Localized Corrosion
of
Friction Stir Spot Welds
in
Magnesium AZ31 Alloy

By Andre James

A thesis submitted in conformity with the requirements
for the degree of Master of Applied Science
Materials Science and Engineering
University of Toronto

© Copyright by Andre James 2012
Localized Corrosion of Friction Stir Spot Welds
in Magnesium AZ31 Alloys

Andre James
Master of Applied Science
Materials Science and Engineering
University of Toronto
2012

Abstract

A scanning reference electrode technique (SRET) apparatus has been designed and commissioned to investigate the corrosion of friction stir spot welds (FSSW) made in AZ31 magnesium alloys. The operational parameters of the apparatus have been calibrated to give good spatial resolution. By combining the SRET data with material flow data and immersion test data it was found that the FSSW process caused the formation of distinct noble and active regimes within the weld area. The noble region was aligned with the stir zone (SZ) and was caused by a dynamically recrystallized grain structure which is void of dislocations / twins, and β Mg17Al12. Localized corrosion attack was observed in both SRET and immersion testing along the thermo-mechanically affected zone (TMAZ). The same effect was consistently observed with a flat versus concave shoulder tool, and dwell times of 1s and 4s.
Acknowledgments

I would like to express my deepest gratitude to my supervisors, Professors Steven Thorpe and Tom North. They have been extremely invaluable throughout the program and I cannot thank them enough.
# Table of Contents

List of Tables........................................................................................................vi
List of Figures........................................................................................................vii
List of Appendices................................................................................................x

1. Introduction.........................................................................................................1

2. Literature Review...............................................................................................3
   2.1 Structure and Properties of Magnesium Alloys.............................................3
   2.2 Main Constituent Phases in Magnesium Alloys.............................................6
   2.3 Microstructural Evolution During Friction Stir Spot Welding.........................8
   2.4 Effects of Microstructural Distribution.........................................................11
      2.4.1 Hardness Profile....................................................................................11
      2.4.2 Residual Stress Profile..........................................................................12
   2.5 Corrosion of Magnesium Alloys.................................................................13
      2.5.1 Effect of Alloying Additions...................................................................15
         2.5.1.1 Deleterious Additions......................................................................15
         2.5.1.2 Beneficial Additions........................................................................18
   2.6 Microstructural Effects on Corrosion of Magnesium Alloys.........................19
      2.6.1 Effect of Grain Size on Corrosion..........................................................20
      2.6.2 Effect of Second Phase Particles on Corrosion......................................21
      2.6.3 Effect of Twins and Dislocations on Corrosion.......................................22
   2.7 Abnormal Grain Growth..............................................................................24
   2.8 Corrosion of Friction Stir Spot Welds in Magnesium Alloys.........................27
   2.9 The Scanning Reference Electrode Technique..............................................28

3. Objectives..........................................................................................................32

4. Experimental Technique.....................................................................................33
   4.1 AZ31 Base Material......................................................................................33
   4.2 Friction Stir Spot Welding.............................................................................34
   4.3 SRET Sample Preparation............................................................................38
4.4 Construction of the SRET Apparatus .........................................................40
4.5 SRET Calibration – Levelling and Aligning the Stage........................................44
4.6 SRET Calibration – Computer Set Up..........................................................46
4.7 Establishing the SRET Operational Parameters..............................................47
4.8 SRET Scanning Procedure ..........................................................................55
4.9 FSSW Immersion Tests .................................................................................57
4.10 Optical Microscopy.......................................................................................57
4.11 Etching for Microstructure and Microstructural Zones.................................57
4.12 FSSW Average Grain Size Analysis ............................................................58
4.13 FSSW Abnormal Grain Growth Analysis .....................................................59

5. Results and Discussion ......................................................................................60
   5.1 Theoretical Calculation of Spatial Resolution of SRET .................................60
   5.2 Error Analysis of SRET Potential Measurements.........................................55
   5.3 Establishing a Baseline Potential for SRET Potential Measurements ..........65
   5.4 SRET Potential Distribution – Flat Shoulder..............................................66
   5.5 SRET Potential Distributions – Concave Shoulder.................................69
   5.6 Effect of Tool Geometry on SRET Potential Distribution............................72
      5.6.1 Influence of Grain Size on Potential Distribution..............................72
      5.6.2 Influence of Abnormal Grain Growth on Potential Distribution..........76
      5.6.3 Influence of Precipitate Distribution on Potential Distribution............78
   5.7 Effect of Dwell Time on SRET Potential Distribution.................................80

6. Conclusions ......................................................................................................85

7. Future Work......................................................................................................87
List of Tables

Table 2.1  Nominal Composition of AZ31 [2] .................................................................3
Table 2.2  Mechanical properties of common alloys [11] ..............................................5
Table 2.3  Principal phases in AZ31 ............................................................................6
Table 2.4  Tolerance limits for magnesium and its alloys [9] .......................................17
Table 2.5  Galvanic potential and galvanic current between different alpha phases and β Mg₁₇Al₁₂ [36] .................................................................19
Table 4.1  Nominal composition of base AZ31 ..............................................................33
Table 4.2  Summary of FSSW parameters ...................................................................38
Table 4.3  Summary of operational parameters for the SRET ...............................55
Table 5.1  Max/min height values for 5 different sample areas .....................................63
List of Figures

Figure 2.1  Al-Mg binary phase diagram [10].................................................................4

Figure 2.2  a) Microstructure of as-cast AZ31 [12]  b) Microstructure of as-cast AZ91 [13].6

Figure 2.3  SEM image of MnAl phase in a) as-cast AZ61 and b) extruded AZ61 [22].........7

Figure 2.4  Optical micrograph of AZ31 rolled 25% at room temperature [20]..................8

Figure 2.5  Schematic diagram of cross section of friction stir spot weld showing the characteristic microstructural regions [25].................................................................8

Figure 2.6  AZ31 B-H24 typical optical micrograph of: a) SZ b) TMAZ c) HAZ and d) base material [19].................................................................9

Figure 2.7  Peak temperatures in FSSW at 3000rpm, 4s dwell time a) AZ91 and b) AZ31 [31].................................................................11

Figure 2.8  Microhardness profile along the centerline in an AZ31 FSW weld [32]..............12

Figure 2.9  Residual stress in a FSW made in AZ31 sheet. Case 1 is for a FSW made with a tool consisting of a pin and shoulder. Case 2 is a FSW made with a tool consisting of only a shoulder. Residual stress was measured using neutron diffraction and contour methods [33].................................................................13

Figure 2.10 SEM surface morphology of AZ 31 after immersed in 1M NaCl at 25°C for 1 hour (left) and 8 hours (right) [35].................................................................15

Figure 2.11 Schematic showing definition of tolerance limit..............................................16

Figure 2.12 Grain size vs. Mn content for high purity Mg alloys [35].................................18

Figure 2.13 Effect of AZ31 grain size on corrosion current in 3.5% NaCl [44]....................20

Figure 2.14 Schematic showing the “positive effect” where a large grain boundary volume fraction supports the fast formation of a passive layer [46].................................21

Figure 2.15 Corrosion current density and anodic current density in the passive state as a function of strain (top), corrosion current density and corrosion potential (bottom) [49]........................................................................23

Figure 2.16 TEM images showing (a) a large abnormal grain containing many dislocations and (b) dislocation-free fine matrix grains in the 2.4-mol%- TiO2-excess SrTiO3 compact annealed at 1470°C for 2 h in air [60].................................................................26
Figure 2.17  The variations of the average grain size and the size of the largest grains with the level of deformation in the specimens heat-treated at 1150°C for 1 h [61]........26

Figure 2.18  The grain size measured in the large grain regions plotted as a function of total strain in compression. The samples were all compressed at 1650°C and then annealed at 1950°C [57].................................................................27

Figure 2.19  Amount of Mg_{17}Al_{12} in a) base material and b) weld nugget (SZ) [62]........28

Figure 2.20  Differences in corrosion attack between stir zone (nugget) and surrounding material [62].................................................................28

Figure 2.21  Schematic showing current flow from anode to cathode in an electrolyte [64].29

Figure 2.22  Potentiodynamic polarization showing pitting potential [65]..................30

Figure 2.23  SRET data from 304 stainless steel in ferric chloride showing increase in the number of pits and pitting activity as a function of time [66].........................30

Figure 2.24  SRET line data above a scratch in the polymer coating showing the potential response against time [68].........................................................31

Figure 4.1  Base material alloys sheets.................................................................33

Figure 4.2  Friction Stir Link Bench-top Welding Unit
a) Sample holder b) 6 axis load cell c) FSSW tool
d) rotary servomotor e) linear servomotor..............................................35

Figure 4.3  a) flat shoulder tool b) 10° concave shoulder tool c) scroll shoulder tool ........37

Figure 4.4  a) pin touch position b) pounce position c) plunge depth position........37

Figure 4.5  SRET sample prepared for testing.....................................................40

Figure 4.6  SRET apparatus.................................................................41

Figure 4.7  Picture and schematic of the CH Instruments reference electrode...............42

Figure 4.8  Burleigh piezoelectric inch worm motors........................................43

Figure 4.9  a) Electrochemical cell surrounded by Faraday cage b) Acrylic electrochemical cell .................................................................43

Figure 4.10  Newport tilt stage.................................................................44
Figure 4.11  Schematic showing locations of 2 pairs of contact points used for establishing the planarity of the stage relative to the scanning reference electrode.................46

Figure 4.12  Schematic diagram of electrochemical cell set up........................................47

Figure 4.13  Schematic drawing of modified AZ31 sample; grey (AZ31) brown (copper) red (scanning path).................................................................48

Figure 4.14  Effect of scanning speed on the SRET sensitivity.........................................49

Figure 4.15  Calculated percent error for the effect of scan speed....................................50

Figure 4.16  Effect of probe height on SRET sensitivity..................................................51

Figure 4.17  Calculated percent error for the effect of scanning height............................52

Figure 4.18  Effect of solution concentration on SRET sensitivity....................................53

Figure 4.19  Calculated decay distances as a function of solution concentration ...............54

Figure 4.20  Schematic representation of SRET scanning procedure. Each arrow represents a single 3250μm line scan.........................................................56

Figure 4.21  a) Macro image of FSSW with red box showing area where grain size measurements are taken, b) Micro image with blue box showing size and location of grain size analysis box, 100μm x 50μm.....................................................58

Figure 5.1  Schematic diagram showing the iso-potential field lines between an anode-cathode galvanic couple in an electrolyte [64].................................................61

Figure 5.2  Oblique plot of area 1 showing surface morphology and height values........63

Figure 5.3  Linear relationship between probe height and SRET potential.......................64

Figure 5.4  Graph of potential vs. time for base AZ31 in 0.086 M NaCl at room temperature........................................................................................................65

Figure 5.5  Collage of images for flat shoulder testing a) Picric acid etched FSSW in AZ31 showing microstructure b)SRET potential distribution c) Overlay of SRET and microstructure  d) Material flow e) Overlay of material flow and SRET f) 2 day immersion of FSSW in room temperature 0.086M NaCl........................................68

Figure 5.6  Collage of images for concave shoulder testing a) Picric acid etched FSSW in AZ31 showing microstructure b)SRET potential distribution c) Overlay of SRET and microstructure  d) Material flow e) Overlay of material flow and SRET f) 2 day immersion of FSSW in room temperature 0.086M NaCl........................................71

Figure 5.7  Comparison of the average grain size measured 50μm below the top surface of three FSSW welds made using different tool designs.................................72
Figure 5.8 SEM images of FSSW welds with incorporated WC tracer element in a) flat shoulder b) concave shoulder c) scroll shoulder [71]......................73
Figure 5.9 Displacement vs. radial position for FSSW with flat shouldered tool...........74
Figure 5.10 Schematic showing the evolution of strain rate as a function of radial position.................................................................75
Figure 5.11 Graph showing the number of abnormal grains as a function of radial position in the FSSW weld.................................................................76
Figure 5.12 Grain size analysis box showing the relative number of grains (and abnormal grains) in spot welds made using the flat shouldered tool (top), the concave shoulder tool (middle) and the scrolled shoulder tool (bottom). Box length = 100um.................................................................77
Figure 5.13 Micrograph of GTA AZ31 fusion zone (FZ) showing α grains and intergranular Mg₁₇Al₁₂ [74].................................................................79
Figure 5.14 SRET potential distributions for welds made with a flat shoulder with a dwell time of a) 1s b) 4s
Approx. areas scanned outlined in red for welds made with c) 1s dwell d) 4s dwell.................................................................80
Figure 5.15 FSSW samples etched in picric acid showing size of SZ and TMAZ in samples made with 1s dwell (left) and 4s dwell (right).................................81
Figure 5.16 Relationship between SZ width and dwell time in FSSW AZ31 [31]........82
Figure 5.17 SRET potential distributions with SZ width drawn in for samples made with a) 1s dwell b) 4s dwell.................................................................82
Figure 5.18 Optical image showing corrosion activity located at 45° along TMAZ interface.83
Figure 5.19 Micrograph of AZ91 showing alignment of Mg₁₇Al₁₂ in deformed TMAZ [76].................................84
List of Appendices

Appendix A – Flat Shoulder 1s SRET Potential Distributions

Appendix B – Concave Shoulder 1s SRET Potential Distributions

Appendix C – Flat Shoulder 4s SRET Potential Distributions

Appendix D – Sample Calculation for Percent Error in Scan Speed

Appendix E – Sample Calculation for Percent Error in Scan Height

Appendix F – Sample Calculation for Decay Distance vs. Solution Concentration
1 Introduction

Magnesium is an alkaline earth metal with many attractive properties making it suitable for use in many engineering applications. Magnesium’s high strength and stiffness to weight ratio, good castability, high workability, low-toxicity, high thermal and electrical conductivity and high damping characteristics can be uniquely exploited in engineering applications. Magnesium is the 8\textsuperscript{th} most abundant element by mass \cite{1} and because of these properties, magnesium is poised to be an economical, sustainable, practical and safe metal for future engineering/structural use.

With a recent push for improved fuel efficiencies and reduced emissions to mitigate the negative impact transportation has on the environment, the low density and high strength of magnesium alloys makes them an attractive solution in all modes of transportation.

