Corrosion Behaviour of Friction Stir Welded AA5xxx Aluminium Alloys

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Friction stir welding (FSW) is a well recognised method for joining aluminium alloys and other engineering materials at a temperature below their melting point. However, the microstructure of the alloys may be modified during the welding process due to frictional heat and severe plastic deformation.

In this study, the microstructures of friction stir welded AA5754-H111 and AA5083-O aluminium alloys have been investigated using optical microscopy, transmission and scanning electron microscopy equipped with electron backscatter diffraction (EBSD) and energy dispersive x-ray (EDX) facilities. Typical weld zones introduced by FSW were observed. Further, a joint line remnant flaw (JLR) within the thermomechanical affected zone (TMAZ) of the welds was also revealed. The formation of the JLR is attributed to dispersion of the magnesium rich oxides within the joining line.

The effect of the modified alloy microstructure on the corrosion behaviour of the welds has been investigated by corrosion susceptibility testing and ex-situ SEM examination. Both parent alloys and welds showed good exfoliation and intergranular corrosion resistance (IGC). However, severe localized corrosion was observed at joint line remnant and the weld root.

Reduced hardness was recorded in the heat affected zone (HAZ) of AA5754-H111 aluminium alloy weldment. This is attributed to the heat generated during welding that led to grain coarsening. In contrast, slightly increased hardness was recorded within the TMAZ. This was related to the grain refinement as a result of the recrystallization process that took place due to the effect of the thermal cycle and the plastic deformation. Little hardness change was recorded within AA5083-O aluminium alloy weldment. This was attributed to the effect of the alloy temper condition.

Thermal simulation of the service environment of the friction stir welded alloys was conducted to assess the resistance to sensitization of welds. After exposure of the welded AA5754 and AA5083 alloys at 50, 70 and 170°C for prolonged time, the resistance of the AA5083 alloy weld to the IGC drastically decreased owing to the precipitation of magnesium rich particles known as β-phase at the grain boundaries. On the contrary, the resistance of the AA5754 alloy weld to IGC remained after the thermal exposure. Thus, the level of Mg content in Al-Mg alloys plays an important role in determining the corrosion characteristics of the alloys. The precipitation of Mg rich particles (β-phase) on the grain boundary is the determining factor for the resistance of the AA5xxx alloys to IGC owing to the difference in the electrode potentials between the β-phase and the grain interior, which leads to the generation of microgalvanic cells and selective dissolution of the grain boundary.
DECLARATION

I declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or any other institution of learning.

Ramadan.R. Abuaisha
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<tr>
<td>AA5754</td>
<td>Aluminum Alloy</td>
</tr>
<tr>
<td>AA5083</td>
<td>Aluminum Alloy</td>
</tr>
<tr>
<td>H111</td>
<td>Some work hardening impacted by Shaping but less than required for H11 temper</td>
</tr>
<tr>
<td>O</td>
<td>Annealed. Applies to wrought products that have undergone a thermal treatment to reduce their mechanical property levels to their minimums. Often described as &quot;dead soft&quot; metal.</td>
</tr>
<tr>
<td>FSW</td>
<td>Friction stir welding</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscope</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Back Scattered Diffraction</td>
</tr>
<tr>
<td>EDX</td>
<td>Electron Depressive X-ray</td>
</tr>
<tr>
<td>SKPM</td>
<td>Scanning Kelvin Probe Microscope</td>
</tr>
<tr>
<td>PM</td>
<td>Parent metal</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat Affected Zone</td>
</tr>
<tr>
<td>TMAZ</td>
<td>Thermo- Mechanical Affected Zone</td>
</tr>
<tr>
<td>AS</td>
<td>Advancing side of TMAZ</td>
</tr>
<tr>
<td>RS</td>
<td>Retreating side of TMAZ</td>
</tr>
<tr>
<td>SZ</td>
<td>Stir zone</td>
</tr>
<tr>
<td>JLR</td>
<td>Joint Line Remnant</td>
</tr>
<tr>
<td>TWI</td>
<td>The Welding Institute</td>
</tr>
<tr>
<td>°C</td>
<td>Degree celsius</td>
</tr>
<tr>
<td>Nm</td>
<td>Nanometre</td>
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<tr>
<td>Cl</td>
<td>Chlorine</td>
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<tr>
<td>Cu</td>
<td>Copper</td>
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<tr>
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<tr>
<td>Mg</td>
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Li…………………………………………….…. Lithium
Zn…………………………………………....… Zinc
Ni……………………………………………..... Nickel
Cr…………………………………………….. Chromium
Ti…………………………………………….. Titanium
Zr…………………………………………….. Zirconium
Sc……………………………………………. Scandium
Fe…………………………………………….. Iron
Si…………………………………………….. Silicon
Mo…………………………………………….. Molybdenum
Ta…………………………………………….. Tantalum
Cr…………………………………………….. Chromium
Sn…………………………………………….. Lead
Ga…………………………………………….. Gallium
Hg…………………………………………….. Mercury
O…………………………………………….. Oxygen
OCP………………………………………….. Open circuit potential
NaCl………………………………………… Sodium chloride
Ecorr………………………………………….. Corrosion potential
Icorr………………………………………….. Corrosion current A/cm²
Ipass………………………………………….. Passivation current density
Epass………………………………………….. Passive potential
H₂O₂……………………………………….. Hydrogen peroxide
HNO₃……………………………………….. Nitric acid
H₃SO₄……………………………………….. Phosphoric acid
e⁻………………………………………….. Electron
Al⁺³………………………………………… Aluminium ion
H₂O………………………………………… Water
Al(OH)₃…………………………………… Aluminium hydroxide
H⁺………………………………………….. Hydrogen ion
OH⁻………………………………………… Hydroxyl anions
Cl⁻………………………………………….. Chloride
HCl………………………………………… Hydrochloric acid
OCP……………………………………….. Open circuit potential
<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>ASTM</td>
<td>American society for testing and materials</td>
</tr>
<tr>
<td>IGC</td>
<td>Intergranular corrosion</td>
</tr>
<tr>
<td>g/l</td>
<td>Gram per litre</td>
</tr>
<tr>
<td>NAMLT</td>
<td>Nitric acid metal loss test</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress Corrosion Cracking</td>
</tr>
<tr>
<td>mm</td>
<td>Millimetre</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometre</td>
</tr>
<tr>
<td>A/Cm²</td>
<td>Amber per centimetre square</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>pH</td>
<td>Negative logarithm (base 10)</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>HV</td>
<td>Vickers Hardness</td>
</tr>
<tr>
<td>Kg</td>
<td>Kilogram</td>
</tr>
<tr>
<td>kV</td>
<td>Kilo volt</td>
</tr>
<tr>
<td>LSM</td>
<td>Laser surface melting</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotation per minute</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>Wt.%</td>
<td>Weight percent</td>
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CHAPTER 1

Introduction

Currently, aluminium alloys are used as alternatives to steel in many applications because of their light weight, good weldability, good formability, good strength and corrosion resistance [1]. AA5xxx aluminium alloys, including AA5754 and AA5083, have become widely used in automotive [2], and marine industries [3]. The growing applications have added challenges for improvement of the welding processes. Friction stir welding (FSW) is a well recognised method for joining aluminium alloys and other materials. The process was invented as a replacement method to fusion joining processes for aluminium alloys and other engineering materials. With use of this process, the porosity and hot cracking defects, often generated with fusion welding, are largely eliminated with resulting improved mechanical and corrosion properties.

The process has a great influence on the microstructure; it substitutes the coarse grains of the post welded aluminium alloy with small equiaxed grains within the stir zone and deformed elongated ones at the thermomechanical affected zone (TMAZ) edges due to the effect of frictional heat and severe plastic deformation.

Although joining with this process takes place below the melting temperature of the parent alloys, the heat generated may alter the alloy microstructure and, consequently, affect the mechanical and corrosion properties.

The aim of the present study is to evaluate the influence of the FSW process on the microstructure of AA5754-H111 and AA5083-O aluminium alloys and the subsequent effect on their corrosion and mechanical properties. Further, the effect of service temperatures on the corrosion behaviour of weldments and the parent alloys has been evaluated.
In this study, ASTM-G66-99 assessment test (ASSEST) was employed for assessing the resistance of friction stir welds and the parent alloys to exfoliation corrosion. ASTM-G67 standard, known as Nitric Acid Metal Loss Test (NAMLT), and phosphoric acid etch response test were used for evaluating the susceptibility of the weldments to intergranular corrosion (IGC). Agar gel testing, and electrochemical measurements were used to verify the galvanic corrosion between the weld regions and parent alloys. Hardness measurement was conducted for evaluating the effect of the FSW process on the mechanical properties of AA5754-H111 and AA5083-O weldments.

Optical microscopy (OM), atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) equipped with dispersive energy X-ray (EDX) analysis and electron backscattered diffraction (EBSD) were utilized for characterizing the weldment microstructures.
CHAPTER 2
-------------------------------------------------------------------------------

Literature Review

2.1 Aluminium and its alloys

Aluminium is a light, soft and reactive metal. It has a low strength when it is in a high purity condition. However, when the metal is alloyed its mechanical properties are enhanced. Aluminium alloys have shown good mechanical properties for low temperature applications. On the contrary, they lose their tensile and yield strengths as well as the corrosion resistance on exposure to elevated service temperature for sufficient periods of time. Aluminium and its alloys are characterised with their resistance to corrosion, owing to the ability to form a thin oxide film on their surfaces due to a high reactivity with oxygen. The naturally formed air oxide film is stable in neutral and some acidic solutions. It works as an insulator and serves to protect the underlying material from the external environments. However, the oxide film is soluble in most acidic solutions and high alkalinity solutions. The electrochemical behaviour of aluminium influences by the variation in the composition of the alloy and the oxide film, concentration of the aggressive species within the solution, solution temperature, pH and the flow rate [4-6].

2.1.1 Characteristics of aluminium and its alloys

Aluminium and its alloys are used in various industrial applications due to a number of advantages [7-8]:

- A combination of high strength, low density, good formability and good weldability give approval for use in critical applications such as automotive and aerospace industry.
- Good corrosion resistance to the atmosphere, neutral solutions and some acidic solutions owing to formation of an insulating, thin, adherent and self healing oxide film on their surfaces. Their corrosion resistance can be enhanced by anodizing and laser surface melting.
• High electrical conductivity allowed their use in electrical power applications.
• Non magnetic property eliminated arc blow problem associated with arc welding processes.
• High modulus of elasticity increased the resistance to impact loading and provided ability to absorb the loading energy.
• Good toughness resistance at low temperature provided advantage for use in cryogenic applications.
• Good formability facilitated their shaping by several ways of forming processes, such as deep drawing, extrusion and cold work forming.
• Non-poisonous and colourless corrosion products facilitated their use in chemical and food-processing industry
• Low melting point made the cost of the aluminium recycling and re-processing cheaper than its extraction.

Unfortunately, aluminium and its alloys have poor fatigue and wear resistance and suffer from losses of mechanical and corrosion properties at elevated and high service temperatures which restricted the use of aluminium and its alloys in high or medium flow turbulences and high temperature application.

2.1.2 Mechanical properties of aluminium and its alloys

The low mechanical property of unalloyed aluminium has restricted its use in fields that require high strength [9]. Addition of alloying elements, such as copper, manganese, silicon, magnesium, and zinc, enhanced the mechanical properties and allowed its use in critical fields that require high strength material. Figure 2.1 presents a comparison between the strength of high purity aluminium alloy and other aluminium alloys. It is evident that both yield and tensile strengths of the pure aluminium are far lower than the alloyed ones [10].

As it can be seen from Figure 2.1, the heat treatable aluminium alloys have higher mechanical properties than non heat treatable alloys owing to their ability to respond to the heat treatment. They develop their good strength from the precipitate hardening effect. However, AA5xxx alloys have the highest mechanical properties among the non heat treatable alloys, i.e. AA 1xxx and 3xxx alloys, due to the magnesium effect.
Magnesium is one of the major alloying elements that is added to aluminium to improve its mechanical properties, formability, corrosion resistance and weld-ability [11].

The aluminium alloys that contain magnesium as a major alloying element are identified as AA5xxx (Al-Mg), non-heat-treatable alloys. AA5xxx alloys obtain their strength from solid solution strengthening and strain hardening. The mechanical properties of these alloys increase with the increase of magnesium content and work hardening rate. For instance, the yield strength of the fully annealed AA5005 alloy containing 0.05-0.1 wt. % magnesium is about 40 MPa. While the yield strength of the fully annealed AA5456 alloy, containing higher magnesium content, i.e. 5.1 wt. %, is about 310 MPa and when the later alloy is subjected to full work hardening (H-16 temper), its yield strength reached to about 352 MPa [11].

The increase in magnesium content and work hardening have been shown to increase both yield and tensile strengths of aluminium at the expense of the ductility, as illustrated in Figures 2.2 and 2.3 [12-13].
Figure 2.2- Effect of Mg on Al and Al-Mg binary alloys mechanical properties [12].

Figure 2.3- Effect of Mg and the cold work on high purity aluminium and aluminium-magnesium binary alloys yield strength [13].
Unfortunately, the solid solubility of magnesium in aluminium is limited. The maximum solid solubility is about 14.9 wt. % at 450 °C which drastically decreases on cooling to 1.7 wt. % at ambient temperature. Therefore, the magnesium that comes out of the solid solution causes precipitation of an undesired, electrochemically active magnesium-rich phase known as the β-phase at the grain boundaries. This phase has been reported to reduce both mechanical properties and corrosion resistance of Al-Mg alloys [9, 14]. Further, the thermal cycling from heating, welding and thermal processing can lead to precipitation of the magnesium-rich phase on the grains boundaries and, subsequently, alters their mechanical properties and corrosion behaviour. The induced heat also has an influence on the microstructure. It can reduce the dislocation density through annealing the post welded or heated alloy microstructure, recrystallize or coarsen the grain and reduce solute atoms (magnesium) which, in turn, results in a decrease in the mechanical properties and corrosion resistance of Al-Mg alloys.

2.1.3 The alloying elements

Copper, silicon, manganese, magnesium, lithium and zinc are added to aluminium in a controlled amount to improve its mechanical properties, corrosion behaviour, formability and weldability. On the other hand, nickel, chromium, titanium, zirconium and scandium are added to achieve specific properties. Generally, the added alloying elements can be classified into two types:

- Those that enhance the mechanical and physical properties through solid solution strengthening and forming fine precipitate hardening phases. These include copper, manganese, zinc, magnesium, silicon and zirconium.
- Those that initially present in aluminium as impurities such as iron (Fe) and silicon (Si). These tend to form a relatively coarse cathodic constituent second phases owing to their limited solid solubility [15].

Effect of the alloying elements on the aluminium properties can be summarized as follows:
Copper (Cu) provides a good level of strength through solid solution hardening. On the other hand, it reduces the aluminium corrosion resistance, ductility and the weldability [16].

- Manganese (Mn) acts as a grain refiner; addition of manganese to aluminium increases the aluminium strength and reduces its ductility [17].
- Silicon (Si) improves fluidity, castability, strength and ductility of the aluminium. It produces precipitate hardening when added with magnesium [11].
- Magnesium (Mg) improves the aluminium weldability, corrosion resistance, strength and work hardening ability [11].
- Zinc (Zn) with magnesium and copper enhances aluminium strength by permitting precipitation hardening. When added in the range of 0.68-0.70 wt. % to standard AA5083 aluminium alloy, it enhances the resistance to IGC [18].
- Iron (Fe) reduces the aluminium corrosion resistance, enhances the electrical conductivity and improves the aluminium strength [9].
- Nickel (Ni) improves the strength of castings and enhances elevated temperature performance of the aluminium.
- Chromium (Cr) improves the stress corrosion resistance of the aluminium alloys.
- Zirconium (Zr) acts as a grain-refiner [19-20].
- Lithium (Li) increases strength, Young’s modulus, provides precipitation hardening and decreases the density [11].
- Scandium (Sc) increases the aluminium strength by an age hardening effect, improves the weldability and acts as a grain refiner [19].
- Lead (Pb) and bismuth (Bi) assist chip formation in free machining alloys [11].

2.1.4 Weldability of aluminium and its alloys

The common methods used for joining aluminium and its alloys are the solid state bonding and fusion welding processes. With solid state joining, the parts are frictioned under pressure to attain bonding. AA5xxx aluminium alloys can be successfully joined with both processes. On the contrary, AA2xxx and AA7xxx have shown difficulty in joining with arc joining processes due to their susceptibility to pitting and solidification cracking. Use of FSW process as alternative to fusion welding processes can eliminate this issue [21-22].
Usually, joining of aluminium and its alloys with fusion welding processes requires attention since the thermal coefficient of expansion for the aluminium is high. For this reason the heat input during joining has to be high to insure proper fusion, particularly for thick sections [7].

Joining with FSW requires proper selection of the welding parameters and the tool design for obtaining welds of a good quality. It is mandatory that the tool should be made from material of a lower thermal conductivity than the components to be joined to avoid absorption of the heat by the tool.

### 2.1.5 Aluminium oxide film

The passive film (Al\(_2\)O\(_3\)) forms from reaction of aluminium with oxygen and aqueous solutions. It forms according to the following reaction:

\[
4 \text{Al} + 3 \text{O}_2 \rightarrow 2 \text{Al}_2\text{O}_3
\]

\[
2\text{Al}(s) + 3\text{H}_2\text{O} (l) \rightarrow \text{Al}_2\text{O}_3(s) + 6\text{H}^+ (\text{aq}) + 6\text{e}^-
\]

The thickness of the oxide film in air and aqueous solutions at room temperature is about 2-3 nm and increases with oxidation at temperatures below 797°F to 20 nm [23]. The formed film is characterised by its ability to self-repair once scratched or mechanically damaged. With anodizing, the thickness of the oxide film can reach 10-20 μm [12].

The film contains two layers known as inner and outer oxide layers. The inner layer has an amorphous structure and it is thinner and less permeable than the outer hydrated oxide layer. The thickness of the inner layer increases with increase of the oxygen pressure and the solution temperature.

The oxide film does dissolve in both acidic and high alkalinity solutions according to the reactions:

\[
\text{Al}_2\text{O}_3(s) + 6\text{H}^+ (\text{aq}) \rightarrow 2\text{Al}^{3+} (\text{aq}) + 3\text{H}_2\text{O} (l)
\]

\[
\text{in acidic solution}
\]

\[
\text{Al}_2\text{O}_3(s) + 3\text{H}_2\text{O} (l) + 2\text{OH}^- (\text{aq}) \rightarrow 2\text{Al} (\text{OH})_4^- (\text{aq})
\]

\[
\text{in alkaline solution}
\]

On the contrary, in neutral solutions, the oxide film is stable and functions as a barrier between the aluminium substrate and the surrounding environment. Thus, it inhibits
passage of electrons and protects the aluminium substrate from the attack of aggressive solutions. Unfortunately, the aluminium oxide film does contain flaws and or defects caused by the heat treatment and the fabrication processes [24]. The latter tend to create roughness and cracks within the oxide film giving accessibility to the surrounding solution aggressive species such as Cl⁻, Br⁻, I⁻ ion that penetrate through the defective locations within the oxide film to the aluminium substrate and attack the substrate locally causing pitting [8, 25-26].

Further, the impurities picked up from the lubricant during rolling processes may have a different chemical behaviour from the surrounding areas, resulting in initiation of localised corrosion in the form of pitting that is driven by the corrosion potential variation [8]. Figure 2.4 demonstrates possible flaws and defects that may exist within the aluminium oxide film.

![Schematic of Possible Defects and Flaws](image)

**Figure 2.4** Possible flaws and defects within the aluminium oxide film [8].

### 2.2 Corrosion of aluminium

Aluminium is an active metal with a corrosion potential of -1.66 mV vs. SCE [9]. The aluminium is anodic to most of the engineering materials. For this reason, it is used as a sacrificial anode for protecting less active materials against corrosion [27].

Aluminium and its alloys have shown good resistance to corrosion in neutral solutions, the atmospheric environment and some acidic solutions, due to formation of a protective oxide film on their surfaces [24, 28].

The formed oxide film has a low rate of dissolution in aqueous solutions of pH 4.0 to 9. However, it does dissolve in a low pH solutions of less than 4 and high alkalinity...
solutions of pH higher than 9. There are some exceptions, where aluminium showed resistance to corrosion in acidic solutions such as concentrated nitric acid > 80 wt. % and sulfuric acid 98 to 100 wt. % [29].

The corrosion process of aluminium in the presence of aggressive solutions is an electrochemical process which involves dissolution of aluminium [8].

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^{-}
\]

The cathodic reactions combine the dissolution of aluminium in acidic, neutral and alkaline solutions in aerated and deaerated condition are as follows [6]

In aerated acidic solutions

\[
\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O} \tag{1}
\]

In aerated neutral and alkaline solutions

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-} \tag{2}
\]

In de-aerated acidic solutions

\[
2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2 \tag{3}
\]

In de-aerated neutral and alkaline solutions

\[
2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-} \tag{4}
\]

In acidic and high alkalinity solutions, the aluminium oxide film is attacked uniformly. Accordingly, the type of corrosion that takes place in this environment is general corrosion. While, in neutral solutions, the oxide film is attacked locally due to increase of alkalinity around the impurities and the intermetallic particles, which exposes the aluminium substrate and accelerates its attack leading to loss of bonding between the matrix and the intermetallic particles and subsequently formation of localized corrosion in the form of pitting corrosion. The susceptibility of the aluminium to localised corrosion increases with increase of chloride and oxygen concentration, pH and solution flow rate, the presence of second phase precipitates, inclusions and grain boundary segregation and the effect of static fluctuating stress [30-31].
2.1.1 Effect of the alloying elements on aluminium corrosion

Beside their effect on the mechanical properties, the alloying elements have an influence on the corrosion behaviour of the aluminium. Copper, manganese and silicon have been shown to increase the aluminium corrosion potential. On the other hand zinc and magnesium reduce the corrosion potential [12]. Such an effect is clearly shown in Figure 2.5. Addition of molybdenum (Mo), tantalum (Ta) and chromium (Cr) to supersaturated aluminium alloys formed by sputter deposition, as showed by Davis et al [32], improved the pitting resistance of Al-Ta, Al-Mo and Al-Cr binary alloys. The improvement was correlated to the presence of oxidized solute species within the oxide film, which served in impeding the passage of the chloride anions through the oxide film and enhanced the resistance to pitting.

Tin (Sn), gallium (Ga), mercury (Hg) and bismuth (Bi) have been reported to increase the rate of aluminium dissolution. For this reason the aluminium contained these alloying elements is used as a sacrificial anode [33-34].

Figure 2.5 presents the influence of Mn, Cu, Si, Mg and Zn on the corrosion potential of solution-treated and quenched high-purity binary aluminium alloys in a solution of 53g/l NaCl and 3 g/l H₂O₂ at ambient temperature [12].

![Figure 2.5](image-url)
However, the effect of alloying elements on the aluminium corrosion behaviour can be detrimental when their limited solid solubility is reached. The alloying elements do have a limited solid solubility in aluminium at certain temperatures and concentration. Therefore, on cooling, they tend to form relatively coarse constituent anodic and or cathodic intermetallic particles that have been reported to cause pitting due to the difference in the corrosion potential with the surrounding matrix. On exposure to solutions containing aggressive anions, such as chloride, the cathodic reaction around the more noble intermetallic particles increases the alkalinity due to production of hydroxyl ions (OH⁻) which aggressively attack the oxide film and the underlying aluminium substrate resulting in pitting formation owing to weakening of the bonding between the aluminium matrix and the second phases. The anodic particles preferentially corrode and leave a hole behind [35]. A typical example on the effect of the intermetallic particles on corrosion behavior of AA2024-T3 is evident in Figure 2.6 where point 1 represents the anodic particle and point 2 the cathodic particle compared with the matrix [36].

![Figure 2.6 SEM images of AA3024-T3 alloy surface before and after immersion in 0.5M NaCl solution](image)

a) Polished surface before immersion testing  b) After immersion in 0.5M NaCl solution

Figure 2.6 SEM images of AA3024-T3 alloy surface before and after immersion in 0.5 M NaCl solution for 4 h [36].

### 2.2.2 Atmospheric corrosion

The corrosion rate of aluminium in industrial environments has been reported to be below 5 μm / year. Normally, at the first year of exposure to the atmosphere the rate of its attack is high, which then starts to reduce as a result of developing a weathered
surface. However, rain washing has been reported to be beneficial in reducing the attack of the aluminium in the atmospheric environment since it helps in washing out the aggressive ions and deposits from the surfaces. AA5xxx aluminium alloys are considered to be resistant to atmospheric corrosion, especially in marine and splash-zone locations. On the contrary, AA2xxx, and AA7xxx were prone to corrosion in atmospheric and sea water environments [34, 37].

2.2.3 Pitting corrosion

Pitting corrosion is known to take place on alloys that form passive films on their surfaces, such as nickel alloys, aluminium alloys and stainless steel, due to the breakdown of their passive films [6, 28, 31].

As a general rule, pitting on the aluminum alloy surface takes place in the neutral solutions of pH in the range of 4.5-8.5 pH [38]. Initiation of pitting requires the presence of oxygen, moisture, aqueous solutions such as rainwater, seawater, etc, and aggressive anions such as chloride, inclusions, second phases and mechanical damage sites [39]. The rate of pit attack in terms of size, density and depth depend on the material homogeneity, intermetallic particle size and type, solution temperature and concentration of the aggressive species. Usually pits are formed in a scattered or clustered form, with different size and irregularity in shape.

The intermetallic particles are believed to responsible for initiation of pitting due to the variation in the corrosion potential with respect to the aluminium matrix. Based on the corrosion potential of the intermetallic particles, the particles either corrode or promote the surrounding aluminium matrix to dissolve, resulting in a pitting corrosion [40-42].

The pitting corrosion can act as an initiation point to other forms of corrosion including stress corrosion cracking and fatigue corrosion and may lead to component failure, loss of product and equipment failure [31, 43].

AA3xxx, AA5xxx and AA6xxx aluminium alloys do suffer from pitting corrosion but to lesser extent than AA2xxx and AA7xxxx aluminium alloys. More often than not, the formed pit in aluminium alloys can be observed by the naked eye and is almost covered with a white alumina gel Al(OH)₃ [9].
2.2.3.1 Pitting corrosion mechanism

For various reasons, the passive film breaks down locally. At the breakdown location, aggressive anions of the solution become in contact with the bulk material. The region of contact becomes acidic owing to the hydrolysis process and starts to corrode rapidly. The result is a hole termed a pit. Work on the pitting corrosion mechanism pointed out that the pitting occurs in three stages, (1) initiation, (2) propagation and (3) termination [9, 44].

Figure 2.7 Schematic drawing showing the pitting mechanism involves metal dissolution inside the pit and oxygen reduction reaction on the adjacent surfaces [10].

2.2.3.2 Pitting initiation

The initiation of pitting in aluminium and its alloys has been related to the local breakdown of the oxide film as a result of its local thickening or thinning and to the galvanic action driven by the corrosion potential variation between the intermetallic particles and the aluminium matrix [5, 45-46].

As explained by Choa et al [47], thickening of the oxide film results from diffusion of cation vacancies from the oxide/solution interface towards the metal/oxide interface. At the metal/oxide interface, the metal atoms oxidize and fill the cation vacancies. The oxide film thickens and breaks when the rate of formation of cation vacancies at the metal/oxide interface is higher than that of anions vacancies filling. Once the oxide film
breaks, the aluminium substrate is not protected any more by the passive film and exhibits susceptibility to pitting corrosion at the surface protective film breakdown location.

The local thinning of the oxide film is attributed to the effect of the adsorbed aggressive anions at the oxide film. The anions enhance catalytically the transfer of the metal cations leading to thinning of the passive layer [5].

