Localized Corrosion of Friction Stir Welded Magnesium AZ Alloys

by

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Department of Materials Science and Engineering
University of Toronto

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Abstract

Magnesium alloys, being the lightest engineering alloys, have the potential to replace ferrous and aluminum alloys in structural applications in the transportation sector. Thus far, their use has been limited largely due to challenges associated with their inherently poor corrosion resistance properties, a problem that is accentuated when the alloys are welded. The work in this dissertation elucidated the mechanisms governing the corrosion behaviour of friction stir welded magnesium AZ alloys. The investigation utilized an integrated approach consisting of several corrosion measurement techniques (both bulk and localized measurements) to examine the effect of individual microstructural features on the overall corrosion behaviour of the joint. Dissolution of second phase precipitates was determined to govern the corrosion behaviour of the joint by enhancing the corrosion resistance of the weld nugget. Based on the findings, a mixed potential theory model correlating changes in second phase particle size and distribution to the corrosion behaviour of friction stir spot welded AZ31 was constructed. The mechanism governing the
corrosion resistance of similar friction stir welded AZ31B joints did not apply to dissimilar AZ31/AZ80 welds. Instead, the corrosion of dissimilar joints was governed by the galvanic coupling between the dissimilar magnesium alloys. Based on the corrosion studies, plasma electrolytic oxidation (PEO) coatings were identified as a promising corrosion mitigating strategy for welded magnesium structures. The application of this coating to friction stir welded specimens improved the corrosion resistance of both similar and dissimilar types of joints. The corrosion mechanism was also altered, as the corrosion of coated specimens was principally governed by the imperfections of the PEO coating, and not by the microstructural changes caused by the welding operation. The findings of this study provide theoretical knowledge that will enable the optimization FSW processing to permit the use of magnesium alloys in the automotive industry.
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In loving memory of my Grandfather

Dr. Lev Reymerov

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<tr>
<td>BM</td>
<td>Base metal</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscatter electron</td>
</tr>
<tr>
<td>CS</td>
<td>Cross-sectional surface</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>ETV-ICP-OES</td>
<td>Electro thermal vaporization – inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>FSSW</td>
<td>Friction stir spot welding</td>
</tr>
<tr>
<td>FSW</td>
<td>Friction stir welding</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat affected zone</td>
</tr>
<tr>
<td>HCP</td>
<td>hexagonal close-packed</td>
</tr>
<tr>
<td>HT</td>
<td>Heat treated</td>
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<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma atomic emission spectrometry</td>
</tr>
<tr>
<td>MCP</td>
<td>Microcapillary Polarization</td>
</tr>
<tr>
<td>ML</td>
<td>Mass loss</td>
</tr>
<tr>
<td>ND</td>
<td>Normal direction</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PDP</td>
<td>Potentiodynamic polarization</td>
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<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PEO</td>
<td>Plasma electrolytic oxidation</td>
</tr>
<tr>
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<td>Rolling surface</td>
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<td>SBF</td>
<td>Simulated body fluid</td>
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<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SRET</td>
<td>Scanning reference electrode technique</td>
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<tr>
<td>SVET</td>
<td>Scanning vibrating electrode technique</td>
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<td>Stir zone</td>
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<td>Transmission electron microscopy</td>
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<tr>
<td>TMAZ</td>
<td>Thermo-mechanically affected zone</td>
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<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>α, β, ϒ</td>
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<td>a, b, c</td>
<td>Lattice constants</td>
</tr>
<tr>
<td>[Al]</td>
<td>Aluminum content in the alloy</td>
</tr>
<tr>
<td>$A_{Total}$</td>
<td>Area of a weight loss specimen</td>
</tr>
<tr>
<td>$A_{UC}$</td>
<td>Uncorroded area of the coating</td>
</tr>
<tr>
<td>$B_O$</td>
<td>Half thickness of a plate-shaped liquid droplet</td>
</tr>
<tr>
<td>$c^{\alpha/\beta}_{T_1}$</td>
<td>Solute concentration in the $\alpha$-Mg phase at room temperature.</td>
</tr>
<tr>
<td>$c^{\alpha/liq}_{T_2}$</td>
<td>Maximum solubility limit of Al in the $\alpha$-Mg phase at the eutectic temperature (437 °C)</td>
</tr>
<tr>
<td>$c^{liq/\alpha}_{T_2}$</td>
<td>Eutectic composition of the two phases ($\alpha$-Mg + $\beta$-Mg&lt;sub&gt;17&lt;/sub&gt;Al&lt;sub&gt;12&lt;/sub&gt;) present in the melted film at the eutectic temperature (437 °C)</td>
</tr>
<tr>
<td>[Cl&lt;sup&gt;-&lt;/sup&gt;]</td>
<td>Chloride concentration</td>
</tr>
<tr>
<td>{Cl&lt;sup&gt;-&lt;/sup&gt;}</td>
<td>Chloride concentration scaling factor</td>
</tr>
<tr>
<td>$CR_{AW}$</td>
<td>Corrosion rate of uncoated specimens (obtained through mass loss testing)</td>
</tr>
<tr>
<td>$CR_{PEO}$</td>
<td>Corrosion rate of PEO coated specimens (obtained through mass loss testing)</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td>$D_{Al \text{ in Mg, } T}$</td>
<td>Diffusion coefficient of aluminum in magnesium at temperature T</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$d_{pounce}$</td>
<td>Pounce position</td>
</tr>
<tr>
<td>$d_{travel}$</td>
<td>Distance between the welding tool at its rest position and the surface of the metal</td>
</tr>
<tr>
<td>$E_{appl}$</td>
<td>Electrode potential when it is anodically polarized</td>
</tr>
<tr>
<td>$E_b$</td>
<td>Breakdown potential</td>
</tr>
<tr>
<td>$E_{corr}$</td>
<td>Corrosion potential</td>
</tr>
<tr>
<td>$E_{OCP}$</td>
<td>Open cell potential</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>$f_{\alpha-Mg}$</td>
<td>Area fraction of the $\alpha$-Mg phase</td>
</tr>
<tr>
<td>$f_{\beta-Mg_{17}Al_{12}}$</td>
<td>Area fraction of the $\beta$-Mg&lt;sub&gt;17&lt;/sub&gt;Al&lt;sub&gt;12&lt;/sub&gt; phase</td>
</tr>
<tr>
<td>$f_{Al_8Mn_5}$</td>
<td>Area fraction of the Al&lt;sub&gt;8&lt;/sub&gt;Mn&lt;sub&gt;5&lt;/sub&gt; phase</td>
</tr>
<tr>
<td>$f_{anode}$</td>
<td>Anodic area fraction</td>
</tr>
<tr>
<td>$H_f$</td>
<td>Height of the welding flash</td>
</tr>
<tr>
<td>$I_o$</td>
<td>Exchange current</td>
</tr>
<tr>
<td>$I_{\alpha-Mg}$</td>
<td>Polarization current of $\alpha$-Mg</td>
</tr>
<tr>
<td>$I_{\beta-Mg_{17}Al_{12}}$</td>
<td>Polarization current of $\beta$-Mg&lt;sub&gt;17&lt;/sub&gt;Al&lt;sub&gt;12&lt;/sub&gt;</td>
</tr>
<tr>
<td>$I_a$</td>
<td>Anodic current</td>
</tr>
<tr>
<td>$I_{Al_8Mn_5}$</td>
<td>Polarization current of Al&lt;sub&gt;8&lt;/sub&gt;Mn&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>$I_{AZ31}$</td>
<td>Polarization current of AZ31</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$I_c$</td>
<td>Cathodic current</td>
</tr>
<tr>
<td>$i_{corr}$</td>
<td>Corrosion current density</td>
</tr>
<tr>
<td>$I_{corr}$</td>
<td>Corrosion rate at OCP</td>
</tr>
<tr>
<td>$i_{corr,BM}$</td>
<td>Corrosion current density of the BM</td>
</tr>
<tr>
<td>$i_{corr,BM-CS}$</td>
<td>Corrosion current density of the base metal on the cross-sectional surface</td>
</tr>
<tr>
<td>$i_{corr,BM-RS}$</td>
<td>Corrosion current density of the base metal on the rolling surface</td>
</tr>
<tr>
<td>$i_{corr,SZ}$</td>
<td>Corrosion current density of the SZ</td>
</tr>
<tr>
<td>$I_H$</td>
<td>Hydrogen evolution reaction rate</td>
</tr>
<tr>
<td>$I_{H,e}$</td>
<td>Theoretical cathodic current when the potential is increased to $E_{appl}$</td>
</tr>
<tr>
<td>$I_{H,m}$</td>
<td>Experimentally measured cathodic current when the potential is increased to $E_{appl}$</td>
</tr>
<tr>
<td>$I_{Mg}$</td>
<td>Magnesium corrosion rate</td>
</tr>
<tr>
<td>$I_{Mg,e}$</td>
<td>Theoretical anodic current when the potential is increased to $E_{appl}$</td>
</tr>
<tr>
<td>$I_{Mg,m}$</td>
<td>Experimentally measured anodic current when the potential is increased to $E_{appl}$</td>
</tr>
<tr>
<td>$I_{obs}$</td>
<td>Observed current when $E_{appl}$ is applied</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$i_z$</td>
<td>Current flux density along the axis of SVET probe vibration</td>
</tr>
<tr>
<td>$k_l$</td>
<td>Driving force solute liquid-state diffusion</td>
</tr>
<tr>
<td>$k_s$</td>
<td>Driving force solute state-state diffusion</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass</td>
</tr>
<tr>
<td>$m_c$</td>
<td>Mass of PEO coated specimens following treatment in chromic acid solution</td>
</tr>
<tr>
<td>$m_f$</td>
<td>Final mass of a weight loss specimen</td>
</tr>
<tr>
<td>$m_i$</td>
<td>Initial mass of a weight loss specimen</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons transferred</td>
</tr>
<tr>
<td>[NaCl]</td>
<td>Sodium chloride concentration</td>
</tr>
<tr>
<td>$N_L$</td>
<td>Number of scanned lines</td>
</tr>
<tr>
<td>${\text{pH}}$</td>
<td>pH scaling factor</td>
</tr>
<tr>
<td>$Q_{\text{diff}}$</td>
<td>Activation energy for diffusion of Al atoms in Mg</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$R_o$</td>
<td>Radius of a spherical dissolving solid particle</td>
</tr>
<tr>
<td>$R_a$</td>
<td>Average surface roughness</td>
</tr>
<tr>
<td>$R_{\text{Al/Mn}}$</td>
<td>Aluminum to manganese concentration ratio</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Polarization resistance</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>Rs</td>
<td>Rotational speed of the welding tool</td>
</tr>
<tr>
<td>SR(_X)</td>
<td>Horizontal scanning rate</td>
</tr>
<tr>
<td>SR(_Y)</td>
<td>Vertical scanning rate</td>
</tr>
<tr>
<td>SX</td>
<td>Horizontal scan distance</td>
</tr>
<tr>
<td>SY</td>
<td>Vertical scan distance</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>({t})</td>
<td>Spray time scaling factor</td>
</tr>
<tr>
<td>(t_{I/II})</td>
<td>Transition time between stage I and stage II of the PEO synthesis process</td>
</tr>
<tr>
<td>(t_{II/III})</td>
<td>Transition time between stage II and stage III of the PEO synthesis process</td>
</tr>
<tr>
<td>(t_{III/IV})</td>
<td>Transition time between stage III and stage IV of the PEO synthesis process</td>
</tr>
<tr>
<td>TD</td>
<td>Dwell time</td>
</tr>
<tr>
<td>t(_{diff})</td>
<td>Diffusion time</td>
</tr>
<tr>
<td>t(_f)</td>
<td>End of the Mg(<em>{17})Al(</em>{12}) dissolution period</td>
</tr>
<tr>
<td>ti</td>
<td>Beginning of the Mg(<em>{17})Al(</em>{12}) dissolution period</td>
</tr>
<tr>
<td>(t_{ML})</td>
<td>Mass loss exposure time</td>
</tr>
<tr>
<td>ti</td>
<td>Transition time</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>$t_{\text{spray}}$</td>
<td>Salt fog spraying time</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Characteristic voltage mode</td>
</tr>
<tr>
<td>$V_m(\text{II})$</td>
<td>Characteristic voltage mode in stage II</td>
</tr>
<tr>
<td>$V_m(\text{IV})$</td>
<td>Characteristic voltage mode in stage IV</td>
</tr>
<tr>
<td>$W_f$</td>
<td>Width of the welding flash</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

1.1 Motivation

A considerable amount of attention has been given to understanding the mechanism(s) governing the corrosion behaviour of magnesium alloys. Much of the research in this area is driven by an automotive industry that seeks to lower the weight of vehicles through the use of innovative lightweight materials. Chassis weight reductions significantly reduce the overall vehicle mass, leading to improved performance and enhanced fuel efficiency. Magnesium alloys, being the lightest engineering alloys, have the potential to replace ferrous and aluminum alloys in structural applications [1]. A study estimated that the use of magnesium alloys can reduce the total weight of automotive components by up to 20% [1]. Thus far, these alloys have seen limited application largely due to challenges associated with their ability to be joined and their inherently poor corrosion resistance properties [1, 2].