One particular magnesium alloy, AZ31, is a commercially available alloy typically used for such purposes as extruded bars, rods, shapes, sheet, structural sections and tubing. The density of AZ31 is approximately 1.77g/cc \cite{2}, whereas the density of steel is about 7.85g/cc \cite{2} making AZ31 4.4 times less dense than the steel. If we consider a simple situation where a force of 10000N is to be supported by a rod in tension, and the yield strengths of steel and AZ31 are 500MPa and 200MPa (typical values according to \cite{2,3}), then the weight of an adequate supporting member would be 43% lighter if made of AZ31 as compared to steel. Extend this to the realm of automobiles and noting the amount of steel used in their production, the overall gain in either performance or fuel economy from using magnesium alloys can be clearly comprehended. This is further illustrated commercially by taking a small component such as the sub frame for a tailgate on a Volkswagen. When the material to be stamped is changed from steel, to aluminum and then to magnesium, the weight reduces from 10.5kg to 8.5kg and to 5.4kg respectively \cite{4}. The theme of weight reduction is seen in many auto manufacturers’ marketing campaigns, e.g. Mazda’s “1g strategy”. All automobile manufacturers are striving to maximize the relationship which states that every 100kg of weight reduction yields a 5% reduction in fuel requirements \cite{5}.
These lightweight, high strength and ease in manufacturing properties are very attractive for the automotive industry when combined with magnesium’s ease of fabrication using a novel process called friction stir spot welding (FSSW). Traditional resistance spot welding (RSW) is not well suited for joining magnesium alloys, since the welded joints contain porosity and are prone to cracking, which has detrimental effects on joint mechanical properties. FSSW was developed by The Welding Institute of England in 1991 and is a variant of the friction stir welding process (FSW). During FSSW, a rotating tool is inserted into the overlap sheet assembly creating a welded joint. This joining process has numerous advantages compared to traditional resistance spot welding. For example, no fumes are created, there is freedom from expulsion of molten metal, no expensive and bulky power transformers are required, there are no electrode wear problems, there is easy machine set-up, there is no noise and completed joints are free from cracking and porosity during fabrication of Mg-alloys.

In spite of the excellent mechanical properties and low density of magnesium alloys and their ease of fabrication using friction stir spot welding, electrochemical activity is the key characteristic that is preventing them from being used on a large scale. Magnesium is the most electrochemically active structural metal, and as such, it corrodes in many aqueous environments. There has been much research investigating the corrosion behavior of cast and wrought Mg-alloys and a limited amount of research evaluating the corrosion resistance properties of Mg-alloy friction stir welds. However, the corrosion resistance behavior of Mg-alloy friction stir spot welds has not been investigated. Research examining the corrosion resistance properties of friction stir spot welds made in magnesium alloys is therefore a prerequisite if magnesium alloys are to be used in the future to help combat greenhouse gas emissions and protect the environment.
2 Literature Review

2.1 Structure and Properties of AZ31 Magnesium Alloys

To achieve the desired mechanical properties, pure magnesium is alloyed with other elements, as pure magnesium alone does not have the required strength, stiffness etc. for many engineering applications. Magnesium has a hexagonal crystal structure with lattice parameters \( a = 0.320 \) nm, \( c = 0.520 \) nm and a \( c/a \) ratio = 1.624. Magnesium’s atomic diameter is 0.320nm, meaning that there is a favourable tendency to alloy with elements who’s atomic diameter is 0.320nm +/- 15% according to the Hume Rothery rules for solid solutions; namely aluminum, zinc, manganese, cerium, yttrium, silver, zirconium and thorium \([6-8]\).

The resulting alloys such as AZ31, AM50 and ZK60, ZE41 have enhanced mechanical properties, however, the corrosion susceptibility of the alloys is increased as compared to pure magnesium. The nomenclature of resulting magnesium alloys can be explained using the following reference code: A-aluminum, E-rare earth, H-thorium, K-zirconium, M-manganese, Q-silver, S-silicon, and Z-zinc. The following two numbers then specify the nominal concentrations in weight percent. Therefore an alloy of designation AZ31 is a magnesium alloy with a nominal composition of 3 wt. % aluminum, 1 wt. % zinc and the balance magnesium. The nominal composition of AZ31, which is the alloy used in this investigation, is outlined in Table 2.1 below. Manganese is present in small quantities, as are other elements such as iron, copper and nickel \([9]\) as trace elements. However, in terms of the main phase formation, the trace elements (Fe, Cu and Ni) do not play a role meaning that the AZ31 alloy can be represented in an aluminum-magnesium binary phase diagram.

<table>
<thead>
<tr>
<th>Element</th>
<th>Aluminum</th>
<th>Zinc</th>
<th>Manganese</th>
<th>Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Percent</td>
<td>3</td>
<td>1</td>
<td>0.2</td>
<td>95.8</td>
</tr>
</tbody>
</table>

Table 2.1 Nominal Composition of AZ 31 \([2]\)
The mechanical properties of common magnesium alloys along with other common aluminum and steel alloys for comparison can be found in table 2.2. When the densities of the magnesium alloys are taken into consideration, it can be seen that magnesium alloys are a possible alternative to both steel and aluminum alloys for structural applications.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Condition</th>
<th>Tensile strength [MPa]</th>
<th>Yield strength [MPa]</th>
<th>Ductility [%EL in 50mm]</th>
<th>Density [g/cc]</th>
<th>Specific tensile strength [MPa cc/g]</th>
<th>Specific yield strength [MPa cc/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aluminum alloys</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al 2024</td>
<td>T4 heat treated</td>
<td>470</td>
<td>325</td>
<td>20</td>
<td>2.77</td>
<td>169.7</td>
<td>117.3</td>
</tr>
<tr>
<td>Al 6061</td>
<td>T4 heat treated</td>
<td>240</td>
<td>145</td>
<td>23</td>
<td>2.7</td>
<td>88.9</td>
<td>53.7</td>
</tr>
<tr>
<td>Al 7075</td>
<td>T6 heat treated</td>
<td>570</td>
<td>55</td>
<td>11</td>
<td>2.8</td>
<td>203.6</td>
<td>19.6</td>
</tr>
<tr>
<td><strong>Steel alloys</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A516 Grade 70</td>
<td>Hot rolled</td>
<td>485</td>
<td>260</td>
<td>21</td>
<td>7.85</td>
<td>61.8</td>
<td>33.1</td>
</tr>
<tr>
<td>AISI 1040</td>
<td>Oil quenched</td>
<td>690</td>
<td>510</td>
<td>26</td>
<td>7.85</td>
<td>87.9</td>
<td>65.0</td>
</tr>
<tr>
<td>AISI 304</td>
<td>Annealed</td>
<td>515</td>
<td>205</td>
<td>8</td>
<td>8</td>
<td>64.4</td>
<td>25.6</td>
</tr>
<tr>
<td><strong>Magnesium alloys</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZ31B</td>
<td>As extruded</td>
<td>262</td>
<td>200</td>
<td>15</td>
<td>1.77</td>
<td>148.0</td>
<td>113.0</td>
</tr>
<tr>
<td>ZK60A</td>
<td>Artificially aged</td>
<td>350</td>
<td>285</td>
<td>11</td>
<td>1.83</td>
<td>191.3</td>
<td>155.7</td>
</tr>
<tr>
<td>AZ91D</td>
<td>As cast</td>
<td>230</td>
<td>150</td>
<td>3</td>
<td>1.81</td>
<td>127.1</td>
<td>82.9</td>
</tr>
</tbody>
</table>

Table 2.2  Mechanical properties of common alloys [11]
In this investigation the wrought magnesium alloy AZ31 will be the main focus for the corrosion study. The reasons for choosing AZ31 are that it has the mechanical properties/formability/machinability and weldability, which make it a viable candidate for use in the auto industry. This explains the current global interest in this Mg-alloy.

### 2.2 Main Constituent Phases in AZ31 Magnesium Alloys

Typical microstructures of common magnesium alloys can be seen in figure 2.2 and the main constituent phases in AZ31 are listed in table 2.3.

![Figure 2.2](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Nominal Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha</td>
<td>3% Al, 1%Zn, balance Mg</td>
</tr>
<tr>
<td>Beta</td>
<td>Mg_{17}Al_{12}</td>
</tr>
<tr>
<td>Gamma</td>
<td>Al₈Mn₅</td>
</tr>
</tbody>
</table>

Table 2.3 Principal phases in AZ31
The primary phase is alpha, a solid solution of magnesium, aluminum, and zinc in their respective concentrations. Typical alpha grain sizes observed in as-cast alloys depends on the casing/cooling conditions, and is on average around 100 µm [12-14]. The beta and gamma phases, Mg_{17}Al_{12} and Al_{8}Mn_{5} respectively, form during cooling when casting the alloy. The beta phase precipitates out along the grain boundaries with a similar size to the alpha grains (~100 µm), effectively surrounding the alpha matrix. The gamma phase can form in either a dendritic or leaf-like structure with sizes ranging from 10-30 µm [15] (figure 2.3) or as uniformly dispersed 5-30 nm particles [16].

To further increase the strength of the alloy, after casting it can be rolled or extruded with varying degrees of reduction ratios to introduce controlled plastic deformation. This effectively decreases dislocation motion, which increases a material's resistance to plastic deformation. However, after rolling/extrusion the microstructure and morphology of the constituent phases change. The alpha matrix transforms from an equiaxed microstructure consisting of relatively large grains (figure 2.2), to a microstructure consisting of smaller grains ranging in size from 5-175 microns depending on the degree of cold working [17-20, 12]. The average alpha grain size in AZ31 is 10 µm [16]. The microstructure also changes to one full of twins (twinning is the main deformation mechanism in magnesium alloys) penetrated by local flow zones [21, 22] (figure 2.4). The brittle beta Mg_{17}Al_{12} particles are broken up after rolling and their size reduces to around 10 µm [23]. As well, after rolling/extrusion the size of the dendrite shaped gamma phase particles decrease from 10-30 µm to 4-5 µm diameter finely dispersed spherical particles [24].

Figure 2.3 SEM image of MnAl phase in a) as-cast AZ61 and b) extruded AZ61 [22]
2.3 Microstructural Evolution in AZ31 During Friction Stir Spot Welding

Performing FSSW on a material introduces both a high degree of plastic deformation and heat into the system which alters the grain structure. Three zones are created during friction stir spot welding (FSSW), namely the stir zone (SZ), the thermomechanically affected zone (TMAZ) and the heat affected zone (HAZ). The base material (BM) beyond the weld area is unaffected (figure 2.5 & 2.6).

Figure 2.4 Optical micrograph of AZ31 rolled 25% at room temperature [20]

Figure 2.5 Schematic diagram of cross section of friction stir spot weld showing the characteristic microstructural regions [25]
Examination of the microstructural features produced following friction stir welding has shown that the stir zone consists of equiaxed grains, which are dynamically recrystallized [19, 26]. The grain structure does not contain twins, and this is indicative of the high temperature nature of the FSW process. [26] Being dynamically recrystallized, and therefore going through processes of recovery and grain growth, the SZ grains are typically larger than the base material and have reported average grain sizes in the vicinity of 10um. [26] Beginning with extremely large base metal grain sizes of 175um, Esparza indicted that a 25um size of the grains in the stir zone was only attained after appreciable post welding grain growth [20]. The TMAZ has a similar microstructure as the SZ, however its exposure to heat and deformation is somewhat less than in the SZ and therefore it has a partially recrystallized grain structure. The HAZ, common to all welding techniques, is essentially an area of the weld that has not undergone any plastic deformation. However, the HAZ region is heated during joining, which produces some grain growth and dissolution of second-phase particles. Wang’s work [27] examining the mechanical
properties of friction stir welded MB3 magnesium alloy shows that failure of the majority of the
tensile test specimens occurred in the HAZ region. Complementing this work, Darras [28]
showed that upon friction stir processing of AZ31, the heat affected zone had the lowest
microhardness values. The reason for such results is that the HAZ does not experience any
deformation leading to any grain refinement or dislocation density increase. However, the HAZ
does experience a sufficient temperature to soften the material.

Although much work has not been completed investigating the phase composition/distribution
and morphology after friction stir spot welding, some hypotheses can be made. The phase
diagram (figure 2.1) shows that above 437°C the beta phase Mg17Al12 dissolves into the
magnesium matrix. It has been shown by Commin and Xunhong [17, 29, 30] that with certain
welding parameters this temperature is achievable during FSW of AZ31 (figure 2.7) and thus
upon cooling, the beta phase distribution throughout the SZ is changed due to the mechanical
stirring and uneven re-precipitation of this phase.

With respect to the gamma phase Al8Mn5, again there is no work done in determining the fate of
these particles during post welding. However, in an investigation where AZ31 was resistance
spot welded, the morphology of the Al8Mn5 particles remained unchanged during post welding.
The reason for this is that the peak temperature during RSW was around 770°C, whereas the
melting temperature of Al8Mn5 is approximately 1050°C [24]. The peak temperatures during
FSSW are around 437°C (eutectic temperature of alpha-Mg + Mg17Al12) and it is expected that
temperature will not have an effect on the morphology of Al8Mn5 particles. However, that is not
to say that the mechanical stirring effect during FSSW will not have an affect the
morphology/distribution of Al8Mn5 particles; in fact, they are broken up into finely dispersed 4-5um spherical particles [24].
Figure 2.7  Peak temperatures in FSSW at 3000rpm, 4s dwell time  
   a) AZ91 and b) AZ31 [31]

2.4 Effects of Microstructural Distribution

2.4.1  Hardness Profile

The FSSW process involves intense plastic deformation and heat generation, which affects the microhardness profile across completed welds. Studies have shown that the microhardness measured in Hv in friction stir welded Mg decreases close to the center of the stir zone [32] (see figure 2.8). The reason for this decrease in the hardness values close to the weld center is due to dynamically recrystallized grain formation typically in the stir zone. Material in this region is softer material than the surrounding base material because of the dissolution of the strengthening precipitates Mg$_{17}$Al$_{12}$ [33] and the lack of dislocations and twins (recrystallized microstructure) in the SZ/TMAZ from the frictional heating of the shoulder. The surrounding base material
retains its many dislocations and twins from the rolling process, and retains the second phase precipitates which both act to increase the resistance to plastic deformation (hardness) of a material.