The intermetallic particles (second phases) have been reported to be the key factor in initiation of pitting in aluminium alloys due to the difference in their corrosion potential with respect to the matrix. Based on the intermetallic particle composition, it may behave in an anodic or cathodic manner with respect to the matrix. In the presence of an aggressive solution, such as sea water, the anodic ones have a tendency to oxidize leaving a pit behind while the cathodic intermetallics cause the adjacent aluminium matrix to be attacked at the area resulting in detachment of the intermetallic particles from the matrix leaving a cavity [41, 48].

### 2.2.3.3 Pitting propagation

Once a pit initiated, it may repassivate or continue to propagate. The pit repassivates when the corrosion products cover its opening, and it continues to grow when the anodic and cathodic reactions are stable. The repassivated pit is called a meta-stable pit and the one that continues to growing is known as stable pit [49].

The corrosion process, involves dissolution of aluminium at the bottom of the pit and production of hydroxyl ions from the oxygen reduction reaction at the pit opening.

\[
2\text{Al} \rightarrow 2\text{Al}^{3+} + 3\text{e}^- \quad \text{Aluminium dissolution}
\]

\[
\frac{3}{2} \text{O}_2 + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow 6\text{OH}^- \quad \text{Oxygen reduction reaction}
\]

The hydroxyl anions (OH\(^-\)) increase the alkalinity of the solution around the cathodic intermetallics and accelerate the dissolution of the oxide film at that location exposing the underlying metal and causing a rapid attack to aluminium for the reason that the aluminium is attacked at a higher rate than its oxide film in high alkalinity solutions.
leading to loss of contact between the cathodic intermetallic and the aluminium resulting in pit formation [49].

The pit propagates due to the increase of the acidity inside it. The hydrolysis of $\text{Al}^{3+}$ produces a local pH decrease at the initiation sites due to formation of $\text{H}^+$

$$\text{Al}^{3+} + 2\text{H}_2\text{O} + \text{Cl}^- \rightarrow 2\text{H}^+ + \text{Al(OH)}_2\text{Cl}$$

Further, the reaction between the cations ($\text{H}^+$) produced from the hydrolysis process and the anion (Cl$^-$ ions in the solution) leads to hydrochloric acid (HCl) formation. The increase of the acidity enhances the aluminium dissolution and causes pit propagation.

The pit re-passivates when $\text{Al}^{3+}$ ions diffuse outward from the pit and react with the hydroxyl ions (OH$^-$) at the pit opening to form a film of metal oxide or hydroxide.

$$2\text{Al} + 3\text{H}_2\text{O} + 3/2 \text{O}_2 \rightarrow 2\text{Al(OH)}_3$$

The formed film acts as a barrier and helps to retard the corrosion of the aluminium through reducing the exchange of ions and electrons at that particular place [9].

The severity of the pitting attack is governed by the alloy and the solution composition, concentration of the aggressive species, temperature and the difference in the corrosion potential between the aluminium and the intermetallic particles [37,49].

The chemical composition plays a role in susceptibility of aluminium alloys to pitting corrosion. High purity aluminium, AA3xxx and AA5xxx aluminium alloys show good resistance to pitting corrosion. On the contrary, AA2xxx and AA7xxx aluminium alloys show lower resistance to pitting [31, 50].

The increase in the chloride concentration has been reported to decrease the pitting potential, consequently increasing the susceptibility to pitting corrosion [31].

### 2.2.3.4 Evaluation of the pitting corrosion

In the laboratory, the pitting corrosion susceptibility of post welded or welded aluminium alloys is generally assessed by immersion and electrochemical corrosion
testing (polarization and electrochemical impedance spectroscopy methods) in aggressive solutions. The electrochemical measurement provides useful information about the corrosion potential, passivity and pitting potential of the material. Following testing, visual, optical and SEM examinations are normally utilised to evaluate the extent of the pitting attack. At site, visual inspection, number, size and the pitting depth are normally used as indications for the extent of the pitting corrosion attack [51].

### 2.2.3.5 Pitting in AA5xxx aluminium alloys

AA5xxx aluminium alloys suffer from pitting corrosion in neutral solutions, but to less extent than high strength AA2xxx and AA7xxx aluminium alloys.

Ezuber et al [38] compared the pitting corrosion resistance of commercial high purity AA1100 aluminium with AA5083 alloy utilising the potentiodynamic polarization technique in a solution of 3.5 wt. % NaCl at 23°C and 60°C. As expected the commercial grade AA1100 aluminium alloy showed better pitting resistance than AA5083 in both cases. That was related to the presence of iron-rich intermetallic particles and magnesium-rich particles within the AA5083 alloy. The iron-rich particles activated the oxide film aluminium dissolution at the area adjacent to them due to their cathodic nature. The hydroxide ions that were generated from the cathodic reaction (oxygen reduction reaction) increased the alkalinity at the adjacent area and facilitated the dissolution of the passive film and the aluminium around the intermetallics. The result is a loss of contact between the cathodic intermetallic particles and the substrate and subsequently pitting initiation.

Similarly, Aballe et al [52-53] studied the resistance of AA5083 to pitting corrosion by immersing the alloy in aerated 3.5% NaCl at 30°C for a period of 1 to 30 days. The results showed the alloy was prone to pitting corrosion. This correlated to the effect of the cathodic activity of Al (Mn,Fe,Cr) phases which accelerated the aluminium matrix dissolution at the area adjacent that led to particle separation and consequently formation of pits. The magnesium silicon rich particles appeared not to have an immediate influence on the corrosion behaviour of the alloy.
Yasakau et al [34] studied the effect of the intermetallic particles on the corrosion behaviour of AA5083 aluminium alloy by immersion of the alloy in aerated 0.005M and 0.5 M NaCl solution utilising atomic force (AFM) and scanning electron microscopy. Prior to immersion, the AFM results showed the iron-containing phase Al (Fe,Mn,Cr) has a higher corrosion potential than the aluminium matrix (cathodic), while magnesium silicon rich (Mg,Si) phase has a lower corrosion potential than the aluminium (anodic). After immersion in NaCl solution, the alloy showed susceptibility to pitting. It was concluded by the authors that the initiation of the pitting corrosion in this alloy was due to the difference in the corrosion potential between the intermetallics and the matrix.

The depth of the pitting for AA5xxx was evaluated after exposing the alloys to a marine atmosphere for a period of 20 years and immersion in sea water for periods of 5 and 10 years. Tables 1 and 2 show the measured pitting depth after the exposure. Generally, the alloys showed resistance to both environments.

After 20 years of exposure to the marine atmosphere, the maximum pitting depth for the alloy AA5754-O was 0.4 mm indicating superior resistance to pitting in this environment. The alloy AA5083 showed a maximum pitting depth of about 0.15 mm after immersion in sea water for 10 years [9].
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Table 2.1 Measured pitting depth for AA5xxx aluminium alloys after 20 years of exposure to marine atmosphere [9].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temper</th>
<th>Year of exposure</th>
<th>Duration of exposure (years)</th>
<th>Site</th>
<th>Pitting depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5005</td>
<td>H14</td>
<td>1955</td>
<td>20</td>
<td>Salin</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>H14</td>
<td>1962</td>
<td>20</td>
<td>Salin</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>H18</td>
<td>1955</td>
<td>20</td>
<td>Salin</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>H18</td>
<td>1962</td>
<td>20</td>
<td>Salin</td>
<td>385</td>
</tr>
<tr>
<td>5754</td>
<td>O</td>
<td>1956</td>
<td>20</td>
<td>Salin</td>
<td>400</td>
</tr>
<tr>
<td>5086</td>
<td>H111</td>
<td>1981</td>
<td>20</td>
<td>Salin</td>
<td>400</td>
</tr>
<tr>
<td>5056A</td>
<td>O</td>
<td>1955</td>
<td>20</td>
<td>Salin</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>H12</td>
<td>1955</td>
<td>20</td>
<td>Salin</td>
<td>350</td>
</tr>
</tbody>
</table>

Table 2.2 Measured pitting depth for AA5xxx aluminium alloys after immersing in sea water for 5 and 10 [9].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Maximum pitting depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 years</td>
</tr>
<tr>
<td>5052 H34</td>
<td>&lt;50</td>
</tr>
<tr>
<td></td>
<td>150</td>
</tr>
<tr>
<td>5056</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>400</td>
</tr>
<tr>
<td>5083</td>
<td>&lt;50</td>
</tr>
<tr>
<td></td>
<td>120</td>
</tr>
<tr>
<td>5086 H112</td>
<td>500</td>
</tr>
<tr>
<td>5154</td>
<td>375</td>
</tr>
<tr>
<td>5454 H34</td>
<td>330</td>
</tr>
<tr>
<td>5456 H321</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>550</td>
</tr>
</tbody>
</table>

2.2.4 Intergranular Corrosion (IGC)

IGC is believed to take place on the entire aluminium alloys surfaces. The IGC corrosion takes place either a grain boundaries or at areas immediately adjacent owing to the difference in the corrosion potential between the precipitated phase and the bulk alloy. Based on the alloy composition, the precipitated phase can be anodic or cathodic with respect to the bulk material. Thus, in the presence of aggressive solution, it can preferentially corrode or cause the surrounding area of the matrix to corrode, resulting
in a localized corrosion attack in form of IGC. Most of aluminium alloys including AA5xxx aluminium alloys do suffer from IGC. The susceptibility of aluminium alloys to IGC increases with subjecting the alloy to excessive cold work and thermal cycles such those experienced during welding and heat treatment due to the change in the alloy microstructure [54]. Generally, non heat treatable AA5xxx aluminium alloys have shown better corrosion resistance to IGC and other forms of corrosion than AA2xxx and AA7xxx aluminium alloys. That is mainly achieved when the magnesium content in aluminium is lower than 3 wt. %, and when it is completely in solid solution or precipitated as Al$_3$Mg$_2$ within the grains interior [55]. On the contrary, increase of the magnesium percent, the amount of applied cold working and the time of exposure to heat have been shown to increase the IGC susceptibility of Al-Mg alloys [56].

The researchers attributed susceptibility of Al-Mg alloys to precipitation of less noble Al$_3$Mg$_2$ phase known as beta phase at the grain boundaries [57]. This phase has been reported to be more anodic than the bulk alloy, where the corrosion potential of the beta phase and AA5083 aluminium alloy matrix in a solution of 53 g l$^{-1}$ NaCl and 3 g l$^{-1}$ H$_2$O$_2$ at ambient temperature with reference to a Calomel electrode has been reported to be -1.24 V and -0.87 V respectively [9, 12, 34].

In the presence of aggressive solutions, the difference in the corrosion potential between β-phase and the adjacent matrix area leads to a dissolution of beta phase at the grain boundaries causing grain detachment and consequent metal loss. The precipitation of the active phase has been related to the limited solid solubility of magnesium in aluminium and high diffusion rate of magnesium [9].

2.2.4.1 Effect of magnesium on corrosion of AA5xxx aluminium alloys

The corrosion susceptibility of AA5xxx aluminium alloys increases with increase the magnesium content and work hardening. AA5xxx alloys that contained below 3 wt. % show better resistance to IGC than ones that contain above 3 wt. %. Above 3 wt. %, the magnesium enhances precipitation of beta β-phase on the grain boundaries.
2.2.4.2 Effect of temperature and cold working on AA5xxx alloys

Depending on the exposure time and aging temperature, a discrete or continuous β-phase precipitation on the grain boundaries of AA5xxx aluminium alloys can be formed.

Searles et al showed non-continuous precipitation of beta phase on the grain boundaries of aged AA5083 aluminium alloy at 150°C for 82.5 h (Figure 2.9) [58].

![Figure 2.9](image.png)

Figure 2.9- A non continuous β- phase precipitation on the grain boundary of aged AA5083 specimen at 150°C for 82.5 h with beta phase diffraction pattern along the {110} zone axis [58].

With increasing time of exposure to 189 h, continuous β-phase precipitates on the grain boundaries were evident Figure 2.10.

![Figure 2.10](image.png)

Figure 2.10- Continuous β precipitates on the grain boundaries of AA5083 specimen aged at 150°C for 189 h [58].
Kaigorodava et al [59] showed continuous β-phase precipitates on the grain boundaries of Al-11% Mg aged for two years at 150 and 200 °C and Yukawa et al [60] observed a continuous precipitation of β phase at the grain boundaries of Al-9% Mg aged at 150°C for 100 h.

Goswami et al [61] studied the effect of temperature on the corrosion behaviour of AA5083-H131 aluminium alloy by sensitizing the alloy at 175°C for 10 days. The TEM results showed the majority of grain boundaries of the as-received specimen were free of precipitates. Quite the opposite, most of the sensitized specimen grain boundaries were decorated with almost continuous beta phase (Al₃Mg₂) precipitates. The beta phase was also revealed in the matrix mainly at the interface between manganese-rich intermetallics and the matrix (Figure 2.11-2.12).

Figure 2.11- β phase precipitated on manganese rich particle in AA5083-H131 aged specimen at 175°C for 10 days [61].

Figure 2.12 a continuous precipitation of beta phase on the grain boundary of aged AA5083-H131 at 175°C for 10 days [61].
Oguocha et al [62] studied the effect of thermal treatment and heating exposure time on the corrosion properties of AA5083-H116 aluminium alloy. The alloy was aged at 80, 100, 150, 175 and 200°C for 24,168, 336,504 and 672 h. The results showed increase in the rate of the IGC attack and a decrease in hardness with increase of the sensitization temperature and heating exposure time. The increase in the IGC susceptibility was attributed to increase of precipitation of the beta phase at the grain boundaries while the reduction in hardness was related to the decrease in the dislocation density within the matrix and the magnesium solute atoms in the solid solution.

Tan and Allen [63] studied the effect of cold working and heating on the IGC corrosion behaviour of AA5083-H116 aluminium alloy. The alloy was cold worked to 25% thickness reduction. Both as-received and cold worked specimens were aged at 100°C for 500 h and immersed in nitric acid at 30°C for 24 h. The IGC resistance was assessed by the nitric acid metal loss test according to standard ASTM-G67. The results showed an increase in the metal loss after cold working and thermal treatment indicating a decrease in their corrosion resistance. Table 2.3 indicates this effect.

<table>
<thead>
<tr>
<th>Alloy condition</th>
<th>Metal Loss in mg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As received</td>
</tr>
<tr>
<td>Unsensitized</td>
<td>$7.264 \pm 0.009$</td>
</tr>
<tr>
<td>Aged at 100°C for 500h</td>
<td>$19.202 \pm 0.015$</td>
</tr>
</tbody>
</table>

Table 2.3 represent the amount of the metal mass loss of the AR and the TMT after NAMLT for 24 h for the AA5083-H116 alloy [63].

Alcan studied the effect of temperature, exposure time and the variation in magnesium content within the filler metal on the IGC behaviour of metal inert gas (MIG) and tungsten inert gas (TIG) welded AA5754 aluminium alloy fabricated with a different temper and thickness. The results showed that the AA5754-O aluminium alloy plate joined by filler metal containing about 5 wt% Mg exhibited a severe degree of sensitization after 3 months and 1 year after exposure to 200°C and 150 °C respectively [64].
The alloy that was joined with filler metal containing the same magnesium content as that of the alloy showed a sign of sensitization after 2 years of exposure at 100°C. However, with increasing the temperature to 125 and 150°C, the sensitization started to take place after six months of exposure. It was concluded that the decrease in the magnesium content within the filler metal enhanced the corrosion properties of the weld. On the contrary, increased temperature and exposure time drastically reduced the corrosion resistance of the weldment.

In the case of un-welded condition, Birol et al [65] studied the resistance of twin roll cast AA5754 aluminium alloy to intergranular corrosion. The results showed that the alloy resists highly the IGC. The alloy was cold rolled to an intermediate gauge (4.5 mm), soaked at 450°C for 8 h, cold rolled again to the final gauge of 1mm and given a softening anneal at 350°C.

### 2.2.4.3 Evaluation of the IGC susceptibility of AA5xxx Al-Mg alloys

ASTM-G67 standard Nitric Acid Mass Loss Test (NAMLT) is a useful assessment method for evaluating the susceptibility of AA5xxx aluminium alloys to IGC. The test involves immersing the relevant specimen in 70% concentration nitric acid at 30 ºC for 24 h. Before immersion, the specimen surface area and weight have to be measured. After immersion, the specimen has to be cleaned with distilled water and weighed. The difference in weight before and after NAMLT determines the susceptibility of Al-Mg alloys to IGC. Specimens that exhibit weight loss of 25 to 75 mg/cm² are considered prone to IGC. Ones that show a metal loss of < 15 mg cm⁻² are considered to be resistant [66].

The other useful method in determining susceptibility of AA5xxx aluminium alloys to IGC susceptibility is the phosphoric acid etch response test. Etching the interested specimen in 10 wt. % phosphoric acid for 90 seconds at 60 ºC has been used as a useful method to identify the presence of anodic β-phase at the grain boundaries [67]. In both cases, it is difficult to observe the IGC by the naked eye. Optical and scanning electron microscopies are used to evaluate the extent of the IGC on the surfaces.
2.2.4.4 Prevention of IGC in Al-Mg alloys

Fabrication processes, heating and welding can sensitise the Al-Mg alloy microstructures and increase their susceptibility to IGC [9, 41]. Accordingly, controlling the fabrication processes and minimizing the heat input during joining can help in minimizing the risk of IGC susceptibility. Further modifying the alloy chemical composition and heat treatment can minimize and eliminate the IGC susceptibility [68]. Unocic et al [69], utilizing NAMLT corrosion testing, SEM and TEM, studied the effect of copper and zinc on the IGC behaviour of a standard AA5083 aluminium alloy. The results showed when high percentages of copper and zinc are added, the alloy IGC resistance enhanced. This was evident from the nitric acid metal loss results which showed a decrease in the metal loss test with increasing the copper and zinc percentages within the alloy. This was further confirmed by TEM images which showed the absence of magnesium-rich phases at the grain boundary of the alloy that contained high percentages of copper and zinc.

2.2.5 Stress Corrosion Cracking (SCC)

SCC is a form of localized corrosion. It takes place in an intergranular or transgranular form. Initiation of SCC requires residual or applied stress and corrosive solutions. It starts by initiation of localised corrosion and propagates when the velocity of the crack is higher than the corrosion velocity. Pure metals can suffer from SCC but do not suffer from intergranular corrosion because of the absence of impurities [6].

Aluminium alloys including AA2xxx, AA7xxx and AA5xxx aluminium are susceptible to SCC in NaCl-H₂O₂, NaCl, sea water and water vapour. However, it may take place even in the presence of moisture alone [5, 6, 39]. High strength aluminium alloys are more susceptible to SCC than low strength alloys and are reported to be more susceptible in directions transverse to rolling direction than that in direction parallel to longitudinal plane due to the difference in the precipitate distribution resulting from the rolling effect [70].

AA5xxx aluminium alloys containing more than 3wt. % magnesium have shown susceptibility to SCC in certain conditions [9] For this, control of the heat input during welding, the alloy chemical composition and the thermo-mechanical processing reduces the risk of the microstructure sensitization and increases its resistance to SCC [71].
In this regard, Alcan studied the SCC resistance of AA5754 and AA5182 aluminium alloys containing 2.5 to 4 wt. % magnesium in the annealed and varied cold worked temper utilizing NAMLT and H$_3$PO$_4$ etching test. The alloys were aged at 75, 100 and 150°C for up to 10 years. The results showed the SCC resistance of the alloys containing low magnesium contents (below 3wt %) remained high even after 10 years of ageing at the specified temperatures. On the other hand, alloys with 3 wt. % Mg became susceptible to SCC after 10 years of ageing at 75°C and above. Quite the reverse, the alloys containing 3.5 and 4 wt. % Mg became prone to SCC after five years and two years respectively. Therefore, the alloys showed increased susceptibility to SCC when the magnesium content exceeded 3 wt. % [64].

### 2.2.5.1 Evaluation of stress corrosion cracking susceptibility

Slow strain rate tension (SSRT), and immersion in 3.5 % sodium chloride in accordance to ASTM G44 [72], tests are widely used for evaluating the SCC susceptibility. Commonly, a strain rate of $10^{-4}$ s$^{-1}$ is appropriate for AA5xxx aluminium alloys [73].

### 2.2.6 Crevice corrosion

Crevice corrosion requires a passive external surface to proceed. It occurs when solution enters between two components. When aluminium is placed in an electrolyte in a slightly loose of contact with its self or other materials, the crevice corrosion starts its action locally between the two surfaces. The corrosion process involves metal dissolution as the anodic reaction and oxygen reduction as the cathodic reaction. With time, the oxygen is gradually consumed by the metal ions at the crevice and the metal ion (positive charges) attracts the Cl$^{-}$ into the crevice for electrostatic balancing [31].

$$M^{+}Cl^{-} + H_2O \rightarrow MOH \downarrow + H^{+}Cl^{-}$$

As a result of hydrochloric acid production, the pH of the solution within the crevice decreases. With decreasing of the pH, the passive film becomes unstable and is attacked rapidly causing crevice corrosion.

Crevice corrosion is quite independent on the alloy type and it occurs even in highly corrosion resistant alloys. Crevice corrosion takes place in a lap and fillet joints and butt welds of partial penetration where crevices cannot be avoided [6].
2.2.6.1 Evaluation of crevice corrosion susceptibility

Immersion, electrochemical and coupon tests are used for investigating the crevice corrosion susceptibility.

2.2.7 Exfoliation corrosion

The exfoliation corrosion is a substrate attack that mainly takes place in heavily cold worked, rolled or extruded products that feature flat and elongated grains. Where selective intergranular attack takes place at the grain boundary, with time the corrosion propagates and the amount of the corrosion products at the grain boundaries increases. The pressure caused by the corrosion products is sufficient to cause detachment of the grains from each other, leading to separate layers of uncorroded metal. This type of attack is known as exfoliation corrosion and termed sometimes as layer corrosion [74].

2.2.7.1 Evaluation of the exfoliation corrosion susceptibility

The aluminium alloys of the 2xxx, 5xxx and 7xxx series are considered susceptible to this type of attack. Susceptibility to exfoliation corrosion in aluminium alloys can be assessed by immersion testing in suitable environments. The susceptibility of Al-Mg alloys to this type of corrosion is assessed by immersing the alloy in a solution containing 53.5 g ammonium chloride, 1.8 g ammonium tartrate, 20.0 g ammonium nitrate, and 10 ml of 30% hydrogen peroxide at 65°C for 24 h followed by SEM examinations at the polished cross section [75].

2.2.8 Filiform corrosion

This type of corrosion initiates beneath surface films, such as lacquers and paints, and/or heavily deformed layers. Once initiated, it can cause a poor visual appearance. The precise mechanism of the filiform corrosion is not fully understood, but it is generally believed to be due to the interaction between humidity, temperature, certain activating agents, such as chlorides, and the alloy composition. Control of the thermomechanical processing, removal of the deformed layer by caustic etching, and controlling the iron content within the aluminium have been found helpful in reducing the susceptibility of the aluminium and its alloys to FFC. Afseth et al [76] studied the influence of heat treatment and surface condition on susceptibility of AA5754 aluminium alloy to filiform...
corrosion. The results showed that the heat treatment increased slightly the alloy susceptibility to filifilm corrosion. This was related to enrichment of the thermally formed oxide film on the alloy surface with magnesium. However, after removal of the thermal oxide film by pre-treatment methods, the corrosion resistance of the alloy to filifilm corrosion resistance was restored.

2.2.9 Galvanic corrosion

Aluminium is anodic to most of the engineering materials with the exception of magnesium and zinc. For this reason, there is always a risk of attack by galvanic corrosion when coupled with a less active material, such as copper, carbon steel or stainless steel, in the presence of an electrolyte. The rate of the galvanic corrosion attack increases with increase the potential variation between the aluminium and other connected components and the surface area of the less active metal [12].

Due to the variation in the corrosion potential, the severity of the galvanic attack can be high. Once initiated, it continues to propagate. Such attack can be avoided by isolating the coupled materials with non conductive materials, coating the cathode area, use of material which has corrosion potential close to aluminium, controlling the environment and by applying cathodic protection.

2.2.9.1 Evaluation of the galvanic corrosion

In the laboratory, the prediction of the galvanic corrosion between two components is evaluated by the electrochemical and immersion testing techniques.

2.3 Surface treatment and protection

Surface treatment is used for protecting the aluminium substrate against corrosion. The surface treatment is used to remove dirt and detritus flaws, provide a uniform physical, chemical and electrical behaviour on the aluminium surface, and to change the surface appearance etc. [8].

Several types of surface treatment are used for improving the corrosion resistance of aluminium alloys including anodizing, laser melting, weld overlaying, painting, lining, electroplating, and cladding.
2.4 Friction Stir Welding

The FSW process is a solid state welding method that joins similar and dissimilar ferrous or non-ferrous materials without melting. It is a relatively new technology [77-79].

The process was invented at The Welding Institute (TWI) by Wayne Thomas at the end of 1991. At the beginning of its use, it was used for joining of aluminium and its alloys [80]. Currently, it is used for joining various engineering metals and alloys [81].

The process has gained an acceptance for use in critical industrial applications, such as within aircraft, aerospace, automotive, railway and shipbuilding production [82].

The process has shown an ability to weld successfully thin and thick plates, in the range of 0.5 to 50 mm in a single pass [83] and thicker sections up to 75mm thick in double pass [84].

![Figure 2.13 Single sided friction stir weld between AA2024 to AA7050 aluminium alloys [85].](image1)

![Figure 2.14 Double side friction stir weld between 75mm thick aluminium plates produced at TWI [84].](image2)
The FSW process has shown the capability to modify the material microstructure. In the case of aluminium alloys, the elongated and coarse grains of the post welded alloy at both top and cross section surfaces are substituted after friction stir welding by much smaller, equiaxed grains within the nugget. It has been reported that the maximum size of the recrystallized grain size within the nugget is about 15 µm and it varies with the variation in the heat input [86]. Such a modification has been related to the dynamic recrystallization process resulting from the frictional heat and severe mechanical deformation [87]. The change in the microstructure due to the effect of the process is evident in Figure 2.15.

Figure 2.15 Backscattered diffraction images represent the effect of the FSW on the grain size where a) represents the parent alloy b) the HAZ on the right and the TMAZ on the left, and c) the stir zone of AA2199 aluminium alloy [83].

2.4.1 Friction stir welding process

Using a suitable downward force, a rotated (at controlled rotation speed) cylindrical threaded or non threaded probe and a circular shoulder made of material with a higher strength and better corrosion, wear and oxidation resistances than the component to be joined is inserted slowly between two rigidly fixed plates.

Once the probe becomes in contact with the edges of surfaces to be joined a heat below the melting point of the parts to be joined is generated. The heat generated softens the material around the probe and helps in inserting the probe and moving the tool along to the required length of joining. The probe has to be inserted to a controlled depth and not touch the backing plate to avoid its damage. However, it should not be too short to avoid formation of lack of penetration at the weld root.
Once the probe has reached the required depth of insertion, and the shoulder becomes in contact with the top surfaces of the parts, the tool is pushed forward at a controlled traverse speed, utilizing a controlled forward pressure and controlled downward forces to keep the tool in position till the end of joining. At the end of the joining line, the tool is retracted leaving a hole behind, which is considered as a common feature and identified as a tilt hole [88].

The presence of the tilt hole as a result of retracting the tool is one of the process disadvantages. However, it is not considered as a serious problem since it can be avoided by the use of a runoff plate [89]. A schematic drawing of the process is shown in Figure 2.16.

![Figure 2.16 Schematic drawing of friction stir welding](image)

**2.4.2 Generation and flow of heat**

During friction stir welding, most of the heat is generated as a result of material deformation due to the tool rotation effect [91-92]. The peak temperature within the weld region is dependent on the used tool size, shape, rotation and traverse speed. The rotating, traverse speed and the probe size play an important role in control the amount of the heat input within the weld region. The larger the tool diameter, the higher the rotation speed and the lower traverse speed, the higher the heat input is expected. On the contrary, the higher traverse speed and or lower rotating speed, the lower the heat input within the weld is generated. This might not be sufficient to soften the material, resulting in improper material flow, pin damage, and formation of defects [93].

