THE EFFECTS OF ZIRCONIUM AND CARBON ON THE
HOT CRACKING RESISTANCE OF IRON ALUMINIDES
Topical Report

by

B.L. Mulac*, G.R. Edwards*, and S.A. David*

*Center for Welding, Joining, and Coatings Research
Department of Metallurgical and Materials Engineering
Colorado School of Mines
Golden, Colorado 80401

*Materials Joining Group
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

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CENTER FOR WELDING, JOINING, AND COATINGS RESEARCH
Colorado School of Mines
Golden, Colorado 80401
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OAK RIDGE NATIONAL LABORATORY
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1.0 Introduction

Iron aluminides have been of interest for about 60 years because of their good high temperature strengths (below 600°C) and excellent oxidation and sulfidation resistance, as well as their relatively low cost and conservation of strategic elements¹. These advantageous properties have driven the development of iron aluminides as potential structural materials. However, the industrial application of iron aluminides has been inhibited because of a sharp reduction in strength at temperatures higher than 600°C and low ductility at ambient temperatures due to hydrogen embrittlement. Oak Ridge National Laboratory has shown in recent years that room temperature properties of alloys containing 28% Al (all compositions are in atomic percent unless otherwise noted) can be improved through thermomechanical processing and alloying.

Iron aluminides must have good weldability if they are to be used as structural materials. A coarse fusion zone microstructure is formed when iron aluminides are welded, increasing their susceptibility to cold cracking in water vapor. A recent study at Colorado School of Mines has shown that refining the fusion zone microstructure by weld pool oscillation effectively reduces cold cracking. Weld pool inoculation has been shown to refine fusion zone microstructures, but coarse carbide distribution caused this approach to reducing cold cracking to be ineffective.

More recently, the addition of zirconium and carbon has been found to improve the mechanical properties as well as the oxidation resistance of iron aluminides. However, zirconium decreases the hot cracking resistance of these iron aluminides. The current study at Colorado School of Mines, in collaboration with Oak Ridge National Laboratory, involves a characterization study of the effects of zirconium and carbon on the hot cracking susceptibility of iron aluminides.

2.0 Background

2.1 Zirconium and Carbon Additions to Iron Aluminides

Zirconium and carbon have been added to the ternary alloy of Fe- 28% Al-5%Cr because of their beneficial effects on mechanical properties. Alven, *et al.*², found that additions of zirconium and carbon

increased the ductility and tensile strength of the basic ternary alloy in hydrogen, oxygen, and laboratory air (relative humidity 21%). Removing the carbon decreased the ductility, and increasing the zirconium content from 0.5% to 0.1% decreased the ductility and tensile strength as well. Alven, *et al.*, also found that zirconium and carbon containing alloys were less susceptible to moisture-induced embrittlement during fatigue crack tests.

2.2 Hot Cracking³

Hot cracking, also referred to as solidification cracking, occurs during the final stages of weld solidification. Continuous thin films of liquid form on the surface of the advancing dendrites, which form a coherent interlocking network. Cracking occurs when stresses induced by thermal contraction and/or solidification shrinkage rupture the liquid film and exceed the strength of the almost solidified weld metal. If enough liquid is present during solidification, it can backfill and "heal" incipient cracks.

There are several factors that affect hot cracking susceptibility of metals. Additions of alloying elements or impurities can increase the freezing range of the alloy. This increases the size of the mushy zone and subsequently the area that is susceptible to hot cracking becomes larger. The distribution of the liquid along grain boundaries has a significant effect and is dependent on surface tension. If the surface tension between the solid and the liquid metal is low, the liquid will be evenly distributed across the interface as a thin film and thus increase the hot cracking susceptibility. However, if the surface tension is high, the liquid will tend to be globular and not wet the interface. Thus, there is no continuous film present and hot cracking susceptibility is minimal. Another metallurgical factor affecting hot cracking susceptibility is fusion zone grain size. Coarse-grained fusion zone structures tend to be more susceptible. Smaller grains can accommodate the contraction strains much easier than larger grains. More grain boundary area is present with a smaller grain structure, so the concentration of low melting point segregates is less.