Figure 2.8 Microhardness profile along the centerline in an AZ31 FSW weld [32]

2.4.2 Residual Stress Profile

The high heat and high axial loads from the shoulder during a FSSW operation produces distinct zones that have different magnitudes of residual stress [33]. These residual stresses are either compressive (negative stress in MPa in Fig. 2.9) or tensile (positive stress in MPa in Fig. 2.9). The residual stress as a function of position within a FSSW in AZ31 can be seen in figure 2.9.
Figure 2.9 Residual stress in a FSW made in AZ31 sheet. Case 1 is for a FSW made with a tool consisting of a pin and shoulder. Case 2 is a FSW made with a tool consisting of only a shoulder. Residual stress was measured using neutron diffraction and contour methods [33].

These plots (case 1 specifically) show that the residual stress sharply decreases near the SZ indicating that the SZ is in a state of compression, while the surrounding material, which has higher residual stress values is in tension. The fact that the residual stress does not drop off as much in case 2 indicates that severe plastic deformation and dissolution of strengthening precipitates causes microstructural softening and decreases residual stress.

2.5 Corrosion of Magnesium Alloys

Despite its potential utility as a structural metal with its low density and adequate mechanical properties, magnesium is the most electrochemically active species and this causes the metal to corrode in many environments. One important indicator of the corrosion susceptibility of a material in a given environment is the exchange current density ($i_{\text{corr}}$) of a metal. The exchange current is the reversible rate, which flows spontaneously in an unbiased material immersed in an environment. A large exchange current density indicates that the corrosion resistance is poor, since a large amount of current can be exchanged between the metal and the electrolyte.
effectively forming the corrosion product and dissolving the metal. This kind of data can be obtained using 3-electrode potentiodynamic anodic polarization tests, where the potential of a metal is varied through a pre-determined range at a specific rate, and the corresponding current density is recorded.

Corrosion of magnesium alloys is controlled by 4 key factors: 1) the composition of the alpha magnesium phase, 2) the electrochemical properties of different phases, 3) the distribution of secondary phases and their galvanic interaction, and 4) the presence of impurities. The corrosion of magnesium alloys in aqueous environments involves some key mechanism considerations: corrosion takes place at the breaks in the partially protective hydroxide [34], giving rise to the following equations, which will be used as a reference for further discussion.

Anodic reaction: \[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \] \[1\]

Cathodic reaction: \[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \] \[2\]

Film formation: \[ \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \] \[3\]

Overall reaction: \[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \] \[4\]

Corrosion can be confirmed visually using scanning electron microscopy following immersion tests in an aggressive environment. Cheng et al. [35] found that after one hour immersion in a solution of 1 M NaCl AZ31 had visible corrosion products (Mg(OH)₂) on the surface. After 8 hours Cheng et al. found that AZ31 suffered from corrosion pits across the whole surface (figure 2.10) This generally uniform attack is due to the galvanic couples of alpha Mg phase and β Mg₁₇Al₁₂ second phase particles (discussed previously) distributed throughout the alloy. Mathieu et al. [36] found that the corrosion potential difference between β Mg₁₇Al₁₂ and alpha AZ91 is likely the reason for the microgalvanic corrosion activity between the phases. A non-uniform distribution of second phase particles will result in a more localized attack.
2.5.1 Effect of Alloying Additions

Alloying additions include any elements that are not present in the nominal composition of the alloy (AZ31). These include both alloying additions to achieve the desired mechanical properties and atomic impurities resulting from the forming process and original alloy stock.

2.5.1.1 Deleterious Additions

While some atomic additions of elements are beneficial to the corrosion resistance, some elements are deleterious to the corrosion resistance. These elements that decrease the corrosion resistance are termed impurity elements. There are four main transition metal impurities, namely, iron, copper, nickel and cobalt that have a major deleterious effect on the corrosion rate [9, 34, 37].
Focusing on iron, copper and nickel one can see from figure 2.11 that a particular concentration exists at which the corrosion rate is increased significantly for each element. This limit is termed the tolerance limit (figure 2.11). The tolerance limit is different for different alloys and different impurities [1] (table 2.4).

![Figure 2.11](image) Schematic showing definition of tolerance limit

The exact mechanism behind the tolerance limit is not known, however, there are two major hypotheses: 1) impurity segregation/phase precipitation and 2) surface deposition. With respect to impurity segregation, it is postulated that after exceeding the tolerance limit the impurities segregate out and precipitate as a high concentration (Cu, Fe, Ni) precipitate and act as active corrosion catalysts, supporting the cathodic reaction of hydrogen evolution (reaction 2). [1, 34]

The surface deposition postulate suggests that an exchange of Mg atoms for impurity (Fe, Ni, Cu) atoms occurs at the surface due to the high concentration of impurity ions at the surface caused by magnesium alloys dissolution. [34] With these possible mechanisms, below these tolerance limits, the corrosion rate of magnesium alloys is significantly reduced. [1]
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe</th>
<th>Mn limit %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM50A</td>
<td>0.01</td>
<td>0.002</td>
<td>0.0049(a)</td>
<td>0.26-0.6(a)</td>
</tr>
<tr>
<td>AM60A</td>
<td>0.35</td>
<td>0.03</td>
<td>...</td>
<td>0.13-0.6</td>
</tr>
<tr>
<td>AM60B</td>
<td>0.1</td>
<td>0.002</td>
<td>0.005(a)</td>
<td>0.24-0.6(a)</td>
</tr>
<tr>
<td>AS41A</td>
<td>0.06</td>
<td>0.03</td>
<td>...</td>
<td>0.20-0.50</td>
</tr>
<tr>
<td>AS41B</td>
<td>0.02</td>
<td>0.002</td>
<td>0.0035</td>
<td>0.35-0.7</td>
</tr>
<tr>
<td>AZ91A</td>
<td>0.1</td>
<td>0.03</td>
<td>0.3(b)</td>
<td>0.13-0.50</td>
</tr>
<tr>
<td>AZ91B</td>
<td>0.35</td>
<td>0.03</td>
<td>0.3(b)</td>
<td>0.13-0.50</td>
</tr>
<tr>
<td>AZ91D</td>
<td>0.3</td>
<td>0.002</td>
<td>0.005</td>
<td>0.15-0.5(b)</td>
</tr>
</tbody>
</table>

Table 2.4 Tolerance limits for magnesium and its alloys [38] (a) In alloys AS41B, AM50A, AM60B and AZ91D if either the minimum Mn limit or maximum Fe limit is not met, then the Fe/Mn ratio shall not exceed 0.010, 0.015, 0.021 and 0.032, respectively (b) not specified but included in the limits for “other metals”.
2.5.1.2 Beneficial Additions

Not all metallurgical additions are deleterious to the corrosion resistance of magnesium alloys. Elements such as manganese, zirconium, aluminum and zinc can increase the corrosion resistance by increasing the tolerance limits.

For magnesium, the main purpose of manganese is to form a precipitate FeMnAl that effectively removes impurities such as iron from the matrix. Removing impurities such as iron can greatly improve the corrosion resistance of the alloy by reducing the impurity levels below the tolerance limit (discussed later) [38]. This can be seen in such alloys as AM60 where manganese can form AlMnFe precipitates which refine the grain structure [35, 9, 39-41] (figure 2.12).

![Figure 2.12](image)

**Figure 2.12** Grain size vs. Mn content for high purity Mg alloys [35]

Although there is no consensus of opinion or data concerning the role of aluminum on the corrosion resistance of magnesium alloys, it has been found that concentrations in the range from 5-62.3% have improved corrosion resistance [35, 42, 43]. By isolating different compositions of alpha-Mg, beta-Mg and the intermetallic phase in AZ91, Mathieu et al [36] found that increasing concentrations of aluminum increase the polarization resistance in ASTM D1384 solution compared to pure magnesium. In addition, the corrosion potential increases linearly as the aluminum content increases (table 2.5) [36]. The influence of the composition of alpha-Mg phase
can be explained by the resulting superficial layer that forms. Increasing amounts of aluminum increase in the aluminum content in this film and thus allow for a more protective film seen as an increase in $R_p$ as function of aluminum content (table 2.5).

<table>
<thead>
<tr>
<th>Phases</th>
<th>$E_{corr}$ (V)</th>
<th>$R_p$ (kΩcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg</td>
<td>-1.55</td>
<td>3.4</td>
</tr>
<tr>
<td>Alpha3Al</td>
<td>-1.49</td>
<td>7.4</td>
</tr>
<tr>
<td>Alpha5Al</td>
<td>-1.45</td>
<td>12</td>
</tr>
<tr>
<td>Alpha9Al</td>
<td>-1.40</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Table 2.5 (adapted from [36]) Galvanic potential and galvanic current between different alpha phases and $\beta \text{Mg}_{17}\text{Al}_{12}$

At a eutectic temperature of 340°C, zinc is soluble in magnesium at levels up to 6.2% [38]. The purpose of zinc additions is to increase the strength of the resulting alloys via a solid solution strengthening mechanism [16]. In addition, zinc makes magnesium-aluminum alloys have a divorced eutectic where particles of $\text{Mg}_{17}\text{Al}_{12}$ are surrounded by alpha magnesium solid solution [38]. As reported by Kim et al., additions of zinc can increase the ductility of Mg alloys [16], which is important for forming operations and failure resistance.

### 2.6 Microstructural Effects on Corrosion of Magnesium Alloys

The FSSW process has a pronounced effect on the microstructure of the weld area and it alters the grain size, precipitate distribution, microstructural twins and dislocation content drastically. Therefore it is important to understand the effect of these individual factors on corrosion in magnesium alloys.
2.6.1 Effect of Grain Size on Corrosion

Grain size has a large effect on the corrosion resistance of magnesium alloys. Having a small grain size leads to decreased corrosion rates as compared to samples with a larger grain size in the same corrosive environment. One study [44] shows that small grain sizes can increase the corrosion resistance by providing more grain boundaries, which act as corrosion barriers. When the grain size increased from 65µm to 250µm, the corrosion rate increased by 30% [44] (figure 2.13). The reason the 35µm grain size had a relatively high corrosion current is because it was an as-received alloy. The as-received alloy did not undergo any heat treatment to increase the grain size and thus it was left full of twins and dislocations, which increased the corrosion rate (discussed later in section 2.6.3).

![Grain Size Vs. Corrosion](image)

**Figure 2.13** Effect of AZ31 grain size on corrosion current in 3.5% NaCl (adapted from [44])

It has been postulated by Lopez et al. [45] that a finer grain size allowed for initial rapid buildup of the corrosion product MgO, which slowed down further corrosion and increased the corrosion resistance. The hypothesis that grain boundaries act as corrosion barriers is confirmed in work done by Ting et al. [46] The small grain size and accompanying high volume fraction of grain boundaries allow for reduced corrosion rates via a mechanism called the “positive effect” (figure...
2.14). The high volume fraction of grain boundaries and the high diffusion coefficient of grain boundaries allows for rapid diffusion of constituents, which ultimately act as nucleation sites for passive layer formation. Therefore, increased grain boundary volume fraction leads to increased passive layer formation and reduced corrosion rates [46].

Figure 2.14  Schematic showing the “positive effect” where a large grain boundary volume fraction supports the fast formation of a passive layer [46]

2.6.2 Effect of Second Phase Particles on Corrosion

The corrosion of magnesium alloys is also controlled by the galvanic couples formed between alpha-Mg and beta-Mg (and other intermetallic phases). The beta phase Mg_{17}Al_{12} also has a controversial role vis-a-vis corrosion resistance. The beta phase particles either act as a cathode with good passive characteristics, or as a corrosion barrier [47]. However, when coupled with alpha grains, Cheng [35] indicated that the beta phase particles form a galvanic couple with the alpha magnesium phase and this was the main source of localized corrosion attack in magnesium alloys. Because the electrode potential of Mg_{17}Al_{12} is higher than the electrode potential of the matrix, adjacent contact forms microcells which increased the corrosion attack. [35] The electrode potential of Mg_{17}Al_{12} was higher than the electrode potential of the alpha matrix (about
150mv higher compared to Mg 9%Al [36]) and this caused micro-galvanic corrosion cells to form within the alloy. Cheng et al believed that the less beta phase Mg$_{17}$Al$_{12}$ that was present in the alpha matrix, the better the corrosion resistance and for this reason AZ31 (3 %Al compared to 9 %Al in AZ91) had higher corrosion resistance than AZ91. [35] This was also observed in Zhao et al’s study involving the corrosion resistance of AZ31, AZ91, AM30 and AM60 [48]. While maintaining a similar alpha grain composition, the corrosion rate of AZ91 and AM60 was higher than AZ31 and AM30, respectively, due to increased amount of second phase micro-galvanic attack.

2.6.3 Effect of Twins and Dislocations on Corrosion

FSSW involves intense plastic deformation to the metal, and thus it is instructive to look at the effect plastic deformation has on the corrosion resistance properties of AZ31 base material. Based on general solid mechanics and mechanical deformation theory, plastic deformation causes the density of dislocations to increase and the grain size to decrease. The effects of increasing the extent of plastic deformation in AZ31 can be seen in figure 2.15, where increasing the extrusion ratio causes the dislocation density to increase. By looking at the AC and DC characteristics of plastically deformed magnesium alloys, and noting the current density as a function of % strain (figure 2.15), Andrei et al. [49] have postulated that a reduction in the equilibrium potential near the dislocations causes the increased anodic dissolution (corrosion attack).
It has been postulated by Hamu et al. and Aung et al. [49, 44] that plastic deformation can lead to increased corrosion resistance by reducing the grain size and increasing the amount of grain boundaries, which act as corrosion barriers. However, further plastic deformation with annealing causes the formation of twins, while still increasing the dislocation density through grain growth, and this causes a drop in the equilibrium potential near the dislocations resulting in a more active AZ31 and an increased corrosion rate. [49]
2.7 Abnormal Grain Growth

Grain growth is a common diffusional phenomenon where grains increase in size and achieve a reduction in grain boundary surface energy. [50] There are two ways that the grains can increase in size: 1) homogeneously, and 2) heterogeneously. The former occurs when all grains grow at a similar rate, and thus have a similar grain sizes once growth has ceased, leaving a uniform grain size distribution. The latter however, occurs when there are discontinuities in the growth process, and large grains form at the expense of smaller adjacent grains. This is termed abnormal grain growth (or secondary recrystallization) and is a phenomenon whereby only a few grains in a matrix grow at an increased rate [51].

