THE CORROSION BEHAVIOR OF AA5086 FRICTION STIR WELDED JOINTS IN 3.15 WT% SODIUM CHLORIDE, ASTM SEAWATER, AND 0.5 M SODIUM SULFATE

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Abstract

Hardness, tensile, and corrosion behavior of friction stir welded (FSW) AA5086-AA5086 joints have been investigated. Vickers microhardness and tensile tests showed that the thermomechanically affected zone (TMAZ) and the heat affected zone (HAZ) had the lowest microhardness values, resulting in tensile failure in this region for transverse specimens. Potentiodynamic polarization experiments conducted using samples cut from each zone indicated that the HAZ had the lowest corrosion rate in deaerated and aerated 3.15 wt.% NaCl. Immersion testing for 90 days showed that corrosion rates were generally mild, but highest in 3.15% NaCl, followed by ASTM seawater and least in 0.5 M Na₂SO₄. Scanning electron microscopy, Raman spectroscopy, and X-ray diffraction were used to characterize the corrosion morphology. Less corrosion products were observed on the HAZ as compared to the other weld zones.

Introduction

The 5xxx series aluminum alloys are widely used in the aerospace and shipbuilding industries due to their good corrosion resistance and high specific strength and stiffness. Friction stir welding (FSW) which is a relatively new welding technique that does not involve liquefying the weld zone, was invented by The Welding Institute (TWI), UK in 1991.[1] FSW has been considered as one of the most significant recent developments in metal joining technologies, and generally results in improved mechanical properties of the weld area due to minimal microstructural changes, as compared to conventional joining techniques including tungsten inert gas (TIG) and metal inert gas (MIG) welding [2].

The FSW joint of aluminum alloys usually contain four microstructural zones: the nugget zone (NZ), the thermomechanically-affected zone (TMAZ), the heat-affected zone (HAZ), and the base material (BM) [3-8]. The NZ is the weld interface region through which a rotating pin traverses and induces the highest amount of plastic deformation and frictional heat in the weld area. The resultant NZ microstructure is fine equiaxed grains due to recrystallization. The TMAZ adjacent to the NZ experiences plastic deformation and heat, but does not recrystallize. The HAZ is only subjected to heat, without mechanical deformation. The microstructural changes induced by the plastic deformation and the frictional heat of the FSW process can have deleterious effects on the mechanical (e.g., hardness and strength), fatigue, and corrosion properties in the weld zones [9]; however, there is much less microstructural changes compared to conventional welding techniques where the weld zone is melted and re-solidified.

The microstructure and mechanical properties of FSW joints of 5xxx series aluminum alloys have been extensively investigated [6, 9-17]. In AA5083 friction stir welds, the microstructural, mechanical properties and residual stresses has been studied as a function of welding speed by Peel et al.[15] They reported that the hardness and yield strength decreased in the weld zone due to recrystallization; and accordingly, during tensile testing, almost all the plastic flow occurred within the recrystallized zone. Cam et al. [10, 11] investigated mechanical properties of FSW AA5086-H32 plate. They found that the heat-induced softening of cold-worked material resulted in lower strength performance (i.e., 75% of the value for the BM). The relatively low ductility was possibly caused by a kissing-bond type defect (where there is no metallurgical bond between adjacent layers of material) and a decrease of strength in the nugget. Ramesh et al. studied the effect of multipass friction-stir processing on mechanical properties of AA5086 [6]. They showed that grainsize, hardness, yield strength and ultimate tensile strength generally decreased in the multipass-processed material compared to single pass-processed materials. Despite extensive research on the mechanical properties of FSW joints of 5xxx series aluminum alloys, little is known about the corrosion performance of such FSW joints. In the present work, the corrosion behavior of FSW joints of AA5086 was investigated by potentiodynamic polarization in 3.15 wt% NaCl, and immersion tests in 3.15 wt.% NaCl, ASTM seawater, and 0.5 M Na₂SO₄ (chloride-free environment). The corrosion products were examined using Raman spectroscopy and X-ray diffraction. Hardness and tensile tests were also conducted on the FSW AA5086 samples.

