Chapter 5
Corrosion of Aluminium

5.1 Corrosion Introduction
Metallic corrosion takes place in wet environments when the chemical or electrochemical reaction between a metal and the surrounding environment results in the oxidation of the metal. For corrosion to occur, electrons are produced by the anodic oxidation of the metal must be consumed in a cathodic reaction. These two processes can take place on different parts of a metal structure providing that there is a conducting path for the electrons between the two, and a continuous electrolyte path for ion transport.

5.2 Corrosion of Aluminium
Aluminium is highly reactive, with a negative standard electrode potential of -1660mV, and is therefore unstable in the presence of water. However aluminium reacts quickly with the oxygen in air or water to form a protective oxide film (alumina, Al₂O₃) that is stable in pH range 4-9 and prevents corrosion of the metal. In aqueous solutions, the oxide film is formed during the reaction:

Eq. 5.1 Oxidation Reaction: \(2\text{Al}(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{Al}_2\text{O}_3(s) + 6\text{H}^+(\text{aq}) + 6\text{e}^-\)

This thickness of the oxide layer can be between 1-10nm [129], and the speed at which it grows is temperature and pH dependent [128]. The oxide layer forms within 1ms in aqueous environments and is protective as it is resistant to dissolution in neutral environments, and blocks the cathodic reaction as it is an insulator.

Although surface oxide layer of aluminium acts as an efficient insulator preventing electron transfer to the surface, commercial alloys contain intermetallic particles that have thinner and more conducting oxide layers allowing electrons to pass through, so that anodic and cathodic reactions can take place [129-130].

Anodic Dissolution
Anodic active dissolution or oxidation is the loss of electrons from an Al atom to leave an Al ion plus electrons. This reaction is given below:

Eq. 5.2 Anodic Dissolution: \(\text{Al} \rightarrow \text{Al}^3^+ + 3\text{e}^-\)

In order for the charge balance to be maintained, the electrons created must be used up in a cathodic reduction reaction.
Cathodic Reduction

The main cathodic reactions involve reduction of oxygen or water as shown in the reactions below depending on the environmental conditions:

Eq. 5.3 Cathodic Oxygen Reduction: \( \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4\text{e}^- \rightarrow 4\text{OH}^- (\text{aq}) \) (Neutral Conditions)

Eq. 5.4 Cathodic Water Reduction: \( 2\text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow 2\text{OH}^- (\text{aq}) + \text{H}_2(g) \) (Neutral Conditions)

Figure 5.1 Pourbaix diagram of aluminium in the presence of water at 25°C, [131]

Under neutral pH conditions the oxide layer is a good insulator in preventing electrons from reaching the surface preventing dissolution. However at highly acidic and highly alkaline pH values aluminium’s passive film becomes unstable and dissolves to leave the bare untreated metal so that active dissolution can take as indicated above in Equation 5.2. Figure 5.1 is a potential/pH, Pourbaix diagram which shows the theoretical regions of
immunity, passivity, and corrosion as potential and pH change, whereby lines a) and b) indicate the lower and upper limits of corrosion with oxygen reduction. The Al$^{3+}$ ions generated at the anode react with water (hydrolysis) to produce local acidity:

\[ \text{Eq. 5.5 Hydrolysis: } \text{Al}^{3+} (aq) + \text{H}_2\text{O}(l) \rightarrow \text{AlOH}^{2+} (aq) + \text{H}^+ (aq) \]

Aluminium can also undergo active dissolution in alkaline conditions:

\[ \text{Eq. 5.6 Alkaline Dissolution: } \text{Al}_4 (s) + 4\text{OH}^- (aq) \rightarrow 3\text{Al}(	ext{OH})_4^- (aq) + 3\text{e}^- \]

Localized corrosion can take a number of forms however is essentially promoted through the same principle; Firstly the passive film becomes damaged or impaired allowing dissolution to take place. Secondly dissolution products (ions) react with water, creating ions and leading to an increasingly acidic environment. Finally the acidic environment increases the rate at which dissolution takes place because it further prevents the passive oxide layer from reforming, thus corrosion continues to worsen.