There are many challenges associated with traditional joining methods for magnesium alloys due to their thermal and electrical properties along with their oxidation characteristics [2]. Conventional fusion welding results in many solidification related problems such as porosity, residual stress, and hot cracking that are present in resistance spot welding or partial segregation and galvanic corrosion present in gas tungsten arc welding [1, 2]. To address the issue a new novel approach was developed by the Welding Institute of England in 1991; the friction stir welding (FSW) technique [3]. There are many advantages to FSW over conventional welding techniques. FSW welds are formed with smaller temperature gradients between the weld and the bulk material in comparison to conventional methods, which results in a crack and pore-free microstructure [4]. The welding process also eliminates smoke, splash, and oxidation issues that are often encountered with conventional welding methods [2].

The development of FSW largely resolved the challenges associated with joining of magnesium alloys and provided manufacturers with a reliable method to produce components. The progress in finding a suitable joining technology for magnesium alloys significantly surpassed the advances made in finding a corrosion mitigations strategy that can be applied on a large commercial scale. Much of the recent work on magnesium alloys focused on understanding the mechanism(s) governing their corrosion behaviour (see discussion in Chapter 3). The new knowledge has
enabled engineers to improve the corrosion resistance of magnesium alloys by altering the chemical composition (e.g. development of new alloys), carefully controlling the microstructure (e.g. optimization of welding parameters), and developing protective barriers that could be applied to the surface of the alloy (e.g. coatings) [1, 2, 5]. While the recent advancements show a promise towards overcoming the challenges associated with corrosion of magnesium alloys, several critical knowledge gaps remain.

To date, most of the work carried on magnesium alloys examined unwelded specimens, and the effect of FSW on the corrosion mechanisms of magnesium alloys remains largely unknown. From the few investigations that attempted to evaluate the effect of FSW on the corrosion resistance of magnesium alloys it can be concluded that the welding process enhanced the corrosion resistance of the weld nugget as compared to the base metal (see discussion in Chapter 5) [6-10]. FSW was also reported to enhance the susceptibility of the alloy for localized corrosion attack at the boundary between the weld nugget and the base metal [11, 12]. It is important to note that while the authors suggested that the changes in the corrosion behaviour were somehow related to the microstructural evolution occurring during the welding process, the exact mechanism leading to these changes has not been identified. If magnesium alloys were to be used within structural applications in the transportation sector, it is essential to understand the effect of welding on the corrosion behavior of magnesium alloys. A better understanding of the effect of thermo-mechanical material flow during welding on the corrosion behavior of the weldment will enable the design of a solution that mitigates the degradation associated with the weld. Overall, the aim of this work is to develop sufficient theoretical knowledge that will enable and optimize FSW processing to permit the use of magnesium alloys in the automotive industry.

Specific attention was given in this work to a commercially available AZ31 magnesium alloy. This alloy is particularly attractive to the automotive industry due to its high specific strength and its superplasticity at high temperatures [13]. Alloys that exhibit superplasticity have better workability that allows them to be shaped using common manufacturing techniques [13]. In the work herein, the mechanism governing the electrochemical properties of FSW joints made in AZ31 was elucidated and a suitable corrosion mitigation strategy was proposed. The work was also expanded to consider dissimilar joints (AZ31/AZ80) to determine if the same corrosion mechanism applied. A suitable corrosion mitigation strategy was determined for dissimilar welds as well. The organization of this thesis is detailed in the following section.
1.2 About This Thesis

The research in this thesis takes on a systematic approach to determine the mechanism(s) governing the corrosion behaviour of FSW joints made in magnesium alloys, with the goal to develop a corrosion mitigation strategy that could be used in an industrial application.

The thesis begins with a critical review of the relevant literature. Chapter 2 discusses the microstructure of magnesium and its alloys, and particular attention is given to the effect of alloying. Chapter 3 presents a detailed literature review of the mechanisms governing the corrosion behaviour of magnesium alloys. The chapter begins by examining the corrosion of pure magnesium and then proceeds to discuss the effect of alloying, microstructure and electrolyte. The chapter concludes with a review of plasma electrolytic oxidation (PEO) coatings, a promising corrosion mitigation strategy. Chapter 4 reviews friction stir welding, and the effect it has on the microstructure of the base metal. Chapter 5 concludes the literature review by presenting a summary of the state-of-the-art research on corrosion of FSW joints made in magnesium alloys. Critical knowledge gaps and the resulting thesis objectives are presented as well.

Protocols for all the experiments detailed in this thesis are given in Chapter 6. The electrochemical properties of individual weld region in friction stir spot welded (FSSW) AZ31B are examined in Chapter 7. The improved corrosion resistance of the weld nugget was confirmed by microcapillary polarization, and mechanistic cause for this improvement was examined in Chapter 8-10. The effect of various microstructural properties changing during the welding process was examined systematically to evaluate the individual effect of each on the corrosion resistance of the joint. Chapter 8 examined the effect of changes in grain size and residual stress, while Chapter 9 evaluated the effect of changes in grain orientation. Finally, Chapter 10 investigated the effect of particle dissolution. In addition to electrochemical characterization, the corrosion properties of the welds were examined using methods that are commonly used in industry. Chapter 10 and 11 present a mass loss testing investigation that evaluated the corrosion resistance of FSSW joints made in AZ31 with and without the flash, respectively. To determine if the conclusions from Chapters 7-12 applied to dissimilar welds as well, Chapter 13 examined the corrosion behaviour of dissimilar AZ31/AZ80 welds.

Chapter 14-15 focused on assessing the feasibility of PEO coatings as a corrosion mitigation strategy for friction stir spot welded structures. Chapter 14 examined the PEO coating formation
mechanism using a novel statistical approach to gain insight on the effect of process parameters. Chapter 15 then evaluated the corrosion resistance of PEO coatings on similar (Section 15.1) and dissimilar (Section 15.2) FSW joints. The conclusions and recommendation for future work appear in Chapter 16.
Chapter 2 Magnesium AZ Alloys

2.1 Chemical Composition

Pure elemental magnesium has a hexagonal close-packed (HCP) lattice with lattice parameters of $a=0.320$ nm, $c=0.520$ nm and a $c/a$ ratio 1.624 [14]. The HCP structure has very few slip systems resulting in low plasticity at room temperature. Deformation is accommodated by the basal slip system $(0001) <11\bar{2}0>$ and through pyramidal twinning $(10\bar{1}0) <11\bar{2}0>$ [15].

In order to improve its mechanical properties, pure magnesium is alloyed with other elements to produce a wide array of alloys. For instance, alloying addition of aluminum and zinc improve the mechanical properties by both solution strengthening and second phase precipitation [16]. The codification of these alloys is based on a system that is described in the ASTM B951 standard [17]. The system utilizes a five-symbol notation to communicate the major alloying elements and their quantity in the alloy (an example is shown in Figure 2-1). The first two letters used in the alloy name correspond to the major alloying elements, where A and Z refer to aluminum and zinc, respectively. Following the letters, the code contains digits that correspond to rounded weight percent of each of the alloying elements (note that in this case 0 indicates 0.5 wt.%). Finally, the last letter in each identification code corresponds to the historical iteration of the alloy design (A-1st, B-2nd, C-3rd, etc.). Additional information on the condition of the alloy is provided following a hyphen, F for as-fabricated, O for fully annealed, H for strain hardened and T for thermally treated. If the alloy was strained hardened the digit “1” will appear after the H, and if the alloy was strain hardened and then annealed, “2” will appear instead. Finally, strain hardened alloys will contain one additional digit in their nomenclature that signifies the hardness of the material on a scale of 1 to 8.

![Figure 2-1 Example of AZ31 nomenclature](image)

Alloying Elements:  
• A - Aluminum  
• Z - Zinc  

Alloying Content:  
• 3 - 3 wt.% Al  
• 1 - 1 wt.% Zn  

Development Stage:  
• B - 2nd
Chapter 2: Magnesium AZ Alloys

The focus of the present work is magnesium-based alloys belonging to the AZ class. The current research is concerned with AZ31B-H24 and AZ80A-F magnesium alloys. Both alloys contain aluminum and zinc, but their concentration varies. AZ31B-H24 is composed of nominally 3 wt. % aluminum, and 1% zinc, and it has been strained hardened and then annealed to half hardness. AZ80 is composed of 8 wt. % aluminum, and 0.5% zinc, and it has been examined in the as-fabricated condition. Finally, both alloys contain minor amounts of manganese, approximately 0.2 wt. %.

2.2 Phase Composition

According to the Hume-Rothery rules for the formation of a substitutional solid solution, the two elements should have similar crystal structures, atomic radii (within 15% of each other), electronegativities, and relative valences [18, 19]. These parameters are summarized in Table 1 for the principal alloying elements. None of the alloying elements meet all rules for the formation of a substitutional solid solution with magnesium. Aluminum meets the criteria of similar atomic radii sizes, and zinc has a similar crystal structure. As a result, these typical alloy alloying elements only exhibit limited solubility (>15 at. %) and are commonly present in two phases, solid solution and intermetallic precipitates [20].

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Radii [nm]</th>
<th>Difference in Atomic Radii [%]</th>
<th>Electronegativity</th>
<th>Crystal Structure</th>
<th>Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.160</td>
<td>0</td>
<td>1.2</td>
<td>HCP</td>
<td>+2</td>
</tr>
<tr>
<td>Al</td>
<td>0.143</td>
<td>10.6</td>
<td>1.5</td>
<td>FCC</td>
<td>+3</td>
</tr>
<tr>
<td>Zn</td>
<td>0.133</td>
<td>16.9</td>
<td>1.6</td>
<td>HCP</td>
<td>+2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.112</td>
<td>30.0</td>
<td>1.5</td>
<td>Cubic</td>
<td>+2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.124</td>
<td>22.5</td>
<td>1.8</td>
<td>BCC</td>
<td>+2</td>
</tr>
</tbody>
</table>

Table 2-1 Characteristics of major elements present in AZ31 magnesium alloy [21]

The principal phases present in AZ31 and AZ80 alloys are $\alpha$-Mg matrix and $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ precipitates as seen from the Mg-Al and Mg-Zn phase diagrams in (Figure 2-2).
Figure 2-2 Binary phase diagrams depicting the effect of alloying elements on the phase composition of AZ alloys: (a) Mg-Al and (b) Mg-Zn (generated from FactSage 7.0 using the FTLite database [22]).