Experimental

AA5086-H32 (UNS A95086) (0.4% Si, 0.5% Fe, 0.1% Cu, 0.35% Mn, 4.0% Mg, 0.15% Cr, 0.25% Zn, 0.15% Ti, balance Al) plates (300 mm × 50 mm × 6 mm) plates were FSW along the rolling direction using an 8 mm-diameter friction-tool of 6.35 mm height and 25 mm shoulder diameter titled at 3° towards the fed material at a 12
mm/min travel speed and 1000 rpm rotational speed. The weld is asymmetric due to the combination of tool rotational and translational motion. The advancing side (AS) of the weld corresponds to the region where the circumferential velocity of the rotating tool is in the same direction as its translation, and the retreating side (RS) of the weld corresponds to the region where the circumferential velocity of the rotating tool is in the opposite direction as its translation.

Hardness and Tensile Testing: Vickers microhardness testing (Wilson Rockwell R5000†) was performed across the welds using a 50 g load. Tensile tests were performed at a crosshead speed of 3 mm/min using an Instron 5500R† testing machine. Tensile specimens were machined parallel (longitudinal) to the weld in the NZ, and transverse to the welds across all zones. The configuration of the tensile specimens is shown in Fig. 1. An axial extensometer with 25 mm gage length was attached to the specimens at the gauge section. The tensile properties of the joints were evaluated using three tensile specimens cut from the same welded plate.

Fig. 1. Schematic diagram showing the orientation of tensile test (L-AA5086-AA5086 and T-AA5086-AA5086) and immersion specimens.

Polarization experiments were conducted using samples (5 mm × 5 mm) cut from different zones (i.e., NZ, TMAZ, HAZ, and BM). The samples were mounted in epoxy resin, polished to a final 0.05 μm mirror-finish using alumina slurries, and immersed in high purity water (18.0 MΩ·cm) prior to polarization experiments in 3.15 wt.% NaCl solutions at 30 °C. The solutions were deaerated with high-purity nitrogen (> 99.999%) or aerated with compressed air. Potentiodynamic polarization experiments were conducted with a PARSTAT 2273† potentiostat (Princeton Applied Research). The working electrodes were kept in the open-circuit condition for 1 hour prior to initiating the potentiodynamic scan at a rate of 1 mV/s. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum mesh was used as the counter electrode. To minimize contamination of the solution, the reference electrode was kept in a separate cell connected via a Luggin probe. Anodic and cathodic sweeps were measured separately on freshly-prepared samples. Polarization experiments for each typical zone were performed using at least three samples to verify reproducibility. To generate polarization diagrams, the mean values of the logarithm of the current density were plotted as a function of potential.

For immersion tests, the FSW samples (70 mm × 25 mm × 4 mm) were degreased in acetone, ultrasonically cleaned in deionized water, dried, and weighted prior to the experiments. Three samples from each zone were placed in a 250 ml beaker. A total of 24 beakers were kept at a controlled temperature of 30 °C by immersing the beakers in a heated and water-circulated tank. Approximately 200 ml of solution (3.15 wt.% NaCl, 0.5 M Na₂SO₄, and ASTM† seawater) was poured into the beakers so that the samples were completely immersed. Beakers were partially covered to minimize evaporation and to maintain an aerated condition. After 90 days of immersion, the samples were retrieved and dried in a dry box (1% RH). The corrosion products were analyzed using scanning electron microscopy (SEM, Hitachi S-3400N†), Raman spectroscopy (Nicolet Almega XR†, Thermo Scientific Corp.), and X-ray diffraction (XRD, Rigaku MiniFlex†). The corroded samples were cleaned in a solution of phosphoric acid (H₃PO₄) and chromium trioxide (CrO₃) at 90 °C for 10 minutes as described in ASTM G01-03. The weight loss of the samples was obtained by recording the weight of the samples before immersion and after chemical cleaning.