The mechanical and corrosion properties of the joined components are highly affected by the amount of the heat induced during joining. Extra heat leads to reduced mechanical and corrosion properties. Minimizing the heat input will possibly reduce
such risk. Ideally, the temperature should not be reduced to an extent that the material softening underneath the probe will not take place. For this reason, proper welding parameters have to be selected to insure that the temperature around the tool is sufficiently high to provide an adequate material flow [94]. The heat generated from the process modifies the post welded microstructure and creates distinct regions with different microstructures.

### 2.4.3 The structure of aluminium friction stir welds

Theadgill and Leonard [94] divided the aluminium alloy friction stir weld structure into four discrete regions, namely (1) nugget, (2) thermomechanically affected zone (TMAZ), (3) heat affected zone (HAZ) and (4) the parent alloy (PA).

#### 2.4.3.1 The nugget or stir zone

The stir zone is the part of the weld located at the TMAZ centre. The microstructure of the nugget is fully recrystallized and refined due to the dynamic recrystallization process, resulting from severe mechanical deformation and thermal cycling. The grain size in this region is much smaller than the rest of the weld regions and the parent alloy. The size of the grain is controlled by the heat input and is influenced by the tool rotation speed and diameter [89, 95]. It has been reported to be in a range of 1 to 10 μm [78, 86, 95, 96].

As a common feature, the nugget of similar and dissimilar aluminium welds is characterised by formation of flow patterns in the form of onion ring shapes, as shown in Figures 2.17 and 2.18 [97]. The shape of the nugget varies with the rotation speed [98].

![Figure 2.17](image-url)  
**Figure 2.17** Flow patterns within the nugget between AA2024 and AA7039 aluminium alloys [99].
2.4.3.2 Thermomechanical affected zone (TMAZ)

The TMAZ is the area of the weld that is located between the heat affected zones and the nugget. It undergoes heating and plastic deformation but to a lesser degree than the stir zone. Its microstructure is different from that of parent alloy, HAZ and the nugget. Usually the grains within TMAZ are not recrystallised as are those in the nugget. Instead they are deformed and elongated specifically at the TMAZ edges due to the tool shearing effect [101]. The TMAZ has two sides namely the advancing side (AS) and the retreating side (RS). The advancing side is characterized by the presence of material flow arm at the top surface of the weld, most likely as a result of dragging the material by the rotated shoulder from the retreating side [98], it also characterized by a clear transition appearance with the nugget, compared with the retreating side, as shown in Figure 2.19 [93].
2.4.3.3 Heat affected zone (HAZ)

The HAZ is a part of the base alloy which is metallurgically affected by the heat of welding, without possessing solid to liquid transformation. The HAZ is generated in all welding processes due to the effect of the heat generated from welding. In some cases, it can be observed by the naked eye in arc welds rather than in the friction stir welds, due to the variation in the heat input between the two processes. Because of the significantly lower amount of heat induced by the FSW process, relative to that generated by fusion welding processes, the effect of the heat generated by the FSW process on the parent alloy is less harmful than that of fusion welding processes [91]. However, although the temperature in this region is lower than in TMAZ, it can be sufficient to modify the post weld microstructure of the alloy. Such a modification can affect the corrosion and mechanical properties of the alloy at the TMAZ and the HAZ. The extent of such an effect is a function of the material composition, alloy temper condition, heat input and the cooling rate. It has been reported that the heat transferred from TMAZ to the HAZ can coarsen the grains, and anneal and sensitise the microstructure, the last through precipitating an electrochemical active or noble phase at or immediately adjacent to the grain boundaries due to the influence of the cooling rate. In general, the HAZ of friction stir welds of heat treatable aluminium alloys show a reduction in hardness compared with the TMAZ and the parent alloy. This phenomenon has been related to coarsening of the constituent phases and or precipitation of reactive phase at the grain boundaries and dissolution of the hardening precipitate. After friction welding, work hardened (non heat treatable) aluminium alloys have shown a reduction in hardness at the TMAZ and the HAZ. This was attributed to dislocation annealing and grain coarsening. The HAZ of the alloys in annealed (O) temper showed no reduction in the hardness [91,103].

In fusion welding processes, the width of the HAZ is governed by the material, welding parameters and the welding process. With a higher material thermal diffusivity and a higher cooling rate, a smaller HAZ is expected and vice versa. The heat input increases with the increase in the current, voltage and the process efficiency. The efficiency is variable from one process to another. It is approximately 0.8 for shielded arc welding process, 0.4-0.6 for the tungsten arc welding process and 0.95 for the submerged arc welding [104].
\[ Q = \frac{E \times I}{S \times 60/1000} \]

Where, \( Q \) is the heat input (kJ/mm), \( E \) is the applied voltage (V), \( I \) is the applied current (A), and \( S \) is the welding speed (mm/min) [105].

In the case of the friction stir welding, the HAZ width is influenced by the tool size and rotation speed.

### 2.4.3.4 The parent alloy

The parent alloy is the part of the component that is not metallurgically affected by the welding process. It represents the original alloy microstructure.

### 2.2.4 Recrystallisation of Al alloys

Several studies were performed to explain the mechanism of the recrystallization (DRX) process that takes place in aluminium alloys. Three types of recrystallization processes have been considered 1) discontinuous dynamic recrystallization (DDRX), 2) continuous dynamic recrystallisation (CDRX) and 3) geometry dynamic recrystallization mechanisms (GDRX) [106].

Etter et al explained that the recrystallization in aluminium alloys takes places either by DDRX, CDRX or GDRX [106]. However, McNelly et al, Bowen et al, Gourdet et al and McQueen et al [90, 107-109] stated that aluminum and its alloys normally do not undergo DDRX due to the high recovery rate of the aluminium owing to its high stacking-fault energy. The dynamic recovery takes place in the metals of high stacking fault energy when subjected to hot working such as aluminium [109].

After friction stir welding, the observed fine, equiaxed grains within the stir zone, have been related to the continuous dynamic recrystallization process that takes place as a result of the frictional heat and the severe plastic deformation, resulting from the tool rotation effect. The dynamic recrystallisation process is defined as the recrystallisation process that takes place during hot deformation [110].

It involves formation of low angle boundaries and an increase in the boundary misorientations during the deformation process, leading to new grain development.
So far, CDRX is the accepted mechanism for the formation of fine grains within the stir zone of the aluminium alloys.

2.2.5 Advantages of the FSW process

For several reasons, the process gained authorization for use in critical industrial applications, such as in the aircraft, aerospace, automotive, railway and shipbuilding industries [111].

- The process provides lower heat input when compared with fusion welding processes. This reduces the risk of component distortion, and provides welds of better mechanical properties than fusion welds [112-113].
- In most cases, removal of the oxide layer from the surface to be joined is not essential, which accelerates the time of executing the welding job [83].
- Absence of porosity and hot cracking defects due to absence of material melting, provide a considerable benefit in joining successfully high strength alloys, such as AA2xxx and AA7xxx aluminium alloys, which do suffer from such defects after joining with fusion welding processes [98, 103, 114].
- The process is environmental-friendly process owing to nonexistence of fumes, spatters and shielding gases [83, 88].
- The friction stir welds generate a refined and recrystallized microstructure compared with the cast structure provided by the fusion welding processes. Such an effect can result in modifying the mechanical properties of the welds [115].
- No requirement for use of consumable filler metals, instead a non consumable tool made of material with better corrosion, physical and mechanical properties than the components to be joined is used. The tool has shown ability to join up to 1000 meter length before replacement [112].
- No extra weld material on the top surface and the root of the weld because no metal deposition takes place. Therefore, there is no need for grinding and machining to remove the slag, sparks and extra material [83].
- The process has the ability to join single and double side butt welds from 0.5 to 75 mm thick [83-84].
2.2.6 Disadvantages of the FSW process

- Clamping is mandatory to keep the parts to be joined in position during joining.
- Sensitivity of the process to the variation in the thickness of the parts to be joined. It is less flexible than the fusion welding processes in this issue.
- FSW is unsuitable for jointing designs that require material deposition, such as fillet welds [116].
- Formation of tilt hole at the tool retraction location. However, the tilt hole is a non serious problem, since it can be avoided by use of a runoff plate or filling the gap by any suitable method.

2.2.7 Factors affecting the friction stir weld quality

Control of the welding parameters and use of proper tool design are the key factors in obtaining welds free of defects. Any deviation in the welding parameters can create a side effect on the corrosion and the mechanical properties of the weld. For this reason parameter windows have to be determined experimentally [117-118].

Therefore, an increase or decrease in the rotation and traverse speed, as well as improper control of the tool plunge depth may affect the weld quality.

2.2.7.1 Tool rotation and traverse speed

The tool rotation speed and traverse speed are the most effective parameters that control the weld mechanical and corrosion properties, via controlling the heat input. High tool rotational speed and or low tool traverse speed generate high heat input. Such an effect is evident in Figure 2.20 [119].

On the contrary, low rotation speed and or high tool traverse speed generate insufficient heat for softening the material, raising the possibility of imperfections within the weld, as well as the tool breakage [90, 120].
Although the heat input within the friction stir welds is below the melting point of the work pieces being joined, the heat generated from the friction can be sufficient to cause adverse effects on the corrosion, ductility, hardness, tensile and fatigue strengths. Such effects have been recorded by Kim et al, who observed a decrease in the tensile strength within the friction stir weld of AA5052 aluminium alloy, with increasing both rotation and traverse speed, as shown in Figure 2.21 [118].

Figure 2.20 The effect of the variation in the weld pitch on the peak temperature within the joint for some of binary aluminium alloys [119].

Figure 2.21 Effect of a) tool rotation speed and b) tool traverse speed on tensile strength of friction stir weld of AA5052 aluminium alloy [118].
Similarly, Sakthivel et al [121] recorded a decrease in tensile strength and ductility of 6 mm commercial grade aluminium alloy friction stir weld with increased tool traverse speed owing to the decrease of the heat input, as shown in Figure 2.22.

Sato observed a reduction in hardness of FS welds of ECA-pressed Al alloy with increase of the rotation speed. This was related to the effect of the heat input on the grain size of the weld. As can be seen in Figure 2.23, increase in the rotation speed reduces the hardness within the weld. This result is in agreement with the Hall Petch equation $\sigma_y = \sigma_0 + kd^{-1/2}$, which relates the increase and the decrease in the strength of the alloy to the grain size [122].
Work by Rajakumar et al [123] is in agreement with the findings of Sato, where the effect of the grain size on the weld nugget hardness is evident in Figure 2.24.

![Figure 2.24 Relation between the grain size and the hardness](image)

**2.2.7.2 Tool tilting and plunge depth**

Tilting the FSW tool by 1 to 3 degree provides a compressive down force behind the tool which has been found helpful in assisting the blending of the material and in obtaining defect free welds [124].

The tool plunge depth and length affect the weld integrity when improperly used. An excessive tool insertion may damage the pin (due to the contact with the backing plate), reduce the thickness of the parts being joined and contaminate the weld. Use of a short pin or improper plunge depth can cause lack of material forging, resulting in lack-of-penetration. Such imperfections may have a considerable affect on the mechanical properties. Therefore, the joint may show susceptibility to cracking when it goes under stresses [125].

**2.2.7.3 Tool design**

The tool serves to generate the heat required for softening the material and mix the softened material while rotating. The heat generated from friction between the tool and the material and is largely influenced by the shoulder, probe size, tool design, rotation and traverse speed. The tool shape determines heating, forging and shearing, while the
tool size determines the rate of friction, temperature as well as the range of the material to which friction stir welding can be applied [126]. Therefore, proper tool selection and optimizing the welding parameters help in obtaining welds of good mechanical and corrosion property.

![Figure 2.25 schematic drawing of the friction stir welding process tool](image)

The tool design is among the factors that affect quality of the welds. With a proper tool design and adequate processes parameters, a weld free of defects can be obtained. As a rule, the FSW process tool has to be made from material of better wear resistance, oxidation, corrosion resistance and mechanical properties and with a higher melting point and lower thermal conductivity than the components to be joined to avoid loss of heat, breakage of the tool and contamination. For this reason, the Welding Institute specialists have developed improved tool designs to provide the ability to join successfully most of engineering materials. At the initial stage of the FSW process use, a cylindrical tool with an unthreaded probe and shoulder was used for joining aluminium and its alloys. The first successful modification in the tool was in 1995. The tool design was named 5651. The 5651 tool was designed with a parallel threaded probe. This design showed better performance than the cylindrical design [127]. Later, several modifications were conducted. TWI developed tools with complex features in
order to improve tool efficiency. Whorl, Triflute\textsuperscript{TM}, Skew-Stir\textsuperscript{TM}, and Trivex tools are among the designs [127].

![Figure 2.26- 5651 tool design [127].](image)

The prototype Whorl\textsuperscript{TM} tool shown in (Figure 2.27) has been designed with a sharpened pin of re-entrant features in a shape of frustum. This design has shown an ability to improve the material flow, reduce the welding force, increase the heat input through increasing the interface between the probe and the softened material and reduce the displaced material volume by 60\% [126]. This tool is applicable for joining butt surfaces but is not suitable for joining lap joints design [90].

![Figure 2.27 - Prototype Whorl\textsuperscript{TM} tool superimposed on a transverse section of 75 mm thick weld in 6082-T6 aluminium alloy [128].](image)

Whorl\textsuperscript{TM} type probes have been designed with different features, as shown in Figure 2.28, to ensure proper functioning of the tool.

![Figure 2.28 - Whorl\textsuperscript{TM} probes have been designed with different features](image)
The Triflute™ design is shown in Figure 2.29. The tool is designed with three deep helical grooves and flutes in the pin to improve the material flow. This design reduces the welding force, increases the heat input and the depth of penetration [126]. That gave the tool an ability to join thick butt surfaces. The tool is not suitable for lap joints [80].

The Flared-Triflute™ design is shown in Figure 2.30. The tool increased the material flow, the material mixing rate, provided wider weld region due to its design feature (flared-out flute lands), reduced the axial force and the loss in the plate thickness that results from the shoulder effect [127-128].
Figure 2.31 illustrates the A-skew™ design. As seen in Figure 2.31 a, the tool is normally inclined by few degrees from the axis of the spindle to increase the material flow from the front to the rear side of the tool. The tool has shown an ability to increase the material mixing rate, provide a wider weld region, improve the welding speed and reduce the axial force [127-129].

Figure 2.31 A-Skew™ tool (a) side view, (b) front view, and (c) swept region encompassed by skew action [129].

With the Twin stir™ design as shown in Figure 2.32, the requirement for component fixation is eliminated. This design is suitable for joining butt and lap joint designs [130].

Figure 2.32 Twin Stir™ tool [130].
2.2.7.4 Shoulder features and effect

Several shoulder designs were invented by the TWI specialists to suit different materials and conditions. The developed shoulders designed with different re-entrant features were used to improve the coupling between the shoulder and the material being joined. The shoulder is usually designed in a concave profile to prevent the softened material from extruding out of the sides of the shoulder and maintain the downwards pressure, and hence good forging of the material behind the tool can be achieved [126].

It has been reported that the friction between the shoulder and top surface of the weld (the weld toe) provides extra heat [131], which in turn is sufficient to cause grain growth at the area close to the weld toe. This feature is mainly observed in weld cross sections, as evident in Figure 2.33 [132].

![Figure 2.33](image)

Figure 2.33 Variation in the grain size within the friction stir welded AA2219-T6 aluminium alloy due to the shoulder effect [132].

Similarly Arora et al [133] observed the grain size at the crown of the AA2219-T87 FS weld was larger than that of the bottom. This was related to the effect of the extra heat provided by the shoulder.
2.4.8 Material flow in FSW process

The material flow in the friction stir welds is quite complex. It depends on the tool geometry and direction, process parameters, material to be joined and the temperature of the work piece.

The material flow during friction stir welding has been studied using a number of techniques, such as tracing by markers and use of dissimilar alloys/metals to follow the material flow pattern within the welds [126].

In this respect, Colligan et al. [134] studied the flow of the material within friction stir welded AA6061-T6 and AA7075-T6 aluminium alloys by embedding small steel spheres at different locations within the weld joints. The results showed not all material in the path of the tool was stirred by the pin. Much of the material movement was simply extruded around the retreating side. However, chaotic mixing at the top surface of the weld was observed. It was concluded that the material movement within the welds is either by simple extrusion or by chaotic mixing. Similarly, Li et al. [135] reported that the material movement within the dissimilar friction stir weld of AA2024 and AA6061 aluminium alloys was due to dynamic chaotic mixing.

Figure 2.34 Material movements from the advancing side point S and deposited at the retreating side point E [136].

Seidel and Reynolds analyzed the material movement in several friction stir welds using marker insertion technique and observed no chaotic mixing at the weld top surface [137]. Schmidt et al. observed a portion of the shear layer rotates with the pin during FSW [138].
2.4.9 Effect of FSW process on the mechanical properties of weld

The mechanical properties of the friction stir weld are largely influenced by the alloy chemical composition and the heat input. In case of friction stir welding, the heat input is controlled by the tool rotation and traverse speed. The induced heat from the joining process can alter the corrosion and the mechanical properties of the joined work-pieces.

In the case of Al-Mg alloys, the alloy temper condition plays a role in the change of the hardness after joining. For instance, the reduction in hardness within cold worked AA5xxx aluminium alloys has been reported to take place within TMAZ owing to the effect of the heat that is generated from the friction. The induced heat can be sufficient to reduce the dislocation density through annealing the alloy microstructure and reduce the post weld alloy mechanical properties. The reduction in hardness within friction stir welded AA5xxx alloys can also take place at the edges of the TMAZ, typically at the HAZ, where the transferred heat to this area can be enough to cause grains coarsening. On the contrary, the hardness of welded fully annealed AA5xxx aluminium alloys has been reported to be slightly higher or the same as the parent alloy due to the effect of the initial alloy temper condition. Therefore, the change in the hardness profile of non-heat-treatable aluminium alloys is sensitive to the alloy temper condition, grain size and dislocation density [120].

In this regard, Fonda et al [139] showed a reduction in hardness within the TMAZ region of a friction stir welded AA5456-H116 aluminium alloy in comparison with the HAZ and the parent alloy (Figure 2.35). This was related to the effect of the heat during welding, which was sufficient to cause a significant recovery in the post weld work hardened microstructure that led to a decrease in the dislocation density within the TMAZ and consequently a decrease in the hardness of the TMAZ area.
In the case of fully annealed AA5xxx aluminium alloys, Sato et al [140] studied the effect of the FSW process on the hardness of AA1080 and AA5083-O non heat treatable aluminium alloys. In case of AA1080, the weld showed better strength than the parent alloy. This was attributed this to the change in the grain size due to the FSW process. After FSW, a significant change in the grain size was observed. TEM investigation revealed a low dislocation density within both the stir zone and the parent alloy. This confirms the effect of the grain size on the hardness, according to the Hall-Petch relationship. In case of AA5083, beside the grain size effect, the results have shown that the increase in the hardness within the TMAZ was due to the effect of the fine and homogenously distributed Al₆(Fe,Mn) particles within the grains interior, which act as obstacles to the mobility of the dislocations [126].

Hirata et al [141] showed clearly the relation between the grain size and the hardness of fully annealed AA5083 aluminium alloy. The decrease in the grain size enhances the hardness within the weld, as is evident in Figure 2.36.

Figure 2.35 Hardness profile a cross friction stir welded AA5654 aluminium alloy [139].
2.4.10 Effect of the process on intermetallics

As a result of the severe mechanical deformation caused by the tool rotation effect, the majority of the coarse constituent particles that are present within the alloy in random distribution are fragmented to finer and more uniformly intermetallics within the TMAZ. That can be seen clearly in the nugget where the probe provides this action. Such an effect was observed by Dilip et al [142] who recorded intermetallic particles of smaller size (in the range of submicron to 5μm) and higher density within the stir zone of friction stir welded AA2219-T87 and AA5083-H321 compared with the ones within the parent alloys.

2.4.11 Corrosion of aluminium alloy friction stir welds

The susceptibility of friction stir welds to localized corrosion is assessed by immersion, agar gel test and electrochemical corrosion testing methods. It is a function of the joined material composition and the implemented welding parameters that control the amount of the heat input [143].
2.4.11.1 AA2xxx aluminium alloys: Friction stir welded AA2xxx alloys showed susceptibility to localized corrosion at the TMAZ and the HAZ in the form of intergranular and exfoliation corrosion owing to precipitation of a copper-magnesium rich phase at the grain boundaries. Leonard et al investigated the susceptibility of as-welded and naturally aged friction stir welded AA 2014A-T651. The results showed that the HAZ and TMAZ were prone to IGC [144].

Zhou et al [145] studied the influence of the FSW process on the microstructure and the corrosion properties of AA2024-T351 aluminium alloy using SEM and TEM techniques as well as the immersion test (EXCO test). The immersion test revealed severe localized corrosion at the HAZ, as shown in Figure 2.37. Close examination on the HAZ using SEM and TEM equipped with EDX showed a continuous network of precipitates rich in copper and magnesium at the grain boundaries, as shown in Figure 2.38. This was attributed to the local micro-galvanic action that was established due to presence of networks of copper and magnesium containing precipitates at grain boundaries.

Figure 2.37 Scanning electron images shows localized attack at HAZ after immersion in EXCO solution for 8 h [145].

Figure 2.38 Transmission electron micrographs of the HAZ showed networks of copper and magnesium containing precipitates at the grain boundaries [145].
2.4.11.2 AA5xxx aluminium alloys: generally, friction stir welds of AA5xxx alloys exhibited a corrosion resistance the same as or slightly worse than the parent alloy [146]. Haver et al [147] tested the pitting and IGC behaviour of friction stir welded 4 mm thick AA5754-H111 aluminium alloy joined at different traverse speeds (100 and 1000 mm/ min) and fixed tool rotation speed and tilt angle (400 rev/min and 2 degree respectively) utilizing anodic polarization measurement. The electrochemical results showed almost similar corrosion behaviour for both welds compared with the parent alloy.

Wadeson, Zhou and Thompson [148] studied the corrosion behaviour of AA5754-O aluminium alloy friction stir weld utilizing immersion and electrochemical corrosion testing to investigate susceptibility of the weld and the parent alloy to exfoliation and pitting corrosion. Their results showed no sign of exfoliation corrosion within the parent alloy and the weld regions and revealed pitting corrosion at the TMAZ edges. They attributed the pitting corrosion to presence of a high population density of Mg$_2$Si particles at the TMAZ edges compared with nugget, parent alloy and HAZ. Their electrochemical tests supported the results obtained from the immersion testing, where the highest corrosion potential and corrosion current density were recorded within the TMAZ advancing and retreating sides compared with the parent alloy and the HAZ.

Compared with fusion welding process, friction stir welds are considered to have better corrosion resistance. Zucchi et al [55] compared the resistance of friction stir welded with metal inert gas welded AA5083-T3 to pitting and SCC resistance utilizing immersion and slow strain rate testing in a solutions of 3.5 wt.% NaCl + 0.3 g/l H$_2$O$_2$ and 4M KCl + 0.5 M KNO$_3$ + 0.1 M HNO$_3$ respectively. The results showed the friction stir weld exhibited resistance to both forms of corrosion, where as MIG weld suffered from pitting and SCC.

Frankel and Xia [149] compared the pitting corrosion resistance between tungsten inert gas (TIG) and friction stir welds of AA5454 aluminium alloy in the annealed (O) and strain hardened (H34) conditions. The susceptibility of the welds to pitting corrosion was tested in 0.1 M NaCl solution using the electrochemical tests. Their results showed that the TIG weld show more susceptibility to pitting corrosion than the friction stir
weld and the friction stir weld showed higher pitting resistance than the parent alloy and the TIG weld.

2.4.11.3 AA6xxx aluminium alloys: Compared with the base metal, the friction stir welds of AA6xxx alloys exhibited similar or slightly worse corrosion. Work by Amini et al compared the corrosion resistance of 7.5 mm thick friction stir welded (Al-1.18Mg-0.3Si) aluminium alloy, utilizing anodic and cathodic polarization measurements in a solution of 3.5% NaCl at ambient temperature. The results showed that the weld exhibited similar corrosion behaviour to that of the parent alloy [150].

2.4.11.4 AA7xxx aluminium alloys: The TMAZ and the HAZ of AA7xxx alloys are the most susceptible parts to corrosion. Davenport et al [151] studied the resistance of the friction stir welded AA7010 aluminium alloy to atmospheric corrosion. The specimen with the weld located at its middle was exposed to the atmosphere for 365 days. The SEM investigation showed the nugget and the HAZ as well as the parent alloy were prone to IGC. The IGC attack was higher in the HAZ and nugget than the parent alloy.

![Figure 2.39 Appearance of friction stir welded AA7010 aluminium alloy after one year of exposure to atmosphere [151].](image)

Wadeson, Zhou, Thompson, Skeldon, Djapic and Scamans [152] studied the corrosion behavior of the AA7108-T79 aluminium alloy using immersion and electrochemical testing. The results showed that the TMAZ edges suffered from intergranular corrosion which was attributed to precipitation of zinc-magnesium rich phase known as η/η'.
(MgZn$_2$) along the grain boundaries of this particular zone due to the effect of the joining process.

Lumsden et al [153] studied the resistance of the friction stir welded AA7075-T651 aluminium alloy to pitting and IGC. The results showed that the HAZ was susceptible to both types of corrosion. The reason was correlated to the presence of copper-depleted regions along the grain boundaries of the HAZ.

### 2.4.12 Improvement of friction stir weld corrosion resistance

The corrosion resistance of friction welds can be improved either during or after welding. Changes can be made in the chemistry of the welds during welding through the addition of alloying elements. Homogenizations of the sensitized microstructure and short term post weld heat treatments after joining appear to be ways to improve the corrosion resistance of the friction stir welds on a long term basis.

Further, the corrosion resistance of friction stir welds can be improved by surface treatments such as laser surface melting, coating and anodizing. Some works on the effect of laser treatment in improving the corrosion resistance of the friction stir welds showed that the process improved the corrosion resistance for both the weld and the parent alloy through the action of dissolving the coarse and fine intermetallics within a few micrometers from the surface. However, the durability of this improvement was short when the treated weldment subjected to IGC and exfoliation corrosion susceptibility testing due to detachment of the laser melted layer that results from the micro galvanic corrosion between the segregated reactive phase (at the interface between the laser layer and the matrix) and the bulk material [145].

### 2.4.13 Flaws in the friction stir welds

No porosity and hot cracking are associated with friction stir welds of aluminium alloys due to solid-state joining nature of the process. However, this does not mean that no imperfections or defects can be generated within the welds. An ideal parameter window has to be selected experimentally to guarantee production of a joint free of defects [126].
As specified by Threadgill, the parameters that play an important role in controlling the friction stir weld joint quality are the tool rotation and traverse speeds, tool plunge depth, tool design, welding gap, variation in the thickness of the components, work-piece thickness mismatch and the tool tilting angle [111].

Blignault et al [154] classified the types of flaws that can be generated within the friction stir welds into three types (1) voids, (2) joint line remnant (JLR), and (3) lack of penetration (LOP).

Figure 2.40 shows the typical imperfections within a friction stir weld of AA-5754-H111 aluminium alloy including, voids, lack of penetration and a joint line remnant flaws.

Figure 2.40 Typical friction stir weld imperfections are presented within friction stir welded 6 mm AA5754-H111 aluminium alloy [154].

### 2.4.13.1 Voids

Voids are generated when a high traverse speed and/or low rotation speed, non adequate joint gap, improper work-pieces fixing and small shoulder are used. Use of a small shoulder can lead to lack of material consolidation due to absence of insufficient forging load, leading to void formation. The void is always seen at the advancing side of the weld due to the complexity of material flow in this zone [155-156]. Leal and Loureiro reported that the probability of void formation increases with increasing the tool traverse speed [157].