The α-Mg matrix is an hcp solid solution of magnesium and substitutional aluminum and/or zinc atoms. The lattice spacing of pure magnesium have been reported as $a=3.2026-3.2099\text{Å}$ and $c=5.1997-5.2108\text{Å}$ [23-26]. These lattice constants have been shown to reduce in size as the solute content in the material increased, see Figure 2-3. It has been previously shown that aluminum and zinc solute atoms occupy a smaller volume in the magnesium lattice than they do in their own respective lattice [24]. The above is caused by greater attraction between the solvent and the solute atoms caused by differences in electronegativity [24]. Greater attraction results in a reduction of the mean interatomic spacing, and contraction of the lattice [24].
The β phase is an intermetallic compound that typically precipitates along the grain boundaries of the α-Mg matrix and corresponds to Mg$_{17}$Al$_{12}$. The β-Mg$_{17}$Al$_{12}$ phase exhibits a cubic crystal structure (BCC structure, cI58 Pearson symbol, and a lattice constant, a=1.054 nm) that can form both coherent and incoherent-type boundaries with the surrounding α-Mg matrix depending on the size of the particle [27]. Larger β-Mg$_{17}$Al$_{12}$ particles were shown to be incoherent while much smaller platelets of the same phase were fully coherent [27]. It has been previously reported that in the AZ family of alloys, zinc can be incorporated into the β-Mg$_{17}$Al$_{12}$ phase to form β-Mg$_{17}$(Al,Zn)$_{12}$ [28]. The β phase particle size and volume fraction is largely related to the overall aluminum content in the alloy (see Figure 2-4) and the processing method used to produce the alloy.
Additionally, intermetallic Al-Mn particles are also formed due to the small addition of manganese into the alloy [30]. Manganese intermetallics can exist in various chemistries within the AZ magnesium alloy system as shown in the Al-Mn phase diagram in Figure 2-5(a). Commonly observed intermetallics include Al₈Mn₅, Al₁₁Mn₄, Al₄Mn, Al₆Mn and Al₁₂Mn [31]. Manganese can also exist in two different solid solutions at room temperature with Al, both α and β-Mn. The crystallographic information of all of these phases is summarized in Table 2-2. The most common intermetallic particles observed in the literature are Al₈Mn₅. Cao et al. measured that of all the Al-Mn particles present in a commercially available AZ31, Al₈Mn₅ represented about 80%, Al₁₁Mn₄ amounted to 10%, with the remainder being largely β-Mn [31]. The Al₈Mn₅ particles occurred in two main morphologies, either dendritic (Figure 2-5(b)) or leaf shaped (Figure 2-5(c)) [32]. These finely dispersed small particles have an average particle size of 15μm when the alloy is cast and about 5μm if the alloy was extruded, as in a commercially available AZ31 [32].
Table 2-2 Crystallographic data of Al-Mn phases found in AZ magnesium alloys

Manganese is added to many magnesium alloys, particularly the AZ series to reduce the deleterious effect of impurities in the metal by forming intermetallics with said impurities. As such it is common to observe Al-Mn intermetallics that contain trace amounts of iron [30]. In this case the crystal structure of the parent phase remains unchanged and iron is incorporated substitutionally.

### 2.3 Grain Size

The grain size of magnesium alloys is largely dependent on the processing methodology employed to produce the alloy and the temper in which it is present. AZ31B is a wrought-magnesium alloy, and thus the grain size is heavily dependent on the thermo-mechanical processing of the sheet. It has been shown that the percent reduction by rolling can be directly correlated to the average grain size. A 9.6 % reduction in thickness is characterized by a grain size of 13.6 μm and a 74% reduction in thickness has an average grain size of 5 μm [36]. Heat treatment at low temperatures (below 200 °C) yields minimal grain growth, however heat treatment at 450°C for five hours resulted in a 60 % increase in average grain size from 8.8 μm to 14.5 μm [37, 38]. Heat treating (tempering) at the same temperature for 10 minutes did not affect the average grain size significantly but did produce recovery by removing a significant portion of dislocations [37].
Grain refinement is observed with the addition of alloying elements. The extent of grain refinement depended on the concentration of the added element as summarized in Figure 2-6 below. Note, that the grain sizes shown in Figure 2-6, are reported for magnesium alloys in the “as-cast” condition. The grain size of these alloys can be further refined through thermo-mechanical processing. Grain refinement due to the addition of manganese occurred through the formation of small Al-Mn intermetallics, $\varepsilon$ (HCP) (see phase diagram in Figure 2-5(a)) that served as crystallographically favourable nucleation sites for magnesium grains [39].

**Figure 2-6 Effect of alloying on grain refinement of Magnesium alloys in the “as-cast” condition for: (a) zinc, (b) manganese, and (c) aluminum [39-41]**

Finally, AZ80A was examined in the “as-fabricated” condition (-F) in this work and so little meaningful comparison can be made between the alloy used in this investigation and previously reported studies.
Chapter 3 Corrosion: Mechanisms and Governing Factors

3.1 Magnesium

3.1.1 Corrosion of Magnesium

Corrosion of magnesium in aqueous environments occurs through an electrochemical reaction between magnesium and water to produce hydrogen gas and magnesium hydroxide [43]. The corrosion attack is governed by micro-galvanic coupling between local anodic and cathodic areas on the surface of the metal. The anodic (metal dissolution) and cathodic (hydrogen evolution) reactions are described by equation (3.1) and (3.2) respectively. Precipitation of magnesium hydroxide is shown by equation (3.3) and the overall reaction is given in equation (3.4). Although the standard reduction potential ($\varphi^o$) for the metal dissolution reaction (equation (3.1)) is -2.36 V$_{SHE}$, the measured corrosion for pure magnesium is much closer to 1.53V$_{SHE}$. The deviation in the potential is caused by the formation of magnesium hydroxide film on the surface of the metal.

\[
\begin{align*}
\text{Mg(s)} & \rightarrow \text{Mg}^{2+} + 2e^- & [\varphi^o = -2.360 \text{ V}_{SHE}]^* \\
2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2\text{OH}^- & [\varphi^o = -0.827 \text{ V}_{SHE}]^* \\
\text{Mg}^{2+} + 2\text{OH}^- & \rightarrow \text{Mg(OH)}_2 & [K_{sp}=5.61\cdot10^{-12}]^{*z} \\
\text{Mg(s)} + 2\text{H}_2\text{O} & \rightarrow \text{Mg(OH)}_2 + \text{H}_2 & [\varphi^o = -1.533 \text{ V}_{SHE}]^* 
\end{align*}
\]

*Standard reduction potentials were obtained from the CRC Handbook of Chemistry and Physics [42].

$^zK_{sp}$ is the solubility equilibrium constant for the reaction.

It is important to note that the metal dissolution reaction shown in equation (3.1) describes the oxidation of elemental magnesium to form divalent Mg$^{2+}$ cations. Initially, the existence of monovalent Mg$^+$ as opposed to divalent Mg$^{2+}$ had been proposed by several independent researchers [44-47]. However, more recent advances concluded that the existence of Mg$^+$ is thermodynamically unfavorable and that the dissolution of magnesium occurs through the formation of the divalent species [48-51].
Most literature suggests the existence of magnesium hydroxide (Mg(OH)$_2$) on the surface of the metal as an outer layer; however, beneath the hydroxide layer a thin compact layer (5-6 nm) of magnesium oxide (MgO) exists [52-54]. Magnesium hydroxide is more stable in the presence of water than the oxide form; thus, the conversion described in reaction (3.5) occurs with only a very thin layer of MgO existing at the metal-oxide interface in aqueous solutions.

$$\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \quad (3.5)$$

Corrosion of magnesium can be characterized by its corrosion mechanism, its general corrosion behaviour, the nature of its susceptibility to different forms of localized corrosion, and its propensity to undergo stress corrosion cracking. There are two main reasons for accelerated corrosion of magnesium, namely internal galvanic corrosion between the second phase particles and impurities and the matrix and/or passive film effects [55]. Breakdown of the quasi passive film generally occurs by aggressive ions such as chloride, sulphate, and nitrate [56]. The passive film is more stable at higher pH levels as can be seen from the Pourbaix diagram in Figure 3-1 [56]. Hence, above pH 11 the corrosion resistance of pure magnesium increases, due to the increasing stability of the hydroxide film.
Some forms of corrosion are not relevant to magnesium. It is important to notice that from these reactions and evidence in literature that dissolved oxygen in the electrolyte has no effect on the corrosion of magnesium [59]. Since the corrosion of magnesium is independent of the presence of oxygen in the solution, then crevice corrosion related to an oxygen depletion cell mechanism does not occur in magnesium or its alloys. True crevice corrosion occurs in narrow gaps where a certain region becomes anodic due to fluid stagnation leading to oxygen depletion in the gap and a separation of anodic and cathodic sites as a function of oxygen concentration. Magnesium is not susceptible to intergranular corrosion in near neutral pH solutions as the grain boundaries (distributed with second phase precipitates) are always cathodic to the grain interior under these conditions [56, 59, 60].

### 3.1.2 Surface Film and Electrochemical Passivity

The corrosion behaviour of magnesium is often governed by the composition and microstructure of the surface film. Under ambient conditions, a thin (2-3 nm) MgO film is formed upon initial contact with the oxygen in the air [61, 62]. Further exposure to air (>1 month) was shown to
increase the film thickness to 4-7 nm as a result of oxide growth and the formation of magnesium carbonate (MgCO₃) [63, 64].

When magnesium is exposed to dilute aqueous solutions the air-formed surface film hydrates to produce a new electrolyte-formed film that comprises a mixture of MgO and Mg(OH)₂ [65]. Literature has shown that when magnesium is first immersed in water, the inner Mg(OH)₂ layer and the outer Mg(OH)₂ layer have approximately the same thickness (2.5 nm) [65]. The thickness of the MgO layer was independent of immersion time, while the Mg(OH)₂ layer increased in thickness over time. Even though the film affects the local electrochemical behaviour of magnesium specimens, their corrosion resistance is not directly related to its thickness as the film exhibits only quasi-passive properties. The MgO layer is incomplete and highly defective due to its low Pilling-Bedworth ratio (0.8), while the Mg(OH)₂ was determined to be porous and permeable [43, 65-67].