Abnormal grain growth is caused by a number of metallurgical factors, including a heterogeneous grain size distribution, differences in dislocation density and low mobility boundaries (which is dependent on grain orientation, grain boundary character distribution and pinning effects). The first catalyst for abnormal grain growth is a heterogeneous grain size distribution. [52] The n-6 rule states that a grain will grow if it has more than 6 neighboring grains, and will shrink if n (neighbors) is less than 6. This rule alone cannot explain abnormal grain growth. [53] Another theory to explain the existence of abnormal grain growth deals with the interfacial energy between grains [51]. Equation 2.1 provides an estimate for the minimum size of a grain to exhibit abnormal grain growth, where D is the minimum grain size, d is the average grain size of the matrix grains, and \( \sigma_{dd} \) and \( \sigma_{dl} \) are the interfacial energies between the abnormal “runaway” grain and the matrix grains, and the interfacial energy between the matrix grains, respectively.

\[
D = \frac{2\sigma_{dl}}{\sigma_{dd}} d \quad \{2.1\}
\]

When this relation is simplified by assuming the interfacial energies \( \sigma_{dl} \) and \( \sigma_{dd} \) are equal, Hillert’s postulation of size advantage exists where abnormal grain growth occurs when the runaway grain is twice the average grain size. [53] Other studies have shown that having a heterogeneous grain size distribution leads to abnormal grain growth. [54-55]
The second factor that affects abnormal grain growth is boundaries with low mobility. Low mobility boundaries (with respect to abnormal grain growth) are influenced by two characteristics of the matrix:

1. The grain boundary character distribution and the presence of low angle sigma boundaries, and
2. The presence of second-phase particles, which lead to grain boundary pinning via the Zener mechanism.

Low angle sigma boundaries are boundaries with special properties such as low energy, low diffusional constants and low mobility. When a matrix has such a grain boundary character distribution consisting of low angle sigma boundaries, only a few grains with increased mobility are allowed to grow, creating large abnormal grains. [56] This was seen in the case of ferritic-type ODS alloys, where abnormal grain growth was only seen at lower annealing temperatures, where deformation induced low angle sigma boundaries remained, leaving low mobility boundaries. [56] Second-phase particles work to pin the grain boundary and stop it from moving. In a microstructure where these second phase particles are heterogeneously distributed, abnormal grain growth is likely to occur. This effect was seen in a study by J. Dennis et al. [50] where they showed in an Al–3.5Cu sample that the boundaries around abnormal grains contained about half the volume fraction of pinning particles in comparison to those in the fine matrix grains.

The last mechanism by which abnormal grain growth can occur is an increase in the dislocation density. Briant et al [57-59] found that increasing the dislocation density in a tungsten sample via plastic deformation caused abnormal grain growth. The same trend was observed by Sung-Yoon et al. and by Kyu et al. while investigating the effect of dislocation density on abnormal grain growth in strontium titanate and in a nickel super alloy, respectively. [60, 61] In each case, the dislocation density was determined from dislocation images taken using transmission electron microscopy (figure 2.16). They concluded that there was a critical extent of plastic deformation (dislocation density) that produced the most abnormal grain growth (figure 2.17). Once this limit had been exceeded, abnormal grain growth started to diminish and the grain size decreased (figure 2.18). Dislocations within a matrix can cause abnormal grain growth by increasing the
mobility of the grain boundary. Chung and Kang showed this in an experiment using a single crystal embedded in a powder compact matrix. The side of the crystal with high dislocation density grew nearly twice as much as the side with low dislocation density. The mechanism underlying the increased growth rate has been documented as elastic relaxation or dissolution into partial dislocations. [60]

Figure 2.16  TEM images showing (a) a large abnormal grain containing many dislocations and (b) dislocation-free fine matrix grains in the 2.4-mol%-TiO$_2$-excess SrTiO$_3$ compact annealed at 1470°C for 2 h in air. [60]

Figure 2.17  The variations of the average grain size and the size of the largest grains with the level of deformation in the specimens heat-treated at 1150°C for 1 h. [61]
2.8 Corrosion of Friction Stir Spot Welds in Magnesium Alloys

Research on the corrosion of FSSW in magnesium alloys is quite limited, and only a few investigations have been performed. These investigations involve stress corrosion cracking and general salt spray test, and to the best of the author’s knowledge, no work has been done on localized corrosion of FSSW in magnesium alloys. Generally speaking, in terms of both the salt spray tests and stress corrosion cracking, it has been found that the weld nugget experiences a higher corrosion attack in aqueous salt solutions [62, 63]. The FSSW process affects the microstructure in a number of ways, and one of those ways is that it dissolves the Mg$_{17}$Al$_{12}$ intermetallic within the stir zone due to the high temperatures and high degree of plastic deformation at this location. It has been postulated by Klag et al. that the reason for higher corrosion rates in the weld nugget (SZ) is due to the absence of the Mg$_{17}$Al$_{12}$ mesh, which effectively acts as a corrosion barrier [62] (figure 2.19-2.20). This postulation goes against what is seen in the literature and one possible explanation for this is that the increased corrosion activity in the SZ could be caused by the presence of the Fe-Mn precipitates.
2.9 The Scanning Reference Electrode Technique

The scanning reference electrode technique (SRET) is a highly localized corrosion technique used to measure micro-galvanic activity in close proximity to an electrochemically active surface located in an aqueous solution electrolyte. The SRET works by utilizing two main features of corrosion in aqueous solutions. The first is that corrosion in aqueous solutions is a combination of anodic oxidation of the metal and cathodic reduction of species in the solution, and the second is that these two reactions are separated spatially by a finite distance. Therefore in order to sustain the chemical reactions that define the corrosion of magnesium alloys, electrons (current) must flow from site A (anode) to site B (cathode) through the solution (figure 2.21). By passing a fine passive probe in close proximity to the corroding surface, the current flow and following
potential variations can be measured. The in-situ and non-destructive nature of the SRET has made the technique suitable for investigating localized corrosion phenomena such as pitting and coating performance. In all cases, the SRET’s ability to detect a change in potential or current is used to measure these phenomena.

![Current flow from anode to cathode in an electrolyte](image)

Figure 2.21 Schematic showing current flow from anode to cathode in an electrolyte [64]

Pitting corrosion is a highly localized form of corrosion and is generally associated with the presence of chloride ions or bromide ions, the presence of other inhibitor anions, with the composition of the metal, the metal surface condition and electrochemical activity of the metal [64]. Pits will form on the surface of a metal when the potential is raised above a certain value called the ‘pitting potential’ (figure 2.22).
H.S. Isaacs [66] investigated the pitting behavior of type 304 stainless steel in ferric chloride. He was able to map out the progression of pitting activity and postulate the mechanisms that contributed to the propagation of pits (figure 2.23). Likewise, Cui et al [67] obtained similar results when employing a modified SRET apparatus to investigate the pitting behavior of carbon steel in neutral media.
Maile et al [68] used SRET to evaluate the delamination of polymer coatings on steel substrates. By using the SRET’s local corrosion characteristics Maile was able to determine the characteristic signature of scratches on the steel substrate via a change in measured potential (figure 2.24). There are numerous examples of how the SRET is applied to study pitting and coating performance, however, when it comes to using the SRET to study the corrosion of magnesium, and FSSW of magnesium in particular, nothing has been published.

**Figure 2.24** SRET line data above a scratch in the polymer coating showing the potential response against time. [68]
3 Objectives

Magnesium alloys and their light weight/high strength properties make them a possible candidate for use in the transportation industry to help improve fuel efficiency and lower emissions. Joints can be made in Mg alloys using the FSSW technique, which produces sound welds free of cracks and porosity. The FSSW process modifies material microstructure, alters the grain size, grain structure, and the precipitate distribution within the weld zone. The FSSW process is a complex thermo-mechanical process, which is known to alter the microstructure of a welded specimen on the micrometer scale. Mechanical stirring creates a stir zone comprising a microstructure consisting of fine equiaxed, dynamically recrystallized grains, a TMAZ region containing partially grains, and a heat affected zone, which experiences a limited amount of grain growth. The second phase precipitate distribution is also changed. Since Magnesium alloys are susceptible to both galvanic corrosion and pitting corrosion, the microstructural changes produced during FSSW markedly affect corrosion resistance properties. Since SRET testing is a localized corrosion technique suitable for investigating changes in corrosion behaviour on the micrometer scale, the objectives of the present thesis are twofold:

1) To determine the effect the FSSW process has on the corrosion resistance behaviour of wrought magnesium AZ31 alloy
2) To explain the corrosion phenomena observed in standard immersion tests and compare them with SRET potential distributions
4 Experimental Technique

The overall approach to the investigation of the corrosion behaviour of friction stir spot welds in AZ31 magnesium alloys involved adopting a conventional welding schedule as noted from literature, and employing SRET testing based on the theory outlined by Isaacs and Vyas [64].

4.1 AZ31 Base Material

The material used in this investigation was a wrought magnesium AZ31 alloy. The alloy was purchased from M & B Mag Ltd. in the form of a 4 foot x 3 foot x 1.5mm thick sheet. The sheet was then cut using a metal band saw into manageable sized coupons having nominal dimensions 10cm x 2.8cm x 1.5mm (figure 4.1). The nominal composition of the alloy system is detailed in table 4.1.

![Base material alloys sheets](image)

Figure 4.1 Base material alloys sheets

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Mn</th>
<th>Al</th>
<th>Zn</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe</th>
<th>Ca</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. %</td>
<td>Balance</td>
<td>0.2</td>
<td>2.5</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Max. %</td>
<td></td>
<td>-</td>
<td>3.5</td>
<td>1.3</td>
<td>0.05</td>
<td>0.05</td>
<td>0.005</td>
<td>0.005</td>
<td>0.04</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 4.1 Nominal composition of base AZ31
4.2 Friction Stir Spot Welding

All spot welds were made using a Friction Stir Link linear displacement bench top welding unit. Figure 4.2 shows the welding unit during experimental use, and also shows the utility of each of the major components. A sample holder provided sufficient clamping force on an overlapping sheet assembly to prevent relative sheet motion during the spot welding operation. A 6 axis load cell was used to collect force and torque data in the x, y and z axes. The rotating welding tool contained a shoulder and threaded pin element that were inserted into the magnesium sheets to create the weld. In this investigation three different tool geometries were used, namely a flat shoulder tool, a 10° concave shoulder tool and a scroll shoulder tool. These tools were made of H14 tool steel, with the thread matching that of the standard M4 metric thread. Images of these tools can be seen in figure 4.3. Note that during SRET testing, only joints made using the flat and concave shoulder tools were investigated. The scroll shoulder tool was only used in the grain size analysis. The flat and concave tools had a shoulder diameter of 10mm, a pin diameter of 4mm and an overall length of 50mm. The scroll tool had a diameter of 15mm and has the same pin dimensions as the flat and concave-shaped shoulder tools. A rotary servomotor capable of producing 28Nm of torque provided rotation for the welding tool and a linear servomotor capable of producing 12kN of normal axial force was used to provide vertical displacement of the welding tool. This linear servomotor was used to force the rotating tool into the overlapped magnesium sheets creating the welded joint.
With the welding apparatus described, the parameters associated with the welding procedure are detailed below:

1) The magnesium base alloys sheets were placed into the sample holder in an overlapping sheet configuration. It is important that the two sheets were arranged in a perfectly congruent fashion, and that sufficient clamping force was used to keep the sheets stationary.

2) In order to obtain the welding parameters, the position of the overlap assembly relative to the welding tool must be determined.
   a. The welding unit was brought to its home (zero) position which is at the top of the linear servomotor’s stroke. This was done by pressing the “run calibration” button on the touch panel in the linear control section. Be sure that the emergency stop switch is disengaged by pulling up on the red “emergency stop” button. The servos will not operate otherwise.
b. The welding tool was then brought down closer to the sample using the “linear jog” buttons on the touch panel under the liner jog section. There are three methods of moving the welding tool; continuous linear jog, 1mm increment, and 0.25mm increment. All methods were used to accurately position the welding tool on top of the alloy sheets. The tool was first brought down quickly initially using the continuous jog button until the probe was 5-10mm from the sample. At this point the 1mm jog button was used until the probe was within 2mm of the sample. Then the probe was moved with the 0.25mm increment button until it contacted the samples. By using the 6 axis load cell and real time computer display, the exact moment when the tool touched the sample was known when the z-axis force signal (read on the computer screen) displayed a change. This linear displacement was then noted. When the load cell was not able to be used, the positioning of the probe can be done manually. In this case, after bringing the probe to within 2mm of the surface, the sample clamp was released and the probe was again incremented by 0.25mm. After each increment of 0.25mm the top sheet must be wiggled to note the drag from the pin touching the surface. The probe is incremented and the drag is checked consecutively until the probe has made solid contact with the top sheet. The clamp must then be re-engaged. Regardless of the method used, this position value describes the point where the tool initially touched the top of the sample (figure 4.4 a), and it is from this point that the positional parameters were developed.

c. If this position is referred to as “x”, then the pounce position (the position at which the welding unit goes into weld mode) will be “x-3” mm. At this point the speed of the linear servomotor changed from its pounce speed of 25mm/s to its plunge speed of 2.5mm/s. During the plunge it is desired that the shoulder penetrate approximately 0.2mm beneath the surface of the top magnesium sheet to provide enough frictional force to sufficiently heat the material to create a proper bond, and to do so at a plunge rate of 2.5mm/s. This required the plunge depth to be the sum of the 3mm pounce position, 2.2mm pin length and 0.2mm penetration, totalling 5.4mm. The tool must weld while vertically stationary for
1s, which requires the dwell time to be 1000ms. Lastly, the retract speed was set to 35mm/s.

d. These parameters which are summarized in table 4.2 were entered into the welding system by navigating to the “welding schedule” section on the touch pad, and entering the values into their respective numerical fields. After entry, it is imperative to download both the linear and rotational parameters into the systems ram by pressing the linear download and rotary download buttons. If this is not done, the FSSW unit will perform the weld with the previously downloaded parameters or null parameters which could cause damage to the unit.