### 2.4.13.2 Joint line remnant (JLR)

The JLR can form when the deforming pressure or the heat input is not sufficient to soften the material. The JLR can only be detected by metallographic examination or destructive testing using the bend test [158-159].
The JLR is also known as lazy S, zigzag line, banded structure and entrapped oxides [156, 160]. It forms as a result of oxide accumulation within the joining line interface. These oxides come from the component surface being joined. Previous studies showed that the JLR usually consists of semi-continuous oxide particles, mainly aluminium oxide, distributed around the original joint line, as shown in Figure 2.41 [161].

![Figure 2.41 a) Optical image showing the JLR, and b) EDX analysis on the JLR showing that the JLR is mainly aluminium oxide [161].](image)

The extent of the oxide particles determines the severity of this imperfection and its effectiveness on the structural integrity [153].

Proper control of the welding parameters and removal of oxides from the surfaces by machining prior to joining can reduce or eliminate formation of such flaws [87, 103]. Sato et al [162] showed that increase in the rotation speed helped in eliminating the JLR imperfection. Such an effect is evident in Figure 2.42.

![Figure 2.42 Effect of the increase in the rotation speed on the JLR formation [162].](image)
2.4.13.3 Lack of penetration (LOP)

The LOP initiates at the root of the weld because of use of a short pin, incorrect plunge depth, and improper tool alignment, and variation in thickness of the work-pieces being joined [156, 159, 163].

Dickerson and Przydatek [160] studied the effect of the root flaws on the mechanical properties of AA5083-O, AA5083-H321 and AA6082-T6 aluminium alloy friction stir welds utilizing destructive and non destructive testing techniques for detecting the root flaws. The used non destructive testing (dye penetrant and radiographic examination) failed to reveal the root flaw within the welds. The destructive test (root and face bend test) managed to show LOP at the welds root. The results showed no significant change in the static or fatigue strength of the friction stir welds of AA5083-O and AA6082-T6 aluminium alloys that contained shallow or small root flaws compared with the welds of the same material that contained no root flaw defects. In contrast, the friction stir weld of 5083-H321 that contained a larger root flaws, exhibited a reduction in the ultimate tensile strength and ductility as well as the fatigue strength compared with that free of root flaw welds.

The LOP can be avoided by selecting the proper probe length and machining. The latter is applicable only for thick welded sections [112].
CHAPTER 3
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Experimental Procedure

3.1 Introduction
The aim of the experimental work is to investigate effect of FSW on the microstructure of non-heat-treatable AA5754-H111 and AA5083-O aluminium alloys in terms of grain structure, size and distribution of intermetallic particles and to correlate the microstructure to corrosion behaviour of the weld and parent alloys.

Corrosion susceptibility of the welds and parent alloys were examined utilizing immersion testing. The recommended ASTM-G66-99 and ASTM-G67-04 standards were used for evaluating the susceptibility of AA5754-H111 and AA5083-O aluminium alloys to exfoliation and intergranular corrosion (IGC) respectively. Optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to determine the microstructure of the weldments.

The susceptibilities of the weldments to galvanic corrosion and pitting were evaluated by agar gel test and electrochemical measurements.

The affect of the welding process on the alloys hardness was assessed by measuring the hardness profile along the weld regions and the parent alloys at the top surface and cross section of the weldments.

3.1 Materials
The investigated alloys are members of AA5xxx non heat treatable aluminium alloys. In both alloys, magnesium (Mg) is the main alloying element with a higher percentage in AA5083 alloy. The chemical compositions of the alloys are presented in Table 3.1.

Friction stir welded 6 mm thick AA5754-H111 and AA5083-O plates were received from The Welding Institute (TWI), with a welding joint located at the centre of the plates.

The welding parameters employed for joining the plates are shown in Table 3.2.
Before proceeding with metallographic examinations and corrosion testing, it is vital to prepare the specimens and solutions according to testing standards requirements. This section describes the specimen preparation procedure for metallographic examination and corrosion testing, as well as the preparation of the testing solutions. The specimen preparation was performed to facilitate characterizing the welds microstructure and to evaluate their corrosion behaviour.

### 3.3 Specimen preparation

The top surface and cross section specimens with the welding line at their centre were ground with 1200 and 4000 grit emery paper, cleaned with ethanol, then dried. The specimens were polished with 3 and 1 μm polishing paste to obtain mirror finish, and cleaned with ethanol in ultrasonic bath for 15 minutes. This allows the second phases to be observed under the scanning electron microscopy (SEM). The distribution, size and composition of the second phases were investigated at the top and cross section of the weld utilizing ZIESS EVO-50 and XL30 SEMs equipped with EDX facilities. For determining the Volta potential of the intermetallic phases, scanning Kelvin probe microscopy (SKPM) was used.

In order to identify the weld regions, macro etching was used to reveal the weld regions. Before etching, as-welded specimens with dimensions of 50 x 3 x 6 mm with the welding line at the centre were mechanically ground at both top and cross section surfaces with 1200-4000 SiC grit papers, polished to 1 μm diamond paste, washed with deionised water, dried in cold stream of air, cleaned with ethanol in ultrasonic bath for 15 minutes and air dried. In order to reveal the welds structure, the interested specimens were etched in a solution of 10 wt. % caustic soda (NaOH) and 90 ml deionised water at 60 °C for 10 seconds, washed immediately with deionised water, dried and rinsed in 70% concentrated nitric acid for 30 seconds before optical microscopy (OM) examination.

For revealing the parent alloys and weld regions grains morphology, etching and electro-polishing were employed to obtain the necessary information about the effect of the FSW on the grains size and the shape. OM, SEM and TEM were utilized to verify such effect.
3.3.1 Etching
50 x 5 x 6 mm specimens were cut in a way that kept the welding at the middle. Before etching, the top and the cross section of the specimens were prepared in the same procedure to that specified in section 3.4.1.

Keller reagent was selected to reveal the microstructure of both welds and parent alloys. The etchant solution was prepared by adding the recommended quantity of acids to 50 ml of deionised water and mixed thoroughly.

The specimens were immersed in a diluted Keller reagent for a period of 10-15 seconds, washed thoroughly with deionised water, and dried in a stream of cold air before examining with OM.

3.3.2 Electropolishing
The specimens were prepared a similar way to that described in section 3.3.1. After the prepared specimens have been dried completely and ensuring that no traces of water exist on the specimen surfaces, the electropolishing was conducted to remove any near surface deformed layer that were generated during mechanical polishing or processing, allowing orientation contrast images and electron backscattered diffraction (EBSD) maps to be produced by FEG-SEM.

To prepare the electropolishing solution, 800 ml of ethanol were poured in a glass beaker and cooled with icy water and then 200 ml of perchloric acid were added in stages. During this process, the temperature of the solution was monitored regularly to keep the solution temperature below 15°C, to avoid the risk of explosion. The same precautions were followed during the electropolishing process.

A thin pure aluminium sheet was used as a cathode in the circuit, a constant potential of 15 V was applied to the electrodes. The specimens were held in solution of 80% vol. % ethanol and 20 vol. % perchloric acid at 5°C for 1 minute. Following removal from solution, the specimens were rinsed thoroughly with ethanol, dried with cold stream of air and examined in FEG-SEM at both top surface and cross sections.
3.3.3 Twin jet electropolishing
Discs of 3mm diameter were punched from the area of interest using a sparking technique. The thickness of the discs was then reduced to 100 µm utilizing 1200 and 4000 grit SiC papers. Using a struers Tenupol twin jet electropolishing machine, electropolishing was conducted in a solution of 30% wt. nitric acid and 70% wt. methanol at -30 ºC. Liquid nitrogen was added gradually to the solution to achieve -30 ºC.

To prepare the electropolishing solution, 700 ml of methanol were poured in glass beaker and cooled with nitrogen, and then 300 ml of nitric acid were added in stages. During this process, the temperature of the solution was monitored and liquid nitrogen was added regularly to keep the solution temperature at -30ºC during the electropolishing process.

3.3.4 Ultramicrotomy
Electron transparent sections for TEM examination were prepared using ultramicrotomy utilizing a Leica Ultracut UCT ultramicrotome. This technique helps in preparing thin foils to allow the prepared sections to be observed in TEM. Detailed information about the type, size of the constituent particles and the dispersoids within the grains interiors and the precipitates at the grains boundaries can be obtained [164].

As-welded and sensitized specimens were cut to a dimension of ~ 6 x 9 x 0.3 cm, and fixed at the centre of standard size plastic capsules with assist of a sticker in a way that kept the interested surface facing the diamond knife. The capsule contained the specimen was filled with epoxy resin made of Agar 100 resin, DDSA, MNA and BDMA in the weight ratio of 24:13:13:1 respectively and kept in an electrical furnace at 60ºC for 24 hours to cure the resin. The cured resin block contained the specimen was taken out of the capsules and fixed on a rotated and movement free arm with the help of specially designed holders. The specimens were trimmed with a glass knife to obtain a rectangle shape of < 0.2 x 0.1 mm from the interested surface and sectioned with a diamond knife at a cutting speed of 0.15 mm·s⁻¹. During sectioning, the water level within the diamond knife bath was controlled to enable floating of the cut sections. The sections of a thickness of 20 nm were collected using nickel grids, dried on filter paper and stored for TEM examination.
3.4 Corrosion testing

The specimens were cut from as-welded plates according to the specified dimensions in ASTM G66-99 and ASTM G67-04 standards. The specimens were cut to 50 mm in the transverse direction and 15 mm in the welding direction and rolling direction in a way that the welding zone is kept at the middle of the specimen as shown in Figure 3.1.

3.4.1 Exfoliation corrosion test (ASTM G66-99)

ASTM G66-99, known as assessment of the exfoliation test (ASSET), is a standard test used for evaluating susceptibility of AA5xxx aluminium alloys to exfoliation corrosion through immersing the interested specimen in the specified test solution (Table 3.3) for 24 hours [75].

The traces of the sharp edges from the cutting process and the cross section surface were ground with 1200 and 4000 silicon carbide grit papers and polished to 1µm utilizing automatically rotated grinding wheels. During grinding, water was injected in a continuous way and the specimens were held gently to avoid over heating of the specimens due to the friction between the specimen and the grinding papers. After insuring smooth and free of scratches surfaces, the specimens were cleaned with deionised water, dried in stream of cold air, cleaned with ethanol for 15 minutes in ultrasonic cleaning bath and dried in stream of cold air. Before immersion in the corrosion testing solution, the interested specimens were etched in a solution of 5% NaOH and 95 ml water for 1 minute at 80 °C, rinsed with deionised water, air dried, and dismutted in 70 % concentration nitric acid for 30 second, washed with deionised water and air dried. Then, immediately specimens were immersed in a freshly prepared exfoliation corrosion testing solution. The chemical composition of the solution is shown in Table 3.3.

To prepare the testing solution, the mixture shown in Table 3.3 was dissolved in a little amount of deionised water, and then the quantity was adjusted with deionised water to one litre. A magnetic stirrer was used to ensure a complete dissolution.

The solution pH was measured before commencing the corrosion test to stick to the standard requirements. The interested specimens were prepared into the ways described in section 3.4.2.1.
A one litre glass beaker was used for containing the prepared solution. The beaker was placed in a water heating bath and held firmly using stand clamps to avoid movement during the experiment running time. The solution temperature was maintained at 65°C utilizing a water heating bath filled with plastic balls for minimizing water evaporation. After verifying that the water level in the heating bath is higher than the solution level in the beaker and the temperature was kept constant at 65°C, the specimens were placed in the beaker in a way that kept standing over the glass rod. In order to minimize the evaporation of the solution, the beaker was covered with a glass cover connected to a condenser. The condenser was connected to the glass beaker cover from one side and to the water tap from the other side.

The temperature and the level of the solutions were monitored regularly till end of the experiment. The specified time for the experiment was 24 hours. After completing the testing, the specimens were taken out of the solution, washed thoroughly with deionised water and allowed to air dry. The specimens were stored in a desiccator for examination.

### 3.4.2 Nitric acid metal loss test (NAMLT)

ASTM G67, known as nitric acid metal loss test (NAMLT), is a standard test for evaluating the susceptibility of AA5xxx aluminium alloys to IGC through immersing the specimens of interest in 70% concentrated nitric acid. According to the standard, the alloy is considered resistant to IGC when the mass loss per unit area is less than or equal to 15 mg/cm², while if it is greater than or equal to 25 mg/cm², then the alloy is considered susceptible to IGC [66].

After removal of the sharp edges traces resulted from the cutting process, the cross section of as-welded specimens were ground with 4000 SiC grit paper, polished to 1µm, cleaned with ethanol, and air dried. Prior to immersion in nitric acid, the surface area of the prepared specimens was measured using a venire calliper. Then the specimens were etched in 5% NaOH at 80 °C for 5 minute, dismutted in concentrated nitric acid for 30 second, washed thoroughly in deionised water, air dried and weighed before commencing the IGC susceptibility test.
The prepared specimens were immersed in nitric acid and kept standing over glass fixed in the glass beaker. The beaker was placed in a water bath to maintain the desired solution temperature and was covered firmly with a glass cap using fixtures to eliminate evaporation of the solution. The nitric acid level was kept below the water level in the bath. The water bath was heated to 30°C. The nitric acid temperature and the water bath level were monitored regularly until end of experiment. After completion of the experiment, the specimens were taken out of the test solution, rinsed thoroughly with deionised water, cleaned softly with a soft tooth brush, allowed to dry in air, weighted and stored in a desiccator for SEM examination. The difference in weight before and after the immersion test was divided by the specimen surface area for evaluating the metal loss per unit area and used as an indicator to reveal the IGC resistance of the weldment.

The cross section of the tested specimens was prepared in the same manner to that specified in section 3.4.2.1 and examined with SEM for verifying the susceptibility of the parent alloy and the weld regions to IGC.

### 3.4.3 Phosphoric acid etching test

Phosphoric acid etching is a useful method for assessing the degree of AA5xxx aluminium alloys to IGC susceptibility. As-welded and sensitised specimens were etched in a solution of 10 % phosphoric acid at 60 °C normally for 90 seconds. This test was used to indicate presence of β-phase at the grain boundaries and to visualise areas of localised corrosion susceptibility for the friction stir welded AA5083-O and AA5754-H111 aluminium alloys.

Before sensitizing, the cross section of the specimens was ground using 4000 SiC grit papers, polished to 1 μm, washed with deionised water, cleaned with ultrasonic bath for 15 minutes and air dried before inserted to the furnace. The prepared as supplied and sensitized ones are then etched in 60°C heated phosphoric acid for 1 ½ minute, washed with deionised water, air dried and examined under SEM.
3.4.4 Agar gel test

Agar gel was placed on the top surface of the as-welded and ground specimens (with 4000 silicon carbide grit paper) with the welding line located at their centre in order to assess the susceptibility of the weld various regions and the parent alloys to localised corrosion through observing the local changes in pH via change in colour. Before commencement of the test, the ground and as-welded specimens were ultrasonically cleaned with ethanol, air dried, and then tested.

In order to prepare the gel, 2.5 g of NaCl was added to 125 ml of deionised water and mixed together in a clean glass beaker using a clean glass rod. The solution was heated to the boiling temperature using a hot plate. Then, 1.5 g of agar gel powder with 3.75 ml of universal indicator were added to the boiled mixture and mixed together. The beaker containing the solution was taken out of the hot plate and left to cool down until the solution becomes viscous. 1-2 mm thick layer of the agar gel were cut using a sharp knife and placed over the prepared specimen surfaces.

The gel test relies on the change in the colour. The colour indicator within the gel is sensitive to the change in pH across the specimen surface. The change in colour is used to identify the net anodic and cathodic regions across the tested specimens.

According to the reference code of the pH indicator, the anodic region within the specimen surface will become orange/yellow due to the effect of the acidity that generated from the hydrolysis of aluminium, the cathodic regions will become blue/green owing to increase of the alkalinity that resulted from the oxygen reduction. The test was repeated several times for reproducibility purpose.

3.4.5 Electrochemical measurements

The weld regions and the parent alloys of as welded specimens were individually assessed utilizing the electrochemical measurements. The specimens were cut to 50 x 50 x 6 mm. The cut specimens were cleaned in ethanol for 15 minutes to remove any dirt. The area of interest on the top surface of the as-welded was kept bare and remained areas were coated with lacquer 45, left to dry for 24 h before proceeding with the electrochemical measurement. De-aerated solution of 3.5 wt. % NaCl at ambient temperature was used for this purpose.
Open circuit potential and anodic polarization were utilized to compare the corrosion behaviour of the weld various regions with the parent alloys. The measurements were carried out using platinum electrode as a counter, saturated calomel electrode (SCE) as a reference electrode and the specimen as a working electrode. A potentiostat from ACM instruments was employed for the measurements. The electrochemical cell is shown in Figure 3.2.

3.5 Hardness measurement

The top surface and the cross section of specimens the welding line at the centre was ground using 1200 and 4000 SiC grit papers, and polished to 1 µm. The Vickers hardness measurement was conducted a cross the top surface and cross section of the prepared specimens using a square-base diamond pyramid indenter fixed on Instron Tukon 2100 micro-hardness tester at a load of 0.1 kg every 200 µm (Figure 3.3).

3.6 Characterisation techniques

In this part we describe briefly the advantages, disadvantages and the operation principles of optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The microscopies are used to provide detailed characterization.

3.6.1 Optical microscopy (OM)

OM was used to reveal the effect of the FSW on the alloys microstructure and to verify the weld regions (structure). Olymus BHM optical microscopy fitted with x5 to x100 magnification lenses and a digital video camera connected to desk top computer was used for examining the welded alloys (Figure 3.4).

The OM is widely used for its simplicity. The interested specimen is illuminated with a focused light to produce the image that can be viewed by the naked eye. Lenses are used to focus the light and to obtain desired magnifications. Unfortunately, the magnification of OM is limited to x 1000 and its resolution to 0.2 mm due to the physical nature of the light. Further, compositional and crystallographic information can not be obtained with OM. For this reason, SEM was developed to overcome such problems [165].
3.6.2 Scanning electron microscopy (SEM)
ZIESS EVO-50 (Figure 3.5) and Philips field emission gun XL30 SEMs equipped with energy dispersive x-ray (EDX) facilities, and the later equipped with electron backscattered diffraction (EBSD), have been used in this study for obtaining necessary information about the microstructure and the corrosion resistance of the friction stir welded AA5754-H111 and AA5083-O aluminium alloys.

A high resolution SEM, Carl Zeiss ULTRA 55, was used to examine the ultramicrotomed blocks. Compared with OM, SEM provides images with higher resolution and greater depth of field [164].

Once the specimen is inserted in the SEM chamber, the vacuum is provided and the beam is switched on, a focused electron beam by the magnetic lenses hits and scans the specimen surface resulting in interaction between the primary electrons and the specimen surface, which leads to emission of secondary, backscattered, Auger electrons and X-rays. The emitted electrons are used for obtaining information about the surface of the specimens. The secondary electrons provide topographic information, the backscattered electrons are used to identify atomic number differences between various regions of the specimen, and the EDX are used to provide information about composition.

Before examining the interested specimens with SEM, the specimens were held on aluminium stub made especially to fit SEM stage with the aid of a carbon tape. Silver paint was applied between the stub and the specimen to eliminate the charging effects.

3.6.3 Transmission electron microscopy (TEM)
JEOL 2000 FX II (Figure 3.6) and TECHNAI F30 transmission electron microscopes, equipped with energy dispersive X-ray (EDX) analysis, operated at 120 and 300KV respectively, were used to examine thin foils taken from the interested area of the parent alloys and welds and prepared by the twin jet electro-polishing and ultramicrotomy. TEM enables examining the grains boundary and the grain interiors in detail on nano scale [165-166]. It is widely used for obtaining detailed information about the thickness and morphology of oxide films on aluminium.
Compared with SEM, TEM operates at higher voltages. JEOL 2000 FX II operates at maximum voltage of 200 KV. High voltages are needed when the specimen is thick.

Once the tungsten filament is electrically heated, the electron beam is produced. The beam passes between fixed condenser lenses system which serve to control the beam alignment. When the beam hits the surface, it interacts with the specimen as result different signals will appear. The electron beam that passes through the specimen without change produces the image. The emitted Auger electrons and X-rays are employed for elemental chemical analyses.

Contrary to OM and SEM, a very thin foil in range of 10-100 nm is required to obtain good results. Normally, the thin foils are prepared by twin jet electropolishing, focussed ion beam (FIB), or by the ultramicrotomy technique, by which transverse sections are cut at 20 nm thickness and collected on grids made of nickel or copper.

### 3.6.4 Scanning Kelvin probe microscopy (SKPM)

The SKPM was used to obtain information about the differences in the Volta potential between the matrix and the second phases within the parent alloys and the weld regions of AA5754-H111 and AA5083-O aluminium alloys. Nanoscope 3100 scanning probe microscope was employed for this purpose (Figure 3.7).

The analysis of the files was performed using Taylor-Hobson Multi map software, where two and three dimensional surface analysis was utilized to illustrate the features on the interested surfaces.

A sharp tip (probe) attached to the end of a cantilever (spring type) is brought very close to the specimen surface to scan the area of interest, when the tip scans the surface, the forces between the tip and the specimen lead to deflection of the cantilever. Photodiodes detector is used for measuring the bending of cantilever during the specimen scanning with the help of a laser light reflected from the top surface of the cantilever into an array of photodiodes. The measured cantilever deflections are used to generate a map of the surface topography [167].
Figure 3.1 Dimensions of the specimen for corrosion testing.

Figure 3.2 Electrochemical measurement cell.

Figure 3.3 The hardness measurement method.
Figure 3.4 Pictures of the optical microscope.

(a)                                                       (b)

Figure 3.5 (a) Picture of ZEISS EVO-50 SEM; (b) specimen stage and detectors.

Figure 3.5 (a) Picture of ZEISS EVO-50 SEM; (b) specimen stage and detectors.
Figure 3.6 Picture of JEOL 2000 FX II- TEM.
Figure 3.7 Picture of Nanoscope 3100 scanning probe microscope.
Table 3.1 Chemical compositions of AA5754 and AA5083 aluminium alloys (wt. %).

<table>
<thead>
<tr>
<th>Material</th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
<th>Cr</th>
<th>Ti</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA5754</td>
<td>2.6-3.2</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td>0.1</td>
<td>0.3</td>
<td>0.15</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>AA5083</td>
<td>4.0-4.9</td>
<td>&lt;0.4</td>
<td>&lt;0.4</td>
<td>0.4-1.0</td>
<td>&lt;0.1</td>
<td>0.05-0.25</td>
<td>&lt;0.15</td>
<td>&lt;0.25</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2 Welding parameters.

<table>
<thead>
<tr>
<th>Material</th>
<th>Traverse speed mm/min</th>
<th>Rotating speed rpm/ min</th>
<th>Pressure</th>
<th>Tilt angle</th>
<th>Probe type</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA5754</td>
<td>500</td>
<td>500</td>
<td>2 kN</td>
<td>2°</td>
<td>Triflute™</td>
</tr>
<tr>
<td>AA5083</td>
<td>380</td>
<td>380</td>
<td>-</td>
<td>0°</td>
<td>Triflute™</td>
</tr>
</tbody>
</table>

Table 3.3 the solution composition used for assessing the AA5754 and AA5083 alloys exfoliation corrosion susceptibility.
CHAPTER 4

Friction Stir Welded AA5754 Alloy

Due to the effect of mechanical deformation and frictional heating, a great modification of the original alloy microstructure takes place during FSW. As a result, distinct regions were generated within the weld, namely, the thermo-mechanical affected zone, the nugget, and the heat affected zone. Each region has a different microstructure feature from the others. The region that experienced highest plastic deformation and temperature exhibits microstructure differences from regions that experienced less heat and deformation. The variations in the microstructure between the weld regions are attributed to the difference in plastic deformation, temperature fields and the post welding cooling rates [168-171].

Understanding the alteration in the microstructure after FSW is an important aspect, as it is the key factor for explaining the reason for the change in corrosion behaviour and mechanical properties of joined materials.

This section covers the microstructural characterization of AA5754-H111 before and after FSW, including grain structure and intermetallic particle compositional analysis and distribution. The effect of the changes in the microstructure on the corrosion behaviour and mechanical property of the alloy is covered in sections 4.3 and 4.4 respectively.

Classification, from Philip Threadgill, of the structure of Al friction stir welds has been used as a guide for identifying the weld structure of AA5754 alloy [94]. For revealing the microstructure, the specimens were electropolished at 15 V for 1 minute in 80% ethanol and 20% perchloric acid solution at 5°C and etched at ambient temperature with diluted Keller reagent. Microstructural characterisation of the alloy before and after FSW was carried out with optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).
4.1 General observation

Figure 4.1 shows optical images of the top surface of the as-welded and electropolished specimens of AA5754-H111 aluminium alloy. The weld region located at the centre is the thermomechanical affected zone (TMAZ). It extends approximately 23 mm, equal to the shoulder diameter. Within TMAZ region, a semicircular pattern can be clearly seen at the contact area with the shoulder.

The edge regions of TMAZ are identified as advancing and retreating sides. The advancing side is located at the right side of the weld in Figures 4.1a-b and marked as ‘AS’. The retreating side is located at the left side of the weld and is labelled as ‘RS’. The AS can be easily recognised since it is characterized by the presence of material arm at the top surface of the weld, as shown in Figure 4.2. This feature does not exist at the RS of the weld. Further, the transition between the stir zone and TMAZ is more obvious at AS than that at RS.

Close examination of the top surface of the as-welded alloy showed that the weld has a relatively smooth surface with a slight reduction in thickness at the shoulder contact area (Figure 4.1a). The interface between TMAZ and the HAZ, as well as between HAZ and the parent alloy was not visible. The width of the HAZ was distinguished by the change in the micro-hardness measurement (See section 4.3). In addition, the weld root can be clearly seen at the centre of the weld at the bottom surface of the weldment, as shown in Figure 4.3.

After electropolishing in a solution of 200 ml perchloric acid and 800 ml ethanol at 15V and 5°C for 1 minute, the expected zones associated with FSW were evident at the transverse section, as shown in Figure 4.4, namely TMAZ, nugget, and the parent alloy. The borders of the HAZ were not visible at the transverse section. At the bottom of the transverse section, the width of the weld is approximately 3 times less than that of the shoulder contact area (weld crown), roughly equal to the probe diameter, i.e. 7 mm.

The TMAZ and nugget appear in a symmetrical and elliptical shape respectively. After etching in a solution of 10g/l NaOH and electropolishing in a solution of perchloric and ethanol (200/800 ml), the nugget showed dark etch profile, as shown in Figures 4.4 and...
4.6. It is located at the TMAZ centre, displaying a flow pattern in the form of an onion ring structure, as shown in Figure 4.5.

After etching the weldment in 10 wt. % NaOH at 60˚C for 1 minute, a semi-continuous dark line in the form of S shape within TMAZ was revealed (Figure 4.6). It is similar in shape to that observed by H. Jin et al [79]. This observed zigzag line at the cross section of the weldment is identified as a joint line remnant (JLR), and its formation has been attributed to the dispersion of oxides that originally exist on the component surfaces prior to joining [172-173].

In this work, SEM examination revealed ultra fine grains within the JLR (Figure 4.7). Similarly H. Jin et al [172] reported the presence of ultra fine grains within the JLR when studied friction stir welded AA5754 and AA5182 aluminium alloys.

The X-ray mapping of the top surface showed that the JLR contains mainly magnesium and oxygen (Figure 4.8). This result came in agreement with that observed by Cantin et al [174] who studied the effect of friction skew-stir welding of lap welding in the microstructure and mechanical properties of AA5083-O aluminium alloy.