The main effect that is induced by the electrolyte-formed film on the corrosion behaviour of magnesium is observed at prolonged exposure times when the film exhibits enhanced catalytic activity for the cathodic reaction [48, 68-70]. It has been shown that the hydrogen evolution reaction occurred 2-3 times faster on magnesium samples that were artificially coated with Mg(OH)₂ than on magnesium specimens that were left untreated. An increase in the cathodic kinetics accelerated the overall corrosion rate due to galvanic coupling between the local anodic and cathodic sites [71]. In addition to the effects caused by the presence of corrosion products, the cathodic kinetics are accelerated by surface impurity enrichment. Several studies suggested that preferential dissolution of magnesium during open circuit corrosion resulted in accumulation of impurity elements that were present in the bulk material [69, 72-74]. For example, Taheri et al. reported small Fe-rich particles embedded in the surface film that was formed on magnesium in a 0.01M NaCl solution as shown in Figure 3-2 [74]. The accumulation of impurity elements on the corroding surface can occur through a replating process as well [75, 76]. According to this hypothesis the impurities present in the bulk metal would leave the surface by non-Faradaic means associated with the dissolution of the surrounding Mg-matrix. The impurities then would dissolve in the electrolyte and re-plate on the magnesium surface. In both cases the impurity particles on the corroding surface act as highly active catalytic sites for the hydrogen evolution reaction that accelerates the overall corrosion rate. Research is still ongoing to determine the mechanism responsible for this phenomenon.
3.2 AZ Alloys

There has been a large interest in understanding the mechanisms governing the corrosion behaviour of not only pure magnesium, but also commercially available alloys such as AZ31 and AZ80. These engineering alloys contain several alloying elements as discussed in the previous chapter, and their impurity levels are much higher than those present in pure magnesium. If magnesium alloys were to be used in an industrial application the mechanisms governing their corrosion must be considered.

3.2.1 Effect of Alloying Elements on Corrosion of AZ Alloys

The discussion on the effect of common alloying elements on the corrosion of magnesium typically starts with the observations reported by Hanawalt et al. (Figure 3-3) [77]. In this study, the authors examined the corrosion resistance of a binary magnesium alloys with varying compositions in 0.51 M NaCl. Since the study was published in 1942 it served as a corner stone for studies examining the effect of alloying on corrosion of magnesium alloys. Over the years, the figure was modified to include new information from recent investigations. Most recently, a new compilation appeared in a review article by Esmaily et al. [5]. Their review article consolidated information from studies conducted in different electrolytes while ignoring the changes in the electrochemical properties of the alloy that could be caused by varying the corrosive environment.
To address this knowledge gap, a new data set was compiled from recent publications (Sections 3.2.1.1-3.2.1.4).

When examining the corrosion behaviour of magnesium alloys it is useful to define the driving force for the corrosive effect of a particular phase. Most commonly the second phase acts as a local cathodic site facilitating the hydrogen evolution reaction. The driving force can then be viewed as the difference in solution potentials of the magnesium and the minor phase minus the hydrogen overvoltage of that minor phase. Magnesium and its alloys can suffer from severe galvanic corrosion in the presence of metals with low hydrogen overpotentials such as nickel, iron, and copper [43]. For these elements (Ni, Fe, and Cu) a tolerance limit is defined as the critical impurity concentration above which the corrosion rate dramatically increases [56]. When magnesium is coupled with metals characterized by high hydrogen overpotentials (Al, Zn, Si, and Cd) the driving force is lower, and the galvanic corrosion is less severe (Figure 3-3).

![Figure 3-3 Effect of alloying additions on the corrosion behavior of binary magnesium alloys in 0.51 M NaCl solution [77].](image-url)
It is often useful to think of the effect of alloying elements, not only in terms of the resulting corrosion rate and the associated tolerance limit, but also the mechanistic influence on corrosion associated with the addition of each of the alloying elements. Gusieva et al. summarized the current understanding of the influence of alloying on the corrosion of Mg in Figure 3-4 [57]. A very large number of alloying additions lead to accelerated cathodic kinetics (cathodic activation) that ultimately accelerate the corrosion rate in a similar fashion to that described for impurity enrichment in the previous section. Anodic activation is not commonly seen for the elements present in the AZ alloy series (Figure 3-4), but it can occur in other systems where elements like Li, Sn, Ca are present [5]. The acceleration of the corrosion kinetics was commonly attributed to the disruption of the quasi-passive film that forms as a result of exposure to corrosive media. Recent advances have shown that in some cases, the corrosion rate of the alloy can even be reduced by microalloying of elements that poison the cathodic and/or anodic reaction as has been shown for As and Ge [78, 79].

![Figure 3-4 Schematic representation of the electrochemical impact of alloying elements studied to date. The plot depicts the ability of alloying additions to modify anodic or cathodic kinetics (or both), leading to changes in the resultant corrosion rate (i_corr), along with changes in corrosion potential (E_corr). C_s corresponds to the solid solution solubility limit. [80].](image)
3.2.1.1 Effect of Aluminum Alloying on Corrosion of Magnesium Alloys

The effect of aluminum alloying on the corrosion resistance of magnesium alloys largely depends on the microstructure [81]. Figure 3-4 shows that as long as the aluminum is retained in solid solution the anodic kinetics will decrease and the overall corrosion potential of the α-Mg matrix will increase with increasing aluminum content. The above observation is confirmed by the experimental data summarized in Table 3-1.

<table>
<thead>
<tr>
<th>[Al]</th>
<th>[Cl]</th>
<th>(E_{\text{corr}}) [V\text{SCE}]</th>
<th>(i_{\text{corr}}) [µA/cm(^2)]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33 wt. % Al</td>
<td>1.0M</td>
<td>-1.61</td>
<td>70</td>
<td>[81]</td>
</tr>
<tr>
<td>3 wt. % Al</td>
<td>0.03M*</td>
<td>-1.49</td>
<td>9</td>
<td>[82]</td>
</tr>
<tr>
<td>5 wt. % Al</td>
<td>0.03M*</td>
<td>-1.45</td>
<td>7</td>
<td>[82]</td>
</tr>
<tr>
<td>9 wt. % Al</td>
<td>0.03M*</td>
<td>-1.40</td>
<td>6</td>
<td>[82]</td>
</tr>
</tbody>
</table>

*As part of ASTM D1384 water [83]

Table 3-1 Effect of aluminum content on the electrochemical properties of α-Mg matrix

If both α-Mg matrix and β-Mg\(_{17}\)Al\(_{12}\) particles are formed, then the situation is more complex and the electrochemical behaviour of the alloy largely depends on the size and distribution of second phase intermetallics. Generally, the presence of β-Mg\(_{17}\)Al\(_{12}\) particles accelerates the corrosion rate of the alloy due to the formation of a microgalvanic cell between the noble β-Mg\(_{17}\)Al\(_{12}\) particles (Table 3-2) and the active α-Mg matrix (Table 3-1) [81, 84, 85]. The overall effect of an increase in aluminum alloying is determined via two competing mechanisms. The corrosion resistance of the alloy increases with increasing aluminum content due to an increase in the aluminum present in the α-Mg matrix, but it also decreases as greater aluminum content in the alloy results in a greater volume fraction of β-Mg\(_{17}\)Al\(_{12}\) particles, and a higher cathode-to-anode ratio. Generally, the deleterious effect of increased cathode-to-anode ratio is more predominant than the improvement associated with increased aluminum content in the α-Mg matrix. Aluminum addition up to 2 wt.% produced minimal changes to the corrosion potential and current density (Figure 3-5). Further increase in the aluminum content caused an increase in the corrosion potential due to the galvanic coupling between the α-Mg matrix and the noble β-Mg\(_{17}\)Al\(_{12}\) particles. The galvanic coupling also reduced the corrosion resistance as evidenced by the
increased corrosion current density in Figure 3-5, and the increased corrosion rate in Figure 3-3. It is important to note that the electrochemical properties of magnesium are highly sensitive to the experimental procedure and so cross study comparison should be done with care. Significant differences are apparent in the absolute values reported by Sudholtz et al. and Hoyer et al., but the trends remain consistent [86, 87].

The presence of noble β-Mg_{17}Al_{12} intermetallics greatly affects the corrosion resistance of magnesium alloys. To assess the full effect of these particles it is essential to understand their electrochemical properties. The cathodic rates of hydrogen evolution are much higher on aluminum rich phases (β particles) than on pure magnesium or the α-matrix [81]. Aluminum enhances the cathodic kinetics in Figure 3-4 when present in concentrations exceeding the solubility limit in magnesium. The β precipitate phase acted as a cathode (Table 3-2) when coupled to the α-matrix and the overall effect results in accelerated localized corrosion. The reason behind the cathodic behavior of the β particles lies with the semiconducting characteristics of the surface film formed on the β particle [81]. The oxide on the aluminum rich particles is far from the ideal Al_2O_3 crystal lattice as it is formed under non-equilibrium conditions, has many defects, and is composed with elements other than Al and O resulting in a highly strained lattice. Due to the high strain found in the lattice, the resulting band gap is narrowed, and the layer can be treated as a semiconductor [81]. The semiconducting nature of the film makes it easier for a proton to obtain an electron and form a hydrogen adatom that recombines to produce hydrogen gas [81]. The experimental results were in agreement with the above theory suggesting that the Ecorr of
the β phase (Table 3-2) was more noble than that of the α-phase (Table 3-1). However, this difference disappeared at higher pH levels due to the anodic dissolution of aluminum. Above pH=11, aluminum was no longer stable while magnesium hydroxide was retained as a stable phase [60].

<table>
<thead>
<tr>
<th>Phase</th>
<th>[Cl]</th>
<th>$E_{\text{corr}}$ [V SCE]</th>
<th>$i_{\text{corr}}$ [μA/cm²]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Mg$<em>{17}$Al$</em>{12}$</td>
<td>1.0M</td>
<td>-1.27</td>
<td>10</td>
<td>[81]</td>
</tr>
<tr>
<td>β-Mg$<em>{17}$Al$</em>{12}$</td>
<td>0.03M</td>
<td>-1.31</td>
<td>14</td>
<td>[82]</td>
</tr>
<tr>
<td>Mg$<em>{17}$(Al,Zn)$</em>{12}$</td>
<td>0.03M</td>
<td>-1.24</td>
<td>7</td>
<td>[82]</td>
</tr>
<tr>
<td>β-Mg$<em>{17}$Al$</em>{12}$</td>
<td>0.1M</td>
<td>-1.35</td>
<td>3.5</td>
<td>[88]</td>
</tr>
<tr>
<td>β-Mg$<em>{17}$Al$</em>{12}$</td>
<td>0.01M</td>
<td>-1.142</td>
<td>N/A</td>
<td>[89]</td>
</tr>
<tr>
<td>β-Mg$<em>{17}$Al$</em>{12}$</td>
<td>0.1M</td>
<td>-1.172</td>
<td>N/A</td>
<td>[89]</td>
</tr>
<tr>
<td>β-Mg$<em>{17}$Al$</em>{12}$</td>
<td>0.85M</td>
<td>-1.222</td>
<td>N/A</td>
<td>[89]</td>
</tr>
<tr>
<td>β-Mg$<em>{17}$Al$</em>{12}$</td>
<td>1.0M</td>
<td>-1.202</td>
<td>N/A</td>
<td>[89]</td>
</tr>
</tbody>
</table>

*As part of ASTM D1384 water [83]

**Table 3-2 Electrochemical properties of β-Mg$_{17}$Al$_{12}$**

### 3.2.1.2 Effect of Zinc Alloying on Corrosion of Magnesium Alloys

Zinc is commonly added to magnesium alloys to reduce the effect of impurities (Cu, Fe, and Ni) and to increase their tolerance limits [43]. An increase in tolerance levels is only seen for additions of 1-3 wt. % Zn additions. Additions of zinc greater than 3 wt. % will increase the corrosion rate. The addition of zinc produces less of an effect on the tolerance limit than the addition of manganese for the same weight percent addition. Addition of zinc also makes the alloy more susceptible to filiform corrosion and stress corrosion cracking [43, 90]. As seen from Figure 3-4, the addition of zinc has been shown to cause cathodic activation largely due to the formation of intermetallic particles. There are no binary Mg-Zn phases in AZ alloys. Zinc is often incorporated into β-Mg$_{17}$Al$_{12}$ to form Mg$_{17}$(Al,Zn)$_{12}$ that are more active than its parent phase, see Table 3-1 [82].
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The effect of zinc on the electrochemical properties of magnesium alloys is summarized in Figure 3-6. At small concentrations (up to 2 wt. % Zn), the addition of zinc had negligible effect on the corrosion current density of magnesium alloys. Further increase in zinc content resulted in an increased corrosion current density due to the formation of a cathodic MgZn phase [91]. Across all concentrations, magnesium alloys did not show clear correlation between the corrosion potential and the zinc content in the alloy. The results in Figure 3-6 (b) further confirm the findings presented Hanawalt et al. (Figure 3-3) [77].