† Trade Name
**Results and discussion**

**Weld zone identification**

Fig. 2 shows the metallographic cross-section of a FSW-AA5086 sample after slight corrosion in acid solution (2.5 vol.% HNO₃). The central NZ has microstructure commonly denoted as onion rings. The NZ is wider on the crown region of the weld because the upper surface was in contact with the tool shoulder.

![Image of weld zones](image.png)

**Mechanical properties**

The microhardness distribution was measured across the top surface of the FSW-AA5086 (Fig. 3). The hardness curve demonstrates a "W"-shaped hardness distribution, which is asymmetrical with respect to the weld centerline. The minimum hardness was observed in the TMAZ/HAZ regions, while the maximum value occurred in the BM. According to the Hall-Petch relationship, the hardness value in the NZ was higher than that of the TMAZ/HAZ because of the fine equiaxed grain structure in the NZ [18]. In addition, because AA5086 is strain hardened and not precipitation hardened, it is possible that high temperatures attained during the FSW process in the TMAZ/HAZ lead to dislocation annihilation that attenuated the strain-hardening mechanism.

The tensile stress-strain curves of the BM and two types of FSW specimens (Fig. 1) are shown in Fig. 4. The elongation, yield strength, and tensile strength of the BM-AA5086 were approximately 17%, 237 MPa, and 300 MPa, respectively. As compared to the BM, all FSW tensile specimens had lower tensile and yield strength values, which can be attributed to the weld zone having lower hardness than the BM. However, the ductility of the two FSW specimens increased as compared to that of the BM. Notice that the longitudinal tensile specimen (L-AA5086-AA5086) had a significant increase in ductility with an elongation value more than 2 times of that of the BM. Because the longitudinal tensile specimens contained only recrystallized, fine equiaxed grains from the NZ (Fig. 1), ductility was significantly better that the BM with relatively large grains and previously strain hardened. The transverse tensile specimens contained all four zones (i.e., BM, HAZ, TMAZ, and NZ), each with different properties due to different grain-size/dislocation-density combinations. Therefore, the observed ductility was measured as an average strain over the gage length. During the tensile test, failure occurred in the weakest region of the weld[19], which was the HAZ for the specimen T- AA5086-AA5086. As a comparison, the BM-AA5086 and L- AA5086-AA5086 fractured in the center of the specimen.

The fractured FSW tensile specimens showed obvious necking/plastic deformation, which was not obvious in the BM-AA5086 specimens. The fractographs of the BM and the two FSW specimens (Fig. 5) revealed dimple structures, which were of various sizes and densities. Compared to the BM-AA5086 and L-AA5086-AA5086 (failure occurred in NZ) specimens, the fracture surface of the T-AA5086-AA5086 specimen (failure occurred in HAZ) appeared to have the highest dimple density. The T-AA5086-AA5086 specimen exhibited lower ultimate tensile strength than the BM-AA5086 and L-AA5086-AA5086 specimens.
Electrochemical measurements

Fig. 6 shows typical polarization curves of the different weld zones in FSW AA5086-AA5086 in deaerated 3.15 wt.% NaCl solutions. All weld zones showed a passive region below $E_{\text{pit}}$, above which the current density increased abruptly due to the breakdown of the passive film. Table 1 summarizes the $E_{\text{corr}}$, $i_{\text{corr}}$, and $E_{\text{pit}}$ values obtained from Fig. 6. The pitting potential became more noble in the weld zones with the highest in the NZ and lowest in the BM: NZ > TMAZ > HAZ > BM. The corrosion potentials increased by approximately 150 mV in the aerated solutions, but the extrapolated corrosion rates $i_{\text{corr}}$ decreased slightly. This is not too unusual since the $E_{\text{corr}}$ values were still below the $E_{\text{pit}}$ values, and the anodic dissolution is still in the passive regime. This was attributed to very little cathodic sites for oxygen reduction on AA5086, which is consistent with its excellent corrosion resistance even in marine environments. The extrapolated $i_{\text{corr}}$ values were consistently lowest for the HAZ in both the deaerated and aerated solutions. The coarsening and resolutionizing of precipitates in FSW AA2219 has been reported to lower corrosion rates [20, 21, 22], likely by the elimination of cathodic sites. In this AA5086, which is a non-heat-treatable alloy, the annihilation of dislocation in the HAZs could potentially be responsible for the improved corrosion resistance. In the aerated solution, the $i_{\text{corr}}$ value was highest in the NZ.