### 5.3 Corrosion Mechanisms in Aluminium

There are four main types of localized corrosion that affect aluminium in aqueous environments: pitting corrosion, intergranular corrosion, exfoliation corrosion and intragranular corrosion, whereby the mode of corrosion that takes place depends strongly on the alloy, its processing history and its environmental conditions.

Pitting can be a severe form of localized corrosion and is the development of cavities in the surface of the metal. There are two steps in the pitting mechanism, firstly pit initiation, followed by pit propagation. Pitting is often initiated by surface defects or intermetallic particles at the surface and the presence of chlorides which damage the oxide layer [132]. Although barely visible from surface observations, pits can often grow unseen beneath the surface of the metal for some time before blistering. Pit propagation does not occur in all initiated pits, however those that do follow the series of steps illustrated in figure 5.2, which can lead to severe pitting as shown in figure 5.3.

- The damaged oxide layer leads to anodic dissolution of Al at the base of the pit, where electrons are transported to the surface and used in cathodic reactions.
- Al$_3^+$ ions are used in hydrolysis reactions leading to acidification within the pit, preventing formation of an oxide film within the pit.
- Chloride ions (Cl$^-$) are drawn into the pit to balance the positive charge generated by anodic reactions, producing a more aggressive environment preventing repassivation of the oxide layer so Al dissolution continues.

![Diagram](image1)

**Figure 5.2** Pitting process in aluminium due to the presence of an intermetallic particle

![Image](image2)

**Figure 5.3** Severe pitting attacks in HAZ of FSW AA7075-T651 [133]

Intergranular corrosion (IGC), as shown in figure 5.4 as a schematic diagram, is attack along grain boundaries or closely adjacent regions, without attack of the grain interior, and is caused by a difference in corrosion potential between grain boundary region and the grain itself. IGC can be caused by precipitation of anodically active intermetallic
particles on the grain boundaries, which corrode preferentially. It can also be caused by precipitation of more noble precipitates, particularly those containing copper, since this leads to formation of a copper depleted region adjacent to the boundary, which is more susceptible to anodic dissolution than the copper-rich matrix in the grains.

Figure 5.4 Schematic diagrams showing the role of the copper depleted zone in IGC

Figure 5.5 illustrates the presence of a Cu depleted zone surrounding Cu rich precipitates that form along a grain boundary. The Cu depleted zone has a lower corrosion potential compared with the surrounding Al matrix and the Cu rich precipitates at the grain boundary and so goes into dissolution preferentially via microgalvanic coupling [134].

Figure 5.5 Initial stages of IGC in the HAZ of FSW AA7075-T651 [133]

Note that the presence of small “white” grain boundary precipitates (arrows) and attack of the precipitate-free zones (black).
IGC can lead to intergranular stress corrosion cracking (IGSCC), which is the simultaneous interaction of sustained tensile stress and corrosion processes, leading to crack initiation and propagation which can result in premature brittle failure of a ductile material. Another form of corrosion often present in aluminium alloys is intragranular corrosion. Intragranular corrosion, sometimes considered as technically a form of pitting, is when the grain interior corrodes preferentially to the grain boundary. Often a result initially of pitting at the surface, followed by intergranular corrosion through the material following grain boundaries, until a grain is reached that will corrode preferentially to the grain boundary. Intragranular susceptible grains are often those with a higher than average dislocation density, leading to either a high degree of precipitation of active precipitates, or a reduction of copper in solid solution through copper rich phases forming at sub-grain boundaries.

Exfoliation corrosion, as shown in figure 5.6 is another form of localized corrosion that propagates along planes parallel to the rolling direction [135]. It is often as a consequence of IGC whereby the voluminous corrosion products are unable to dissolve into the environment and instead form along the paths of attack causing internal stresses leading to layers of metal being lifted from the surface [136]. It is a process that more often occurs in metal with strong directionality which creates highly elongated grains.

![Figure 5.6 Exfoliation corrosion on the surface of an Al-Li alloy [135]](image)

5.4 Influence of Alloyming Elements

Due its surface oxide layer, high purity aluminium is very corrosion resistant. However, it has insufficient strength for most practical applications [128], so is usually alloyed with elements such as Cu, Mg, Li, Zn, Mn, Si. The effect of additional alloying elements is often detrimental with regards to corrosion resistance [137]. When the alloying elements
are in solid solution the alloy generally remains corrosion resistant, however precipitation and the formation of second phase particles reduces the alloys corrosion resistance by increasing the corrosion potential by providing sites for the cathodic reaction, and also sites for the initiation of localized corrosion.