![Figure 3-6 Effect of zinc alloying on the corrosion (a) potential, and (b) current density of magnesium in 0.1 M NaCl. Data summarized from Xia et al. (Jan 2015) [92], Xia et al. (Nov 2015) [93], and Cai et al. [91].](image)

3.2.1.3 Effect of Manganese Alloying on Corrosion of Magnesium Alloys

In absence of aluminum, manganese addition to magnesium alloys has little effect on their electrochemical properties. As can be seen from Figure 3-7, addition of up to 2 wt.% Mn has been shown to slightly reduce the corrosion potential and current density. This minor improvement in the corrosion resistance of the alloy was attributed to the reduction in cathodic kinetics that occurred when manganese was dissolved in magnesium as a solid solution [94]. The study did not identify the exact mechanism responsible for the reduction in cathodic kinetics, and thus far this area has remained largely unexplored.
In the presence of aluminum (as discussed in Section 2.2), the addition of manganese results in the formation of various Al-Mn intermetallics and Mn-rich phases. Cathodic activation occurs on the intermetallic phases when Mn is added to the alloy in agreement with the trend shown in Figure 3-4. The corrosion potential of intermetallic particles containing manganese is significantly higher than that of the \( \alpha \)-Mg matrix (Table 3-3) resulting in the formation of microgalvanic couples between the active matrix and the noble particles. Though all Al-Mn particles are noble to the \( \alpha \)-Mg matrix, the \( \text{Al}_8\text{Mn}_5 \) phase represents the most noble composition in this family of intermetallics. It is interesting to note that as mentioned in Section 2.2, \( \text{Al}_8\text{Mn}_5 \) is also the most frequently occurring phase in AZ31. At present, with the exception of the corrosion potential, the electrochemical properties of the phases in Table 3-3 have not been thoroughly researched. This lack of readily available information presents a challenge in assessing the effect of these phases on the corrosion behaviour of magnesium alloys.

The overall effect is still beneficial since the addition of manganese can increase the tolerance limits for nickel and copper in magnesium [56]. Manganese can also improve the tolerance limits for iron in magnesium via two possible mechanisms. Addition of manganese, up to its solubility limit, greatly reduces the solubility of iron in the magnesium melt causing its precipitation [96]. The precipitate iron is removed during the production process reducing the final iron content in the alloy [43, 96]. The alloyed manganese serves a secondary function by producing a series of Al-Mn-Fe intermetallics, which create a smaller galvanic couple than pure iron with magnesium (see Table 3-3) [56]. The extent of cathodic activation that occurs as a result of Mn additions are outweighed by improvements to the tolerance limits for iron and other harmful impurities.
### Table 3-3 Summary of electrochemical properties of Al-Mn intermetallics present in AZ alloys.

The corrosion potential of Fe, Ni and Cu is provided for reference as well.
3.2.1.4 Effect of Iron Impurities on Corrosion of Magnesium Alloys

Iron is the most common impurity in Mg alloys; it has a low solubility limit and so it remains largely in its elemental form. Iron is very active (Table 3-3) and as such it forms a strong galvanic couple with magnesium when iron particles are scattered throughout the \( \alpha \)-matrix. It enhances the cathodic kinetics that could occur on the surface of a corroding magnesium specimen, thereby reducing its corrosion resistance (Figure 3-4).

The effect of iron content on the electrochemical properties of magnesium is summarized in Figure 3-8 (a) and (b). The corrosion potential of magnesium specimens (Figure 3-8(a)) varied drastically for the specimens summarized in the figure. Surprisingly no trend clear relation was observed between the corrosion potential and the iron content in the specimen. Determining a relation between the corrosion current density and the iron content (Figure 3-8(b)) was equally difficult. It is worth mentioning that the lack of dependence between the iron content in the specimen and its electrochemical properties is likely caused by the experimental methodologies employed in the studies summarized in the figure. The absolute values of the electrochemical properties of magnesium alloys are highly sensitive to experimental procedure, making cross comparison of the results challenging. Instead of comparing the individual values across various studies it is often more useful to compare the trends emerging from each study.

An example of such study is shown in Figure 3-8(c). In this study the effect of iron on the corrosion of magnesium was examined through mass loss testing [77]. It can be seen from the figure that the corrosion rate of magnesium was relatively independent of iron content up to its tolerance limit (0.017 wt. %). At concentrations above the tolerance limit, the corrosion resistance of magnesium reduced rapidly with increasing iron content. Iron has an even more serious effect on the corrosion of magnesium when aluminum is alloyed [56]. Iron creates FeAl\(_3\) particles which are more active than iron particles; thus, the iron tolerance limit decreases dramatically in Mg-Al alloys, typically on the order of a few ppm [43].
Figure 3-8 Effect of iron alloying on the corrosion (a) potential, and (b) current density of magnesium in 0.1 M NaCl. For discussion purposes (c) the effect of iron on mass loss of magnesium (modified from Hanawalt et al. [77]) is included as well. The data in (a) and (b) was summarized from Gandel et al. [95], Xia et al. [93], Sudholtz et al. [86], Hoche et al. [76], and Hoyer et al. [87].
3.2.2 Passivity of AZ Magnesium Alloys

3.2.2.1 Film Structure

The presence of Al and Zn in AZ alloys increases the number of phases that can be found in the surface film. In addition to the phases described in Section 3.1.2 (for pure magnesium), the film formed on AZ magnesium alloys has been shown to contain aluminum and zinc rich phases [81, 98]. The presence of an aluminum rich phase in the surface film formed on AZ alloys was determined by x-ray photoelectron spectroscopy (XPS) in a study conducted by Song et al. [81]. The results have shown that alloys from the AZ series comprises three layers that differed in their composition [81]. While there is no distinctive boundary between the layers they are fundamentally different in their chemistry. The inner layer is alumina (Al$_2$O$_3$), the middle layer consists of MgO, and finally the outer most dissolving layer is made of Mg(OH)$_2$ [81]. It was noted that inner aluminum rich layer was unlikely to match the exact crystal structure of Al$_2$O$_3$ due to non-equilibrium formation conditions [81]. The XPS results were independently confirmed by Feliu et al. [61, 67]. The presence of this three layer structure (Al$_2$O$_3$/MgO/Mg(OH)$_2$) was also observed by transmission electron microscopy (TEM) [99, 100]. The outer platelet-like film was composed of crystalline Mg(OH)$_2$, the intermediate compact layer was composed of Al enriched MgO, while the inner layer was a cellular aluminum rich layer (Al$_2$O$_3$).

The presence of an aluminum enriched layer was not unanimously accepted in literature. In a recent TEM investigation, Kish et al. reported that the film exhibited a higher Al:Mg ratio than that of the base metal [98]. Aluminum enrichment was not related to the formation of an Al$_2$O$_3$ layer, but instead it was related to preferential dissolution of magnesium that left the aluminum in the $\alpha$-Mg matrix behind. Interestingly, in the same investigation a thin Zn rich filament was observed at the metal/film interface. This enrichment was related to preferential dissolution of Mg and Al from the $\alpha$-Mg matrix leaving the Zn present in AZ31 at the metal oxide interface.

3.2.2.2 Electrochemical Properties

Alloys from the AZ series can exhibit passive behavior in near neutral saline solutions [85]. Wang et al. have examined the effect of applied overpotential during a potentiostatic polarization experiment on the film formed on the surface of AZ alloys [85]. The films were characterized using x-ray diffraction (XRD) and XPS, and the effect of chloride concentration was examined as well. The results obtained from XRD and XPS were correlated to the overpotentials used to form
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the film and a corrosion map for the alloy was constructed. This map outlined the electrochemical behavior based on the electrode potential and chloride ion solution concentration as shown in Figure 3-9 [85]. $E_{ocp}$ is the open cell potential of the sample in a given solution. The critical potential, $V_c$, is the potential between the passivation and corrosion regimes, also known as the breakdown potential. The transition from the passive zone to the corrosion zone is characterized by pit initiation and accelerated localized corrosion. The authors attempted to estimate the critical potential using two different approaches. $V_c$ was measured from a potentiostatic polarization experiment while $V_{c,100}$ was measured from a potentiodynamic polarization tests as the potential corresponding to a current density of 100 $\mu$A/cm$^2$. It is evident from Figure 3-9 that both pitting and critical potentials decreased with increasing concentration of chlorine ions. Pure Mg, and AZ31 only exhibited passive behavior at open circuit in solutions that have a chloride concentration less than 0.03M, and 0.2M respectively (Figure 3-9). At higher concentrations, the open circuit potential is higher than $V_c$ preventing passivity. In direct contrast AZ91 remained passive in all solutions examined in the study.

When the alloy is in its passive state, anodic charge transfer occurs below the porous surface film, at the metal/electrolyte interface. Anodic dissolution is then controlled by the rate of diffusion through the passive compact alumina layer and/or diffusion through the film/solution interface [101]. Most industrial applications for magnesium alloys occur in conditions in which the alloy does not passivate and so research on the corrosion behaviour of magnesium under passive conditions is scarce. Instead, researchers focus attention towards understanding the quasi-protective film on magnesium alloys and its role in governing the localized corrosion mechanism occurring at the surface of the alloy.
Several models have been proposed to explain the localized corrosion mechanism occurring at the surface of magnesium alloys in chloride containing media, see summary in Table 3-4. In all cases the corrosion mechanism was directly related to the structure of the surface film, and activity of each of the phases present in the film. The most simplistic model was proposed by Zeng et al. who suggested that localized corrosion occurred due to galvanic coupling between the active α-Mg matrix and noble Al-Mn particles [102]. In their model the surface film comprised a bi-layer structure comprising an inner MgO and outer Mg(OH)$_2$ layer. Anodic dissolution occurred near local cathodes on adjacent α-Mg phase where film defects were present. Their model assumed that all of the cathodic reaction occurred exclusively on noble intermetallics, and the contribution arising from the oxide/hydroxide film itself were not considered. Enrichment of Al and Zn near the surface film was not discussed either [102].

Song et al. provided a more complete mechanism by describing a film with a trilayer structure comprising an inner non-equilibrium Al$_2$O$_3$ layer, an intermediate MgO layer, and an outer Mg(OH)$_2$ layer [81]. Like the previous model, anodic dissolution occurred near local cathodes on adjacent α-Mg phase where film defects were present. The main difference between the two models was that in Song’s model the cathodic contribution arising from the film itself was also considered. Even though the presence of an aluminum rich layer was identified, its cathodic contribution was not considered since the authors assumed it would act as an insulator. Such assumption cannot be made, since the Al rich layer would act as a semiconductor due to the many defects present in its structure. Much like in the case of the oxide formed on β-Mg$_{17}$Al$_{12}$ (see discussion in Section 3.2.1.1), the defects in its structure would introduce lattice strain that would narrow the band gap and promote semiconducting properties. The Al rich phase is therefore expected to act as a cathode for hydrogen evolution.