2.2.1 The Sigmajig Apparatus

The Sigmajig hot cracking test was developed in the mid 1980s⁴. Unlike the Varestraint and the Tigamajig test, the Sigmajig is used to evaluate hot cracking susceptibility of thin sections. The Sigmajig

applies a transverse stress to the specimen, which is then gas tungsten arc welded. As the stress is increased from specimen to specimen, the threshold hot cracking stress of the material is eventually reached and hot cracking occurs.

3.0 Experimental Procedure

3.1 Alloy Compositions

Several alloys of base composition Fe -28% Al - 5% Cr were developed to study the effects of zirconium and carbon on hot cracking resistance. Table 1 gives all compositions used. The alloys can be split into three distinct groups. The first group of alloys consisted of five alloys, having a fixed zirconium to carbon ratio of 10 and varying concentrations of zirconium and carbon. This group was developed to determine the effects of increasing zirconium content on hot cracking susceptibility. The ratio of 10 was used because it was assumed that at that ratio, a sufficient amount of zirconium would be tied up as carbides. Another group consisted of two alloys with fixed carbon content and a varying zirconium content. These alloys contained a high zirconium content relative to the other alloys and were prepared to determine the zirconium concentration needed to generate sufficient liquid for backfilling. For the final group of two alloys the zirconium content was fixed and the carbon content was changed to determine the effect of carbon content on hot cracking resistance. All alloys were melted in a vacuum furnace and cast in a copper mold. They were then hot rolled down to an approximate thickness of 0.76 millimeters. These alloy preparations were completed during the 1997 student summer internship at ORNL.

3.2 Hot Cracking Tests

Specimens 50mm x 50mm square were sheared from each alloy sheet. The specimens were annealed in air at 650°C for one hour and then pickled in a solution of 20 parts water, 10 parts nitric acid, and 1 part hydrofluoric acid to remove any oxide.

Gas tungsten arc welding was used in conjunction with a Sigmajig test apparatus. Figure 1 is a photograph of the Colorado School of Mines testing device. Welding parameters used are as follows: current 60-65 amps, arc gap 0.159 cm (0.0625 in.), and travel speed 76.2 cm/sec (30 in/min). Before welding, specimens were wiped clean with acetone. For each alloy, an estimate of the threshold stress

was made (depending upon zirconium content), which was used as a starting point. Depending upon the results (hot crack or no hot crack), the stress was then increased or decreased by an increment of 2 to 5 ksi for the next test. This procedure was followed until the threshold stress was found. The threshold stress was defined as the stress just less than the stress required for hot cracking to occur.

3.3 Metallography and Fractography

Metallographic specimens were polished using an automatic polisher and were wet ground to 600 grit, followed by polishing with 6- μ m diamond suspension. A 1- μ m diamond suspension was used for the final polish. The specimens were etched with a solution of 60 ml methanol, 20 ml hydrochloric acid, and 40 ml nitric acid. The specimens were dipped into hot water first, followed by dipping into the etchant for 15 to 20 seconds, and then rinsed with water.

The hot crack fracture surfaces were analyzed with a scanning electron microscope. Surfaces were analyzed for evidence of bridging and tearing that may have occurred during failure.

4.0 Results and Discussion

4.1 Microstructural Analysis

The bulk microstructure was found to be partially recrystallized in all alloys (Figure 2). As the zirconium content went up, an increase in the number of second phase particles was observed. The second phase particles are believed to be zirconium carbides (ZrC). Preliminary analysis with EDS, as seen in Figure 3, showed the particles to have a very high zirconium content. Further analysis to determine the exact composition of the particles is in progress. The carbide concentration profoundly affected the grain size in the heat-affected zones (HAZ) of the alloys. The low zirconium content alloy had large grains in the HAZ while a high zirconium content alloy showed significantly smaller grains with a larger concentration of carbides (Figure 4). The grain size difference is a function of carbide concentration and is caused by the carbides pinning grain boundaries, preventing further grain growth.