4.2 Microstructure feature of FSW AA5754-H111

4.2.1 Parent alloy

The parent alloy is the part of the weldment that was not metallurgically affected by the welding process. It is located far from the weld. That means its microstructure remained unchanged throughout the entire welding process. The alloy was supplied in H111 temper, which means that the alloy was strain hardened via the manufacturing processing to develop minimum property requirements. The AA5754 aluminium alloy is widely used in automotive industry due to its light weigh, excellent weldability, good formability and good resistance to corrosion [175].

Figures 4.9- 4.11 show optical and BSE images, and electron backscattered diffraction map (EBSD), presenting the alloy microstructure at the rolling plane. The size of the grains is in the ranges of 10-50 μm, similar in shape to that observed by T Hausöl et al [176].
Within the grains, white and grey spots are evident in Figure 4.9 and 4.10 respectively. These spots represent the constituent intermetallic particles. Some of them were seen attacked by the electropolishing and etching processes. The grains in BSE imaging mode showed different brightness (Figures 4.9). This is due to the variation in the orientation of the grains. As can be seen, some grains were slightly elongated in a direction parallel to the rolling direction.

The alloy fabrication process has shown its impact on the distribution of intermetallic particles as well. The intermetallic particles (Figure 4.12) were seen aligned along the rolling direction.

At the transverse section, the shape and size of the grains is almost similar to that observed at the rolling plane. The grains varied from fine, equiaxed of approximately 10 µm in diameter to slightly flatten in a direction perpendicular to the rolling plane and the welding direction in range of about 20-70 µm. Figure 4.13 represents the parent alloy microstructure at the transverse plane. It is evident in the SEM micrograph that the majority of the intermetallic particles are distributed within the grain interior. The compositional analyses of the intermetallic particles are presented in section 4.2.5.

At the longitudinal plane, the grains were seen elongated in a direction parallel to the rolling direction and the intermetallic particles were aligned along the rolling direction (Figure 4.14). The grains at the transverse plane are in the range of 50-100 µm.

### 4.2.2 Heat affected zone (HAZ)

The HAZ is the part of the alloy that is affected by the heat generated from welding. It is located between TMAZ and the parent alloy. It should be noted that this region is far from the probe and the shoulder. For this reason, no mechanical deformation took place within the HAZ. As the HAZ experienced heat without deformation, the microstructure of this region is sensitive to the amount of the heat transferred from the TMAZ, as well as to the cooling rate after FSW. The heat input to the HAZ of friction stir welds increases with increasing tool rotation speed and the tool size [177]. The induced heat at this region and the cooling rates after FSW can significantly modify the microstructure.

In the literature, grains coarsening, reducing the solute atoms within the matrix by precipitating electrochemically active phase at the grain boundaries and/or annealing
the microstructure by reducing the density of the dislocation within the alloy matrix have been reported within FSW aluminium alloys [171].

By examining the microstructure of weldment at rolling and transverse planes, it was evident that the HAZ exhibited larger grains than that of the parent alloy, as shown in Figures 4.9, 4.11 and 4.15. The size of the grains was in the range of 50-100 μm. The white spots seen in the HAZ represent the constituent particles. The majority of the intermetallic particles are located within the grain interior. Their composition, size and distribution are presented in section 4.2. Since the borders between the TMAZ, the HAZ and the parent alloy were not evident, the width of the HAZ was determined by the hardness measurement along the weldment. The hardness profile along the weldment at the top surface of the weld is presented in section 4.4.

4.2.3 Thermomechanical heat affected zone (TMAZ)

The TMAZ is located between the nugget and the HAZ. At the rolling and transverse planes, the TMAZ region showed a different microstructure in terms of grains size and shape compared with the parent alloy and the HAZ. At the TMAZ edges, the grains were heavily deformed without the presence of recrystallized structure, with size of approximately 10 x 80 μm. Figures 4.16 shows clearly the presence of the elongated grains at AS edge of TMAZ at both top surface and cross section respectively. The grains were elongated in a direction parallel and perpendicular to the welding and rolling directions at the top surface and the cross section of the weld respectively.

Away from the edges, TMAZ exhibited partially recrystallized microstructure. This is evident in Figures 4.17 and 4.22b. The grains were seen oriented following the shoulder movement at the advancing and retreating sides. Such an effect is apparent in Figures, 4.17 and 4.22 b.

At the TMAZ advancing side, a sharp transition from highly refined grains to deformed grains was detected. At the retreating side, the transition was not clear as the AS. Figure 4.18 shows the transition between the stir zone (nugget) and TMAZ at the advancing and retreating sides of the weld respectively.
Examining the variation of the microstructure inwardly through the weld at the transverse (cross) section, the difference in the grain size within the weld area was evident (Figures 4.19-4.20). It has been found that the size of the grains increases as moving from the bottom of the weld toward the weld crown.

### 4.2.4 The stir zone

The stir zone displays completely different microstructure in terms of the size and the shape of grain than that of the parent alloy and the HAZ. This region of the weld is located in the centre of TMAZ and experienced the highest level of deformation and heating, resulting from the friction between the profiled probe and the material during its rotation and travelling along the joining line; as a result, a recrystallization process took place at this region [178-179]. Consequently, fine, equiaxed grains of approximately 5 μm in diameter were generated. Figure 4.21 shows the stir zone microstructure at the top surface and the cross section of the weld. The grain size of the nugget was resolved by SEM as the grains were too small to be measured by optical microscopy. However, it should be mentioned that the nugget is free of defects such as voids and cracks.

In addition to that, the stir zone was observed to contain submicron intermetallic particles within the grains interior, as a result of the rotated tool effect, as shown in Figure 4.29, smaller in size than that observed within the parent alloy and the HAZ.

The effect of the FSW on the microstructure of the AA5754-H111 is evident in Figure 4.22. It is obvious that the FSW process resulted in a significant change in the grains size and morphology, owing to the severe mechanical deformation and frictional heating, which generated from the contact between the tool and the material during rotating and travelling of the probe and the shoulder along the joining line.

### 4.2.5 Effect of FSW on intermetallic particles

It is well known that FSW process relies on the mechanical action served by the shoulder and the probe. A rotated profiled pin and shoulder made of high strength and wear resistance material are used to soften the material by stirring action to achieve
bonding. Thus, the tool forging action serves to break-up and redistribute the insoluble intermetallic particles. Additionally, the heat generated from the friction between the tool and the material can also be sufficient to cause particle dissolution, typically to those having lower melting point than the welding heat input [180-181].

Generally, the second phases within Al-Mg alloys and the other aluminium alloys are divided into two groups, constituents and dispersoids. The constituent particles can be readily seen with SEM due to their relatively large size (micro-scale). The dispersoids are of nano-scale dimensions and are normally identified by transmission electron microscopy [182]. The type, size and distribution of the intermetallic particles before and after FSW were examined utilizing scanning Kelvin microscopy, SEM and TEM.

SEM and TEM equipped with EDX analysis conducted on the top surface showed the presence of two types of intermetallic particles within the parent alloy and the weld regions. These are iron (Fe) containing particles and magnesium-silicon rich particles (Figures 4.23-4.25).

The iron-containing particles are divided into two categories, Al (Fe,Mn) rich and Al(Fe,Mn,Sn) particles, as shown in Figures 4.23-4.26. Coarse iron-rich particles with irregular shape, different size and a random distribution were observed within the parent alloy and the HAZ. On the contrary, fine and uniformly distributed particles were observed within the TMAZ and the stir zone, as illustrated in Figures 4.29-4.31. Within the parent alloy and the HAZ, some areas were observed to contain high population density of intermetallic particles; in other areas, low population density was recorded. The iron rich intermetallic phases exhibited a good contrast with the surrounding alloy matrix in both secondary and backscattered imaging mode. The white spots within the alloy matrix represent the iron-rich intermetallic phases.

The other detected phase was found to be rich in magnesium and silicon, displaying a good contrast with the adjacent alloy matrix in both secondary and backscattered imaging modes, as shown in Figures 4.27 and 4.28. The black spots seen in the micrographs represent this phase.
The size of the iron and magnesium rich particles varies. It is estimated to be in the range of approximately 1 to 15 µm within the parent alloy and the HAZ and in submicron to 5 µm within TMAZ region.

It has been reported that the intermetallic particles are the main factor that controls the corrosion behaviour of the alloy and that the corrosion resistance of the alloy is largely influenced by the composition, density and distribution of the intermetallic particles within the alloy matrix [183].

4.3 Corrosion behaviour of FSW AA5754-H111

Although the heat input during FSW is far lower than that generated by fusion welding processes, and it does not cause material melting, however, the process may alter the alloy microstructure and, consequently, affect its corrosion property.

The main alloying element in AA5xxx, including AA5754 alloy, is magnesium, which is added to improve the mechanical and corrosion properties of these alloys [184-185].

However, the corrosion resistance of AA5xxx aluminium alloys can be decreased drastically when subjected to heating and excessive deformation due to diffusion of magnesium from the grains interiors to the grain boundaries to form a non continuous and/or continuous magnesium rich phase known as β-phase (Al₃Mg₂). In a corrosive environment, such as sea water, β-phase behaves anodically with respect to the interior of the grains, leading to preferential attack at the grain boundaries [64].

In order to look at the effect of FSW on the corrosion behaviour of the AA5754-H111 alloy, agar gel test was used to determine the electrochemical nature of the various weld regions and parent alloy. Further, the susceptibility of the weldment to localised corrosion was assessed by immersion testing according to standards ASTM-G66 and G67. The standard ASTM-G66-99 was used for determining the susceptibility of the weld regions and the parent alloy to exfoliation corrosion [75]. Nitric acid metal loss test (NAMLT) was used to evaluate the resistance of the weldment to intergranular corrosion [66]. In addition, electrochemical measurement was also used to assess the variation in the resistance of the weld regions to corrosion.
### 4.3.1 Agar gel test

Figure 4.32 shows the appearance of as-welded, ground to 4000 SiC grit, and polished to 1µm weldment after the agar gel test. No difference or change in the colour between TMAZ, HAZ, and the parent alloy regions was observed, suggesting that there is no significant variation in the corrosion behaviour between the weld regions and the alloy.

### 4.3.2 Exfoliation corrosion susceptibility

Figures 4.33-4.34 show the appearance of top and bottom surface following exfoliation immersion testing for 6 and 24 h respectively. Localised attack was observed at the top surface within TMAZ, HAZ and the parent alloy. It can be seen clearly from the micrographs that the most severe attack is located within TMAZ mainly at the JLR and the root of the weld (Figures 4.35 and 4.36). A small number of scattered pits were observed within the HAZs and the parent alloy. High magnification SEM images at the top surface and cross section revealed that the width and the depth of the largest pit are in the range of 160 µm and 450 µm respectively (Figures 4.37). The majority of the parent alloy and the weld regions showed resistance to pitting corrosion, indicating that the weld regions have similar corrosion behaviour to that of the parent alloy.

At the bottom surface of the specimen immersed for 6 h in the testing solution, a high population density of pits were seen at the location of the contact with the glass supporting rods (Figure 4.33b). During testing, the bottom surface of the specimen was lying on the glass supports, thus, most likely the contact with the glass rod supports induced crevice corrosion, which increased the localised corrosion at this surface. Examining the cross section of the tested weldments with SEM using BSE imaging mode failed to detect the presence of the exfoliation corrosion neither at the weld regions nor at the parent alloy Figures 4.38-4.39.

### 4.3.3 Intergranular corrosion susceptibility

The results of the weight loss test (NAMLT) are shown in Table 4.1. As it can be seen, after 24 h of immersion in nitric acid, the amount of metal loss was - 2.70 mg/cm². This is a low value compared with the amount of metal loss specified in the standard ASTM-G67 at which and above the alloy is considered to be susceptible to IGC, i.e. 25 mg/cm². Examining the top surface and the cross-section of the tested specimens by SEM
revealed no evidence of IGC either in the parent alloy and nor in the weld regions (Figures 4.40-4.41). This result revealed that the alloy has maintained its low susceptibility to IGC after FSW. Additionally, the phosphoric acid etching test showed also no IGC attack, indicating the absence of the magnesium-rich phase at the grain boundaries (Figure 4.42).

For further confirmation, twin jet electropolished foils prepared in a solution of 300 ml nitric acid and 700 ml methanol at -30 °C, as well as thin foils prepared by the ultramicrotome were examined by TEM and SEM for verifying the absence of the electrochemically active phase (β-phase) at the grain boundaries, which reported to be responsible for the IGC initiation within the AA5xxx aluminium alloys. The resolution TEM and SEM images (Figures 4.40-4.46) showed that the grain boundaries of the weld regions and the parent alloy were free of β-phase. This result came in consistency with the weight loss and phosphoric acid tests. However, examining the weld by SEM following the NAMLT and the phosphoric acid response test revealed preferential corrosion attack at within the JLR, as shown in Figures 4.41 and 4.42a.

4.3.4 Electrochemical measurements

4.3.4.1 Open circuit potential

The open circuit potential (OCP) versus time of FSW AA5754-H111 aluminium alloy in as-welded condition is presented in Figure 4.47. On initial immersion in a de-aerated 3.5 wt. % NaCl solution, it can be observed that the OCP of the parent alloy and the TMAZ-AS is nobler than that of the HAZ and TMAZ-RS.

The TMAZ-RS and the HAZ exhibited lower potentials than those experienced within the TMAZ-RA and the parent alloy. However, after approximately 1000 seconds, the potential of the TMAZ-RS and the HAZ increases and reached the value of the corrosion potential of the parent alloy and the TMAZ-AS respectively. After approximately 3200 seconds immersion the corrosion potential of the weld regions and the parent alloy reached the stability with a slight difference in the $E_{\text{corr}}$ with a magnitude of 25 mV. It can noted that the unique difference was the rate to reach the stable potential (corrosion potential), following the order $E_{\text{PM}} > E_{\text{HAZ}} > E_{\text{TMAZ-RS}} \geq E_{\text{TMAZ-AS}}$. The OCP of the different regions is presented in Table 4.2
4.3.4.2 Anodic polarization

Figure 4.48 shows the potentiodynamic anodic polarization curves of the parent alloy and the weld regions in as welded condition. The parent alloy curve presents a passivation phenomenon with a breakdown of passivity at potential of approximately -720 mV. The current density increases with the electrode potential to reach a current plateau named passivation plateau or passivation zone. The passive current density remains almost constant and then increases hurriedly when the pitting potential $E_{\text{pit}}$ is exceeded. This potential denotes the film breakdown and pitting corrosion. On the other hand, the HAZ, TMAZ-AS and TMAZ-RS present an approximately similar passive current density slightly higher than the parent alloys. In addition, the $E_{\text{corr}}$ shows a slight difference in the area affected by the welding process compared to the parent alloy.

Generally, the curves of the weld regions and the parent alloy exhibit almost similar trends. The electrochemical parameters such as the corrosion potential ($E_{\text{corr}}$), the corrosion current density ($I_{\text{corr}}$) was determined by extrapolation of cathodic Tafel lines to the corrosion potential ($E_{\text{cor}}$). The passivation current density ($I_{\text{pass}}$) and the pitting potential ($E_{\text{pit}}$) are reported in Table 4.2.

4.4 Effect of FSW on mechanical property

It is well known that the mechanical property of any materials is influenced significantly by the heating, deformation and alloying. The deformation and heating during FSW, as well as the cooling rates after FSW are reported to cause a change in the microstructure of the joined material(s). Thus, the change in the microstructure can lead to alteration in the material mechanical property [186].

The effect of FSW process on the alloy strength was determined using hardness testing. The hardness measurements were conducted utilizing micro hardness machine at load of 0.1 kg. Figure 4.49 illustrates the hardness profile along the top surface of the welded specimen. The parent alloy has a Vickers hardness of about 60 HV, similar to that measured by T Hausöl et al for the same alloy in the same temper condition [176].

After FSW, a decrease in hardness was observed at the HAZs when compared with the parent alloy, the hardness of the HAZ was reduced by approximately 20%. On the
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contrary, the TMAZ hardness was slightly higher than the parent alloy. It increased by 10% to about 65-70 HV.

4.5 Discussion

4.5.1 Microstructure of FSW AA5754 alloy

After FSW, the welded alloy showed a typical structure at both top surface and the transverse section, similar to that observed by other researchers. The width and appearance of the weld as well as the heat input are controlled by the design and size of the tool (the shoulder and the probe). Depending on the nature of the tool design, the profiled (scrolled) shoulder generates semi-circular patterns. On the contrary, smooth (featureless) shoulders produce smooth surfaces.

As the tool rotates, it drags the softened material from the RS to the AS, resulting in a material flow arm at the edge of the advancing side (AS) similar to that observed in Figure 4.2. The amount of the material at this edge is largely influenced by the heat generated from the friction of the tool with the material. The higher the heat input, the more material is expected to be seen at the AS of the TMAZ, due to the increased of the material plasticity during processing [187].

As a characteristic of FSW, the interface between the stir zone and TMAZ is generally very sharply defined on the advancing side compared with the retreating side of the weld. The difference in the clarity between the stir zone to TMAZ transition on between the AS and RS has been reported [188-189]. It is attributed to the difference in the intensity of the deformation between both sides [178, 190-195] due to the difference in the velocity fields. The velocity fields are having opposite direction on the advancing side and same directions on the retreating side [195].

Similar to the observations of other researchers, flow patterns in the form of onion rings structure within the stir zone are observed. The formation of the onion ring structure within the stir zone is directly dependent on the welding parameters [178] and related to the extrusion of the material around the [196-197] variation in texture and grain size [168, 186, 196] and referred to be associated with the forward motion of the tool in one revolution [109, 176] as well as to the second phase rich band [103].
It is well known that combination of the profiled shoulder and the probe is responsible for generating the heat required for softening the material during welding process. The heat generated is normally sufficient to raise the temperature to the range of 0.8-0.9 from the melting point of the joined material [199]. According to literature, the highest temperature is revealed within the stir zone due to the intensive deformation of the material under the tool, and it gradually reduces as moving towards the parent alloy. The difference in the thermal gradient results in generation of inhomogeneous microstructure across the plate. As moving from the parent alloy to the centre of the weld, the alteration in the microstructure becomes remarkable [200].

The parent alloy is the part of the weldment that locates far from the deformation and heating during processing. It shows a typical microstructure of AA5754-H111, similar to that observed by Hausöl [176] in terms of grains shape. Conversely, after welding, the developed grains at the HAZ are coarser than the parent alloy. The current observation is consistent with the findings of Yadipour [188] who reported grain growth within the HAZ of FSW AA5083-H321 alloy. The observed enlargement in the grain size within the HAZ of the alloy AA5754 is attributed to the heat resulted from the welding, where the thermal transition during welding was sufficient to cause grain coarsening [201].

At the TMAZ edges, the alloy grain structure is rotated by about 90° due to the effect of the tool, which shears the material during its rotation generating enough strain to deform and elongate the structure at this region without recrystallization. The absence of the recrystallized microstructure at TMAZ edges has been reported by several authors and it is attributed to the absence of the sufficient amount of deformation and heating at the TMAZ edges [202]. The grains within TMAZ showed different crystallographic orientations. This most probable caused as a result of the plastic deformation effect [203-204].

The stir zone exhibits completely different microstructure feature relative to the TMAZ edges, the HAZ and the parent alloy. This region of the weld experiences the highest level of deformation and heating due to the direct friction with the probe. The stir zone composed recrystallized and small grains formed under high temperature and deformation owing to the probe stirring action [179,194, 205]. The generation of recrystallized and fine microstructure within the stir zone is attributed to effect of the
severe mechanical deformation and heating that leads to the dynamic recrystallization process to take place [206]. According to literature, the recrystallization starts initially by introducing dislocations in the grains structure of the post welded material through the plastic deformation, followed by the formation of subgrains by dynamic recovery, as a result the temperature causes the grains to move and become arranged, leading to reducing the residual stress in the grains. The recrystallization and recovery steps continue until stresses within the grains diminishes, at this point grain growth takes over. There is an agreement in the literature that the continuous dynamic recystallization (CDRX) is the accepted mechanism, it involves a continuous increase in the subgrain boundary misorientation within the microstructure of the material. This achieved by the continuous heat and deformation [207].

The size of the grains within the stir zone is normally varies with the variation of the welding parameters. It has been reported that the grain size increases with increasing the peak temperature within the stir zone [89, 114, 168, 186, 208].

Previous works has shown a relatively high population of dislocation within the stir zone. Similarly, in this study, the TEM investigation showed the presence of the dislocation within the stir zone. The generation of the dislocations within the stir zone has been related to effect of the mechanical deformation resulted from forging action of the probe [209].

In the present work, a difference in the grains size between the TMAZ top surface (weld crown), the middle region and the weld bottom surface at the transverse section is observed, as shown in Figures 4.19 and 4.20. Zhang et al and Liu et al [131-132] reported similar observation within the FSW AA2219-T6 aluminium alloy. Sutton et al and K. Arora et al [103-210] revealed difference between the grains size of the TMAZ top and the bottom surface of FSW AA2219-T87 aluminium alloy. The variation in the grains size can be attributed to effect of the extra heat generated at the top surface of the weld, as a result of the friction between the shoulder and the material underneath. The extra heat provided by the shoulder resulted in a variation in the temperature between the top and the bottom surface of the weld, consequently in a change of the grain size between the top, middle bottom of the weld at the cross section as it is evident in Fig. 4.
In addition to effect of FSW process on grains size and shape, a great impact on the intermetallics particles size and distribution due to the effect of FSW process is observed in the present study. The influence of FSW on size and distribution of the intermetallic particles is evident in Figures 4.29-4.31. AA5xxx alloys contain intermetallics particles in the form of constituent and dispersoids. The constituent particles are divided into insoluble and soluble phases. The Al₆(Fe,Mn) and Al(Fe,Mn)Si are classified as insoluble due to their high melting. These phases form interdendritically by eutectic decomposition during ingot solidification. Their melting point is reported to be > 700°C, which higher than the temperature of the homogenisation treatment process, which takes place at approximately 500-600°C. The second type of the constituent particles is Al₃Mg₂ and Mg₂Si, these phases are reported to dissolve in range of 550-600°C.

According to literature, the melting point of the AA5754 alloy is reported to be about 610°C [211] and 539-640°C for the AA5083 alloy [212]. Since FSW, takes place below the melting point of the material, it is expected that the temperature is not enough to dissolve Fe rich particles. On the other hand, it may dissolve partially Al₃Mg₂ and Mg₂Si if the temperature within the stir zone reaches or exceeds 550°C [142, 213-214]. However, based on the SEM examination, shown in Figure (4.30 b), it seems, that the temperature was not sufficient to dissolve the Mg₂Si phases. Instead, the rotated tool breaks up the coarse particles of the mentioned phases into smaller ones and increased their population density, as evident in the Figure.

Capability of FSW process to join materials at temperatures lower than their melting point gave it ability to produce welds free of solidification cracks and porosity that normally generate with fusion welding processes [103, 114]. However, when improper welding parameters are employed, incorrect tool location relative to the joining line is used, and or the surface being joined is improperly cleaned, flaws and defects can be generated within the weld [142, 213-214].

According to literature, three imperfections are reported to be generated within the friction stir welds, namely, 1) lack of penetration (LOP) that result from the use of a short tool plunge depth, 2) voids, which normally generate at the AS of the weld due to improper material stirring owing to use combination of low rotation speed and high
traverse speed and 3) the joint line remnant (JLR) generates, which generates as a result of insufficient breaking and mixing of the oxides layer at the welding line interface meaning that the formation of the JLR is associated with the low heat input [162, 215]. The oxides originated from the component surface prior to joining [215-216].

In this study, the JLR is revealed clearly after the metallographic examination, the JLR is evident in Figure 4.6. Several authors reported the formation of the JLR based on the metallographic examination and bend testing [215-217]. However, Savolainen et al [217] reported that the JLR becomes more evident with increasing the oxide scale at the surfaces to be joined. This was confirmed by Leonard et al [218] who were able to observe clearly the JLR within FSW of AA2014A after anodizing without etching.

The extent of the oxide particles, as reported by Benavides et al [78], determines the severity of this imperfection and its effectiveness on the structure integrity. However, up to date, no work has focused on the effect of the JLR on the corrosion behaviour of the welds. The majority of the research work concentrated on its effect on the welds mechanical properties and fatigue strength. Some authors reported no effect on the mechanical property of the weld, while others reported a reduction in the mechanical properties of the weld due to the formation of the JLR [215, 219-221].

In this study, the FSW process generates a weld free of voids, indicating that the employed welding parameters were sufficient to soften the material. However, it seems that the heating was not sufficient to break and mix the surface oxides. Sato et al [162] reported that the formation of the JLR can be avoided with the use of a high rotation speed. This was supported by Buffa et al [222] when studied the factors that influence the bonding mechanics in FSW of AA5754 and concluded that a flaw free weld can be generated with proper selection of the tool rotation and travelling speed. Cleaning of the surface to be joined by machining prior to joining has also been reported to reduce the formation of the JLR [215, 220].

The detailed SEM examination revealed the formation of the JLR within the weld (Figures 4.7 and 4.8). The X-ray mapping performed on the JLR at the top surface of a polished specimen showed that the JLR is rich in magnesium and oxygen (Figure 4.8). Similarly, the EDX analysis conducted by Cantin et al [174] revealed the presence of magnesium and oxygen within the JLR when studies effect of friction skew-stir welding
on the microstructure and mechanical properties of AA5083-O aluminium alloy. On immersion in the etching solutions, the JLR preferentially attacked. Its elimination will lead to produce sound weld with good corrosion resistance.

4.5.2 Corrosion behaviour of FSW AA5754-H111 alloy

Previous studies on friction stir welding of heat treatable and non-heat-treatable aluminium alloys showed that in some cases, the FSW process does not affect the corrosion behaviour of the welded materials. In others, it sensitized either the TMAZ or the HAZ and increased susceptibility to corrosion. Generally, the influence of FSW process on the alloy corrosion properties is determined by composition and temper condition of the alloy being joined.

The aluminium magnesium alloys (AA5xxx) specially those containing less than 3% Mg are considered not prone to exfoliation and IGC unless subjected to moderately elevated temperature for sufficient time and or excessive cold working, then they may show susceptibility to IGC and exfoliation corrosion. Thus, the degree of the susceptibility to such forms of corrosion increases with increasing the magnesium content and degree of deformation. The susceptibility of AA5xxx aluminium alloys to exfoliation and IGC is linked to the magnesium content within the alloy, and attributed to the precipitation of magnesium rich phase known as beta phase (Al₃Mg₂) at the grains boundary caused by exposure to heat for sufficient time and or the mechanical deformation. This phase has been reported to have a more negative corrosion potential than the solid solution matrix [223]. Thus, in the presence of corrosive environment such sea water, the variation in the corrosion potential generates micro galvanic coupling and leads to dissolution of the magnesium rich phase. The result is the initiation of a localised corrosion in form of intergranular and/or exfoliation corrosion. Therefore, the chemistry of the grains boundary is the main factor for susceptibility of AA5xxx alloys to exfoliation corrosion and IGC [172, 222].

In the present study, the SEM investigations on the cross section of the weldment after the corrosion testing did not reveal evidence of exfoliation (Figures 4.35 and 4.36) and low population density of pits in the parent alloy, HAZ, and TMAZ. The weight loss after immersion in nitric acid was 2.70 mg/cm², was also far lower than the amount of
metal loss specified in the standard ASTM-G67 at which the alloy is considered to be susceptible to IGC, i.e. 25 mg/cm$^2$, indicates resistance to IGC. This resistance of the alloy and the weld to exfoliation and the IGC was confirmed by SEM examination of the cross section of the tested specimens, which showed no attack at the weld regions and the parent alloy and by the phosphoric acid testing, which showed the weld regions and the parent alloy are resistance to IGC, indicating no difference between the chemistry of the grain boundaries and the grain interiors, which is confirmed by the TEM investigations which revealed that grain boundaries of the parent alloy, the TMAZ, the stir zone and the HAZ are free of beta phase as evident in the Figures 4.40, 4.41 and 4.43. The high resistance of the welded alloy to the exfoliation and IGC may be attributed to the low content of magnesium, low applied amount of deformation during the alloy manufacture process and the proper control of the welding parameters, which reduced the presence of active precipitates at the grain boundaries. Hence, it can be concluded that FSW did not create any adverse effect on the resistance of the alloy to IGC.