Table 1. $E_{\text{pit}}$, $E_{\text{corr}}$, and $i_{\text{corr}}$ and values of different zones in FSW AA5086-AA5086 in 3.15 wt.% NaCl solutions.

<table>
<thead>
<tr>
<th>Weld Zone</th>
<th>Deaerated</th>
<th>Aerated</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$E_{\text{pit}}$ (mV SCE)</td>
<td>$E_{\text{corr}}$ (mV SCE)</td>
</tr>
<tr>
<td>BM</td>
<td>-767</td>
<td>-953</td>
</tr>
<tr>
<td>HAZ</td>
<td>-762</td>
<td>-929</td>
</tr>
<tr>
<td>TMAZ</td>
<td>-748</td>
<td>-924</td>
</tr>
<tr>
<td>NZ</td>
<td>-730</td>
<td>-924</td>
</tr>
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</table>
**SEM analysis**

The SEM images of FSW AA5086-AA5086 samples that were immersed in the three different solutions for 90 days are shown in Figs. 8-10. Generally, the SEM images showed that the amounts of corrosion products on FSW AA5086-AA5086 samples immersed in the three solutions were highest for 3.15 wt.% NaCl, followed by ASTM seawater, and least for the 0.5 M Na$_2$SO$_4$ solution. This trend indicates that among the three solutions, 3.15 wt.% NaCl solutions is the most corrosive environment for AA5086-AA5086 samples while 0.5 M Na$_2$SO$_4$ is the least corrosive environment. In addition, the SEM images showed that, in all three environments, the HAZ had much less corrosion products than the other three zones (i.e., NZ, TMAZ, and BM). However, it is difficult to differentiate the other three zones in terms of the amounts of corrosion products on them. The conclusion that HAZ is the most corrosion-resistant zone in FSW AA5086-AA5086 is in good agreement with the polarization results.

![SEM images](image)

**Fig. 8.** SEM images of different zones in FSW-AA5086 after 90 days immersion in 3.15 wt.% NaCl: (a) TMAZ, (b) BM, (c) Nugget, and (d) HAZ.
Fig. 9. SEM images of different zones in FSW-AA5086 after 90 days immersion in ASTM seawater: (a) TMAZ, (b) BM, (c) Nugget, and (d) HAZ.

Fig. 10. SEM images of different zones in FSW-AA5086 after 90 days immersion in 0.5 M Na$_2$SO$_4$: (a) TMAZ, (b) BM, (c) Nugget, and (d) HAZ.

**Raman spectroscopic and XRD analysis**

Fig. 11 shows Raman spectra obtained from the corrosion products formed on different zones in FSW AA5086-AA5086 after 90 days immersion in 3.15 wt.% NaCl, ASTM seawater, and 0.5 M Na$_2$SO$_4$ solutions. Raman bands
for bayerite (α-Al(OH)₃) were detected from all zones in FSW AA5086-AA5086 immersed in 3.15 wt.% NaCl solution (Fig. 11a) that were close to the characteristic bands at 237, 296, 322, 388, 435, 545, and 569 cm⁻¹ [23]. Notice that the strong Raman band at 237 cm⁻¹ might be partially from system noise [24-26]. On the sample immersed in ASTM seawater (Fig. 11b), only weak Raman signals of α-Al(OH)₃ at 435 and 569 cm⁻¹ were detected. The sharp bands at 982 and 996 cm⁻¹ are from Na₂SO₄ in the ASTM sea salt. On the sample immersed in Na₂SO₄ solution (Fig. 11c), only Raman signal of Na₂SO₄ (457, 615, 636, 996, 1075, and 1131 cm⁻¹) was observed and that from Al(OH)₃ was not detected. The characteristic bands of Na₂SO₄ associated with internal vibrations of SO₄²⁻ are 449, 466, 620, 632, 647, 992, 1101, 1131, and 1152); and the presence of other cations or hydration can cause some peak shifts.[27]