The fusion zone microstructure of welds in all alloys tested was found to be coarse-grained. At lower magnification, only small differences between alloys were seen in the fusion zone. The grains in the low zirconium content alloy had smooth grain boundaries, while the grains in the higher zirconium content

alloy exhibited a roughening of the grain boundaries (Figure 5). Analysis at higher magnifications revealed the cause of the grain boundary roughening. A second phase was found decorating the grain boundaries in the higher zirconium content alloy (Figure 6). This second phase was not present in the low zirconium alloy. Additional particles of this phase were found within the grains themselves. The second phase clearly outlines the dendrites formed during weld solidification, providing evidence that the phase was the last liquid to solidify. Preliminary analysis with EDS showed the second phase to be zirconium rich (Figure 7a). An EDS spectrum, shown in Figure 7b, was taken of the matrix next to the second phase and no zirconium was found. During solidification, it is assumed that the zirconium segregates ahead of the advancing solidification front, decreasing the liquidus temperature of the alloy, thus the last liquid to solidify would be high in zirconium content and the already solidified metal would be significantly depleted of zirconium. Further experimentation to quantitatively identify the zirconium-rich phase is in progress.

4.2 Hot Cracking Tests

The threshold stress determined for each alloy is plotted in Figure 8. The first graph (Figure 8a) is for alloys in group 1, having a fixed Zr/C ratio of 10, with varying concentrations of zirconium and carbon. The data clearly show a trend of decreasing threshold stress with increasing zirconium and carbon content. Figure 8b gives the results of alloy group 2, containing alloys with fixed carbon content and varying zirconium content. Increasing the zirconium content to levels higher than 0.5% provided enough liquid to allow for backfilling of incipient cracks and hence, increased the threshold stress for cracking. The results from group 3 (Figure 8c) show that fixing the zirconium level at 0.1% and increasing carbon levels above 0.01% had little effect on the hot cracking susceptibility of the alloys.

To more quantitatively compare the threshold stresses of all the alloys, the amount of excess zirconium in each alloy was calculated. The threshold stress of the alloys was then plotted as a function of excess zirconium (Figure 9). The excess zirconium was calculated by subtracting the amount of carbon in the alloy from the zirconium content. It was assumed that all available carbon would combine with an equivalent amount of zirconium to form ZrC. Any zirconium not used in the formation of ZrC was considered excess. The graph in Figure 9 clearly shows the effects of small increases in excess

zirconium concentrations on the hot cracking threshold stress. The threshold stress drops significantly for the alloys containing from 0 to 0.5% excess zirconium. The trend follows what was seen in Figure 8a. The drop in threshold stress is due to the fact that zirconium lowers the liquidus temperature of the iron aluminide alloy. During solidification, the zirconium segregated ahead of the advancing solidification front, significantly reducing the solidification temperature of the remaining liquid. As a result, the contraction stresses exceeded the strength of the liquid and caused hot cracking to occur. Increasing the zirconium levels from an initially low concentration increased the amount of liquid present and consequently reduced the threshold stress. The second phase found along the grain boundaries in the fusion zone microstructures of the alloys of higher excess zirconium (Figure 6) provides further evidence of the phenomenon. However, Figure 9 also shows that at high excess zirconium concentrations, the threshold stress increased to levels comparable to those achieved when very little excess zirconium was present. This trend corresponds with that found in Figure 8b. Once a critical amount of excess zirconium was reached (greater than 0.5%), enough liquid was generated to allow for the backfilling and healing of incipient cracks. Thus the threshold stress for the onset of hot cracking increased with increasing concentrations of excess zirconium.

4.3 Fractography

The hot crack surfaces of each alloy were analyzed for evidence of bridging and tearing. Figure 10 shows hot crack surfaces for: a) 0% excess zirconium ($\sigma = 14$ ksi), b) 0.45% excess zirconium ($\sigma = 4$ ksi), and c) 1.95% excess zirconium ($\sigma = 14$ ksi). The high stress, low excess zirconium surface showed evidence that the remaining liquid solidified on the surface after cracking but was not evenly distributed across the whole surface (Figure 10a). This shows that only a small amount of liquid was present when cracking occurred. Since the excess zirconium was very low, it would be expected that the amount of liquid present would be minimal. The hot crack surface of the mid-level excess zirconium composition exhibited no evidence of bridging or tearing. An even layer of solidified liquid covered the surface of the dendrites, providing evidence that a large amount of liquid was present at the time of cracking (Figure 10b). This follows the expected trend of a large amount of liquid present at the time of cracking in alloys with high zirconium content. The final fractograph shows evidence of tearing on the fracture surface.

This means that part of the surface had already solidified when the crack formed. At high levels of zirconium, sufficient liquid was present to backfill into incipient cracks, which were healed by solidification before constraint imposed stresses were large enough to fracture the fusion zone.