Cano et al. accounted for this and provided three pathways for the cathodic reaction to occur. In addition to the oxide layer and noble intermetallics, the cathodic reaction that can occur on the enriched layer (Zn rich layer in their case) was considered as well [98]. The mechanisms in Table 3-4 suggest one or more pathways for the cathodic reaction to proceed. A common weakness to all these models is that the relative strength of each cathodic site was not considered. Though all pathways mentioned in the table could theoretically proceed, it is currently uncertain which cathodic site type, or a combination of cathodic site types governs the corrosion behaviour of magnesium alloys.
Table 3-4 Summary of proposed mechanisms governing localized corrosion of magnesium alloys

<table>
<thead>
<tr>
<th>Schematic</th>
<th>Model Description</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Film Structure</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Bilayer structure comprising an inner MgO layer and an outer Mg(OH)$_2$ layer.</td>
<td>[102]</td>
</tr>
<tr>
<td></td>
<td><strong>Anodic Reaction</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Occurs near local cathodes on adjacent α-Mg phase where film defects were present.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Cathodic Reaction</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Occurs on noble Al-Mn intermetallic particles</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Important Notes</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Developed for AM60 in 0.6M NaCl electrolyte</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• No enrichment was found in the film</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• The cathodic contributions from the film or enriched layers were not considered</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Film Structure</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Trilayer structure comprising an inner non-equilibrium Al$_2$O$_3$ layer, an intermediate MgO layer, and an outer Mg(OH)$_2$ layer.</td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td><strong>Anodic Reaction</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Occurs on the α-Mg phase where film defects were present.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Cathodic Reaction</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Occurs on intermetallic particles, surface film and on α-Mg phase that is not covered with a surface film.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Important Notes</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• No zinc enrichment was found in the film</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• The cathodic contribution from the inner non-equilibrium Al$_2$O$_3$ layer was not considered</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Film Structure</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Bilayer MgO structure comprising an outer air formed layer (pre-existing surface film) and an inner solution formed layer (corrosion filament).</td>
<td>[98]</td>
</tr>
<tr>
<td></td>
<td>• Zn enrichment at the metal oxide interface.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Anodic Reaction</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Occurs near local cathodes on adjacent α-Mg phase.</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Cathodic Reaction</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Occurs on Al-Mn intermetallic particles, the corrosion product, and Zn-rich filament</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Important Notes</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• No Al$_2$O$_3$ layer was found</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Mg(OH)$_2$ was not considered</td>
<td></td>
</tr>
</tbody>
</table>
3.2.3 Effect of Microstructure on Corrosion of Magnesium Alloys

3.2.3.1 Grain Size

The effect of grain size on the corrosion resistance of magnesium alloys has been examined in literature over the past few decades. Table 3-5 and Table 3-6 summarize the effect of grain size on the electrochemical properties of magnesium and magnesium alloys as they were reported in literature. It is evident that a debate is ongoing, and that the exact relation between grain size variation, and corrosion resistance properties remains poorly understood.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Grain Size Range [µm]</th>
<th>Results</th>
<th>Reported Trend</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Grain Size</td>
<td>icorr [µA/cm²]</td>
<td>Ecorr [V SCE]</td>
</tr>
<tr>
<td>0.1M NaCl</td>
<td>3.5-1000</td>
<td>3.5</td>
<td>30</td>
<td>-1.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11</td>
<td>2</td>
<td>-1.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>20</td>
<td>-1.60</td>
</tr>
<tr>
<td>0.1M NaCl</td>
<td>2.5-100</td>
<td>2.5</td>
<td>6.5</td>
<td>-1.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>8</td>
<td>-1.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>8.2</td>
<td>-1.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>10</td>
<td>-1.64</td>
</tr>
<tr>
<td>Simulated Body</td>
<td>233-500</td>
<td>233</td>
<td>1,580</td>
<td>-1.90</td>
</tr>
<tr>
<td>Fluid</td>
<td></td>
<td>355</td>
<td>2,510</td>
<td>-1.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>396</td>
<td>1,500</td>
<td>-1.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>452</td>
<td>1,260</td>
<td>-1.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>890</td>
<td>-2.01</td>
</tr>
</tbody>
</table>

Table 3-5 Effect of grain size on the electrochemical properties of pure magnesium

The main challenge preventing progress in this field is the lack of appropriate experimental design that would allow grain refinement without inducing additional physical or chemical changes to the material [57]. Consideration must be given to the materials processing approach and the testing methodology as grain size influence has been recorded only under very specific conditions. For
example, the corrosion resistance properties of as cast pure magnesium does not exhibit dependence on grain size variation when the metal is exposed to 0.6M NaCl [103]. However, when the material processing methodology was changed from casting to equal channel angular pressing, with everything else kept constant, the corrosion current density was proportional to the logarithm of the grain size [103]. Determining the effect of grain size on the corrosion resistance of magnesium alloys is even more complicated than in the case of pure metal, as special consideration must be given to changes in the size and distribution of second phase intermetallics which are frequently encountered when the alloy is subjected to heat treatment. The effect of grain size on the electrochemical properties of magnesium alloys is summarized in Table 3-6.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat Treatment</th>
<th>Electrolyte</th>
<th>Results</th>
<th>Reported Trend</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grain Size [µm]</td>
<td>( i_{\text{corr}} ) [µA/cm²]</td>
<td>( E_{\text{corr}} ) [V SCE]</td>
</tr>
<tr>
<td>AZ31B-H24</td>
<td>As-received</td>
<td>0.6M NaCl</td>
<td>35</td>
<td>455</td>
<td>-1.46</td>
</tr>
<tr>
<td></td>
<td>3 Hrs at 200°C</td>
<td></td>
<td>50</td>
<td>77</td>
<td>-1.40</td>
</tr>
<tr>
<td></td>
<td>3 Hrs at 300°C</td>
<td></td>
<td>65</td>
<td>67</td>
<td>-1.38</td>
</tr>
<tr>
<td></td>
<td>3 Hrs at 400°C</td>
<td></td>
<td>90</td>
<td>152</td>
<td>-1.42</td>
</tr>
<tr>
<td></td>
<td>3 Hrs at 500°C</td>
<td></td>
<td>250</td>
<td>480</td>
<td>-1.48</td>
</tr>
<tr>
<td>AZ31B-H24</td>
<td>24 Hrs at 400°C</td>
<td>0.6M NaCl</td>
<td>6</td>
<td>72</td>
<td>-1.50</td>
</tr>
<tr>
<td></td>
<td>72 Hrs of natural aging</td>
<td></td>
<td>17</td>
<td>117</td>
<td>-1.53</td>
</tr>
<tr>
<td>AZ31B-H24</td>
<td>As-received</td>
<td>0.6M NaCl</td>
<td>4.5</td>
<td>67</td>
<td>-1.60</td>
</tr>
<tr>
<td>AZ31B-O</td>
<td>As-received</td>
<td>0.6M NaCl</td>
<td>11</td>
<td>179</td>
<td>-1.59</td>
</tr>
</tbody>
</table>

Table 3-6 Effect of grain size on the electrochemical properties of AZ31B
Examination of Table 3-6 revealed that negligible correlation existed between the corrosion potential and the grain size of the alloy. A much stronger trend, with the exception of a few data points, was observed for the corrosion current density as it generally increased with increasing grain size. A notable outlier is the corrosion current density measured for specimens in the as-received condition in Aung’s study [106]. With the exception of samples in this condition, Aung et al. were able to achieve a good correlation between the results obtained from immersion testing, hydrogen evolution measurements, and potentiodynamic polarization [106]. The cause for the deviation is uncertain, but for the purpose of the present study, it was decided not to consider this data point.

Aung et al. reported that grain boundaries acted as corrosion barriers and thus the corrosion resistance of AZ31B improved with decreasing grain size [106]. While the study suggested that grain size had an effect on the corrosion behaviour of AZ31B, it also noted that this effect was relatively weak as compared to the effect of other microstructural features such as the presence of twins. Twins dominated the corrosion resistance of the alloy when present in the microstructure their effect, and the effect of changes in grain size could not be separately measured. It was suggested that the presence of twins accelerated the anodic metal dissolution due to local reduction in corrosion potentials in the vicinity of dislocations [106]. While this explanation fit the experimental data, it is important to note that the number of twins in the various specimens examined in the study was not quantified, and that the corrosion potential in the vicinity of dislocations was not measured either. Further characterization of the specimens used in the study is required to draw definitive conclusions about the relative effect of twins and grain size.

An investigation of the corrosion behaviour of heat treated AZ31B by Jang et al., also reported the corrosion current density to increase with increasing grain size [107]. In an attempt to explain their experimental observations, the authors hypothesized that the fine-grained microstructure lead to the formation of a denser and a more uniform passive film that exhibited superior corrosion resistance properties. Some evidence in support of their claims was later provided by Cristobal et al. who suggested that grain size of AZ31B could be affecting the rate at which atmospheric CO$_2$ reacted at the surface of the alloy to form a protective surface film [10]. The authors noted that this proposition was yet to be proven and that further work was required to support or refute it. Even if this hypothesis is proven to be true, it still fails to explain why grain size dependence was only observed for specimens manufactured using specific processing techniques.
It is interesting to note that in all cases the grain size in the studies summarized in Table 3-6 was varied through the use of a heat treatment that induced grain growth. It is likely that in addition to the desired grain growth changes, the size and distribution of second phase intermetallics were also altered in the alloy. As such, the changes in the electrochemical properties that were attributed to varying grain size could also be caused by the changes in the size and distribution of second phase intermetallics. A similar proposition was made by Kish et al. who suggested that the differences in the corrosion resistance of AZ31B in different heat-treated conditions were related to changes in the size and distribution of intermetallic particles and not by the differences in grain size [108]. The proposition explained the data presented in the manuscript but lacked experimental evidence to support its validity. If variation in the size and distribution of second phase intermetallics was responsible for the difference in the corrosion resistance of various heat-treated specimens, a measurement of these particles is needed to support the explanation provided by the authors. A knowledge gap exists in this area, and an experiment capable of altering the grain size while keeping all other microstructural features constant is required to elucidate the role of grain size in the corrosion resistance of magnesium alloys.

3.2.3.2 Residual Stress

The effect of residual stress on the corrosion resistance of magnesium alloys is not well documented. One of the few studies, by Aghion et al., reported that the corrosion resistance of AZ80 decreased when internal stresses were introduced into the alloy [109]. Although it was shown that the corrosion rate was shown to increase from 0.5 to 26 mm/year following an extrusion process that introduced internal stresses in the alloy, the study had two limitations that introduced uncertainty into the conclusions [109]. The study did not separate the changes caused by introduction residual stress from the changes caused by increased iron content that occurred as a result of extrusion. The mechanism governing the effect of residual stress was not elucidated either. In this context, Clarke suggested that residual stresses present in metallic specimens would generally impact the electrochemical behaviour of the metal by introducing internal strain and increasing its internal energy [110]. The alloy chemistry and the nature of the residual stresses (tension versus compression) play an important role in determining the corrosion resistance properties of metallic substrates. Tensile residual stresses accelerated the corrosion rate of AZ80, while compressive residual stresses increased the corrosion resistance of AA2024 metallic samples [109, 111]. The influence of residual stress on the corrosion behaviour of magnesium
alloys is not clearly defined and may affect the corrosion behaviour of welded structures. Understanding the influence of residual stress on the overall corrosion resistance of magnesium alloys is therefore essential.

