechanical property improvement.

The distribution of particles in the metal matrix is controlled by the particle composition, size and density, the liquid composition, and the solidification velocity [49]. A critical solidification velocity, V_{cr} , has been defined by Stefanescu et al. [50] which is dependent upon the particle size and the material system. Below the critical velocity, particles are pushed ahead of the solidification front, leading to a concentration of particles in the interdendritic regions as well as at the grain boundaries. The solidification velocity is controlled by the welding process. Reducing the heat input is one method of increasing the solidification velocity; however, with titanium inoculation, grain refinement was inconsistent with lower heat inputs. Increasing the travel speed also increases the solidification velocity. With the current welding sample configuration, the travel speed was limited due to the formation of an atypical weld pool at higher travel speeds. An alternative addition method such as welding over alloyed rods or using powder filled wires may allow for higher travel speeds. Higher travel speeds would improve the conditions for grain refinement by decreasing the temperature gradient in the weld pool. Increased travel speed might also result in a solidification velocity which is greater than the critical velocity, giving a more uniform distribution of second phase particles and possibly improving the mechanical properties of the weldment.

Conclusions

1. Arc oscillation was shown to be an effective method for refining fusion zone microstructures in iron aluminide alloy FA-129 by altering the thermal gradients in the weld pool.
2. Slow strain rate tensile tests showed fine-grained iron aluminide fusion zones to be less susceptible to hydrogen cracking and more tolerant of high hydrogen concentrations than coarse fusion zone grain structures. The fracture strength was found to obey the Hall-Petch relationship.
3. Microstructural refinement by arc oscillation is suitable for well-controlled fabrication environments. Optimal refinement parameters were sensitive to numerous processing variables including welding water vapor concentration, material composition, and heat input.
4. Titanium inoculation was shown to be an effective method for refining fusion zone microstructures in iron aluminide alloy FA-129.
5. Titanium inoculation changed the composition and distribution of second phase particles in the fusion zone.
6. Slow strain rate tensile tests showed that titanium inoculation reduced the fracture strength of FA-129 weldments.
7. Further characterization of second phase particle composition, size and shape as a function of titanium concentration is required to determine the role of the particles as cleavage nucleation sites.

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