Work done by other researchers showed the resistance of the AA5754 alloy to exfoliation corrosion and IGC. For example, Birol et al [65] reported low weigh loss of 0.411 mg/cm$^2$ after the immersion of the AA5754 alloy in nitric acid for 24 h at 30°C for 24 h, indicating superior resistance to IGC. A study by Alcan showed resistance to IGC even after ageing at 75, 100 and 150°C for 10 years [64].

Wadeson [148] utilising ASTM-G67 showed that the FSW AA5754 resist the exfoliation corrosion. The results are identical to those of the present study, showed no evidence of exfoliation corrosion within the parent alloy and weld regions.

Besides, its resistance to exfoliation and IGC, the AA5754 aluminium alloy, the AA5754 is also characterized for the resistance to pitting. Its corrosion resistance feature gives its acceptance of use in marine and automotive industry [224-225].

However, localized attack took place at the JLR. This is evident in the SEM examination after NAMLT, phosphoric acid response test and the exfoliation corrosion testing. The EDX analysis revealed that the JLR is rich in magnesium and oxygen. Due to the fact the magnesium corrodes faster than the aluminium due to the difference in their corrosion potential, therefore the reason of the severe attack at the JLR could be
attributed to the micro galvanic corrosion between the rich in magnesium and oxygen band and the adjacent bulk material.

The agar gel test is used to indicate the presence of areas sensitive to localized corrosion. With the help of the agar gel test, the net anodic or cathodic regions on the weldment can be identified. Once the specimen surface is covered with a layer of 1-2 mm viscous agar gel, the active region starts to corrode, producing $\text{Al}^{3+}$ according to the following reaction \[159\].

\[
\text{Al (solid)} \rightarrow \text{Al}^{3+} + 3 \text{e}^{-}
\]  
\[4.1\]

The produced $\text{Al}^{3+}$ enters the moisture-laden gel and reacts with water producing hydrogen ions. Due to the hydrolysis process, the acidity increases, consequently, the gel pH indicator furnishes this region with a colour that differs from the remained regions.

\[
\text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}^{2+} + \text{H}^+ \]  
\[4.2\]

The electrons that produced from the corrosion process {reaction 4.1} are consumed by the oxygen reduction reaction at the other area of the weldment surface, producing hydroxyls and area with basic nature.

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]  
\[4.3\]

Utilizing the agar gel visualization test, Jariyaboon et al [226] managed to verify the sensitive region to corrosion within FSW AA2024-T351 aluminium alloy. The obtained result was consistent with the results of the immersion testing, which showed IGC attack took place at the active areas detected by the agar gel test. Similarly Younes [227] with the help of the agar gel test showed that the HAZ of FSW AA2024-T351 aluminium alloy behaved anodically with respect to other regions of the weldment. This was confirmed with the immersion testing which revealed that the HAZ was prone to exfoliation and IGC.

From the above, it can be concluded that the agar gel test is a simple and useful method for determining the susceptible region to corrosion within the weldment. In this study, the agar gel test did not reveal any difference or change in the colour between TMAZ, HAZ, and the parent alloy regions of as welded, ground and the polished specimens (
Figure 4.29), suggesting that the structure is homogenous within the weldment, and no indication of galvanic corrosion between the parent alloy and the weld regions is evident.

The OCP or the free corrosion potential represents the corrosion potential of the specimen that immersed in an electrolyte without subjecting it to external current as a function of time. The specimen that has a more positive corrosion potential is considered more resistance to electrochemical dissolution than the one of a more negative corrosion potential.

From the OCP measurements shown in Figure 4.44, it is evident that the weld regions and the parent alloy reached a stable corrosion potential after a relatively short time of immersion with a difference of 25 mv between the more positive (the parent alloy) and the more negative region i.e. TMAZ-RS, indicating that the parent alloy and the weld region have almost similar corrosion behaviour.

The anodic polarization measurement provided information about the corrosion potential, range of passivity, breakdown of the passivity and the passive current density ($i_{pass}$). As shown in Table 4.2 and Figure 4.45, the HAZ, the TMAZ-AS and the TMAZ-RS exhibited almost similar current densities ($i_{pass}$) that were slightly higher than the parent alloy. Therefore, the electrochemical behaviour of the weld regions and the parent alloy is considered the same because the corrosion potential, breakdown potential and the passive range are almost the same within the weldment. The obtained breakdown potential from this study is similar to that reported by Trueba et al [228].

From the above, it can be concluded that there is no difference in the electrochemical behaviour across the weldment. Indicating, the selected FSW process generated a weld of corrosion behaviour as good as the alloy.

The electrochemical measurements of this study are consistent with that recorded by Wadeson [148] who observed similar electrochemical behaviour for the FSW and the parent alloy of AA5754-O aluminium alloy in de-aerated 3.5% NaCl medium at ambient temperature.

In summary, the electrochemical measurements are consistent with the agar gel testing which failed to detect any difference in the corrosion behaviour between the parent
alloy and the weld regions. This was supported by the exfoliation corrosion testing results, which showed very low population density of pits within the weldment at the top surface, indicating that the alloy has a good resistance to pitting.

4.5.3 Mechanical property

Al-Mg alloys are non heat treatable alloys, which mean that their mechanical properties do not rely on the precipitate hardening effect. It should be mentioned that most particles in Al-Mg alloys, either the constituent or the dispersoid ones are originated from the impurity elements (Fe, Mn, Si), and are predominantly insoluble during the welding cycle [229].

Instead, Al-Mg alloys strength is gained from solid solution strengthening, grain size and/or strain hardening effects [11, 137]. The strain hardening increases the dislocations density within the microstructure improving the tensile and yield strengths. However, when the cold worked alloy is subjected to thermal cycling such as that experienced during welding, the heat increases the dislocations mobility, allowing them to annihilate by interacting with other dislocations of opposite sign and thus removing their effects on the material. This leads to softening the material [207].

As shown in Figures 4.9, 4.15a and 4.21a, the FSW replaced the original alloy microstructure with coarser grains at the HAZ and finer, recrystallized ones within the stir zone. In this study, the FSW softens slightly the material at the HAZ and increases its hardness at the TMAZ (Figure 4.49).

According to Hall-Petch formula presented below [230] there is a strong relationship between the grain size and the strength. The strength increases with decreasing the grain size and increases with increasing the grain size. Therefore, the observed increase in the hardness within TMAZ can be explained by the grain refinement associated with the dynamic recrystallization during FSW and the reduction in the HAZ hardness can be related to the grain coarsening resulted from the effect of the transferred heat during joining.

\[ \sigma_y = \sigma_0 + kd^{-1/2} \]
Where, $\sigma_y$ is the yield stress, $\sigma_0$ is the frictional stress, which reflects the strengthening due to Mg (and/or other solute species) in solid solution, $k$ is constants and $d$ is the grain diameter [17].

Work by Sato et al [120] showed that the strength of non heat treatable aluminium alloys is largely influences by the variation in the microstructure, in particularly, the grain size. Their optical and TEM investigations showed a big variation between the size of the parent alloy and the nugget grains, where, the average grains size was 40 $\mu$m within the parent alloy and 0.6 $\mu$m within the nugget. A low dislocation density was observed within both zones, indicating that the variation in the hardness is correlated to the change in the grain size rather than the annealing effect.

Similarly, Leitao et al [231] reported an increase in the TMAZ hardness of FSW AA5182-H111. The authors attributed the improvement in the hardness to the effect of the grain refinement within this region. Further, Attallah et al [232] showed an increase in the hardness of the TMAZ. This was related to the refinement of the grain with the TMAZ and increasing the density of the submicron Al$_6$ (Fe, Mn) intermetallics particles. The presence of fine Al$_6$ (Fe, Mn) reported to obstacle the dislocation movement.
Chapter 4: Friction Stir Welded AA5754-H111 Alloy

Figure 4.1 Appearance of the weld top surface: a) as-welded and b) electropolished specimen.

Figure 4.2 Optical image showing a material flow arm at the AS of TMAZ.

Figure 4.3 Appearance of as-welded specimen at the bottom surface.
Figure 4.4 Optical image of the weld cross section after electropolishing in 200 ml HPO$_4$ and 800 ml ethanol, showing: a) nugget, b) TMAZ, and c) the parent alloy.

Figure 4.5 Optical images of the cross section of the weld showing the presence of circular flow patterns within the stir zone.

Figure 4.6 A montage at low magnification image of the cross section of the weldment after etching in a 10 g/l NaOH at 60°C for 1 minute, showing the presence of the JLR within TMAZ.
Figure 4.7 BSE image and EBSD map taken from the top surface of the TMAZ, showing the presence of ultra fine grains within the JLR.
Figure 4.8 (a) BSE image shows the JLR at the top surface of the weld, and (b)-(e) elemental maps showing Mg, O and Al distribution at the JLR.
Figure 4.9 BSE image of the parent alloy at the rolling plane after electropolishing.

Figure 4.10 Optical image of AA5754-H111 parent alloy at the rolling plane after etching in diluted Keller region.
Figure 4.11 EBSD map shows the grains structure within the parent alloy at the top surface.

Figure 4.12 BSE image of mechanically polished specimen shows the intermetallic particles distribution within AA5754-H111 parent alloy.
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Figure 4.13 BSE image of the parent alloy at the transverse plane.

Figure 4.14 BSE image of the parent alloy at the longitudinal plane.
Figure 4.15 SEM images of the HAZ: a) rolling plane, and b) the transverse section.
Figure 4.16 EBSD image of TMAZ AS edge: a) the top surface, b) the transverse section.
Figure 4.17 BSE images: a) TMAZ advancing side and b) TMAZ retreating side.
Figures 4.18 SEM image of cross section: a) the advancing side and b) the retreating side of the weld at the transverse section, showing the transition from highly refined zone to the deformed grains.
Figure 4.19 EBSD images show variation in the grain size within the TMAZ.

Figure 4.20 BSE images show variation in the grain size within the TMAZ.
Figure 4.21 SEM image of the stir zone: a) the rolling plane, and b) the transverse section.
Figure 4.22 SEM image of the top surface of: a) the parent alloy, b) the TMAZ.
Figure 4.23: a) SEM micrograph taken from the top surface of the AA5754 parent alloy, and b) the EDX line scan of the corresponding regions.
Figure 4.24: a) SEM micrograph taken from the top surface of the AA5754 parent alloy, and b) the EDX line scan spectrum acquired along the line indicated in (a).
Figure 4.25 BSE image revealing the microstructure of as received AA5754-H111 aluminium alloy and corresponding X-ray maps of Al, Mg, Si, Fe and Mn, showing the distribution of elements in the matrix (α-Al), Al(Fe,Mn) and Al(Mg,Si).
Figure 4.26 BSE images of the AA5754 aluminium alloy and associated EDX analysis taken at the indicated locations.
Figure 4.27 (a) TEM micrograph taken from the AA5754 parent alloy, (b)-(d) associated EDX spectra of the locations indicated in (a)
Figure 4.28 (a) TEM image of AA5754 aluminium alloy, (b) the EDX analysis showing Mg/Si rich particle.
Figure 4.29 Surface potential maps showing the effect of FSW process on the intermetallic particles.
Figure 4.30 SEM images showing distribution of intermetallic particles within: a) parent alloy, and b) the TMAZ at the top surface of the weldment.

Figure 4.31 SEM images showing distribution of intermetallic particles within: a) parent alloy, and b) the stir zone at the transverse section.
Figure 4.32 Optical images of the top surface of FSW AA5754-H111 aluminium alloy after agar-gel testing for 2 h.
Figure 4.33 Surface appearances of: a) top surface and b) the bottom of the weldment after exfoliation testing for 6 h.

Figure 4.34 Surface appearances of: a) top surface and b) the bottom of the weldment after exfoliation testing for 24 h.
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Figure 4.35 Localised corrosion at the JLR during exfoliation testing

Figure 4.36 Corrosion at the weld root during exfoliation testing

Figure 4.37 Micrograph of the weld following ASTM-G66 immersion testing of a) parent alloy top surface and b) cross section of the pit shown in (a).
Figure 4.38  BSE micrographs of the cross section of: a) parent alloy and b) the weld after exfoliation testing for 6 h, showing that the weld and the parent alloy were resistant to exfoliation corrosion.
Figure 4.39  BSE micrographs of the cross section of: a) parent alloy and b) the weld after exfoliation testing for 24 h, showing that both regions were resistant to exfoliation corrosion.
Figure 4.40 BSE micrographs of the cross section of: a) parent alloy and b) the weld after NAMLT testing for 24 h, showing that both regions were resistant to IGC.
Figure 4.41 Surface appearances of the weldment after NAMLT at a) top surface, b) transverse section, and c) the bottom surface.
Figure 4.42 Appearance of a) stir zone, b) parent alloy, and c) the HAZ at the transverse section following immersion in 10 wt.% H₃PO₄ at 60°C for 90 second.
Figure 4.43 TEM micrographs of thin foil obtained by electropolishing for a) parent alloy; and b) the HAZ.
Figure 4.44 TEM micrographs of thin foil obtained by electropolishing for a) TMAZ-AS; and b) the stir zone.
Figure 4.45 SEM micrograph of the stir zone taken from the top surface of the weld of specimen prepared by the ultra microtome process showing (free of precipitates) grains boundaries.

Figure 4.46 TEM micrograph of thin foil obtained by ultramicrotomy for the stir zone at the transverse section, showing grains boundaries free of precipitates.
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Figure 4.47 OCP as function of time of the weld regions and the parent alloy in de-aerated 3.5 wt. % NaCl solution.

Figure 4.48 Anodic polarization curves for FSW AA5754 H111 alloy in 3.5 % NaCl in de-aerated 3.5 wt. % NaCl solution at room temperature in as received and after FSW process.
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Figure 4.49 Hardness profile across the weld at the top surface.

<table>
<thead>
<tr>
<th>Area</th>
<th>Weight before</th>
<th>Weight after</th>
<th>Difference in weight</th>
<th>Weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.43 cm²</td>
<td>10.0663 g</td>
<td>10.0300 g</td>
<td>36.3 mg</td>
<td>2.70 mg/cm²</td>
</tr>
</tbody>
</table>

Table 4.1 Weight loss for the FSW AA5754 alloy

<table>
<thead>
<tr>
<th>Area</th>
<th>( E_{\text{corr}} ) (V SCE)</th>
<th>( I_{\text{pass}} ) (A/cm²)</th>
<th>( E_{\text{pit}} ) (V SCE)</th>
<th>( E_{\text{pit}} - E_{\text{corr}} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent alloy</td>
<td>-0.99</td>
<td>9x10⁻⁷</td>
<td>-0.72</td>
<td>0.27</td>
</tr>
<tr>
<td>HAZ</td>
<td>-0.995</td>
<td>6x10⁻⁷</td>
<td>-0.74</td>
<td>0.255</td>
</tr>
<tr>
<td>TMAZ-AS</td>
<td>-1.00</td>
<td>8x10⁻⁷</td>
<td>-0.72</td>
<td>0.28</td>
</tr>
<tr>
<td>TMAZ-RS</td>
<td>-1.02</td>
<td>6x10⁻⁷</td>
<td>-0.74</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 4.2 Differences between \( E_{\text{pit}} \) and \( E_{\text{corr}} \) determined from anodic polarization curves.
Chapter 5

Friction Stir Welded AA5083 Alloy

As a result of the friction between the rotated hard and profiled tool with the material, the material at the contact and near the tool is deformed and heated. Hence, the alloy grain shape and size are no longer maintained and is replaced after FSW with recrystallized grains within the stir zone and a deformed structure at the TMAZ edges. The difference in the deformation, the temperature and the cooling rates between the centre and the edges of the weld is believed to be the reasons for the modification of the alloy microstructure [188-191]. The thermal cycling can modify the microstructure, hence, altering the mechanical properties and corrosion behaviour of the regions subjected to heating.

The aim of this chapter is to study the effect of FSW on the size, as well as the shape of the grains and the intermetallic particles of the AA5083-O aluminium alloy, and, consequently, the influence of the change in the microstructure on the alloy’s corrosion behaviour and mechanical property.

Electropolishing at 15 V in a solution of 80% ethanol and 20% perchloric acid at 5°C for 1 minute, as well as etching at ambient temperature with diluted Keller reagent, were used to reveal the weld regions and the parent alloy microstructures. Specimens mechanically polished to a 1 μm diamond finish were utilized for assessing the influence of FSW process on the intermetallic particles.

Optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning Kelvin probe microscopy (SKPM) were employed for characterizing the weldment microstructure.
5.1 General observation

As previously found for the FSW AA5745-H111 aluminium alloy, FSW of AA5083-O alloy generated well defined TMAZ and nugget, typical of most friction stir welded aluminium alloys. At the top surface, the thermomechanical heat affected zone (TMAZ) is evident at the specimen centre (with a width of approximately 23 mm, equivalent to the used shoulder diameter), containing a semicircular patterns, as shown in Figure 5.1. At the edges of the weld, there are the commonly named TMAZ advancing and retreating sides denoted by ‘AS’ and ‘RS’ respectively. The AS is distinguishable with the presence of a material arm, as shown in Figure 5.1. The weld appears to be a relatively smooth, with a slight reduction in the thickness at the area of the contact with the shoulder relative to the original thickness of the joined plates. As with FSW AA5754-H111, the interface between the TMAZ, HAZ and the parent alloy was not clear under this imaging condition. At the top surface, the rolling marks are perpendicular to the welding direction.

At the traverse section (cross section), a typical FSW structure divided into three zones (as previously described in chapter 4) is evident, as shown in Figure 5.2. The width of the weld is reduced from 23 mm at the top surface to approximately 7 mm at the bottom surface of the TMAZ, indicating full penetration of the tool. The HAZ was not discernible.

The stir zone displays characteristic concentric rings in its interior, as shown in Figure 5.2. The dark region on either side of the stir zone shown in Figure 5.3 corresponds to the TMAZ. Generally, the utilized welding parameters generated a weld free of voids and cracks with the presence of a joint line remnant, as shown in Figure 5.3. The JLR formed in a similar shape to that recorded in the FSW AA5754-H111 aluminium alloy. This line contains ultra fine grains, as shown in Figure 5.4.

5.2 Microstructure feature of FSW AA5083-O alloy

5.2.1 Parent alloy

The parent alloy is the part of the weldment that is located sufficiently far from the tool contact region. It does not experience deformation and heating during the welding process. It represents the original microstructure. In this study, the SEM examination
revealed that the AA5083-O alloy contained different microstructural features. The grains are irregularly shaped at the rolling direction and thin, elongated at the transverse section, as shown in Figures 5.5 and 5.6. The average size of the grains of the rolling plane is about 10-50 μm. At the transverse section, the grains are longer, about 150 μm length and approximately 10-20 μm width, as shown in Figure 5.6. SEM examinations showed that the grains exhibited different contrast, indicating various crystallographic orientations of the grains.

Undissolved coarse intermetallics particles, randomly distributed within the grains interiors along the rolling direction, at the rolling plane and the transverse section, are evident (Figures 5.5 and 5.6). The type and size of these particles is discussed in section 5.2.5.

### 5.2.2 Heat affected zone (HAZ)

By definition, the HAZ experiences heating without mechanical deformation during welding. Therefore, the corrosion behaviour and the mechanical property of the HAZ of aluminium alloys and other alloys are determined by the heat input, the cooling rates, the chemical composition of the alloy and the original alloy temper condition. The heat transferred from the TMAZ can be sufficient to alter the corrosion behaviour and the mechanical property of this region, through changing the chemistry of the grain boundaries, annealing the work hardened microstructure and recrystallizing or coarsening the grains.

In the case of Al-Mg alloys, the alloy temper condition in addition to the heat input are the effective factors in controlling the corrosion behaviour and the mechanical property of the HAZ. The heat transferred from the TMAZ anneals the microstructure of the severely cold worked alloy, and, consequently, reduces the dislocation density within the alloy; the result is softening of the HAZ. On the contrary, the HAZ of fully annealed Al-Mg alloys (O-temper) usually exhibits no apparent difference compared with the parent alloy owing to the starting temper condition.

In the present study, the SEM examinations, as shown in Figures 5.7-5.8, showed that the HAZ exhibited no apparent difference in terms of the shape and size of the grains relative to the parent alloy, with an average grain size of approximately 50 μm and 150
μm at the rolling plane and the transverse section respectively. SEM micrographs and EBSD map illustrate differences in the contrast between the grains, indicating the presence of a variation in the crystallographic orientation. Within the grains interiors, randomly distributed white spots, aligned along the rolling direction, represent the intermetallic particles. The compositional analysis of the insoluble intermetallic particles is presented in section 5.2.5.

5.2.3 Thermomechanical heat affected zone (TMAZ)

The TMAZ surrounds the nugget at either side. The microstructure of this region differs from the parent alloy and the HAZ in terms of the grains size and shape.

At the top surface, the TMAZ exhibited recrystallized grains, as shown in Figure 5.9, similar to that observed by Peel et al [171]. The edges of TMAZ presented a highly distorted structure. The grains exhibited elongation in a direction parallel to the welding direction and perpendicular onto the rolling direction without the presence of recrystallization, as shown in Figures 5.10 and 5.11. The intermetallics particles in TMAZ (white spots) appeared smaller in size compared with that of the parent alloy and the HAZ.

The transition between the TMAZ and the nugget (stir zone) is more evident at the advancing side than the retreating side, as shown in Figure 5.12. At the top surface, the grains are deflected downward towards the edges of the weld, as shown in Figure 5.9.

Examining the variation of the microstructure inwardly through the weld at the transverse section, the difference in the grain size within the weld area is evident, as shown in Figure 5.13. The size of the grains at the weld crown is bigger than that of the weld bottom.

5.2.4 The stir zone

The nugget or the stir zone experienced the highest level of deformation and thermal cycle during welding, resulting in a formation of fine equiaxed recrystallized grains at the expense of the original parent alloy elongated grains owing to the recrystallization process. The SEM micrographs of the nugget, taken from the top surface and the cross section of the weld respectively, as shown in Figures 5.14 and 5.15, demonstrate the
presence of a small equiaxed grains. The nugget contains fine homogenously distributed white particles spread along the grain interiors representing the intermetallics particles.

5.2.5 Effect of FSW on intermetallic particles

For achieving a weld free of defects and contaminations, the probe and the shoulder are always made from a harder and more wear resistant material than the welded Al-Mg alloys known to contain coarse and fine intermetallics particles. When, the tool rotates the interaction between the tool and the material, leads to break up and/or dissolution of the intermetallic particles.

In this study, the SEM and TEM analysis showed that the AA5083 alloy contains coarse white and black particles known as constituent particles and fine particles known as dispersoids. The EDX analysis revealed that the white particles indexed as Al (Fe, Mn) and Al (Fe, Mn, Si, Cr) and the black particles as Mg and Si rich phase (Figures 5.16 - 5.17).

After FSW, the non-uniformly distributed coarse intermetallics particles of the parent alloy, as shown in Figure 5.18a, are crushed by the rotated tool during its travelling into uniformly distributed small particles, as shown in Figure 5.18b. The SEM images show comparison between the size and distribution of the intermetallic particles within the weld regions and the parent alloy at the top surface and the cross section of the weldment, as shown in Figures 5.19 and 5.20 respectively. The scanning Kelvin probe microscope results shown in Figure 5.21 were in agreement with the SEM analysis. The presence of lesser in size and higher in density intermetallics particles within the TMAZ compared with the parent alloy and the HAZ is obvious.

5.3 Corrosion behaviour of FSW AA5083-O alloy

The Al-Mg alloys including AA5083 are characterized by their resistance to corrosion. This feature drastically decreases when these alloys are subjected to excessive deformation and/or heating in range of 50-200°C for sufficient time.

Generally, the welding of materials, including Al-Mg alloys, requires sufficient amount of heating to reach bonding. The heat in FSW generates from the friction between the tool and the material. Therefore, during processing, the material is subjected to both
deformation and heating at the area of the contact with the tool. This can lead to alteration in the alloy corrosion behaviour. The aim of the employed corrosion testing in this study is to evaluate the influence of FSW on the corrosion behaviour of the weldment.

Agar gel testing, immersion testing according to standards ASTM-G66 and ASTM-G67 for determining the susceptibility of the weld regions and the parent alloy to exfoliation and IGC respectively, and electrochemical measurements were utilized to assess the corrosion behaviour of the weld regions relative to the parent alloy.

5.3.1 Agar gel test
The appearance of as-welded specimen after agar gel testing is shown in Figure 5.22. Looking at the top surface, there is no obvious change in the colour between TMAZ, HAZ and the parent alloy regions, suggesting no significant change in the corrosion behaviour of the alloy after FSW.

5.3.2 Exfoliation corrosion susceptibility
The surface appearance of the specimens following the exfoliation immersion testing for 24 h is shown in Figure 5.23. Similar to FSW AA5754-H111 alloy, a localised corrosion attack took place mainly at the JLR, as shown in Figure 5.24. Generally, the weld regions and the parent alloy are almost free from exfoliation corrosion, indicating similarity in the corrosion behaviour of the parent alloy and the weld regions.

SEM images of the tested specimen cross section taken from the parent alloy and TMAZ, as shown in Figures 5.25 and 5.26, showed no sign of exfoliation corrosion either at the parent alloy or the weld. Thus, after FSW, the alloy retained its resistance to exfoliation corrosion, indicating that the FSW process did not influence the corrosion behaviour of the alloy.

5.3.3 Intergranular corrosion (IGC) susceptibility
The presence of the electrochemically active phase (β-phase) at the grain boundaries of the aluminium-magnesium alloys is believed to be the factor for initiation of IGC within these alloys. It has been reported that the precipitation of the β-phase at the grain
boundaries increases with increasing the magnesium content and the material deformation. The alloy of study (AA5083-O) has a higher magnesium content than the previously studied AA5754-H111. Therefore, it is considered that the alloy may show susceptibility to IGC due to the increased chance of the precipitation of rich in magnesium phase. However, since the AA5083 alloy is supplied in the fully annealed temper, it is also expected that the alloy will show resistance to IGC. This is because this treatment is reported to reduce the precipitation of magnesium rich phase at the grain boundaries and the grains interior, hence, most of the grain boundaries are free of the β-phase, consequently the resistance of the alloy to IGC is likely to be high.

According to standard ASTM-G66, the weight loss per unit area is the measuring unit by which the IGC susceptibility of the alloy is determined. If the metal loss is at or above 15 mg/cm², then the alloy is considered prone to IGC when. In this study, the obtained metal loss after immersing the weldment in nitric acid for 24 h is about 4.88 mg/cm², as shown in Table 5.1, indicating good resistance to IGC. The SEM results obtained from the cross section surface of the tested specimen also showed that the weld regions and the parent alloy are free of IGC attack (Figure 5.27).

The SEM images after phosphoric acid etching at 60°C for 90 s, showed no preferential attack at the grain boundaries of the parent alloy and the weld, as shown in Figure 5.28 and 5.29. Additionally, the resistance of the weld and the parent alloy is further confirmed by the TEM analysis. The TEM investigations showed that the grain boundaries of both regions are free of β-phase, as shown in Figures 5.30-5.33.