### 3.2.3.3 Grain Orientation

The effect of grain orientation on the corrosion resistance of magnesium and its alloys has been the subject of debate in recent years [37, 112-115]. Several studies have shown that closed packed magnesium basal planes (0001) in AZ31B exhibited better corrosion resistance than prismatic planes like ((1010) and (1120)) [37, 112, 113]. The findings reported in these studies are summarized in the first three rows of Table 3-7. In the studies examining the effect of grain orientation on the corrosion properties of AZ31, two planes of a wrought sheet were compared. The rolling surface (RS) of AZ31 exhibited a strong basal texture and lower corrosion rates than those found for the cross-sectional surfaces (CS) containing primarily prismatic planes [37, 112, 113]. It was also found that close-packed planes exhibited more uniform corrosion, while planes of lower atomic density suffered from highly localized corrosion characterized by deep pits [113]. This proposition was further supported by Shin et al. who examined the effect of grain orientation on corrosion of single crystal magnesium specimens [114]. Their study established a correlation between high atomic packing factors and low corrosion rates by systematically examining changes in grain orientations.

Theoretically, the variation in the electrochemical activity of different crystallographic planes has been correlated to their surface energy. Close-packed planes have a higher binding energy due to their higher atomic coordination, which in turn leads to lower surface energy along with lower corrosion rates. Fu et al. reported that the close-packed plane in magnesium have a surface energy that is two times smaller than that of the planes ((1010) and (1120)) [116]. In attempt to quantify the change from first principles, Song et al. have shown that the theoretical dissolution rate of the basal closed packed planes is almost twenty times lower than on other planes [113].

The proposition that grain orientation significantly influenced the corrosion behaviour of magnesium alloys was recently challenged by Bland et al. [115]. The authors suggested that the differences in the corrosion resistance of different surfaces of the wrought metal specimen were caused by different distribution of Al-Mn intermetallic particles and not by the intrinsic properties of the grain orientations that were examined. Their study suggested that the corrosion rate on basal
planes was the highest due to its poor film forming ability (line 4 in Table 3-7) [115]. Although the authors acknowledged that differences in surface energy would enhance the corrosion resistance of the basal plane, it was suggested that grain orientation would have a negligible effect on the overall corrosion behaviour as its effect would be easily masked by other factors (such as differences in second phase size and distribution).

Table 3-7 Effect of grain orientation on the corrosion of magnesium alloys

As it stands, the cause for the discrepancy between the studies remains unknown. The difference cannot be attributed to varying intermetallic content alone as it has already been reported that the rolling surface and the cross-sectional surface had a similar area fraction of Al₈Mn₅ intermetallics (0.28 % on RS and 0.31 % on CS) [37]. Finally, their theory did not account for differences in the corrosion behavior of various planes seen in a magnesium single crystal specimen (containing no intermetallic particles) [114]. Further research is required to determine the effect of grain orientation on corrosion of magnesium alloys.

3.3 Effect of Electrolyte on Corrosion of Magnesium and Magnesium Alloys

3.3.1 Chloride Ions

Several investigations have studied the effect of chloride ion concentration on the corrosion resistance of magnesium alloy AZ31 [117, 118]. A summary of the electrochemical parameters associated with the corrosion of AZ31 in NaCl environment is given in Table 3-8. As seen from

<table>
<thead>
<tr>
<th>Material</th>
<th>[NaCl]</th>
<th>Basal Plane (0001)</th>
<th>Prismatic Plane ((10\overline{1}0))</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31</td>
<td>0.86 M</td>
<td>Corrosion Rate 0.009 $\frac{mg}{cm^2\cdot hr}$</td>
<td>Corrosion Rate 0.091 $\frac{mg}{cm^2\cdot hr}$</td>
<td>[113]</td>
</tr>
<tr>
<td>AZ31</td>
<td>0.6 M</td>
<td>Corrosion Rate 0.105 $\frac{mg}{cm^2\cdot hr}$</td>
<td>Corrosion Rate 0.205 $\frac{mg}{cm^2\cdot hr}$</td>
<td>[112]</td>
</tr>
<tr>
<td>Single Crystal Mg</td>
<td>0.6 M</td>
<td>Corrosion Rate 0.009 $\frac{mg}{cm^2\cdot hr}$</td>
<td>Corrosion Rate 0.020 $\frac{mg}{cm^2\cdot hr}$</td>
<td>[114]</td>
</tr>
<tr>
<td>Polycrystalline Mg</td>
<td>0.6 M</td>
<td>Corrosion Rate 0.417 $\frac{mg}{cm^2\cdot hr}$</td>
<td>Corrosion Rate 0.036 $\frac{mg}{cm^2\cdot hr}$</td>
<td>[115]</td>
</tr>
</tbody>
</table>
the table below, the corrosion potential of the alloy varied as the concentration of the electrolyte changed. When the NaCl concentration varied from 0.01M to 2M the corrosion potential was measured to be between -1.47 \( V_{SCE} \) and -1.55 \( V_{SCE} \) [84, 117, 118]. When the chloride concentration increased in the range between 0.01M and 0.5M NaCl the corrosion potential of AZ31 specimens decreased. At concentrations above 0.5M NaCl, no direct correlation was observed between the corrosion potential and the concentration of the electrolyte, since chloride concentration does not directly affect the corrosion potential.

<table>
<thead>
<tr>
<th>Concentration [M]</th>
<th>( E_{corr} ) ([V_{SCE}])</th>
<th>( i_{corr} ) ([mA/cm^2])</th>
<th>( R_p ) ([Ω/cm^2])</th>
<th>Corrosion Rate ([mm/year])</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-1.47</td>
<td>10</td>
<td>2633</td>
<td>0.220</td>
<td>[117]</td>
</tr>
<tr>
<td>0.01</td>
<td>-1.48</td>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>[118]</td>
</tr>
<tr>
<td>0.05</td>
<td>-1.49</td>
<td>0.05</td>
<td>--</td>
<td>--</td>
<td>[118]</td>
</tr>
<tr>
<td>0.1</td>
<td>-1.52</td>
<td>0.05</td>
<td>--</td>
<td>--</td>
<td>[118]</td>
</tr>
<tr>
<td>0.2</td>
<td>-1.51</td>
<td>10</td>
<td>2067</td>
<td>0.298</td>
<td>[117]</td>
</tr>
<tr>
<td>0.5</td>
<td>-1.55</td>
<td>0.3</td>
<td>--</td>
<td>--</td>
<td>[118]</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.47</td>
<td>65</td>
<td>582</td>
<td>1.480</td>
<td>[117]</td>
</tr>
<tr>
<td>1.0</td>
<td>-1.52</td>
<td>105</td>
<td>237</td>
<td>2.400</td>
<td>[117]</td>
</tr>
<tr>
<td>2.0</td>
<td>-1.54</td>
<td>142</td>
<td>196</td>
<td>3.260</td>
<td>[117]</td>
</tr>
</tbody>
</table>

**Table 3-8 Magnesium alloy AZ 31 corrosion properties in NaCl environment**

Though direct comparison between two separate studies is not possible due to the high sensitivity of the measurement to the experimental procedure, the trends in the investigations summarized in Table 3-8 are the same. Corrosion resistance of Mg AZ31 decreased with increasing chloride concentration due to local breakdown of the surface film leading to pitting corrosion. This is the predominant form of corrosion observed by many investigators [1, 52]. The localized breakdown of the surface film on the metal contributed to the Negative Difference Effect (NDE) observed in this system as discussed in Section 2.6. When the sample was polarized at potentials near the open cell potential it showed passive behavior. The study conducted by Wang et al. on Mg AZ31 in 0.01M NaCl showed that polarization at potentials near OCP (+/- 50 mV) resulted in the
precipitation of corrosion products inside the pits and retarded further pit growth; however, at larger overpotentials pits continued to grow and no passivation behavior was present [119].

### 3.3.2 Perchlorate Ions

The corrosion behaviour of magnesium alloys in perchlorate ($\text{ClO}_4^-$) containing solutions is not very well documented in literature. Preliminary studies have shown that the corrosion attack caused by perchlorate anions is similar in nature (localized pitting) to that caused by chloride ($\text{Cl}^-$) anions, but its rate is reduced [52]. The difference between the two is related to the ability of the corrosive species to complex with the surface of the metal specimen. The perchlorate anions tend to complex less with the surface metal atoms as compared to chloride anions [120]. As a result, perchlorate ions are less corrosive than chloride anions but still cause localized pitting corrosion on magnesium alloys [52].

### 3.4 Negative Difference Effect

Following the Butler-Volmer relationship, the anodic rate will increase, and the cathodic rate will decrease with an increase in applied anodic potential. Therefore, it is expected that when the applied potential increases, the corrosion rate will increase while the hydrogen evolution rate will decrease. However, experimental work on magnesium has shown a different phenomenon [43]. As seen in Figure 3-10 both hydrogen evolution and corrosion rates increased with increased applied potential (or current).

The explanation to this phenomenon is given by the negative difference effect. Figure 3-10 shows a schematic of the expected electrochemical response to polarization. The cathodic and the anodic currents marked by $I_c$ and $I_a$ respectively intersect at $I_o$, which is the current at the open cell potential. If the potential was to increase to a new potential $E_{\text{appl}}$, the anodic current should increase to a new value $I_{\text{Mg,e}}$ and the cathodic rate should decrease to a new value denoted by $I_{\text{H,e}}$. However, as seen in Figure 3-10, the anomalous behavior of Mg deviates and the corresponding actual values are marked by $I_{\text{Mg,m}}$ and $I_{\text{H,m}}$ [43].
The negative difference effect occurs when the sum of the corrosion and applied currents is smaller than the observed current as given in the equation below:

\[ I_{\text{corr}} + I_{\text{app}} < I_{\text{obs}} \]  

(Where \( I_{\text{corr}} \) is the corrosion rate at open circuit conditions, \( I_{\text{app}} \) is the current needed to hold a specimen at a given potential, and \( I_{\text{obs}} \) is the observed corrosion rate when \( I_{\text{app}} \) is applied). The negative difference effect is given by a quantity, \( \Delta \), that has to be negative and is given by:

\[ \Delta = I_0 - I_{H,m} < 0 \]  

A number of possible reasons (detailed below) for this phenomenon have been reported, however, none of the given postulates were able to put forth a comprehensive explanation [43, 56, 121]:

1. Existence of monovalent magnesium ions, \( \text{Mg}^+ \), can explain the negative difference effect. Experimental work suggested that the valence of dissolved magnesium was found to be in
the range of 1.33-1.66, which indicates the presence of monovalent Mg\(^+\) ions formed by the electrochemical reaction \([43, 44, 47, 84]\):

\[
\text{Mg} \rightarrow \text{Mg}^+ + e^- \tag{3.8}
\]

The monovalent magnesium ions will react to produce divalent ions and hydrogen gas following the chemical reaction described below. The increase in hydrogen evolution is due to a chemical reaction rather than an electrochemical one.

\[
2\text{Mg}^+ + 2\text{H}^+ \rightarrow 2\text{Mg}^{++} + \text{H}_2 \tag{3.9}
\]

This theory failed to explain the significant reduction in corrosion current at potentials that are about 1V higher than the Mg\(^+\)/Mg equilibrium potential. The existence of the monovalent magnesium ion has been the subject of several debates. Following extensive investigations by independent research groups over the past decade it was concluded that the monovalent magnesium ion does not exist, proving the theory above to be incorrect \([48, 49, 51, 122]\).