Figure 4.3 a) flat shoulder tool b) 10° concave shoulder tool c) scroll shoulder tool

Figure 4.4 a) pin touch position b) pounce position c) plunge depth position
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pin touch</td>
<td>x mm</td>
</tr>
<tr>
<td>Pounce position</td>
<td>x-3 mm</td>
</tr>
<tr>
<td>Pounce speed</td>
<td>25 mm/s</td>
</tr>
<tr>
<td>Plunge rate</td>
<td>2.5 mm/s</td>
</tr>
<tr>
<td>Plunge depth</td>
<td>5.4 mm</td>
</tr>
<tr>
<td>Dwell time</td>
<td>1000 ms</td>
</tr>
<tr>
<td>Retract speed</td>
<td>35 mm/s</td>
</tr>
</tbody>
</table>

Table 4.2 Summary of FSSW parameters used in this study

3) With the FSSW parameters established, the welding procedure was simply executed by running the welding schedule comprised of the aforementioned parameters. Once the welding operation was completed (when the linear servomotor brings the welding tool back to the home position and the rotary servomotor stops spinning), the red emergency stop button was pressed, the welded sample was released from the clamp and the FSSW tool was removed from the welding unit. The tool was then cleaned from all adhered magnesium before fabricating the next weld by cleaning it in 30% HCl until all of the magnesium had dissolved, and then rinsed with water.

4.3 SRET Sample Preparation

1. Once the sample was welded it was slowly cut in half using a Struers Accutom-2 diamond saw using water cooling to minimize any effects on the microstructure from plastic deformation. Cutting was performed using 1800rpm and 1.25bar of loading pressure.
2. The sample was then ground from the backside with wet 320 grit silicon carbide paper, so that the overall thickness of the actual welded sample was in the range of 4-6mm (this thickness allowed the sample to fit within the SRET) and then mounted in a 2 part Buehler Epoxycure epoxy. Care must be taken to ensure that epoxy fills the characteristic FSSW void between the two alloy sheets.

3. Four holes were drilled in the hardened epoxy: 3 X 4.8mm diameter clearance holes for plastic screws which fixed the sample in the SRET, and a 1X 1.6mm diameter press fit hole for the working electrode lead wire. Plastic screws were used so that no corrosion occurred once the aqueous solution was added to the cell. The three holes were aligned so that two of the holes were parallel with the top surface of the welded sheets (figure 4.5). The 1 press fit hole was the same diameter as the copper wire, and lead into the AZ31 sheet that allowed for intimate physical contact between the alloy and the copper lead wire to achieve the lowest electrical resistance. To be sure good electrical contact had been made between the copper wire and the magnesium sample, the resistance was measured with a digital ohm-meter which should read $\leq 0.2\Omega$. If the resistance was more than $0.2\Omega$, then either the wire or the hole was adjusted until this value was achieved.

4. Specimens for SRET testing were ground and polished according to the following procedure:
   a. The bottom of the epoxy puck (where the AZ31 surface is not exposed) was first ground to reduce the height of the puck to within the range of 6-10mm.
   b. Next, the AZ31 surface was progressively ground using 320, 600 and 1200 grit silicon carbide wet grinding wheels. In between each grit level the sample was rinsed with water.
   c. Following grinding, the surface was progressively polished using 15µm, 6µm, 3µm and 1µm diamond suspension solutions on a felt pad. In between each micron size the sample was rinsed with isopropanol to avoid cross contamination of different sized diamond particles. During the grinding/polishing stages it was
important to orient the sample so that the bottom sheet was the leading edge on the grinding/polishing wheel. Polishing in this manner avoided the “edge effect” on the important upper sheet surface where the edge is rounded and the height is not maintained.

After polishing, the sample was cleaned in an ultrasonic bath of isopropanol for 5 minutes, rinsed with isopropanol, and air dried. If the samples were not tested immediately, they were stored in a vacuum desiccator until testing was commenced.

d. The copper lead wire was then inserted into the alloy through the hole in the epoxy, and any exposed copper was masked with low temperature thermal glue to prevent copper ions dissolving into solution. The result of sample preparation can be seen in figure 4.5.

![SRET sample prepared for testing](image)

**Figure 4.5** SRET sample prepared for testing

### 4.4 Construction of the SRET Apparatus

The SRET is a combination of individual components each with their own specific purpose, assembled together with custom mounting hardware. A picture of the apparatus can be seen in
A 10µm diameter platinum wire counter electrode from CH Instruments (model CHI 116) was used as the scanned (reference) electrode (figure 4.7). High electrical conductivity is also especially important in this application since the small diameter of the wire increases its impedance. As an estimate to the resistance of a 10µm diameter 5cm long wire the simple relation of $R = \frac{\rho L}{A}$ where $R$ is the resistance, $\rho$ is the resistivity, $L$ is the length of wire and $A$ is the cross sectional area can be used. This resulted in a resistance on the order of $10^{2} \Omega$. This was much less than the input impedance on the order of $10^{11}$ of the Hokuto Denko potentiostat, thus any noise resulting from the fine platinum tip would not be significant. To keep the probe in optimum working condition it must be polished with 0.25µm diamond paste and distilled water on a nylon polishing pad before every experiment. The condition of the exposed platinum tip can be viewed under a microscope, and conditioning is needed when the probe does not have a smooth shiny appearance. This removed any accumulation of surface contaminants which could affect the voltage/current readings. Platinum was also used for a second macroscopic reference electrode as it has a high chemical stability, high electrical conductivity high reproducibility, fast response time and it is not easily contaminated.
The scanning reference electrode was moved horizontally in the x-y plane using 2 piezoelectric inch worm motors from Burleigh Instruments (figure 4.8). One motor was used for motion in each axis. The motors have a resolution of 4nm and a travel of 25mm, however, when connected to the Heidenhain positional encoders, the resolution dropped to 0.1µm. The motors and encoders were connected to the Burleigh 7000 Controller. The motion of the motors was controlled using a Burleigh 7004 keypad. The keypad allowed for continuous, pulsed and stepped travel and at the same time the stabilization parameters, tolerance and dwell, were set. For the x-axis, the tolerance and dwell were 1µm and 11ms, respectively, whereas for the y-axis the tolerance and dwell were 1µm and 82ms, respectively. Motion in the z-axis (height control) was provided by a conventional inch micrometer. Consistent accurate positional changes were not required in the z-axis as the height of the probe remained constant during the SRET scans.
The electrochemical cell provides the corrosive environment in which the AZ31 will be tested. The cell was constructed out of Plexiglas and utilized 2 o-rings to seal in the aqueous solution. The cell had a working volume of 50mL. Inside the cell were 3 tapped holes which allowed the sample to be rigidly fixed within the aqueous solution. Also inside the cell were 2 counter electrodes made of a platinum mesh. They were rigidly fixed to the sidewall of the cell in an electrochemically ‘inert’ area (i.e. far from the sample) to avoid disruption of the electrochemical activity occurring on the surface of the AZ31 welded sample. To increase the signal to noise ratio an electrically grounded Faraday cage completely surrounded the electrochemical cell to block out any external static and non static electric fields and radio frequency signals (figure 4.9).
The flat polished cross sectional surface of the welded AZ31 sample set in epoxy will have a different plane normal when going from sample a to sample b, and as such the whole electrochemical cell was situated on a 2 axis Newport tilt stage (figure 4.10) to facilitate leveling the top surface. The stage had a sensitivity of approximately $1.94 \times 10^{-4}$° and is brought into the same plane as the plane traced by the motion of the probe by a 4 point contact leveling system.

![Newport tilt stage](image)

All of the previous components were rigidly fixed to a steel base plate which was in turn situated on a vibration isolation system. When dealing with such small distances on the micrometer scale, it is important to eliminate any vibrations and this was achieved by using both mass and dampening media. The vibration isolation system consisted of two heavy masses measuring 22.7kg, one mass measuring 5kg, and three sets of rubber damping media with a hardness classified as either soft, medium or hard. Using three different hardness values allowed for dampening a wider range of external vibration frequencies, and using heavy masses offset the inertial effect of vibration on the SRET apparatus.

### 4.5 SRET Calibration- Leveling and Aligning the Stage

Calibrating the SRET apparatus consisted of leveling and aligning the stage, setting up the computer software for data recording, and establishing the operating parameters of the SRET.
Since the probe output in mV will change as a function of height, it was important that the surface of the sample be in the same plane as that traced by the motion of the probe otherwise the SRET would interpret changes in voltage that are caused by changes in height rather than changes in surface chemistry or surface morphology. As well, to obtain the highest spatial resolution it was important to optimize both the operational parameters and data collection methods.

1. A 4 point contact system was used to level the stage. First, the angle of the x-axis was adjusted using the x axis screw knob until 2 contact points had the same height. The contact points were separated by the largest distance possible governed either by the motor’s travel (25mm) or spatial restrictions on the sample itself (figure 4.11). The heights at the points of contact were known by employing a digital ohm meter connected to the probe and the surface of the sample and noting the moment when an infinite resistance (zero load) becomes a finite resistance of “x” ohms on contact.

2. Once the electrical resistance was registered the height as denoted by the z-axis inch micrometer was noted, and the stage angle was adjusted accordingly so that the height on either side of the sample in the same axis was equivalent. The same procedure was then used to level the stage in the y-axis direction. These adjustments must be made extremely slowly and accurately to determine the point when the probe just touches the surface of the sample. When performed in this manner, the high impedance electrical junction registered a very high resistance characteristic of 2 electrical contacts only just touching.

3. This process was iterated and the stage angles (contact heights) were adjusted until the 4 points had the same height. This was synonymous to orienting the top surface of the sample so that its plane normal is [0,0,1]. Performing the levelling in this manner allowed for the most accurate levelling of the stage.
4.6 SRET Calibration- Computer Set Up

The SRET is a 4 electrode electrochemical cell consisting of two working electrodes, a counter electrode and the reference electrode.

1. With this design one platinum wire mesh was connected to the counter electrode (CE), and the other was connected to the first working electrode (WE1). These were used only as stable counter electrodes so the fact that it is connected to WE1 is not an issue.

2. The sample itself was connected to the second working electrode (WE2)

3. The SRET probe was connected to the reference electrode (RE). These terminals lead into the Hokuto Denko potentiostat, which was controlled by its accompanying software. Refer to figure 4.12 for a schematic of the electrochemical cell.

4. The potentiostat was set to record open circuit potentials and voltages at a frequency of 1 Hz.

5. The intrinsic data filter was switched on to minimize data fluctuations. The intrinsic data filter is a low pass filter (a capacitor with a large time constant) which provided dampening to the electrical circuit.
4.7 Establishing the SRET Operational Parameters

The resolution and sensitivity of the SRET was governed by the parameters under which it operated. More specifically, the parameters that control the sensitivity of the SRET and that affect the electrochemical interaction between the sample, solution and probe include: the scanning speed, scanning height and the ionic concentration of the solution. These parameters were then used in conjunction with the spatial dimensions of the sample to develop a scanning procedure.

With higher scanning rates the probe and potentiostat are less likely to record the steady state voltage as the probe may not have sufficient time to come to equilibrium at a given location. Therefore, slower scan speeds are recommended to achieve the highest resolution. To determine an appropriate scanning speed a special sample, termed the modified AZ31 sample, was developed to show the sensitivity of the SRET. This special sample was a piece of AZ31 base alloy, with a copper wire inserted into the middle (figure 4.13). The copper wire makes full contact with the surrounding AZ31 resulting from the press fit insertion method.
Scanning horizontally through the middle of the copper wire moving from AZ31 to copper and back to AZ31 while monitoring the change in potential/current measured by the SRET, provided a means to establish the spatial resolution of the SRET. The sharpness of the transition region (slope and length) between the magnesium and copper in a potential/current vs. distance plot is related to the spatial resolution of the SRET. A sharper (steep and short) transition region signified increased resolution, while a broader (not steep and long) transition region signified decreased resolution. Figure 4.14 shows the effect of scanning speed on the resolution of the SRET in an aerated aqueous solution of 8.55E-2 M NaCl at a temperature of 24°C with a scan height of 30μm and probe diameter of 30μm (this was done with a preliminary probe).
Figure 4.14 SRET response in scanning over modified AZ31 sample showing the effect of scanning speed on the SRET sensitivity

The blue trace (10μm/s) had a very long and broad transition region compared to the red trace (1μm /s). Also, scanning at 10μm /s a potential produced a drop off from about 2500μm to 2800μm which does not occur when scanning at 1μm /s. Scanning at 1μm/s in comparison to 10 μm/sec increased the sensitivity of the SRET because scanning the higher speed did not allow sufficient time for the probe to reach equilibrium at a discrete location. By looking at the distance over which the probe must travel to stabilize at the magnesium potential (perceived diameter of copper wire) and comparing it to the actual diameter (1.6mm) , the percent error for each scan speed can be calculated (figure 4.15). See appendix D for sample calculations.
However, it was found that scanning at such a slow speed allowed the samples to corrode to the point where the morphology of the sample was dynamically changing too fast as a result of its high corrosion rate. Thus, the scan speed was increased to 2 µm/s to facilitate scanning the whole sample effectively in a period where large macroscopic changes are not observed.

Increasing the scanning distance between the probe and sample will affect the SRET output as the probe will intersect different iso-potential lines as described in the literature review. To determine the optimal scanning distance the same modified AZ31 sample was scanned to check the voltage response when going from AZ31 to copper (1.6mm diameter) and back to AZ31 at varying scan heights in an aerated solution of 8.55E-2 M NaCl at a temperature of 24°C with a probe diameter of 10µm and scan rate of 1µm/s. The results can be seen in figure 4.16.
The sensitivity was again measured by the slope and length of the trace in the transition region, as well as the extent of potential drop-offs. When the scan is performed at a distance of 30μm (purple x’s in figure 4.16), a large transition region was experienced with large potential drop-offs observed at approximately 1000μm. Decreasing the scan height from 20μm to 15μm improved the potential drop-off and narrowed the transition region. However, using a scan height of 10μm resulted in the least potential drop-off (the blue trace is nearly flat between the 1.6mm markers), and the transition region is steep and sharply defined. Probe heights less than 10μm were not considered since having a probe height less than the probe diameter results in interference with the potential distribution over the sample [64]. Also, when scanning at 10μm above the surface the SRET was able to detect the presence of precipitates indicated by the peaks at 2900μm and 3300μm. Again, the difference in the perceived diameter of the copper wire versus the actual diameter was calculated to give the percent difference as a function of a scan height (figure 4.17), and it can be seen that scanning at closer distances resulted in the lowest error. Thus, scanning at 10μm away from the surface of the sample provided the highest sensitivity while using a 10μm probe diameter. See appendix E for sample calculations of the percent error.
Figure 4.17  Calculated percent error for the effect of scanning height. Percent error is calculated for the difference in the perceived diameter of the copper wire (length of stable copper signal between 1.6mm markers) vs. actual diameter of the wire.