5.3.4 Electrochemical measurements

5.3.4.1 Open circuit potential

Open circuit and the anodic polarization measurements are used in this study for comparing the anodic reactivity of the weld regions relative to the parent alloy. The anodic polarization measurements provided information about the breakdown potential \( E_{\text{pit}} \), the passive range and the passive current density \( I_{\text{pass}} \) for each region. Hence, they provided information about the corrosion behaviour of each region. The open circuit potential (OCP) versus time of the FSW AA5083-O aluminium alloy in as-welded condition in deaerated 3.5 % NaCl is shown in Figure 5.34.
As it can be seen from the measurements, on the initial immersion, the OCP of the parent alloy and the TMAZ-RS showed a tendency to move through more negative potential, the potential of the TMAZ-RS moves from a approximately -1.17 vs. SCE to -1.27 vs. SCE, after approximately 500 s the potential start to increase until it reaches a stable potential of -1.02 vs. SCE after 3500 s. The potential of the parent alloy shifted from -1.03 to -1.09 vs. SCE and then increased until reached the stability at a potential of approximately -0.95 vs. SCE after 2000 s of immersion.

The potential of the AS region reached the stability after approximately 3500 s at a corrosion potential of approximately -1.01 vs. SCE. The potential of the HAZ reached stability after approximately 2000 s of immersion at a corrosion potential of approximately -0.9 vs. SCE. After stability, the difference between the region of the most negative potential (RS) and the region of the most positive potential i.e. HAZ is of magnitude about 40 mV.

### 5.3.5.2 Anodic polarization

Anodic polarization was performed, starting at 20 mV below the OCP, in 3.5 wt. % NaCl deaerated solution, at a sweep rate of 0.1667 mV/s. The measurements were taken from the parent alloy, HAZ, TMAZ advancing side and the stir zone. Figure 5.35 shows the potentiodynamic anodic polarization curves of the parent alloy and the weld regions in as-welded condition. The weld regions and the parent alloy curves present a passivation phenomenon with a breakdown of passivity at potential of approximately -680 mV, -690 mV, -710 mV and -685 mV vs. SCE for the TMAZ-AS, TMAZ-RS, the parent alloy and the HAZ respectively. Following the transition from the cathodic branch of the polarization curve, the anodic branch exhibited an increase in the current density with an increase in the corrosion potential until reaching the passive current density, and then it remained almost constant in all regions and finally increased above the pitting potential \(E_{\text{pit}}\). The pitting potential indicates the film breakdown and pitting corrosion. Generally, the HAZ, TMAZ-AS and TMAZ-RS present an approximately similar passive current density which is slightly higher than the parent alloys. The passive current density of the RS is approximately \(1 \times 10^{-7}\) A/cm\(^2\), the AS is approximately \(2 \times 10^{-7}\) A/cm\(^2\), the parent alloy is approximately \(5 \times 10^{-7}\) A/cm\(^2\) and the HAZ is approximately \(6 \times 10^{-7}\) A/cm\(^2\).
The electrochemical parameters, such as the corrosion potential ($E_{corr}$), the corrosion current density ($I_{corr}$), were determined by extrapolation of cathodic Tafel lines to the corrosion potential ($E_{corr}$). The passivation current density ($I_{pass}$) and the pitting potential ($E_{pit}$) are reported in Table 5.2.

5.4 Effect of FSW on mechanical property of AA5083-O alloy

The hardness measurements were performed with 200 μm spacing along the top surface and the cross section in the mid section position of polished specimen containing the weld at its centre. The profiles of the hardness are shown in Figures 5.36 and 5.37. No softening in the HAZ and the TMAZ at both surfaces is observed. The hardness of the TMAZ is almost similar to that of the HAZ and the base material.

The parent alloy has a Vickers hardness of approximately 90 HV, similar readings were recorded within the HAZ and TMAZ. Compared with the FSW AA5754-H111, the hardness profile is not significantly influenced by the grain size variation in the TMAZ. However, the hardness of AA5083-O parent alloy and the weld regions is significantly higher compared with AA5754-H111 alloy owing to the increased magnesium content within AA5083 compared with the AA5754 alloy.

5.5 Discussion

5.5.1 Microstructure of FSW AA5083-O alloy

Similar to the previously investigated alloy AA5754-H111, the zones generated by FSW composed a typical FSW structure. It is in agreement with that observed by Reis et al [178]. Three regions were revealed, namely, the nugget (stir zone), the TMAZ and the HAZ though it is not remarkable.

At the cross section of the weld, the TMAZ appeared wider at the top than the bottom surface of the weld. This is due to the difference between the diameter of the shoulder and the probe. Normally, the shoulder is designed in a bigger size than the probe for maintaining the plasticized material and increasing the heat input for insuring proper material softening. Within the stir zone circular lines in the form of onion rings were
generated. These represent the plastic deformation developed as a result of the movement of the rotated profiled probe along the joining line [233].

It is evident that the heat input, the mechanical deformation and the post weld cooling rates are the factors responsible for generating a distinct microstructure within the weldment. It is well documented that the temperature generated from the friction between the tool and the material is below the material melting point [187]. The highest level of deformation and the peak temperature have been recorded within the stir zone (probe contact region). Rhodes et al [179] measured the temperature during FSW of AA7075-T6 at the area adjacent to the rotating probe and found that the maximum peak of temperature was in range of 400-480°C, which is considered below the melting point of this alloy because there was no evidence of melting in the weld region. Grujicic et al and Steuwer et al [234-235] reported that the peak temperature during FSW increases with increasing the rotation speed of the tool and the tool contact pressure. This temperature decreases with moving towards the parent alloy. For instance, the maximum recorded temperature during FSW of AA6063 alloy as reported by Sato et al [236] is about 402°C at the centre of the weld. At 10, 12.5 and 15 mm from the centre of the weld, the measured temperature at the centre of the weld (stir zone) reduced to 353°C, 302°C and less than 201°C respectively [200].

The duration of the temperature incubation and the cooling rate at a specific position during welding as reported by Chao et al [236] are the main factors that affect the formation of the material microstructure and the mechanical properties of the generated regions. Chao et al also compared the temperature remaining time between the centre of the weld and the area adjacent and found that the duration time for the materials stayed at temperatures above or near 250°C in the weld centre of the AA 2195-T8 alloy is about 1.6 times to 2.14 times longer than those located 5 mm to 12.7 mm away from the weld centre. Therefore, the difference in the temperature resulted in different microstructural characteristics.

In the stir zone, the combination of deformation and heating develops recrystallized fine grains due to the recrystallization process [187, 236-239]. A recrystallized structure in the centre of friction stir welded AA5083 aluminium alloy has also been reported by
other researchers. Chen et al [240] found a similar fine equiaxed grains within the stir zone of the AA5083-H18 alloy, El-Danaf et al [241], reported the same result for the same alloy. Sato et al [242] studied the FSW AA5083-O and observed recrystallized grains within the stir zone in the range of 4.5 μm similar to the observation of this study.

At the edges of the thermo mechanical affected zone, the grains are elongated and bent vertically on the welding direction at the cross section. This is due to the tool rotation effect. This phenomenon has been reported by many authors in several materials and alloys. All did not observe recrystallized grains at the edges and related this phenomenon to the non presence of sufficient magnitude of strain deformation to generate recrystallized microstructure.

In this study, a variation in the microstructure is also observed between the top and the bottom of the weld, indicating the presence of a temperature variation between these regions. The SEM result is similar to that reported for the alloy AA5754-H111 and that reported by Xu et al [200] on study of the microstructure of the FSW AA2219-T6. The contact area between the shoulder and workpiece is much larger than between the pin and workpiece, hence, the heat generated from the shoulder contact is larger than that generated by the probe which explains the difference in the grains size between the top and bottom surface of the weld [233].

According to Mishra et al [126], some of the heat transfers by conduction into the backing plate, as a result of the contact with the workpieces, hence, at the bottom region, the thermal cycle is expected to be shorter and the peak temperature of the weld is lower compared to the shoulder contact region. Therefore, the difference in the heat input between the top and the bottom surface of the weld results in a generation of microstructure of unlike feature.

In the HAZ, the microstructure shows no apparent difference from the base material, indicating clearly that the thermal cycle during joining does not create any significant influence on the microstructure of this alloy. As shown in the results, both the HAZ and the parent alloy exhibit long and thin grains (pancake shaped grains) at the transverse section. This alloy is characterized by its excellent formability, hence, both regions exhibited typical rolled microstructure [141].
In addition to the influence of FSW on the grain shape and size, FSW has shown a great impact on the distribution of intermetallics particles. As showed in the previous section, increase in the population density and decrease in size of the intermetallics particles were revealed, which is in agreement with that presented in Chapter 4, section 4.2.5. Both the iron containing particles (white spots) and the magnesium-silicon rich particles (black spots) are fragmented into smaller sizes, indicating that the temperature during joining was not sufficient to dissolve these intermetallic particles and the crushing caused by the contact between the particles and the rotated tool.

As discussed above, due to the difference in the mechanical deformation level and the heating rate between the centre and the edges of the weld, the FSW generated distinct regions with a dissimilar microstructure feature, hence, it is expected that each region may exhibit different corrosion behaviour from others. For this reason, the weldment is tested in accordance to the specified standards for evaluating the corrosion behaviour of weld regions and compared with the parent alloy.

5.5.2 Corrosion behaviour of FSW AA5083-O alloy

Generally, Al-Mg (AA5xxx) alloys including AA5083-O are resistant to exfoliation and IGC [141]. This characteristic diminishes with the increase of magnesium content and the rate of work hardening. Additionally, Al-Mg alloys can suffer from exfoliation and IGC when the thermomechanical processing is improperly applied or when subjected to heating for sufficient time at moderate temperatures either in service or during joining due to precipitating of anodic Al$_2$Mg$_3$ phase, known as β-phase [41, 243].

This is the case of the alloy of the present study. The alloy contains a higher magnesium content than the AA5754-H111 alloy. Since the AA5083 alloy is subjected to heating during joining, its corrosion behaviour may alter. However, in the present study, the results of the agar gel testing showed that parent alloy, TMAZ, HAZ and the stir zone exhibited similar colour, indicating no difference in the corrosion behaviour between the weld regions and the parent alloy. This is due to the proper control of the thermomechanical processing during the alloy manufacturing steps, which did not give chance for the magnesium to precipitate at the grain boundaries, and the short time of heating during joining with the FSW process. This is confirmed by the TEM
examinations, which showed that the grain boundaries of the parent alloy and the weld regions are free of beta phase precipitates and the SEM examinations of the tested specimens by the nitric acid metal loss testing (NAMLT), which revealed no attack at the grain boundaries of the weld regions and the parent alloy. After NAMLT, the weldment exhibited a low amount of metal loss (4.88 mg/cm$^2$) compared with that specified by the standard ASTM-G67 i.e. 25 mg/cm$^2$, at or above the specified value the alloy is considered susceptible to IGC. The results are further supported by the phosphoric acid etching test, which gave evidence for the resistance of the alloy to IGC and exfoliation. No attack at the grain boundaries is observed, indicating the absence of the electrochemically active phase ($\beta$-phase), which is reported to be the responsible for IGC and exfoliation corrosion initiation. The obtained results from this study are in agreement with the previous observations reported by Chang et al [243] who recorded a low metal loss i.e. 5.6 ± 0.4 mg/cm$^2$ after immersion of the AA5083 alloy in nitric acid for 24 h. Hence, it can be said that the FSW joint and the parent alloy are resistant to exfoliation and IGC.

**Electrochemical behaviour**

According to the previous works, the deaeration was observed to decrease the open circuit potential of the AA5083 alloy [53], which is in agreement with this study, where a decrease in the OCP of AA5083 is reported compared with the alloy OCP in aerated 3.5 wt. % NaCl. Jafarzeh et al [244] related this phenomenon to the lowering of the cathodic sites activity on the aluminium surface in deaerated solutions. However, in the present study, the OCP, the break down potential and the passive current density values of the parent alloy are not greatly influenced after FSW. This is evident in the obtained results which showed that the anodic polarization curves exhibited similar polarization behaviour and the breakdown potential of the parent alloy and the weld regions is almost similar, which is in agreement with that reported by Ezuber et al [38], indicating that FSW generates a weld of good quality.
5.5.3 Mechanical property

The hardness profile of Al-Mg alloys is very much dependent on what temper the alloy begins with. Generally, the work hardened alloys exhibit local softening in TMAZ, or the HAZ owing to the effect of the recovery, and coarsening of the grains resulting from the heat generated during FSW [103]. Quite the opposite, the HAZ and TMAZ of the Al-Mg alloys supplied in annealed (O) condition remain unchanged and retain the parent alloy hardness [83]. However, an increase in the hardness within TMAZ is expected owing to the grain refinement. The same increase can also be observed in strain-hardened conditions within the WN, where the minimum hardness occurs within the HAZ, similar to that obtained from the FSW AA5754-H111 alloy.

From the obtained hardness readings, the parent alloy has Vickers hardness of approximately 90 HV. Similar readings are recorded within the HAZ and the TMAZ. As the alloy is supplied in annealed condition, the dislocation in the parent alloy is already low, hence it is expected that the heat generated during FSW will not influence the original mechanical properties of the alloy. This is evident from the hardness profile, which showed similar hardness trend for the weld regions and the parent alloy. Hence, it can be said that the FSW results in a weldment of homogeneous mechanical properties.
Chapter 5: Friction Stir Welded AA5083 Alloy

Figure 5.1 Optical micrograph of the top surface of friction stir welded AA5083-O aluminium alloy

Figure 5.2 Optical micrographs of the cross section of as welded AA5083 alloy after electropolishing in 200 ml HPO$_4$ and 800 ml ethanol for 1 minute

Figure 5.3 Optical micrographs of the cross section of as welded AA5083 alloy after electropolishing in 200 ml HPO$_4$ and 800 ml ethanol for 1 minute

Figure 5.4 Electron backscattered diffraction map showing ultra fine grains within the TMAZ at the top surface.
Figure 5.5 a) SEM image and b) optical image of the AA5083 parent alloy at the rolling plane
Figure 5.6 a) SEM image and b) EBSD map showing elongated grains with a variation in grain orientation within the parent alloy at the transverse section.
Figure 5.7 a) SEM image and b) EBSD map of the HAZ at the rolling plane
Figure 5.8 SEM images of the HAZ at the transverse section
Figure 5.9 SEM micrographs of: a) TMAZ advancing side and b) TMAZ retreating side.
Figures 5.10 (a) Optical and (b) electron backscattered diffraction map within the nugget (left) and TMAZ transition (right).
Figure 5.11 Electron backscattered diffraction map recorded at: a) the cross section and b) the rolling at the edge of TMAZ-AS, showing elongated grains.
Figure 5.12 Optical images of cross section: a) the advancing side and b) the retreating side of the weld at the transverse section, showing the transition between the stir zone and TMAZ.

Figure 5.13 EBSD maps showing variation in the grain size within the TMAZ.
Figure 5.14 SEM image of the stir zone at the rolling plane.

Figure 5.15 SEM image of the stir zone at the transverse section.
Figure 5.16 (a) SEM image and associated with X-ray mapping for Al, Si, Fe, Mn, Cr, and Mg
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Figure 5.17 (a) SEM image of the stir zone, (b) and (c) associated EDX spectra corresponding to the points indicated in (a).
Figures 5.18 Top surface of: a) the AA5083-O alloy and b) the stir zone.
Figure 5.19 SEM images taken from the top surface of the weldment showing effect of the FSW on the intermetallic particles.
Figure 5.20 SEM images of the cross section showing the distribution of the intermetallic particles within: a) the stir zone and b) the parent alloy.
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Figure 5.21 SKPM images taken from the top surface of the weldment showing effect of the FSW process on the intermetallic particles.
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Figure 5.22 Optical image of the top surface of friction stir welded AA5083-O aluminium alloy after agar-gel testing for 2 h.

Figure 5.23 Micrograph of the top surface of the friction stir welded AA5083 alloy after ASTM-G66 immersion testing

Figure 5.24 SEM image showing attack at the JLR after ASTM-G66 immersion testing

<table>
<thead>
<tr>
<th>pH</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td></td>
<td>Yellow</td>
<td>Green</td>
<td>Blue</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

5 μm 5 μm
5.25 SEM micrographs of the parent alloy after ASTM-G66 immersion testing: a) cross section of the parent alloy and b) increased magnification.
5.26 SEM micrographs of the TMAZ after ASTM- G66 immersion testing: a) cross section of the TMAZ and b) increased magnification.
Figure 5.27 SEM micrographs after IGC testing of: a) the parent alloy top surface and b) the TMAZ.
Figure 5.28 SEM micrographs after phosphoric acid etch testing of: a) the parent alloy top surface and b) increased magnification of a.
Figure 5.29 SEM micrographs of the TMAZ-AS at the top surface after phosphoric acid etch testing
Figure 5.30 TEM micrographs of thin foil obtained by electropolishing from: a) the parent alloy and b) increased magnification
Figure 5.31 TEM micrograph obtained from TMAZ advancing side.

Figure 5.32 TEM micrograph obtained from TMAZ retreating side.
Figure 5.33 TEM micrograph for the stir zone

Figure 5.34 Open circuit potential versus time of the as-welded AA5083-O aluminium alloy in deaerated 3.5 wt. % NaCl solution.
Figure 5.35 Anodic polarization curve of as-welded AA5083-O aluminium alloy in deaerated 3.5 wt. % NaCl solution.

Figure 5.36 Hardness profile across the weld at the transverse section
Chapter 5: Friction Stir Welded AA5083 Alloy

Figure 5.37 distribution of the hardness within the TMAZ.

<table>
<thead>
<tr>
<th>Area</th>
<th>Weigh before</th>
<th>Weigh after</th>
<th>Difference in weigh</th>
<th>Weigh loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.32 cm²</td>
<td>10.69713 g</td>
<td>10.61735 g</td>
<td>79.79 mg</td>
<td>4.88 mg/cm²</td>
</tr>
</tbody>
</table>

Table 5.1 Metal weigh loss after NAMLT

<table>
<thead>
<tr>
<th>Area</th>
<th>$E_{corr}$ (V) SCE</th>
<th>$I_{pass}$ (A/cm²)</th>
<th>$E_{pit}$ (V) SCE</th>
<th>$E_{pit}$ - $E_{corr}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent alloy</td>
<td>-0.95</td>
<td>$5 \times 10^{-7}$</td>
<td>-0.71</td>
<td>0.24</td>
</tr>
<tr>
<td>HAZ</td>
<td>-0.99</td>
<td>$6 \times 10^{-7}$</td>
<td>-0.685</td>
<td>0.30</td>
</tr>
<tr>
<td>TMAZ-AS</td>
<td>-1.01</td>
<td>$2 \times 10^{-7}$</td>
<td>-0.68</td>
<td>0.33</td>
</tr>
<tr>
<td>TMAZ-RS</td>
<td>-1.02</td>
<td>$1 \times 10^{-7}$</td>
<td>-0.69</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 5.2 Open circuit potential, the passive current density and the breakdown potential determined from the anodic polarization curves.
CHAPTER 6

Effect of thermal exposure on corrosion of FSW AA5083 and AA5754 alloy

This chapter will present and discuss the effect of a simulated service condition on the intergranular corrosion (IGC) resistance of the friction stir welded AA5083-O and AA5754-H111 aluminium alloys. The welds were exposed to various temperatures i.e. 50˚C, 70˚C and 170˚C for 25, 50, 75, 100, 230, 570, 790 and 1000 h.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), nitric acid mass loss tests (NAMLT) and phosphoric acid etching test were used to evaluate the effects of thermal exposure. The as-welded alloy was initially examined for comparison of resistance to IGC.

6.1 Effect of thermal exposure on the corrosion behaviour of FSW AA5083-O alloy

After immersion of the as-welded specimen in the nitric acid for 24 h at 30˚C, the weldment exhibited metal loss of 4.88 mg/cm$^2$, as shown in Table 6.1. This value is considered low when compared with that specified by standard ASTM-G67, i.e. 25 mg/cm$^2$, at which and above the alloy is considered prone to IGC \[66, 72\]. The resistance of the alloy to IGC indicates that FSW did not influence the corrosion behaviour. This is confirmed by SEM investigations after NAMLT, which showed no IGC at the specimen cross section, as shown in Figure 6.1. The resistance to IGC is further confirmed by the phosphoric acid etching, which showed clearly no sign of IGC attack at the grain boundaries in the TMAZ and the parent alloy, as shown in Figures 6.2 and 6.3, indicating the absence of β-phase at the grain boundaries of the weld and the parent alloy. Firm evidence for the resistance of the weldment to IGC obtained from the microstructure examinations of the as welded specimen. The SEM and TEM images showed that the grain boundaries of the alloy and the weld regions are free of precipitates, as shown in Figure 6.4 and 6.5 respectively. Hence, it can be said that the AA5083-O alloy has good resistance to IGC.
In order to evaluate the service temperature effect on the corrosion behaviour of the FSW AA5083 and AA5754 alloys, heating of the specimens was carried out in an air furnace at 50°C, 70°C and 170°C for various lengths of time from 25 h up to 1000 h.

### 6.1.1 Thermal exposure at 50°C

Table 6.2 shows the mass loss test (NAMLT) results. As can be seen, after heating of the specimen containing the welding line at its centre at 50°C for 25, 50, 75 and 100 h, the metal loss has increased slightly compared with as-welded specimen. However, the obtained metal loss values are still far lower than 25 mg/cm² at which the alloy is considered susceptible to IGC. It is also evident from the metal loss results that the weight loss exhibited a slight increase with increasing heating exposure time. The maximum weight loss after 100 h of exposure to 50°C is about 5.05 mg/cm², which is very close to that for the as-welded specimen, indicating that the alloy kept its resistance to IGC after heating at the specified temperature and exposure time.

The appearance of the cross section of FSW AA5083 alloy following the NAMLT is shown in Figures 6.6 and 6.7. The surfaces appear smooth with no sign of attack at the grain boundaries at the weld regions or the alloy. The phosphoric acid etching test shows no sign of attack at the grain boundaries of the weldment as evident in Figure 6.8, which is in agreement with the NAMLT results, indicating that the alloy is resistant to IGC after heating at 50°C for 25-100 h. However, with increase of the exposure time to 230, 570, 790 and 790 h, the metal loss increased to approximately 2 times than that obtained after exposure for 100 h, as shown in Figure 6.9 and Table 6.2.

Examining the surfaces of the specimen heated for 790 h after immersion in nitric acid for 24 h at 30°C, revealed signs of attack at the grain boundary of the alloy, as shown in Figure 6.10. Corrosion attack in the weld is also observed after etching in 10 wt. % phosphoric acid at 60°C for 90 s, indicating a change in the nature of the grain boundary chemistry. It is evident that the prolonged exposure time influenced the corrosion behaviour of the alloy. Hence, it is expected also that the increase of thermal exposure temperature from 50 to 70 and 170°C will influence the corrosion resistance of the welded alloy.
6.1.2 Thermal exposure at 70°C

With increasing the thermal exposure temperature from 50 to 70°C, the weight loss values, after 25, 50, 75 and 100 h of exposure, have increased slightly compared with specimens heated at 50°C for the same time of exposure, as shown in Table 6.3 and 6.2 respectively. The weight loss after exposure to 25, 50, 75, 100 h is 5.25, 5.38, 5.78 and 6.09 mg/cm² respectively. However, these values are still far below that specified by standard at which the alloy is considered prone to IGC.

Following NAMLT, the surfaces of the weld appeared slightly rougher than the surfaces exposed to 50°C for the same period of exposure, as evident in Figures 6.11 and 6.6 respectively, indicating that heating for the specified period of exposure does not influence the IGC corrosion resistance of the alloy. Examining the cross section of the exposed weld after NAMLT confirmed the observations, the SEM micrographs showed free surfaces from any sign of IGC, as shown in Figure 6.12. This is further confirmed by the phosphoric acid etching results, which were in agreement with the NAMLT results. The SEM examination of the heated specimens after immersion in 10% wt. H₃PO₄ at 60°C for 90 s revealed no attack at the grain boundaries of the parent alloy and the TMAZ, as apparent in Figure 6.13. However, with increasing the exposure time to 230, 570, 790 and 1000 h the metal loss increased, as evident in Table 6.3 and Figure 6.14. The metal weight loss value for the specimens heated for 790 and 1000 h approached 15 mg/cm². Hence the susceptibility of this material to IGC, which is measured in terms of mass loss per unit area (mg/cm²), increased. This becomes obvious in the obtained SEM images of the heated specimens after immersion in nitric acid at 30°C for 24 h and etching inside 10 wt. % phosphoric acid at 60°C for 90 s, as shown in Figures 6.15-6.17. The grain boundaries were attacked indicating the presence of active phase at the grain boundaries.

The SEM and TEM examination of the specimen heated for prolonged time showed the presence of discrete precipitates at the grain boundaries, as shown in Figures 6.18-6.19. The EDX analysis showed that the prolonged holding at 70°C leads to the precipitation of intermetallic compounds rich in magnesium at the grain boundaries, as shown in Figure 6.19.
6.1.3 Thermal exposure at 170°C

Following the nitric acid metal loss test (NAMLT), the obtained metal weight loss values, as shown in Table 6.4, are much larger than the welds after exposure at 50 and 70°C. After exposure for 25, 50, 75 and 100 h, the values of the metal loss exceeded 25 mg/cm² indicating that the alloy becomes susceptible to IGC. After NAMLT, a drastic change in the surface morphology is also observed, as shown in Figure 6.20. The heated specimens exhibited rougher surfaces when compared with the as-welded and the heated specimens at lower heating temperatures i.e. 50°C and 70°C. It is evident that the surfaces roughness increases with increasing the temperature and the heating exposure time.

The susceptibility to IGC is clearly revealed by SEM, which showed grain detachment within the TMAZ and the parent alloy, as evident in Figures 6.21 and 6.22. This explains the reason for the increased metal weight loss. Examination of the cross sections of the heated specimens following the NAMLT showed IGC attack within the weld and the alloy, as shown in Figure 6.23.

The SEM examination of the phosphoric acid etched weld showed that the grain boundaries of the parent alloy and the weld have been severely attacked by the etchant to the extent that they are completely corroded, as shown in Figure 6.24, which is in agreement with the NAMLT results.

TEM examination of the parent alloy and the weld grain boundaries of the specimen after exposure at 170°C for 75 and 100 h revealed the presence of almost continuous precipitates at the grain boundaries within both the TMAZ and the parent alloy, as shown in Figures 6.25-6.27. Compositional investigation using EDX analysis showed that the precipitated phase is rich in magnesium, as shown in Figure 6.28. This finding is consistent with the work done by Goswami et al and Adigun [61, 245].

From above, it is evident that the IGC resistance of the as-welded AA5083 alloy to IGC decreased with increasing the temperature and the exposure time. This is obvious from the difference in the weight loss values between the specimens exposed at 50°C, 70°C and 170°C for 25, 50, 75 and 100 h, as shown in Figure 6.29. The effect of the temperature can also be seen clearly in Figure 6.30, which is in agreement with the metal weight loss test for all cases. The weldment heated at 50 and 70°C exhibited
resistance to IGC up to 100 h of exposure. However, after increasing the exposure time, the attack at the grain boundaries becomes evident, indicating a change in the chemistry of the grain boundaries.

The EDX analysis on the specimens exposed at 170°C revealed the presence of magnesium rich phase at the grain boundaries. This phase is electrochemically more active than the alloy. Hence, in the presence of the corrosive media, the grain boundaries are attacked at a higher rate than the adjacent alloy matrix owing to the difference in the corrosion potential. This explains the drastic change in the corrosion behaviour of the as welded specimen after heating.

6.2 Effect of thermal exposure on corrosion of AA5754 alloy

The susceptibility of the friction stir welded specimen has been assessed in the as-welded condition. After thermal exposure, only the parent alloy was tested for the reason of the shortness of the welded material. The phosphoric acid etching is a simple and reliable test and it is used as indicator for the presence of the beta phase at the grain boundaries. It is the only method used for determining the susceptibility of the thermally exposed AA5754 at 50, 70 and 170°C to IGC. The grain boundaries that contain beta phase precipitates will be preferentially attacked and decorated with a black line as a sign of corrosion. While the boundaries free of precipitates will not be attacked and hence, can not be observed under optical microscopy and the SEM.