These second phase intermetallic particles can form during solidification either through cellular/dendrite boundaries, or by precipitation from the supersaturated solid solution (SSSS), and can be anodic, inert, or cathodic to aluminium [130,132]. Those particles that are more electrochemically active than aluminium act as localized anodes and go into dissolution themselves, while those that are less electrochemically active become net cathodes relative to the aluminium matrix where dissolution will occur [129].

### 5.5 Corrosion of Friction Stir Welded Aluminium Alloys

As discussed in chapter 4, FSW results in generation of various microstructural zones, i.e., the nugget zone, the TMAZ, and the HAZ. These zones exhibit different microstructural characteristics such as grain size and dislocation density, residual stress and texture, and precipitate size and distribution. Therefore, it is expected that the various microstructural zones will exhibit different corrosion susceptibility. For practical applications, it is very important to understand corrosion behavior of the FSW welds and elucidate the prevailing mechanisms for corrosion in various FSW alloys and various microstructural zones. In the past few years several studies were conducted with the aim to understand the effect of FSW on the corrosion and stress corrosion cracking (SCC) [138-143]. Generally, it has been found that the weld zones are more susceptible to corrosion than the parent metal. Friction stir welds of aluminium alloys such as 2219, 2195, 2024, 7075 and 6013 did not exhibit enhanced corrosion of the weld zones [138,144,145]. FS welds of aluminium alloys exhibit intergranular corrosion mainly located along the nuggets heat-affected zone (HAZ) and enhanced by the coarsening of the grain boundary precipitates. Coarse precipitates and wide precipitate-free zones promoted by the thermal excursion during the welding are correlated with the intergranular corrosion. The effect of FSW parameters on corrosion behaviour of friction stir welded joints was reported by many workers [142,146]. The effect of processing parameters such as rotation speed and traverse speed on corrosion behaviour of friction stir processed high strength precipitation hardenable AA2219-T87 alloy was investigated [146,147]. The results indicate that rotation speed has a major influence in determining the rate of corrosion, which is attributed to the breaking down and dissolution of the intermetallic particles. Jariyaboon et al. [142] studied the effect of welding
parameters (rotation speed and travel speed) on the corrosion behaviour of friction stir welds in the high strength aluminium alloy AA2024–T351. It was found that rotation speed plays a major role in controlling the location of corrosion attack. Localized intergranular attack was observed in the nugget region for low rotation speed welds, whereas for higher rotation speed welds, attack occurred predominantly in the HAZ.

Many investigators studied the corrosion resistance of aluminium alloys weld joints made by using FSW and other conventional fusion welding techniques such as metal inert gas (MIG) and tungsten inert gas (TIG) [148-150]. The results indicated that joints welded using FSW are more resistant to corrosion than those welded using MIG. In FSW joints, however, the differences between the weld nugget (WN), thermo-mechanically affected zones (TMAZ) and heat affected zones (HAZ) were not as evident as in TIG joints; what is more, inside FSW weld bead, the retreating zone showed a behaviour nobler than the advancing one. It has been found that most of the work carried out in the field of corrosion resistance of FSW is focusing on wrought aluminium alloys [138-152], especially, high strength alloys such as 7xxx and 2xxx series. A very few literature papers are reported on corrosion resistance of FSW joints of aluminium alloys AA6082 and AA6061.

5.6 Summary of Literature Review

From the above literature study it is evident that there is a potential for Friction Stir Welding of aluminium alloys in various fields. FSW continues to be the subject of investigations and further development and improvements in the joining of aluminium alloys remains one of the aims. Even many studies have been performed; there is still a considerable need to further examine existing and new combinations of process parameters. Despite the large amount of published literature about the FSW process, systematic information does not exist on the influence of the tool geometry and the process parameters on the weld quality for a large range of materials, thicknesses and joint configurations. The objective of present research work aims to acquire the fundamental knowledge of the FSW process and to investigate the feasibility of incorporating this technology with existing resources to weld aluminium alloys 6xxx series in the abutting configuration and characterize the optimum operating parameters while establishing sound mechanical integrity of the friction stir welded joint.