5.0 Conclusions and Future Work

The results of this study to date show that increasing the excess zirconium concentration from 0% to 0.5% decreased the hot cracking resistance of the ternary alloy. Increased hot cracking susceptibility is due to the lowering of the liquidus temperature by the zirconium, which generates more liquid at the final stages of weld solidification. Further increasing the zirconium content, beyond the critical level, causes the threshold stress to increase again because even more liquid is generated, allowing for backfilling and healing of incipient cracks before constraint stresses become high. Fractography shows evidence of both bridging and tearing in the samples representing both low excess zirconium and high excess zirconium. No evidence of bridging was revealed in fracture surfaces of specimens containing the critical zirconium concentration. Microstructural analysis showed evidence of an as yet unidentified second phase in samples containing high zirconium content alloys.

Future work will be focused on further analysis of second phases in the microstructure as well as on more quantitative fractography to more completely show the function of zirconium and carbon in the hot cracking susceptibility of iron aluminides.

Table 1. Alloy Compositions (values in atomic percent).

Alloy	Fe	Al	Cr	Zr	C	Zr/C Ratio	Excess Zr
Group1							
16854	Bal.	28.0	5.0	0.05	0.005	10	0.045
*16853	Bal.	28.0	5.0	0.10	0.01	10	0.09
16596	Bal.	28.0	5.0	0.20	0.02	10	0.18
16595	Bal.	28.0	5.0	0.35	0.035	10	0.215
*16594	Bal.	28.0	5.0	0.50	0.05	10	0.45
Group 2							
*16594	Bal.	28.0	5.0	0.50	0.05	10	0.45
16858	Bal.	28.0	5.0	1.50	0.05	30	1.45
16857	Bal.	28.0	5.0	2.00	0.05	40	1.95
Group3							
*16853	Bal.	28.0	5.0	0.10	0.01	10	0.09
16855	Bal.	28.0	5.0	0.10	0.02	5	0.08
16856	Bal.	28.0	5.0	0.10	0.10	1	0.00

** These alloys are the same.

Figure 1. Hot cracking test setup at Colorado School of Mines.

Figure 2. Micrograph of the partially recrystallized structure found in the bulk material.

Intensity, counts

(a)

(b)

Figure 3. a) Results from EDS analysis of second phase particles found in matrix. b) Second phase particles. These particles are believed to be ZrC.

(a)

(b)

Figure 4. HAZ structures found in alloys containing: a) low zirconium concentrations (0.05%), b) high zirconium concentrations (0.5%).

(a)

(b)

Figure 5. Fusion zone microstructures of: a) low zirconium content (0.05%), and b) high zirconium content (0.5%). Note the difference in grain boundary texture between alloys.

(a)

(b)

Figure 6. Fusion zone microstructures of: a) low zirconium concentration (0.05%), and b) high zirconium concentration (0.5%). Note the second phase present along grain boundaries and within the grains in the high zirconium containing alloy.

Figure 7. Results from preliminary analysis with EDS of: a) second phase found along fusion zone grain boundaries, and b) the matrix next to the second phase.

(a)

Figure 8. The threshold hot cracking stress as a function of alloy content. a) Alloys of group 1 with a fixed Zr/C ratio of 10.

(b)

(c)

Figure 8. (cont.) b) Results from alloy group 2, with a fixed carbon content of 0.05%. c) Alloy group 3, with fixed zirconium content of 0.1%.

Figure 9. Summary plot of hot cracking threshold stresses of all alloys tested, as a function of excess zirconium content.

(a)

(b)

(c)

Figure 10. Hot crack fracture surfaces of: a) 0% excess zirconium ($\sigma = 14$ ksi), b) 0.45% excess zirconium ($\sigma = 4$ ksi), c) 1.95% excess zirconium ($\sigma = 14$ ksi).

6.0 References

1. McCamey, C.G., DeVan, J.H., Tortorelli, P.F., and Sikka, V.K. 1991. J. of Mat. Sci. Res. 6: 1779.
2. Alven, D.A., and Stoloff, N.S. 1997. Final Report: Investigation of Moisture-Induced Embrittlement of Iron Aluminides. ORNL/Sub/90-SF521/05: 54.
3. Kou, S. 1987. Welding Metallurgy. New York: John Wiley and Sons.
4. Goodwin, G.M. 1987. Welding Journal 66(2): 33s.

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