The last parameter that affected the sensitivity of the SRET was the solution concentration. Aqueous NaCl solutions are used in this investigation to simulate the corrosive environment experienced in service. Again, the modified AZ31 sample (figure 4.13) was used to check the voltage response against varying concentrations when scanned across with a probe scan rate of 1μm/s, 10μm probe height and 24°C solution temperature. The results can be seen in figure 4.18.
Changing the solution concentration had a profound effect on the output of the SRET as can be seen in the magnitude of the SRET output, and slope of the line in the transition region. With a very dilute solution at 0.00086 M NaCl there was some potential drop-off which occurred at about 600µm. The transition region (time/distance to reach a stable voltage characteristic of the AZ31) is also comparatively large. As the solution concentration was increased, the potential drop off disappeared, and the transition region narrowed until it was at its shortest width at a concentration of 0.086 M. Although the potential drop off remained unaffected, as the concentration is increased further to 0.43 M NaCl the transition region broadened representing a loss in SRET sensitivity due a higher count of Na⁺ and Cl⁻ ions. Increasing the concentration of Na⁺ and Cl⁻ ions will increase the conductivity k, of the electrolyte. Based on the following equation which defined the spatial resolution of the SRET, l, an increase in k will increase the spatial resolution of the SRET apparatus. As well, either decreasing the change in voltage, dV or increasing the current di, will cause an increase in the spatial resolution.
Changing the solution concentration did not have a large effect on the perceived diameter of the copper wire as the potential plateau over the copper is identical for each concentration value (length of the plateau between the dotted markers in figure 4.18). However, the rate of decay of the potential to reach a quasi-steady signal over the magnesium was affected by concentration. By looking at this decay distance for each, the effect of solution concentration on the sensitivity of the SRET was calculated (figure 4.19). See appendix for F for sample calculations of decay distance.

Therefore, the SRET sensitivity is highest when a solution concentration of 0.086 M NaCl is used since the decay distance is the least. Below is a table summarizing the operational parameters used in the SRET.
### Table 4.3 Summary of operational parameters for the SRET

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan Speed</td>
<td>2µm /s</td>
</tr>
<tr>
<td>Probe Height</td>
<td>10µm</td>
</tr>
<tr>
<td>Solution Concentration</td>
<td>0.086 M NaCl</td>
</tr>
</tbody>
</table>

### 4.8 SRET Scanning Procedure

The SRET scanning procedure used these optimized parameters in conjunction with the spatial dimensions of the welded sample (figure 4.5), and the procedure was developed so that half of the sample can be completely covered by the SRET. Since the FSSW process is a rotational process and the weld is cut through the centre axis, it can be assumed that the left side of the weld is metallurgically identical to the right side of the sample. This allowed for only one side of the sample to be scanned, and this was hypothesized to accurately describe the corrosion behaviour within the whole weld. As well, scanning only one side of the sample saved time to prevent the sample from corroding sufficiently during the period of measurement and preserved the microstructural features present.

1. The sample was placed into the cell and rigidly fixed using 3 plastic screws.

2. The same levelling technique as described earlier was used again to level the FSSW sample, along with the same cell connections. One platinum wire mesh was connected to the counter electrode (CE), and the other was connected to the first working electrode (WE1).
3. The FSSW sample itself was connected to the second working electrode (WE2), and the SRET probe was connected to the reference electrode (RE). These terminals lead into the Hokuto Denko potentiostat, which was controlled by its accompanying software.

4. The potentiostat was set to record open circuit potentials at a frequency of 1 Hz, and the low pass filter was switched on to minimize data fluctuations.

5. The SRET was only able to scan in either a horizontal or vertical manner, therefore, to completely cover one side of the sample, a series of stepped linear scans were combined (figure 4.20).

   a. The scans were made with a scan distance of 3250μm which allowed the probe to scan across the 3000μm shoulder area

   b. The individual line scans were separated by a step down distance of 250μm which allowed for adequate depth coverage within eleven scans for the flat shoulder samples and 14 scans for the concave shoulder samples.

---

Figure 4.20 Schematic representation of SRET scanning procedure.
Each arrow represents a single 3250μm line scan
4.9 FSSW Immersion Tests

The immersion tests were performed in order to reveal the effects of long term exposure of the FSSW to the corrosive environment. For these tests, the polished sample was placed in a beaker filled with 50mL of an aerated aqueous solution of 0.086 M NaCl for 48 hours at 24°C. Once the time had elapsed, the sample was taken out of solution, washed with distilled water, air dried and the extent of corrosion assessed using optical microscopy.

4.10 Optical Microscopy

Optical microscopy was the main imaging technique used in this investigation. Using certain preparation and etching techniques, the grain size, microstructure, and flow zones of the FSSW welds were revealed. Micrographs were taken using an Olympus SZ-PT stereo-zoom microscope and a Jenaphot 2000 reflected light photomicroscope.

4.11 Etching for Microstructure and Microstructural Zones

To reveal the microstructural and flow zones, the samples were first polished in the same manner as samples tested in the SRET. To reveal the macrostructure and flow zones the samples were immersed in a room temperature #7 picric acid solution containing 20mL acetic acid, 50mL ethanol, 20mL distilled water and 3g of solid picric acid [2] for approximately 30 seconds. To reveal the microstructure and grain sizes, the samples were immersed in a room temperature #8 picric acid solution containing 10mL acetic acid, 70mL ethanol, 10mL distilled water and 4.2g of solid picric acid [2] for approximately 5 seconds. The samples were then rinsed thoroughly in isopropanol, and then ultrasonically cleaned in isopropanol. To view the flow zones the samples were viewed under an Olympus SZ-PT stereo microscope.
4.12 FSSW Average Grain Size Analysis

Grain size analysis was carried out on the FSSW welds for 3 different tool designs; flat shoulder, concave shoulder and scroll shoulder. The samples were cut, ground and polished in the same manner as the samples used in the SRET tests, and were etched in the same manner as the samples used for analysis of microstructural and flow zones. The grain size measurements were taken at the top surface to investigate the effect on the tool geometry on the resulting grain size distribution (figure 4.21).

Figure 4.21   a) Macro image of FSSW with red box showing area where grain size measurements are taken, b) Micro image with blue box showing size and location of grain size analysis box, 100μm x 50μm
To determine the grains size as a function of position across the surface of the shoulder, a series of 100\(\mu\text{m}\) by 50\(\mu\text{m}\) boxes were constructed along the shoulder length. The average grain sizes were calculated by manually circling each grain within a box, taking the Feret diameter as the grain size for each grain, and then calculating the average with the box. By assigning a positional value to each box, the average grain size as a function of radial position could then be established. In total, there were 30 boxes for each sample, consisting of approximately 100-300 grains depending on the sample. The standard deviation for a typical data set is approximately 2.55 \(\mu\text{m}\).

4.13 FSSW Abnormal Grain Growth Analysis

To determine the extent of abnormal grain growth and to determine a function of abnormal grain size versus radial position, the number of abnormal grains had to be counted. This was accomplished by using the list of individual grain sizes within each of the grain size boxes from the average grain size measurements, and the actual average grain size within that box. Hillert’s postulation of size advantage which states that a grain is abnormal when it is at least twice the average grain size is used for the analysis. By using excel and counting the number of grains that are larger than 2\(d_{\text{ave}}\) for each individual grain size box, a relation of abnormal grains across the surface was established.
5 Results & Discussion

The results found using the SRET potential distributions arising from welding with the flat and concave FSSW tools are presented. The results of the grain size analysis and the results of the microstructural analysis and immersion tests are presented as well. Particular emphasis will be placed on trends in the SRET potential distributions, and these trends will be linked to the data found during the grain size analysis, microstructure evaluation and immersion testing.

5.1 Theoretical Calculation of Spatial Resolution of SRET

The theoretical spatial resolution of SRET testing is defined by a parameter that describes how accurate the apparatus is in terms of the smallest distance over which the SRET can differentiate potential values. This output is governed mainly by the distance between the probe and the surface of the sample and the conductivity of the electrolyte as discussed earlier. Certain factors may limit either of these two variables. For example, specific solution concentrations are needed to study certain types of corrosion. In addition, the distance between the probe and the sample is limited by the diameter of the probe itself [48]. If the probe is positioned closer to the sample than the diameter of the probe itself, it will disturb the natural potential distribution in the solution [69]. If we model the system as described in figure 5.1, the smallest spatial resolution is important in isolating the individual iso-potential field lines to be interpreted as independent from the overall signal.
The model used in this analysis is that described by Waber [75] where the juxtaposed anode/cathode couple has equal polarization parameters, typical of a local corrosion situation. The potential variation results from the current flow (from anode to cathode) and the corresponding IR drop. The critical dimension that affects the spatial resolution is called the polarization parameter, l, as described by Wagner [62]:

\[ l = k \frac{\partial V}{\partial i} \quad \text{(eq. 5.1)} \]

In this equation l is the polarization parameter (μm), k is the specific conductivity of the electrolyte (μS/cm), \( \partial V \) is the potential of the metal (V), and \( \partial i \) is the current density (A/cm\(^2\)). For simplicity, \( \partial V \) is taken as the resolution of the potentiostat (0.2mV), and \( \partial i \) is taken as \( i_{corr} \) for the corroding species in the appropriate electrolyte (2.5μA/cm\(^2\) – measured separately) and the solution specific conductivity, k is 9.57μS/cm (measured in a 0.086M NaCl solution using a Hach Sension 5 conductivity meter).

\[ l = \frac{uS}{cm} \times \frac{mV}{A/cm^2} \]

\[ l = \frac{uA}{Vcm} \times \frac{mV \ cm^2}{A} \]
Therefore, the theoretical spatial resolution during SRET testing was on the order of 10um, meaning that SRET testing can differentiate potential values of magnitude 0.2mV that are at least 10um apart in a 0.086M NaCl aqueous solution.

This is of course the theoretical spatial resolution. However, in experimental situations this is not possible to achieve. One of the main factors limiting the resolution is the sample to probe distance. The tip of the probe must be placed at least one tip diameter away from the sample to avoid any significant disturbance to the local field over the sample. At the same time, the potential difference over the anode cathode couple decreases exponentially over the first few micrometers when the height is increased, meaning that a compromise must be made between probe height and test resolution.

\[
l = 10^{-5}m
\]

\[
l = 9.57 \times \frac{0.2}{2.5}
\]

\[
l = 7.7\mu m
\]

5.2 Error Analysis of SRET Potential Measurements

Errors during experiments can arise from three possible sources. One source involves the piezoelectric inchworm motors that control motion of the probe in the xy plane. When they are connected to the positional encoders, they have a resolution of 0.1um in either direction, meaning distances measure x um +/- 0.2um. Another source of error is due to the potentiostat, which has a resolution of 0.2mV. The other source of error is due to the variations in height on the FSSW sample, which create changes in the potential measured by the SRET apparatus. Tretheway et al [70] found that the probe output in mV varied as a function of probe height according to the formula:

\[
y(mV) = -0.052x (um) + 43
\]
To test the levelness of the FSSW sample surfaces, an optical surface profilometer was used to measure the height differences in five areas (table 5.1) on a representative polished sample (figure 5.2).

![Oblique plot of area 1 showing surface morphology and height values](image)

Figure 5.2 Oblique plot of area 1 showing surface morphology and height values

<table>
<thead>
<tr>
<th>Area</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. height (um)</td>
<td>2.2898</td>
<td>0.65793</td>
<td>1.02622</td>
<td>0.21783</td>
<td>0.20435</td>
<td><strong>0.879226</strong></td>
</tr>
<tr>
<td>Min. height (um)</td>
<td>-1.10768</td>
<td>-1.51415</td>
<td>-1.65124</td>
<td>-0.84839</td>
<td>-0.77589</td>
<td><strong>-1.17947</strong></td>
</tr>
</tbody>
</table>

Table 5.1 Max/min height values for 5 different sample areas
This amounts to an overall peak to peak height difference of 2.06um, which corresponds to a flat surface having a height error of +/- 1.03um for all FSSW samples. Similar to Tretheway et al’s work where the potential reading varied linearly within the first 500um of separation between the sample and the SRET probe, it is assumed that the recorded potential varied linearly within the first 100um of sample/probe separation with the SRET set-up used in this investigation. The linear relation was determined by tracking the recorded potential at a range of probe heights from 5um to 100um (figure 5.3). This was done with polished base AZ31 material, and in the same 0.086 M NaCl solution at room temperature.

![Corrosion Potential Vs Height](image)

**Figure 5.3** Linear relationship between probe height and SRET potential. Data was taken outside of the exponential range (~ 0-10μm)

The slope of the line in figure 5.3 is -0.0028mV/um, which means that for every 1um change in height between the FSSW surface and the probe, the potential varies by 2.8mV. By combining this measurement (2.8mV/μm) with the surface roughness measurement (+/- 1.03μm), the error in potential as a result of the surface roughness is easily calculated as +/-2.88mV. Considering that the potential spread during testing of joints is approximately 500mV, this means that there is an error of 2.88mV in 500mV, or an error of 0.58%.
5.3 Establishing a Baseline Potential for SRET Potential Analysis

In a separate experiment the SRET probe was held over the base material to record the potential value. Figure 5.4 shows the results. The initial drop in potential from 0s to 400s indicated the transient period where the electrochemical system was coming to equilibrium. The transient potential stabilized at approximately -0.91V which is the open circuit corrosion potential for base AZ31 in 0.086 M NaCl. However, the plateau in figure 5.4 is not actually a plateau. The slope of the plateau line is slightly negative and this shows that there are two regimes with respect to potential vs. time. Stage 1 is the initial transient occurring from 0 to 300s, and stage 2 occurring from 300s onward. The negative slope in stage 2 represents the slight decrease in measured potential as a function of time. This decrease is very small, thus, this shows is that the negative potential measured in the SRET scans (blue and purple regions) are correct and do actually represent the potential signature of base AZ31.