After immersion in 70% concentrated nitric acid at 30°C for 24 h (NAMLT), the FSW AA5754 alloy exhibited less weight loss when compared with weight loss values of the tested AA5083-O alloy (shown in chapter 5), i.e. 2.7 mg/cm², as shown in Table 6.5, indicative of a superior resistance to IGC. This result is confirmed by the SEM examination following the NAMLT. The SEM micrographs of the cross section revealed no evidence of any IGC attack at the weld or the parent alloy, as shown in Figure 6.31. The phosphoric acid etching also revealed no attack at the grain boundaries of both regions, as shown in Figures 6.32, indicative of grain boundaries free of the anodic precipitates. The SEM and TEM results were in agreement with the NAMLT and the phosphoric acid etching, where the grain boundaries are seen to be free of precipitates, as shown in Figures 6.33 and 6.34. Hence, the chemistry of the grain
Chapter 6: Effect of thermal exposure on corrosion of FSW AA5083-O and AA5754

boundaries remains unchanged after FSW, which clearly explains the reason of the high resistance of the alloy to IGC in this condition.

6.2.1 Thermal exposure at 50°C

Similar to the AA5083 alloy, the AA5754 alloy has kept its resistance to IGC after heating at 50°C for 25, 50, 75 and 100 h. This is evident in the SEM micrographs shown in Figure 6.35 obtained from the top surface of the heated as-supplied and ground specimens after etching in 10 wt. % phosphoric acid at 60°C for 90 s. No attack at the grain boundaries was observed. With increasing the thermal exposure time to 230, 570, 790 and 1000 h, the AA5754 alloy exhibited good resistance to IGC when compared with the AA5083 exposed at the same temperature. SEM examination following etching in 10 wt. % H₃PO₄ for the specimen thermally exposed for 230-1000 h revealed no apparent attack at the grain boundaries, as shown in Figure 6.36, suggesting the absence of the active precipitate (β-phase) at the grain boundaries.

6.2.2 Thermal exposed at 70°C

Similar to the AA5083 alloy, the AA5754 alloy has maintained its resistance to the IGC after heating at 70°C for 25, 50, 75 and 100 h. This is evident in the SEM micrographs obtained from the top surface of the thermally exposed alloy after etching in 10 wt. % phosphoric acid at 60°C for 90 s, as shown in Figure 6.37, which confirms no attack at the grain boundaries. The alloy has kept its resistance to IGC even after increasing the heating exposure time to 230, 570, 790 and 1000 h, the AA5754 alloy exhibited good resistance to IGC when compared with the heated AA5083 at the same temperature and time (as shown in section 6.1). Again, the SEM examination following etching in 10 wt. % H₃PO₄ revealed no evident of attack, as shown in Figure 6.38, indicating that the heating at the specified temperature and time did not sensitize the alloy microstructure.

6.2.3 Thermal exposure at 170°C

Compared with the AA5083-O alloy, the AA5754-H111 alloy showed better resistance to IGC after exposure at 170°C for 25-100 h, indicative a good resistance to IGC. No drastic change in the surfaces morphology is observed compared with as-welded and the heated specimens at lower temperatures i.e. 50 and 70°C, as shown in Figure 6.39. As
well, no precipitates at the grain boundaries were observed after heating, as shown in Figure 6.40. This alloy contains less magnesium than the AA5083. As shown previously in chapter 3, the AA5754 contains about of 2.7 wt. % Mg, and the alloy AA5083 contains 4.7 wt. % Mg about two times more than the AA5754 alloy. Increase of the magnesium content is reported to increase the susceptibility of the Al-Mg alloys to IGC. The alloys that contain 3.5 percent of magnesium and over are found suffering from the IGC [246].

From the obtained results, it is evident that the IGC resistance of the as-welded AA5083 alloy decreased with increasing sensitization temperature and time. For the alloys AA5083-O and AA5754-H111, the heated specimens at 50°C and 70°C for 25, 50, 75 and 100 h exhibited resistance to IGC. However with increasing the heating exposure time to 230, 570, 790 and 1000 h, the resistance of the AA5083-O to IGC decreased drastically, this is evident from the increase of the metal loss values after NAMLT. In contrast, the resistance of the AA5754-H111 alloy to IGC remained unchanged. Increasing the heating temperature to 170°C increased significantly the susceptibility of the AA5083 alloy (containing 4.7 wt. % Mg) to IGC. The attack of the grain boundaries becomes evident. On the contrary, the heated alloy AA5754 (containing 2.7 wt. % Mg) at the same temperature and exposure time maintained its resistance to IGC. Thus, beside the temperature and the heating exposure time effect, the magnesium content within the alloy plays an important role in increasing the susceptibility of the Al-Mg alloys to IGC.
6.3 Discussion

The mechanical properties of Al-Mg alloys, including the alloys of the present study, namely AA5754 and AA5083 alloys, are determined by the Mg content in the solid solution (solute strengthening), work hardening and grain size [17]. The good strength, formability, corrosion resistance to atmospheric conditions and sea water make the Al-Mg alloys suitable for use in marine and automotive applications [247-248]. The higher the magnesium content the better strength. However increased magnesium decreases drastically the corrosion resistance of Al-Mg alloys, due to precipitation of magnesium rich phase at the grain boundaries [249].

According to the literature, the susceptibility of the Al-Mg alloys to IGC increases with increasing the Mg content and the cold working [4]. Below 3 wt % Mg, there is almost no precipitation of β-phase at grain boundary, while above this content, the Mg starts to precipitate along the grain boundaries especially when subjected to thermal exposure in range of 50-200°C for sufficient time [58, 248, 250-252].

The low solid solubility of Mg in aluminium at lower temperature and its high diffusivity at elevated temperatures are the reasons for precipitation of magnesium rich phase known as beta phase. The solid solubility level for Mg in aluminium is about 2 wt % at 200°C [251, 253]. For this reason, the Al-Mg alloys containing 3.5 wt % Mg and above become unstable with time at service temperatures as low as 65°C [254].

According to the literature, the fabrication processing, the chemical composition and the crystallographic misorientation play determining roles in the susceptibility of Al-Mg alloys to IGC. The population density, size and distribution of β-phase within the grain boundaries are also factors in determining the intensity of the attack at the grain boundary [255].

Work by Davenport et al [57] on the effect of the crystallographic misorientation on the susceptibility to IGC of AA5182 aluminium alloy, (containing 4.5 wt % Mg) solution heat treated at 450°C for 30 minutes, air cooled and aged at 70 and 150°C for 100, 250, 500, 1000 and 1800 h, showed different level of β-phase precipitation on the grain boundaries. The low angle boundaries (< 20°) were found free of β-phase precipitates. On the contrary, the higher angle boundaries exhibited a continuous film of β-phase
precipitates. This is due to the fact that the low misorientation angles result in low energy boundaries and hence, this decreases level of segregation and precipitation compared with high energy boundaries [256]. Davenport et al [57] and Unwin et al [257] al showed that the precipitation of beta phase is also influenced by the grain boundary characteristics such as misorientation and boundary plane.

From the above, it can be concluded that the corrosion behaviour of Al-Mg alloys including the alloys of study is determined by the presence of β-phase precipitates on grain boundary. Such a phase has a more negative corrosion potential than aluminium due to differences in composition and, therefore corrodes preferentially [246, 258-259].

In general, the increase in the susceptibility of Al-Mg alloys including the alloys of study is usually related to the magnesium content of their solid solution. This means that when the magnesium content is lower than 3 wt. % and the Mg is completely is in solid solution or distributed at the grain interiors, the risk of susceptibility to IGC will be decreased. As shown in Chapter 3, the AA5083 alloy contains a magnesium concentration above the specified value in the literature i.e. 3 wt % Mg at which the AA5xxx alloys become prone to IGC. The AA5754 alloy contains less Mg content, which is 2.7 wt %.

Based on the above, it should be expected that increasing the magnesium content within aluminium, as the case of the AA5083 alloy (4.7 wt. % Mg) will increase the susceptibility of the aged Al-Mg alloys to IGC.

The results of this study showed that the AA5083 alloy and AA5754 in as-welded condition are resistant to IGC, which indicates proper control of the fabrication and joining processes. The result is consistent with that observed by Goswami et al [61] for the AA5083 alloy and by Birol et al [65] for the AA5754 alloy. The high resistance to IGC may be attributed to the combination of various effects, which reduced the presence of active precipitates at the grain boundaries: 1) low content of Mg within the AA5754 alloy and 2) proper control of the manufacturing processes and the welding parameters for the AA5083 alloy.

However, after exposure to thermal heating at 50 and 70˚C a slight increase in the metal weight loss of the alloy AA5083 was found, where as ageing at 170˚C results in a significant increase in the susceptibility of the alloy to IGC. On the contrary, the
AA5754 exhibited resistance to IGC even after exposure to thermal heating at 170˚C for 25-100 h.

The increase in the susceptibility of the AA5083 to IGC as a result of increase in temperature and the exposure time has been frequently reported. For example, Sampath et al [260] have observed an increase in the metal weight loss for the AA5083-O and AA5083-H116 alloys with increasing the ageing temperature from 100 to 150 and 175˚C and the thermal exposure time from 168 to 336 h. Oguocha et al [62] have also observed a decrease in the IGC resistance of the alloy following ageing at 80, 100, 175 and 200˚C for up to 672 h.

The resistance of the alloy AA5754 to IGC after ageing at elevated temperature is also reported by Alcan [64]. The study compared the resistance to IGC of some aged Al-Mg alloys containing below and above 2 wt. % Mg at 70, 100 and 150˚C for up to 10 years, utilizing the NAMLT and phosphoric acid etching tests. The results showed that the alloys containing below 3 wt. % Mg have superior resistance to IGC and the IGC resistance decreases with increasing the Mg content, which is constituent with the results of this study.

These examples clearly illustrate that, when any Al-Mg alloy is subjected to elevated temperatures for a prolonged period of time, IGC will certainly take place in the presence of aggressive environments.

In the present study, TEM and SEM investigations show the presence of discrete magnesium rich particles at the grain boundaries of the AA5083 alloy aged at 70˚C and 170˚C and severe corrosion attack at the grain boundaries following the NAMLT and the phosphoric acid etching.

Jain et al [261] suggested a hypothesis to explain the reason for occurrence of the continuous attack at grain boundaries despite the presence of distinct precipitates at the grain boundary. The corrosion initially starts as a pitting corrosion at the exposed β-phase, causing local acidification and high chloride ion concentration within pits. As a result the chemistry of the solution will be more aggressive leading to decrease of the breakdown potential, subsequently triggering corrosion of neighbouring β-phase precipitates. The close isolated pits then progress into a network of corroded grain boundaries. This was evident in specimen which exhibited high degree of sensitization,
where short distances between the β-phase particles is observed allowing coordinated attack to occur on the surface, providing networks of IGC sites. On the contrary, at low degree of sensitization, the β-phase particles are not in close enough proximity to enable the progress of the chain of pits, allowing random pitting events to dominate instead. Therefore, the distance between the precipitates plays a role in controlling the severity of the IGC.

Similarly, work done by Winsley [262] on effect of the thermal exposure on corrosion of FSW AA5083-H116 showed that in as-supplied and solution heat treated condition; the alloy is resistant to IGC. However, after ageing at 100, 150, 200 and 250°C for 10 and 100 h, it becomes susceptible to IGC due to precipitation of β-phase at grain boundary. The author observed the presence of non continuous precipitates at the major of the grain boundary of highly sensitized specimen. On the contrary, the SEM examination after NAMLT showed extensive grain boundary corrosion. He explained the mechanism for the propagation of the corrosion attack at the boundary as summarized in Figure 6.41.

![Figure 6.41 Sketch illustrating hypothesis for propagation of the IGC at the grain boundaries of Al-Mg alloys [262].](image)

Since the β-phase particle is anodic with respect to the bulk alloy, it would be expected to corrode rapidly when exposed to aggressive solution as Cl⁻. As a result of dissolution
of β-phase, the Mg$^{2+}$ ions are liberated into the localised solution cavity making the solution more aggressive to the surrounding aluminium matrix. This leads to preferential attack of the surrounding matrix. As the area of attack widens it may (as the case of highly sensitised conditions) reach another coarse grain boundary β-phase particle, which again dissolves rapidly, providing a ‘burst’ in localised solution aggressivity. Again this aggressive localised solution attacks the surrounding aluminium matrix and with the presence of another close active coarse precipitate at the grain boundary, the localised solution again becomes inherently more aggressive, as again it is saturated with a ‘burst’ of Mg$^{2+}$ ions. In this manner, discontinuous grain boundary precipitates could cause the continuous IGC as the case observed for the sensitised AA5083 at 70°C.

Hence it can be concluded that when Al-Mg alloys contain more than 3 wt. % Mg are used in applications that involve exposure to elevated temperatures, such as those used in this study, there is a risk of sensitization occurring.
Figure 6.1 SEM micrographs of the as-welded AA5083-O aluminium alloy of: a) the TMAZ and b) the parent alloy following nitric acid metal loss test.
Figure 6.2 SEM micrographs of as-welded AA5083-O aluminium alloy at: (a) and (b) the parent alloy, (c) the HAZ and the TMAZ after etching in phosphoric acid at 60°C for 90s.

Figure 6.3 SEM micrographs of as-welded AA5083-O aluminium alloy at the TMAZ after etching in phosphoric acid at 60°C for 90s.
Figure 6.4 Backscattered scanning electron micrographs of friction stir welded AA5083 aluminium alloy at: (a) and (b) the parent alloy, (c) and (d) the HAZ and (e) and (f) the stir zone.
Figure 6.5 TEM micrographs of friction stir welded AA5083 aluminium alloy at: (a) and (b) the parent alloy and (c) and (d) the TMAZ.
Figure 6.6 Cross section of the weld after exposure to 50°C for: a) 25 h, b) 50 h, c) 75 h and d) 100 h then, NAMLT.
Chapter 6: Effect of thermal exposure on corrosion of FSW AA5083 and AA5754

Figure 6.7 Cross section back scattered scanning electron micrographs of heated specimens at 50°C for 25, 50, 75 and 100 h at: (a-d) the parent alloy, and (e-g) the TMAZ after NAMLT.
Figure 6.8 Surface appearance of: (a) and (b) the TMAZ, (c) and (d) the stir zone and (e) and (f) the parent alloy of heated specimens at 50°C for 100 h following phosphoric acid etching.
Chapter 6: Effect of thermal exposure on corrosion of FSW AA5083-O and AA5754

Figure 6.9 Effect of the heating exposure time on the IGC corrosion behaviour of FSW AA5083 alloy heated at 50°C.

Figure 6.10 SEM images of heated specimen at 50°C for 790 h of: a) the stir zone after phosphoric acid etching and b) the parent alloy following NAMLT.
Figure 6.11 Cross section micrographs of heated specimens at 70°C for: a) 25 h, b) 50 h, c) 75 h, d) 100 h.
Figure 6.12 Cross section back scattered scanning electron micrographs of heated specimens at 70°C for 25, 50, 75 and 100 h at: (a-d) the parent alloy, and (e-g) the TMAZ after immersion in nitric acid for 24 h at 30°C.
Figure 6.13 Surface appearance of: a-d the TMAZ and e) the parent alloy of heated specimens at 70°C following phosphoric acid etching.

Figure 6.14 Effect of the exposure time on the IGC corrosion behaviour of FSW AA5083 aluminium alloy exposed to heating at 70°C.
Figure 6.15 Cross section micrographs of heated specimens at 70°C for: a) 230, b) 790 and c) 1000 h following NAMLT showing effect of exposure time on IGC resistance of the FSW AA5083-O alloy.
Figure 6.16 Cross section and top surface microstructure of FSW AA5083 alloy heated at 70°C for (a) and (b) 570 h and (c-f) 1000 h after NAMLT.
Figure 6.17 Cross section and top surface SEM micrograph of the AA5083 alloy heated at 70°C for 790 and 1000 h following immersion in H₃PO₄.
Chapter 6: Effect of thermal exposure on corrosion of FSW AA5083-O and AA5754

Figure 6.18 SEM micrographs of: a) the stir zone and b) the alloy heated at 70°C for a) 230 h and b) 790 h respectively.

Figure 6.19 a) TEM image of the parent alloy after heating at 70°C for 1000 h with b) corresponding EDX line profile analysis showing the presence of β-phase.
Figure 6.20 Cross section appearance of the heated specimens at 170°C for: a) 25 h, b) 50 h, c) 75 h and d) 100 h following NAMLT.
Figure 6.21 Cross section scanning electron images of the heated stir zone at 170°C for:
(a) 25 h, (b) 50 h, (c) 75 h and (d) 100 h

Figure 6.22 Cross section scanning electron images of the heated parent alloy at 170°C for:
(a) 25 h, (b) 50 h, (c) 75 h and (d) 100 h.
Chapter 6: Effect of thermal exposure on corrosion of FSW AA5083-O and AA5754

Figure 6.23 Cross section back scattered scanning electron micrographs of the heated specimens at 170°C for 25, 50, 75 and 100 h at: (a-d) the parent alloy, and (e-g) the TMAZ after NAMLT.
Figure 6.24 Top surfaces back scattered scanning electron micrographs of heated specimens at 170°C for 25, 50, and 75 at: (a-d) the TMAZ and (e-h) parent alloy after etching in 10% wt. H₃PO₄ at 60°C for 90s.
Figure 6.25 TEM micrographs of the parent alloy after heating at 170°C for 75 h.
Figure 6.26 TEM micrographs of: (a) the parent alloy and (b) the TMAZ after exposure to 170°C for 100 h.
Figure 6.27 SEM micrographs of the TMAZ after heating 170°C for 100 h.
Figure 6.28 EDX spectrum of the precipitate at the grain boundaries of the heated specimen at 170˚C for 100 h, showing rich in Al and Mg precipitate (β-phase) at the grain boundaries.

Figure 6.29 Influence of the temperature and the heating exposure time on the susceptibility of the FSW AA5083-O alloy to IGC.
Figure 6.30 Surface appearance of the cross section of FSW AA5083 alloy heated at (a) and (b) 50°C, (c) and (d) 70°C and (e) and (f) 170°C for 100 h following NAMLT, representing the influence of the temperature increase on the IGC resistance of the alloy.
Figure 6.31 BSE images of the cross section of: a) parent alloy and b) the weld after NAMLT testing for 24 h, showing that the parent alloy and the weld are resistant to IGC.
Figure 6.32 BSE images of the cross section of: (a) the parent alloy and (b) the weld after phosphoric acid etching at 60°C for 90 s, showing that the weld and the parent alloy are resistant to IGC.
Figure 6.33 Electron backscattered SEM images of: (a) parent alloy; and (b-d) the TMAZ.
Figure 6.34 a) TEM image of the AA5754-H111 alloy with b) corresponding EDX line profile analysis showing grain boundaries free of β-phase.
Chapter 6: Effect of thermal exposure on corrosion of FSW AA5083-O and AA5754

Figure 6.35 Top surface SEM micrographs of the AA5754 alloy heated at 50°C for: a) 25 h, b) 50 h, c) 75 h and 100 h after etching in 10% wt. H$_3$PO$_4$ at 60°C for 90 s.
Figure 6.36 Top surface SEM micrographs of the AA5754 alloy heated at 50°C for: a) 230 h, b) 570 h, c) 790 h and 1000 h following phosphoric acid etching.
Figure 6.37 Top surface SEM micrographs of the AA5754 alloy heated at 70°C for: a) 25 h, b) 50 h, c) 75 h and 100 h after etching in 10% wt. H₃PO₄ at 60°C for 90 s.
Figure 6.38 SEM micrographs of the AA5754 alloy heated at 70°C for: a) 570 h, b) 790 h and c) 1000 h after etching in 10% wt. $\text{H}_3\text{PO}_4$ at 60°C for 90 s.
Chapter 6: Effect of thermal exposure on corrosion of FSW AA5083-O and AA5754

Figure 6.39 Top surface SEM micrographs of the AA5754 alloy heated at 170°C for: a) 25 h, b) 50 h, and c) 75 h after etching in 10% wt. H₃PO₄ at 60°C for 90 s.

Figure 6.40 TEM micrographs of a) the parent alloy, b) HAZ and c) the TMAZ after exposure to 170°C for 100 h.
Chapter 6: Effect of thermal exposure on corrosion of FSW AA5083-O and AA5754

Table 6.1 Weight loss for the FSW AA5083 alloy

<table>
<thead>
<tr>
<th>Area (cm²)</th>
<th>Weight before (g)</th>
<th>Weight after (g)</th>
<th>Difference in weight (mg)</th>
<th>Weight loss (mg/cm²)</th>
</tr>
</thead>
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<tr>
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<td>10.69713</td>
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<td>4.88</td>
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Table 6.2 Weight loss obtained from the NAMLT for weld of AA5083 after exposure to 50˚C for 25, 50, 75, 100, 230, 570, 790 and 1000 hours

<table>
<thead>
<tr>
<th>Exposure Time (h)</th>
<th>Surface area (cm²)</th>
<th>Weight before (g)</th>
<th>Weight after (g)</th>
<th>Difference in weight (mg)</th>
<th>Weight loss (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
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<td>8.8331</td>
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<tr>
<td>50</td>
<td>19.3696</td>
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<td>8.6731</td>
<td>93</td>
<td>4.80</td>
</tr>
<tr>
<td>75</td>
<td>19.3696</td>
<td>8.9738</td>
<td>8.8774</td>
<td>96.4</td>
<td>4.97</td>
</tr>
<tr>
<td>100</td>
<td>19.3712</td>
<td>8.9616</td>
<td>8.87636</td>
<td>98</td>
<td>5.05</td>
</tr>
<tr>
<td>230</td>
<td>17.7300</td>
<td>8.7632</td>
<td>8.6137</td>
<td>149.8</td>
<td>8.40</td>
</tr>
<tr>
<td>570</td>
<td>18.5600</td>
<td>8.8498</td>
<td>8.6244</td>
<td>225.4</td>
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<tr>
<td>790</td>
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<td>8.6514</td>
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<td>1000</td>
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<td>9.1145</td>
<td>8.829</td>
<td>288.2</td>
<td>15.30</td>
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Table 6.3 Weight loss obtained from the NAMLT for weld of AA5083 after exposure to 70˚C for 25, 50, 75, 100, 230, 570, 790 and 1000 hours

<table>
<thead>
<tr>
<th>Exposure Time (h)</th>
<th>Surface area (cm²)</th>
<th>Weight before (g)</th>
<th>Weight after (g)</th>
<th>Difference in weight (mg)</th>
<th>Weight loss (mg/cm²)</th>
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<td>Exposure Time (h)</td>
<td>Surface area (cm²)</td>
<td>Weight before (g)</td>
<td>Weight after (g)</td>
<td>Difference in weight (mg)</td>
<td>Weight loss (mg/cm²)</td>
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<td>57.58</td>
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<tr>
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<td>6.9708</td>
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Table 6.4 Weight losses obtained from the NAMLT for heated specimens at 170°C for 25, 50, 75 and 100 hour.

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<th>Area</th>
<th>Weight before</th>
<th>Weight after</th>
<th>Difference in weight</th>
<th>Weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.43 cm²</td>
<td>10.0663 g</td>
<td>10.0300 g</td>
<td>36.3 mg</td>
<td>2.70 mg/cm²</td>
</tr>
</tbody>
</table>

Table 6.5 Metal weight loss results for the FSW AA5754 alloy.
CHAPTE R 7

Conclusions and Suggestions for Future Work

7.1- Conclusions

1- High quality welds, free of cracks, distortion and voids, were produced by friction stir welding of AA5754 and AA5083 aluminium alloys. It has been shown that FSW has a great impact in modifying the microstructures of AA5754 and AA5083 aluminium alloys. The coarse alloys grains have been replaced by a much smaller recrystallized microstructure within the stir zone or elongated and deformed grains at the TMAZ edges. Such a modification is attributed to severe plastic deformation and frictional heating between the tool and materials.

2- Grain coarsening was also observed in the HAZs of the AA5754 alloy due to the effect of transferred heat during welding.

3- The grain size is significantly reduced from the top surface region to the bottom regions of the TMAZ within the welds. This is probably due to the effect of the extra heat generated at the top surface by the friction between the shoulder and the material.

4- Slight reduction in the hardness of AA5754-H111 weldment at the HAZ is observed. This is related to the grain coarsening owing to the transferred heat from the thermomechanical affected zone (TMAZ).

5- FSW also modified the size and distribution of the intermetallics particles. The tool breaks up the coarse particles into small and homogenously distributed ones owing to mechanical deformation action.

6- An increase in hardness within the TMAZ of AA5754 alloy welds was observed. This is attributed to the grain refinement that resulted from the dynamic recrystallization within TMAZ.
7- No significant change in the hardness of the weld of AA5083 alloy was observed when compared with the parent alloy. This is probably because the alloy is supplied in annealed condition and the only treatment that can occur in the weld region is an annealing cycle. Therefore, no drastically change in the mechanical properties of the weld is observed.

8- The FSW did not create any adverse affect on the corrosion properties of both alloys. After FSW, the various welding zones exhibited resistance to exfoliation, pitting and IGC, indicating that the alloys were not sensitized by the welding process and they maintained their good corrosion resistance after welding, indicating the ability of FSW to produce good quality welds. This was evident from the agar gel test, the electrochemical measurements as well, the exfoliation and the IGC susceptibility testing.

9- Increased susceptibility to localized corrosion at the joint line remnant was revealed after etching and corrosion testing. This might be due to the micro galvanic corrosion between the magnesium and oxygen rich band and the adjacent bulk material. However, cleaning the surfaces prior to joining may reduce this effect.

10- Both alloys exhibited resistance to IGC and exfoliation in as-welded condition. The high resistance to IGC may be attributed to the combination of various effects, which reduced the presence of active precipitates at the grain boundaries: 1) low content of Mg within the AA5754 alloy and 2) proper control of the manufacturing processes and the welding parameters for the AA5083 alloy.

11- After exposure of the friction stir welded AA5754 and AA5083 alloys to thermal heating at 50, 70 and 170°C for prolonged time, the resistance of the AA5083 alloy (4.7 wt% Mg) to the IGC drastically decreased owing to precipitation of magnesium rich particle known as β-phase at the grain boundaries. On the contrary, the resistance of the AA5754 alloy (2.7 wt% Mg) to IGC remained after the thermal exposure. Thus, the level of Mg content in Al-Mg alloys plays an important role in determining the corrosion characteristics of the alloys. The precipitation of Mg rich particle (β-phase) at the grain boundaries is the determining factor for the resistance of AA5xxx alloys to IGC owing to the
difference in the electrode potentials between β-phase and the grain interior, which lead to the generation of microgalvanic cells and selective dissolution of the grain boundaries.

12- The combination of temperature and aggressive environment can potentially bring negative effects to the friction stir welded AA5083 alloys under service conditions.

7.2- Suggestions for Future work

1- The obtained results have provided information on the effect of the friction stir welding process on the alloy microstructure, mechanical and the corrosion properties. Further focus on the crystallographic orientation and the texture of the alloy at the welds utilising electron backscattered diffraction is required for investigating their effect on the corrosion behaviour of the individual weld zones.

2- It is known that joints free of imperfections can be produced within AA5083-O alloy using higher rotation speed than that employed in the present study. Hence, increasing the rotation speed to avoid the formation of the joint line remnant is recommended. Once the correct window is established, the produced weldments need to be subjected to detailed microstructure characterization, corrosion and mechanical testing for determining effect of the increased heat input on corrosion and mechanical properties of the weld.

3- Surface treatment of the weld, including anodising and laser surface treatments, should be investigated in order to improve the resistance of the alloys to localized corrosion across the weld.

4- Post welding heat treatment should be assessed for stabilizing the microstructure to reduce the risk of sensitization of the weld during service.
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