The Raman spectroscopic analysis agreed well with the SEM results and showed that more corrosion products (i.e., Al(OH)₃) formed on FSW AA5086-AA5086 samples immersed in 3.15 wt.% NaCl than in ASTM seawater and 0.5 M Na₂SO₄. Another agreement between the Raman analysis and SEM observation is that they all differentiate the HAZ from the other three zones on FSW AA5086-AA5086 immersed in 3.15 wt.% NaCl, in terms of the amount of corrosion products. This is evidenced by the two Raman bands at 296 and 321 cm⁻¹ for bayerite having the lowest intensities in the Raman spectra (Fig. 11a) from HAZ as compared to the other three zones. Fig. 12 shows the XRD patterns obtained from FSW AA5086-AA5086 samples immersed in the three solutions for 90 days. Notice that XRD patterns were collected from both the upside and downside of the FSW weld zone and the BM with an area of approximately 1 × 1 in². Fig. 12a shows strong peaks of α-Al(OH)₃ which indicates that a considerable amount of α-Al(OH)₃ formed on the samples immersed in NaCl solution. On the contrary, only extremely weak peaks of α-Al(OH)₃ were observed for ASTM seawater and 0.5 M Na₂SO₄ solution (Fig. 12b and c), implying the formation of small amounts of corrosion products. The XRD analysis generally agrees well with SEM and Raman results.

![Fig. 11. Raman spectra obtained from the corrosion products on different zones in FSW-AA5086 after 90 days immersion in (a) 3.15 wt.% NaCl, (b) ASTM seawater, and (c) 0.5 M Na₂SO₄ solution.](image1)

![Fig. 12. XRD patterns obtained from FSW-AA5086 samples after 90 days immersion in (a) 3.15 wt.% NaCl, (b) ASTM seawater, and (c) 0.5 M Na₂SO₄ solution.](image2)
Weight loss measurements

The corrosion rates of FSW AA5086-AA5086 immersed in the three different solutions for 90 days are shown in Fig. 13. The corrosion rates of FSW AA5086-AA5086 from the highest to the lowest for three solutions was as follows: 3.15 wt.% NaCl > ASTM seawater > 0.5 M Na₂SO₄, which agrees with SEM, Raman, and XRD results.

![Graph showing corrosion rates](image)

Fig. 13. Corrosion rates of FSW-AA5086 specimens after 90 days immersion in 3.15 wt.% NaCl, ASTM seawater, and 0.5 M Na₂SO₄ solution.

Conclusions

All FSW AA5086-AA5086 specimens showed significant decreases in both tensile and yield strengths, but an increase in ductility. The T-AA5086-AA5086 tensile specimens failed in the TMAZ/HAZ regions, where the lowest hardness values were detected. The BM and L-AA5086-AA5086 (NZ) failed in the center of the specimen. In deaerated and aerated 3.15 wt.% NaCl solutions, the lowest corrosion rates were in the HAZ and the highest corrosion rates were in the NZ (aerated) and BM (deaerated). SEM observation, Raman spectroscopic and XRD characterization of the corrosion products on FSW AA5086-AA5086 immersed for 90 days in three air-exposed solutions indicated that corrosion was most severe in 3.15 wt.% NaCl, followed by the ASTM seawater, and then 0.5 M Na₂SO₄, which was also consistent with corrosion rates determined by weight-loss calculations. SEM and Raman results also showed that the HAZ had the least amount of corrosion as compared to the other three regions. The main corrosion product was identified as α-Al(OH)₃ (bayerite) using Raman and XRD analyses.

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References