![Steady State Ecorr Measurement](image)

Figure 5.4 Graph of potential vs. time for base AZ31 in 0.086 M NaCl at room temperature
Obtaining the corrosion potential for base AZ31 allowed for the potentials measured with the SRET (arbitrary relative potentials vs. the platinum mesh) to be normalized against the corrosion potential for base AZ31 (see Appendix G).

5.4 SRET Potential Distribution – Flat Shoulder

The results of SRET scanning when using the flat shoulder are shown in figures 5.5. For additional SRET scans using the flat shoulder FSSW tool please refer to appendix A. Figure 5.5 a shows the right side of the FSSW etched in a picric acid solution to show the boundary of the SZ. The boundary of the SZ is highlighted by the darker upward curved region adjacent to the keyhole, which extends approximately 500µm (measured at half depth) from the keyhole periphery.

The SRET potential distribution can be seen in figure 5.5 b. The graph is a 2-dimensional contour plot with distance on the x and y axis while the colors represent different magnitudes of recorded potentials (V). Areas in red have a higher noble potential signature and areas in dark blue have a lower active potential signature. With the flat shoulder tool design, the noble potential regions represented by red and yellow are segregated and lie adjacent to the keyhole and beneath the shoulder surface. The active potential region, which is blue and purple colored, then extends out into the base material. Therefore a boundary is established between the noble and active areas, which in the graph correspond with the green regions. The horizontal green line in the SRET image for the flat shoulder is simply due to the un-bonded region between the 2 AZ31 sheets and is an artifact arising from the joining process.

When the SRET data is correlated with the microstructure image by overlaying figure 5.5 b on top of 5.5 a, there is very good one to one congruency of the SZ with the noble (red/yellow) region of the weld (figure 5.5 c). This shows that the yellow region in the SRET distributions represents the edge of the SZ and that the SZ has the noblest potential signature. Figure 5.5 d shows the material flow data in a FSSW made with a flat shoulder [71]. To show the material flow a tungsten carbide powder was placed under the tool shoulder pre-welding and due to the influence of the shoulder and threads the powder was mixed into the spot weld. The tungsten carbide tracer elements which show up as white particles (due to atomic contrast in the SEM
image) indicated regions of the weld that had undergone mechanical mixing [71]. From the image it can be seen that the area adjacent to the keyhole and beneath the tool shoulder had undergone mechanical mixing. Since the white marks the edge of the mechanically mixed zone, the boundary between the white particles and the grey AZ31 marked the edge of the TMAZ (the outer most mechanically mixed zone).

When the SRET data is correlated to material flow data in the same manner by overlaying figure 5.5 b on top of figure 5.5 d, it can be seen that all of the noble potential values occurred in areas of the weld that had undergone mechanical mixing (figure 5.5 e). The tungsten carbide powder was added pre-welding beneath the tool shoulder, and due to mechanical mixing from the shoulder and threads of the pin, the powder was incorporated into the SZ and TMAZ. Thus, due to the alignment of the green zone with the edge of the mechanically mixed region identified by the white particles, the green region in the SRET distribution must be the TMAZ.

Figure 5.5 f shows a FSSW made with a flat shoulder that has been immersed in 0.086M NaCl for 2days. The black regions in figure 5.5 f are areas that have undergone significant corrosion resulting in pitting (see arrows in figure 5.5 f). The pits appear black, since the light was shone oblique to the samples when taking optical macrographs, and thus no light can reflect from within the pit. The rough and somewhat wavy regions surrounding the pits have also undergone some corrosion. The immersion tests reveal that preferential corrosion had taken place in that the corroded areas (black pits and rough areas) are segregated at the bottom right section of the welded joint. The top left areas adjacent to the keyhole and beneath the tool shoulder have suffered relatively less corrosion. When the results from the SRET scanning, microstructure, material flow and immersion data are correlated, it is clear that long term corrosion occurred in regions of the weld that had not undergone mechanical mixing. The un-corroded region of figure 5.5 f (adjacent to the keyhole and beneath the shoulder) align perfectly well with the mechanically mixed region, SZ/TMAZ and noble potential regime (figure 5.5 c).
Figure 5.5  Collage of images for flat shoulder testing a) Picric acid etched FSSW in AZ31 showing microstructure b) SRET potential distribution c) Overlay of SRET and microstructure  d) Material flow e) Overlay of material flow and SRET f) 2 day immersion of FSSW in room temperature 0.086M NaCl
5.5 SRET Potential Distribution – Concave Shoulder

The results of SRET scanning when using the concave shoulder are shown in figures 5.6. For additional SRET scans using the flat shoulder FSSW tool, please refer to Appendix B. Figure 5.6 a shows the right side of the FSSW etched in a picric acid solution to show the boundary of the SZ. The boundary of the SZ is highlighted by the darker upward curved region adjacent to the keyhole, which extends approximately 750µm (measured at half depth) from the keyhole periphery.

The SRET potential distribution can be seen in figure 5.6 b. The graph is a 2-dimensional contour plot with distance on the x and y axis while the colors represent different magnitudes of recorded potentials (V). Areas in red have a higher noble potential signature and areas in dark blue have a lower active potential signature. With the concave shoulder tool design, the noble potential regions represented by red and yellow are segregated and lie adjacent to the keyhole and beneath the shoulder surface. The active potential region, which is blue and purple colored, then extends out into the base material. Therefore a boundary is established between the noble and active areas, which in the graph correspond with the green regions.

Figure 5.6 d shows the material flow data in a FSSW made with a concave shoulder [71]. To show the material flow a tungsten carbide powder was placed under the tool shoulder pre-welding and due to the influence of the shoulder and threads the powder was mixed into the spot weld. The tungsten carbide tracer elements which show up as white particles (due to atomic contrast in the SEM image) indicated regions of the weld that have undergone mechanical mixing. From the image it can be seen that the area adjacent to the keyhole and beneath the tool shoulder had undergone mechanical mixing. Since the white marks the edge of the mechanically mixed zone, the boundary between the white particles and the grey AZ31 marked the edge of the TMAZ (the outmost mechanically mixed zone).

Comparing to figure 5.6 a to 5.5 a the change in tool geometry from flat shoulder to concave shoulder caused the SZ to increase in size and causes the TMAZ to be pushed farther into the BM. When comparing the SRET data (figure 5.5 a and 5.6 a) the change in tool geometry caused the noble region to be pushed upward closer to both the keyhole and the beneath the surface.
When the SRET data is correlated to material flow data in the same manner by overlaying figure 5.6 b on top of figure 5.6 d, it can be seen that all of the noble potential values occurred in areas of the weld that had undergone mechanical mixing (figure 5.6 e). The tungsten carbide powder was added pre-welding beneath the tool shoulder, and due to mechanical mixing from the shoulder and threads of the pin, the powder was incorporated into the SZ and TMAZ. Thus, due to the alignment of the green zone with the edge of the mechanically mixed region identified by the white particles, the green region in the SRET distribution must be the TMAZ. Comparing figures 5.5 d and 5.6 d showed that there is more intense mechanical mixing close to the keyhole and beneath the surface for the shoulder, indicated by the higher concentration and lamellar flow of tungsten carbide particles at this location. This explains and is consistent with the differences seen in the SRET images for the flat and concave tool designs.

Figure 5.6 f shows a FSSW made with a concave shoulder that has been immersed in 0.086M NaCl for 2 days. The black regions in figure 5.6 f are areas that have undergone significant corrosion resulting in pitting. The pits appear black, since the light was shone oblique to the samples when taking optical macrographs, and thus no light can reflect from within the pit. The rough and somewhat wavy regions surrounding the pits have also undergone some corrosion. The immersion tests reveal that preferential corrosion had taken place in that the corroded areas (black pits and rough areas) are segregated at the bottom right section of the welded joint. The top left areas adjacent to the keyhole and beneath the tool shoulder have suffered relatively less corrosion. When the results from the SRET scanning, microstructure, material flow and immersion data are correlated, it is clear that long term corrosion occurred in regions of the weld that had not undergone mechanical mixing. The un-corroded region of figure 5.6 f (adjacent to the keyhole and beneath the shoulder) aligns perfectly well with the mechanically mixed region, SZ/TMAZ and noble potential regime (figure 5.6 c). When comparing the immersion test profiles from figure 5.5 f and 5.6 f it can be seen that a similar corrosion profile is maintained. In each case, the un-corroded noble region remains under the surface of the shoulder and adjacent to the keyhole where mechanical mixing takes place and the corroded active region is perfectly congruent with the un-mixed region of the weld.
Figure 5.6 Collage of images for concave shoulder testing a) Picric acid etched FSSW in AZ31 showing microstructure b) SRET potential distribution c) Overlay of SRET and microstructure d) Material flow e) Overlay of material flow and SRET f) 2 day immersion of FSSW in room temperature 0.086M NaCl
5.6 Effect of Tool Geometry on SRET Potential Distribution

This section will be used to compare the similarities and differences in FSSW made with a flat and concave shoulder tool design. Specific emphasis will be placed on the reason behind the similarities and difference based on microstructure.

5.6.1 Influence of Grain Size on Potential Distribution

The average grain size as a function of radial position was determined for the three different FSSW tool designs. The grain sizes were measured 50µm below the top surface of the FSSW welds since this surface makes initial contact with the environment when the fabricated component is in use. It is therefore the most relevant for the present corrosion investigation. The results produced during grain size measurement are shown in figure 5.7.

![Comparison of Average Grain Sizes Across Different Tools](image)

Figure 5.7 Comparison of the average grain size measured 50µm below the top surface of three FSSW welds made using different tool designs
Figure 5.7 shows a number of interesting trends that change as a function of FSSW tool geometry and radial position. Firstly, it can be seen that welds made with the flat shouldered tool have the smallest average grain size variations across the radius of the tool shoulder. Welded joints having much larger average grain sizes are produced by the concave shoulder and scrolled shoulder tools. The reason for this lies in the differing tool geometries and particularly, how they influence the flow and amount of deformation of material during welding. Both the concave and scrolled shoulder tools have a 10° concave section machined into the tool shoulders and based on data from Horie [71] this tool geometry enhances the flow of material by forcing material from beneath the shoulder periphery inwards towards the tool centerline (figure 5.8). This causes increased amounts of shear and plastic deformation and heat generation, and increased the extent of grain growth at the surface in contact with the base of the tool shoulder.

![Figure 5.8 SEM images of FSSW welds with incorporated WC tracer element in a) flat shoulder b) concave shoulder c) scroll shoulder [71]](image-url)
Figure 5.7 also shows that the average grain size decreased, as the radial position increased from the edge of the SZ to the shoulder periphery. This trend is quite clear for all three tool designs. It is interesting to note that the trends produced by the concave tool and the concave section of the scrolled tool are very similar in that they have similar slopes and similar average grain size values. This suggests that particular FSSW tool geometries have distinct, unique effects on the grain size distribution at the top surface. The concave section of the FSSW tools produces a grain size distribution that has a stronger dependence on radial location than the flat shouldered tool, since the slope of the average grain size vs. radial position relation is steeper. The drop-off in grain size with increasing radial location may be explained as follows. The reason for the drop-off in grain size must be due to the extent of plastic flow that occurred along the shoulder of the tool. North et al [72] showed the amount of displacement (radial, axial and angular) and by taking the sum of these values a new plot of total displacement vs. radial position can be derived (figure 5.9).

![Displacement of Material During FSSW](image)

**Figure 5.9** Displacement vs radial position for FSSW with flat shouldered tool [72]
The total displacement (sum of radial, angular and axial displacements) has a parabolic shape, which does not match any of the trends in grain size vs. radial position. Therefore, material displacement alone does not account for the decrease in grain size 50μm beneath the shoulder. The strain rate increases as a function of radial position due to the increase in tool linear velocity as r increases (figure 5.10). Increased plastic strain rates leads to increased plastic deformation and thus the grain size is expected to decrease. The effect of strain rate and the resulting plastic deformation helps to better explain the decrease in average grain size as a function of radial position in the weld.

\[
\begin{align*}
  v &= \omega r \\
  \dot{\varepsilon} &= f(v)
\end{align*}
\]

Figure 5.10  Schematic showing the evolution of strain rate as a function of radial position

When the average grain size data from the flat and concave shouldered tools are correlated with the appropriate SRET potential distributions, only the top portion of the data needs to be analyzed since this is where the grain size data came from. Seeing that the SRET potential does not change as a function of radial position (only concerning the top 50um below the shoulder of the weld) while the grain size decreases by approximately 44% and 40% for the concave and flat shoulder samples respectively, it suggests that grain size alone did not have a major contribution to the potential distribution and corrosion behavior in FSSW.
5.6.2 Influence of Abnormal Grain Growth on the Potential Distribution

Abnormal grains (where the grain size is greater than twice the average grain size) are related with radial location in figure 5.11 below.

![Abnormal Grain Growth](image)

**Figure 5.11** Graph showing the number of abnormal grains as a function of radial position in the FSSW weld.

The trend lines in figure 5.11 are used only for reference to separate the data points found when examining the average grain size values found when using different tool designs. The flat shouldered tool produced the highest number of abnormal grains, while the concave and scrolled shoulder tools produced similar, but lower amounts. The flat shoulder tool produced on average four times more abnormal grains than the concave or scrolled shoulder tools. The abnormal grain count dependence with radial location was similar for all tool designs, since the slopes of all the lines are similar. Increased amounts of abnormal grain growth in spot welds made using the flat shouldered tool is explained partly by statistics. The grain size analysis indicated that the flat shoulder produced the smallest grain sizes across the length of the shoulder surface. Within the
specified grain size analysis box (see Fig. 4.21 in the experimental section of this thesis) there are more grains when using the flat shouldered tool. For example, the average grain sizes at the location 1000\(\mu\)m from the keyhole periphery are 4\(\mu\)m, 7.5\(\mu\)m and 9\(\mu\)m for spot welds made using the flat, concave and scrolled shoulder tools, see fig. 5.12. As a result, it would be expected that there would be more abnormal grains in the spot weld made using the flat shouldered tool.

Figure 5.12 Grain size analysis box showing the relative number of grains (and abnormal grains) in spot welds made using the flat shouldered tool (top), the concave shoulder tool (middle) and the scrolled shoulder tool (bottom). Box length = 100\(\mu\)m
Comparing the abnormal grain growth data to the SRET potential distribution revealed that there is no concrete relationship between the two. Although the number of abnormal grains increased as a function of radial position, the SRET potential remained unchanged, showing that abnormal grain growth did not affect the potential distribution in FSSW welds.

5.6.3 Influence of Precipitate Distribution on Potential Distribution

A number of factors result from the mechanical deformation during FSSW welding that cause the SZ to have a lower corrosion rate than the surrounding base material. These factors include: (a) the formation of a fine dynamically recrystallized grain structure in the SZ, and (b) the dissolution of the secondary phase Mg\textsubscript{17}Al\textsubscript{12}. The fine recrystallized grain structure in the SZ is produced by the intense plastic deformation and heat generation from the rotating pin and shoulder. Within the SZ there are very few precipitates as the β Mg\textsubscript{17}Al\textsubscript{12} dissolve at 437°C, and this leaves an equiaxed alpha-Mg microstructure with equally few micro-galvanic cells between the α-Mg primary and β Mg\textsubscript{17}Al\textsubscript{12}. Secondly, the dynamic recrystallization process removes many of the dislocations and twins within the microstructure. The combined effect of having little β Mg\textsubscript{17}Al\textsubscript{12} and low dislocation/twin density can explain the increased corrosion resistance in the SZ. The surrounding base material undergoes significant corrosion and this is due to the nature of the base alloy. AZ31 is a wrought alloy and as such has a deformed microstructure containing dislocation and twins. In addition, β Mg\textsubscript{17}Al\textsubscript{12} still remains as a divorced eutectic and this allows for the formation of micro-galvanic cells. These factors contribute to the base alloy suffering increased corrosion activity. Therefore, the FSSW process, in particular the mechanical deformation resulting in decreased amounts of β Mg\textsubscript{17}Al\textsubscript{12}, dislocation and twins, causes a change in the electrochemical interaction of the SZ compared to the unstirred region surrounding the SZ. The SZ is protected during immersion in aqueous NaCl solutions, and corrosion attack initiates at the TMAZ and continues into the base material.

It is interesting to note that in a study done by Benhamu [73] where the corrosion behaviour of Gas Tungsten Arc (GTA) welded AZ31 was investigated via polarization testing, the opposite trend was found. Benhamu found that the weld nugget, or fusion zone (FZ) (analogous to the SZ in FSSW), displayed active corrosion activity, while the surrounding material a relatively noble
activity. This meant that the weld nugget suffered pitting, while the surrounding material exhibited less corrosion. GTA welding involves no mechanical deformation and is a high temperature fusion joining technique. In a study done by Liu [74] the microstructure of GTA welds in AZ31 was investigated and it was found that the weld nugget consisted of fine equiaxed grains with a large amount of intergranular Mg\(_{17}\)Al\(_{12}\) (figure 5.13).

![Figure 5.13](image)

**Figure 5.13** Micrograph of GTA AZ31 fusion zone (FZ) showing \(\alpha\) grains and intergranular Mg\(_{17}\)Al\(_{12}\) [74]

Mg\(_{17}\)Al\(_{12}\) is retained in the fusion zone of GTA welds, since melting followed by a longer cooling time provides sufficient time for the Mg\(_{17}\)Al\(_{12}\) to re-precipitate at the grain boundaries. Therefore, the results found during SRET and immersion testing in the present thesis are consistent with Liu’s work; the SZ regions containing fine grained alpha-Mg is not corroded in FSSW joints and the fusion zone region in GTA welds made in AZ31 material are corroded, since they comprise a mixture of alpha-Mg and \(\beta\) Mg\(_{17}\)Al\(_{12}\). This provides further proof to the postulate that the mechanical stirring of the FSSW process is the cause for the shift in potential in the stirred region of the FSSW weld (figure 5.5, 5.6). The immersion tests confirm that the Blue and purple regions observed in the SRET potential distributions (relative anodic areas) are in fact active areas.

Therefore the TMAZ is the region between the active and noble regions of the FSSW when immersed in aqueous NaCl solutions. Being between these two areas the TMAZ serves as a transition region and must play a critical role in the corrosion of FSSW in magnesium alloys. In
order to see the transition region and see its effect on the corrosion process, the welding parameters (i.e. Dwell time) can be varied to accentuate the presence of the TMAZ.

### 5.7 Effect of Dwell Time of SRET Potential Distribution

The influence of dwell time on the SRET potential distributions can be seen in figure 5.14. The same analysis developed for the effect of tool geometry on corrosion behavior was applied. Areas in red have a higher noble potential signature and areas in dark blue have a lower active potential signature. The relative size of the noble area and the TMAZ boundary will be used to analyze the effect of dwell time on corrosion behavior.

![SRET Potential Distributions](image)

**Figure 5.14** SRET potential distributions for welds made with a flat shoulder with a dwell time of a) 1s b) 4s. Approximate areas scanned outlined in red for welds made with c) 1s dwell d) 4s dwell.
Figure 5.14 shows that again the noble potential area is located adjacent to the keyhole and beneath the shoulder of the weld. The main differences between the microstructures of welds made with 1s and 4s dwell times were the size of the SZ and how far the TMAZ extended out into the base material. Figure 5.15 shows the difference in SZ width in FSSW samples made in this investigation using dwell times of 1s and 4s. The 1s dwell sample had a SZ width of approximately 500μm, while the 4s dwell sample had a SZ width of approximately 1300μm (taken at half depth of the weld). North et al. [31] also investigated the SZ width as a function of dwell time in FSSW AZ31. Their results can be seen in figure 5.16, and they agree with the SZ sizes produced with 1s and 4s dwell times in this investigation (figure 5.15).

![Figure 5.15](image-url)  
**Figure 5.15**  
FSSW samples etched in picric acid showing size of SZ and TMAZ in samples made with a) 1s dwell and b) 4s dwell

![Figure 5.16](image-url)  
**Figure 5.16**  
Relationship between SZ width and dwell time in FSSW AZ31 [31]
This same trend continues in the SRET potential distributions, in test samples made using 1s and 4s dwell times (figure 5.14). If the SZ boundary is the red/yellow region as previously established, then the SZ widths indicated during SRET testing can be seen in figure 5.17. The SZ width was considerably larger in the 4s compared to the 1s dwell sample, and using the SRET data (figure 5.17) or the microstructure data (figure 5.15), the increase in size was approximately the same, at roughly 1300μm. This proves that the SRET monitored the change in microstructure produced during joining, and the TMAZ was the boundary between the noble and active regions in the welded test samples.

Figure 5.17 SRET potential distributions with SZ width drawn in for samples made with a) 1s dwell b) 4s dwell

Figure 5.18 shows a magnified image of the 4s dwell sample following SRET testing and focuses on the boundary between the noble and active areas. Along the boundary between the noble and active areas there were many corrosion sites, which appeared as elongated pits oriented at a 45° angle. These corrosion sites were the only corrosion sites seen anywhere on the sample, and the fact that these corrosion sites are elongated and angled at 45° suggests that the corroded region corresponded with the TMAZ.
The TMAZ contains deformed and elongated grains displaced upwards at a 45° angle due to the upward shear produced at the edge of the SZ (figure 5.19). In addition, being only a partiality recrystallized grain structure there is a large amount of secondary phase Mg$_{17}$Al$_{12}$ surrounding the elongated grains. It would be expected that this region of the weld would have a moderate amount of dislocations and residual twins due to the partial recrystallization in this zone. All three of these factors contributed to accelerated corrosion within magnesium alloys. The last effect, which explains the concentrated corrosion activity along the interface is caused by a micro-galvanic cell, which is established due to the fact that there are two regions with different corrosion potentials in electrical contact within an electrolyte. Because of the small current and high resistance of the electrolyte, galvanic corrosion is limited to the immediate areas surrounding the anode/cathode boundary. Therefore, concentrated corrosion attack at the interface between the noble and active areas of the welded joint was caused by the presence of second phase precipitates, moderate levels of dislocations and twins and the limited galvanic current at the interface. The TMAZ is the boundary between the noble SZ region, which had higher potential values, and active areas adjacent to the SZ, which had negative potentials. This explains why this region was the region that is attacked first.

Figure 5.18 Optical image showing corrosion activity located at 45° along TMAZ interface
Figure 5.19  Micrograph of AZ91 showing alignment of Mg17Al12 in deformed TMAZ [76]
6 Conclusions

A scanning reference electrode technique apparatus has been successfully commissioned based on SRET electrochemical theory outlined by Isaacs and Vyas. The operational parameters have been optimized to give adequate spatial resolution and sensitivity for investigating corrosion of FSSW in AZ31 magnesium alloys.

The SRET output showed that a noble potential region was created following FSSW joining and was segregated to the locations beneath the base of the tool shoulder and adjacent to the periphery of the keyhole. This trend was observed in spot welds made with the flat and concave shouldered tools and welds made with 1s and 4s dwell times. However, spot welds made with the concave shoulder had the noble potential region pushed up closer to the top of the weld. In order to determine the cause of the noble potential region formed, a number of secondary investigations were carried out, such as grain size analysis (average grain size and abnormal grain growth), material flow and immersion testing.

The average grain size data showed that when using three different tool designs the average grain size changed markedly as a function of radial position. When the change in average grain size as a function of radial position was correlated to the SRET data, there was no concrete trend that could be relate with the SRET corrosion testing output. Similarly, there was no relation between the number of abnormal grains measured across the weld surface and SRET corrosion testing output.

Correlating the SRET data with the material flow data showed that the noble regions in FSSW welds coincided well with the weld region that had undergone mechanical stirring during the joining operation. This was true for welds made with both the flat and concave shouldered tools and welds made using 1s and 4s dwell times.

Correlating the immersion test images with the SRET potential distribution shows that the noble region of the weld is located below the tool shoulder and adjacent to the keyhole and the remainder of the welded joint is an active region. The images revealed that pitting corrosion occurred mainly in the active region of the weld. When comparing the 1s and 4s dwell time immersion tests it was found that the 4s sample had increased corrosion attack along the TMAZ boundary.
Based on the observations made through SRET testing, grain size analysis, and immersion testing a series of conclusions have been developed.

1. High temperature mechanical mixing causes large amounts of mechanical deformation leading to changes in grain size and changes in the amount of abnormal grains. Since there was no correlation between the grain size or abnormal grain growth with the SRET data, and since the SRET testing output aligned with material flow output, the mechanical deformation of the FSSW process causes the shift in potential values, creating distinct noble and active regions within the joint.

2. Changing the tool geometry changes the material flow pattern and using a concave shoulder profile leads to increased mechanical mixing closer to the top of the shoulder and adjacent to the keyhole. Therefore, when making a joint with the concave shoulder tool, the noble region follows the material flow pattern and is pushed up closer beneath the shoulder and adjacent to the keyhole.

3. Changing the dwell time pushes the TMAZ outward farther into the base material and close examination reveals that there is heavy localized corrosion along the TMAZ boundary between the noble and active regions. This suggests that there is a micro-galvanic electrochemical cell formed between the anodic and cathodic regions of the welded joint, and increased localized corrosion takes place at the boundary between them.

4. The FSSW welding operation raises the corrosion potential above the pitting regime in the mechanically mixed zone and facilitates preferential pitting attack in the surrounding areas. The large amount of mechanical deformation and high temperatures experienced in the mechanically mixed region causes the dissolution of the second phase precipitate Mg$_{17}$Al$_{12}$, and a recrystallized grain structure with few dislocations and twins. The reduced amount of Mg$_{17}$Al$_{12}$ causes less micro-galvanic cells within the mechanically mixed region. The reduced amount of twins and dislocations in the mechanically mixed region leaves less corrosion initiation sites and thus it suffers less corrosion attack. The combination of having less Mg$_{17}$Al$_{12}$ dislocations and twins explains the noble potential signature recorded in the mechanically mixed zone during SRET testing.
7 Future Work

1. The investigation of FSSW corrosion in AZ31 has been successful, however it would be instructive to perform further work to ascertain the reason for the shift in the potential observed in the mechanically mixed zone. Some possible reasons for the potential shift include preferential grain orientation, compositional changes, or residual stress variations. These aspects could be investigated using techniques such as EBSD, SEM/EDX analysis, and stress relieving heat treatments.

2. Furthermore, it would be interesting to examine the SRET corrosion performance of welds made with FSSW tools that create markedly different material flow pattern within the stir zone region. Different flow patterns could be produced by using FSSW tools with different thread pitches, shoulder geometries and different degrees of shoulder concavity. Performing the SRET analysis on these samples would further confirm the conclusion that the noble regions are caused by mechanical mixing, and establish a trend between material flow in the stir zone region and SRET corrosion testing output.
References


Appendix A - Flat Shoulder 1s SRET
Appendix B- Concave Shoulder 1s SRET
Appendix C - Flat Shoulder 4s SRET

SRET Across 4s Flat FSSW

SRET Across Flat 4s FSSW
*Coloured dashed lines represent the perceived edges of the copper wire, taken as the point on the curve where the potential begins to plateau.

Perceived width for 10µm/s:

\[ = 1600 \mu m + 400 \mu m + 200 \mu m \]

\[ = 2200 \mu m \]

Percent error for 10µm/s:

\[ = \frac{(2200 \mu m - 1600 \mu m) \times 100}{1600 \mu m} \]

\[ = 37.5\% \]
Appendix E - Sample Calculation for Percent Error in Scan Height

*Coloured dashed lines represent the perceived length of copper wire, taken as the point on the curve where the potential begins to deviate from the plateau level.

Percent error for 20 µm:

\[
= \left( \frac{1600 \text{ µm} - 1200 \text{ µm}}{1600 \text{ µm}} \right) \times 100\%
\]

\[= 25\%\]
Appendix F- Sample Calculation for Decay Distance vs. Solution Concentration

*Coloured dashed lines represent the decay distance measured from the right edge of the copper wire to the point on the curve where the potential begins to level off representing a steady magnesium signal.