2. Breakdown of the quasi-protective passive film during anodic dissolution could be responsible for the deviation from the behaviour predicted by the Tafel equation. In this proposition, the film coverage is assumed to decrease as the external potential applied to the surface is increased. The Tafel equation assumes that the active area remains unchanged, and the active area changes caused by passive film deterioration violate this assumption. The model has been criticized due to insufficient evidence to support the passive properties of the film. The model also does not explain the negative difference effect in solutions where film formation is not favourable.

3. Spalling of metallic particles can occur as the \(\beta\) particles are cathodic to the \(\alpha\)-matrix and the interphase boundary would be highly active, resulting in them being undermined and falling out of the matrix. As a result, more localized dissolution of metal into the solution would occur than predicted by Tafel behavior. Experimental results showed that the
concentration of impurities in the electrolyte solution did not increase as expected if $\beta$ particles dissolved into the electrolyte [43].

4. Hydride formation would result in subsequent hydride decomposition into hydrogen gas and divalent magnesium ions. This would increase the hydrogen evolution and corrosion rate simultaneously, as seen in reaction 3.10. It is important to note that production of magnesium hydride follows a cathodic reaction and thus should decrease with an increase in applied potential (in the anodic direction). The hydrogen evolution rate should decrease as well, which is in contradiction to that observed experimentally.

$$\text{MgH}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{OH}^- + 2\text{H}_2$$ \hspace{1cm} (3.10)

At present, the general consensus is that the negative difference effect can be explained by anodically induced cathodic activation that has been cited to occur in several Mg systems that are corroding at open circuit potential. This terminology refers to the increase in the cathodic kinetics of an electrode (magnesium specimen) following exposure to corrosive media. Anodically induced cathodic activation is particularly detrimental to magnesium alloys, as faster cathodic kinetics accelerate the anodic dissolution of the alloy which in turn accelerates the hydrogen evolution reaction even further. Williams et al. have shown that anodically induced cathodic activation does not require anodic polarization, and it can occur following exposure to corrosive media at open circuit potential [70]. The exact mechanism responsible for anodically induced cathodic activation is not fully understood, but it is generally accepted that it is caused by noble metal (as compared to magnesium) enrichment on the surface of the specimen that occurred through incongruent dissolution or replating. It was proposed that the enhancement in cathodic kinetics was caused by increased concentration of impurity and/or alloying elements on the surface of the specimen [69, 72, 98, 123]. Since common impurity and/or alloying elements found in magnesium alloys exhibit strong catalytic properties for the hydrogen evolution reaction, an increase in their concentration would result in an overall enhancement in the cathodic kinetics exhibited by the specimen [88].
3.5 Corrosion Protection: Plasma Electrolytic Oxidation Coatings

3.5.1 Formation Mechanisms and Effect of Process Parameters

Plasma electrolytic oxidation is a process for producing hard and corrosion resistant oxide coatings on the surface of metallic substrates such as aluminum, magnesium and titanium alloys [124, 125]. In this process, a high voltage is applied to a metal specimen immersed in an electrolyte bath causing dielectric breakdown accompanied by local plasma discharges. The plasma on the surface of the specimen converts the metallic substrate into an oxide coating. The process is particularly attractive for industrial applications due to its relatively short cycle time (5 - 30 minutes) and the ability to coat complex geometries [8, 126].

The research pertaining to the formation mechanism of the coating focused on two major areas: the mode of plasma discharging and the chemical reactions occurring during the oxidation process. In terms of plasma discharging mode, previous research by Hussein et al. reported three different plasma discharge types that could occur on a surface of a PEO treated specimen [127, 128]. The type of discharge was determined by the location at which it occurred; Type “A” referred to a discharge on the top surface of the oxide, Type “B” was designated as a discharge through the existing oxide layer, and type “C” referred to a discharge inside the mesoporous structures within the coating film [127]. Cheng et al. further expanded the mechanism by adding two more discharge modes, to describe the discharges that occur on ceramic coatings that were partially detached from the surface, or those containing micro-voids at the metal-oxide interface [129]. Type “D” describes the discharges taking place at the bottom of the voids between the coating and the base metal, while type “E” refers to discharges occurring on the top surface of the partially detached ceramic layer. While these mechanisms provide a description of the broad range of possible discharge behaviour that could occur at the electrode interface, not all apply in every PEO process. Further experimental evidence is required to distinguish between these mechanisms and to identify where in the coating process they may dominate.
Figure 3-11 PEO discharge mechanisms. Summarized from the conclusions reported in [127-129].

The chemical reactions occurring during the oxidation process are directly linked to the process parameters and electrolyte chosen to produce the coating [129-134]. Electrolytes containing silicate are commonly used in PEO processing of magnesium alloys [135]. The formation of PEO coatings in these electrolytes has been previously described in literature [135, 136]. During the PEO process, a voltage is applied between an inert cathode and the workpiece which serves as the anode. Oxygen evolution occurs due to the electrolysis of water as described by equation (3.11):

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \tag{3.11}
\]

The oxygen is then ionized and diffuses towards the metal substrate where it reacts with metal cations (Mg\(^{2+}\)) forming magnesium oxide (MgO), as shown in equation (3.12):

\[
\text{Mg}^{2+} + \text{O}^2^- \rightarrow \text{MgO} \tag{3.12}
\]

Silicate anions arising from the electrolyte penetrate into the micro-discharge channels due to the existing electrical field where they are reduced forming both silica (SiO\(_2\)) and oxygen (O\(_2\)) according to equation (3.13):

\[
\text{SiO}_3^{2-} \rightarrow \text{SiO}_2 + \frac{1}{2}\text{O}_2 + 2\text{e}^- \tag{3.13}
\]
Silica then reacts with magnesium oxide to form forsterite (Mg$_2$SiO$_4$) via equation (3.14):

$$\text{SiO}_2 + 2\text{MgO} \rightarrow \text{Mg}_2\text{SiO}_4$$  (3.14)

The resulting oxide layer was reported to be a rough surface morphology comprising a bilayer structure: a porous outer layer with microscopic cracks and pores that grows outward from the substrate, and a more compact inner layer that grows into the substrate [8, 125]. Hwang et al. conducted a transmission electron microscopy (TEM) investigation to characterize the structure of PEO coatings produced on AZ91 (see Figure 3-12) [137]. Following this investigation it was proposed that the outer layer (Figure 3-12 (a)) consisted primarily of an amorphous phase that was formed when the molten oxide, ejected following a discharge event, rapidly solidified upon contact with the electrolyte [137]. In contrast, the inner layer (Figure 3-12 (b)) exhibited a dense nanocrystalline microstructure that was determined to be similar to magnesium oxide (MgO) [137]. It is likely that, unlike the outer layer, the inner layer was formed by solid state diffusion of oxygen into the substrate. EDS measurements of the coating cross-section showed that the outer layer had higher concentrations of Si than the inner layer [125, 138, 139]. As such the outer layer comprised a partially amorphous MgSiO$_4$/MgO phase, while the inner contained primarily nanocrystalline MgO.

Figure 3-12 TEM micrographs of a cross section of a PEO coating produced on AZ91: (a) bright field image of the porous outer layer, and (b) bright field image of the compact inner layer. Adapted from [137].
Chapter 3: Corrosion: Mechanisms and Governing Factors

Much of the research investigating PEO coatings on magnesium alloys has been focused on optimization of treatment conditions to improve the corrosion resistance of these coatings [124, 138, 140-144]. Lee et al. reported that the corrosion resistance of PEO coatings produced on AZ31 magnesium alloy decreased with increasing current density due to increased porosity [145]. On the contrary, several other papers documented that corrosion resistance of the coating can be increased by increasing the applied current density up to an optimum value [146, 147]. Ultimately the optimization of applied current density would be based on balancing the beneficial properties of a thicker coating with the harmful characteristics of a coating with increased porosity. Similar observations were made for the effect of oxidation time [146].

The temperature of the electrolyte during PEO coating is generally regarded as an important parameter that should be controlled in the range between 20-40 °C [148]. It was suggested that if the temperature of the electrolyte was too low the oxide growth rate would slow down, while excessively high temperatures of the electrolyte would result in coating dissolution both of which would result in production of a thinner coating [148]. It is interesting to note that these recommendations were given as a general suggestion, and that the specific role of electrolyte temperature in PEO treatment of AZ31 is still not clearly understood.
3.5.2 Corrosion resistance of PEO Coatings on AZ31 Magnesium Alloy

PEO coatings have been shown to dramatically increase the corrosion resistance of magnesium alloys [138, 149-153]. Table 3-9 presents a summary of the electrochemical properties of silicate based PEO coatings on AZ31 in 0.6 M NaCl. It is evident from the table that the corrosion resistance properties of the coatings were two orders of magnitude better than the substrate material regardless of the electrolyte composition or the oxidation time used to produce the coating. While the results in Table 3-9 are specific to PEO coatings on AZ31, similar observations were made for PEO coatings on AZ91 [151]. The corrosion performance of the coating is dependent on its thickness, compactness, and the chemical stability of the oxide formed during PEO processing [138]. The physical properties of the coating are largely dependent on the electrolyte composition. Various additives are added into the electrolyte to improve the corrosion of PEO coatings made on AZ31 (see Table 3-9).

Chen et al. reported that the corrosion resistance of PEO coatings on AZ31 can be improved through the addition of NaF into the electrolyte [138]. The presence of fluoride ions in the electrolyte promoted their incorporation into the oxide film to form a stable MgF$_2$ phase, which enhance the corrosion resistance of the coating. Alternatively, the corrosion resistance of PEO coatings can be improved by reducing their porosity, as has been shown with the addition of Na$_2$B$_4$O$_7$ [152]. The density of the coating can be further increased through the addition of 10 g/L of polyethylene glycol (PEG) to sodium silicate electrolytes [153]. Microscopically, PEG was adsorbed on the surface of the anode, resulting in a higher breakdown potential via changing the discharge mechanism [153]. The altered oxidation process resulted in greater Mg$_2$SiO$_4$ incorporation into the coating, as compared to coatings made without the addition of PEG, leading to a denser corrosion resistant coating. Electrolyte additives present an opportunity to enhance the properties of PEO coatings on magnesium alloys. Much research is still required to develop sufficient fundamental knowledge to enable optimized electrolyte design.
Table 3-9 Electrochemical properties of silicate based PEO coatings on AZ31 in 0.6 M NaCl. The electrochemical properties of the substrate material used in each study are provided as well for reference. Note that EG stands for ethylene glycol, and PEG stands for polyethylene glycol (the subscript represents polymer number average).
The corrosion behaviour of PEO coatings on magnesium alloys can be improved not only by altering the oxidation process, but also by pore sealing post treatments following the application of the coating. In this approach, the porosity of the coating is reduced by blocking and/or filling the pores in order to minimize the number of pathways exposing the substrate to the corrosive medium. One example of such a treatment involves heating the coated sample in boiling water to produce oxides and/or hydroxides within the pores [153, 155]. Similarly, pore filling can be attained by immersing the coating into aqueous solutions containing various salts to induce precipitation within pores and reduce the porosity. In this connection, a recently published article has shown that immersion of PEO coated AZ91 in cerium and sodium stannate containing electrolytes can improve the corrosion resistance of the oxide coating [139]. Finally, the porosity of PEO coatings can be minimized by application of an organic top coating, such as a polymer, to penetrate the pores and improve the corrosion resistance of the coating [156].

Most of the research on PEO coatings is focused on evaluating their corrosion resistance properties. Through this assessment authors are able to fine tune process parameters and secondary treatments to produce PEO coatings with superior corrosion resistance properties. So far, little attention has been given to the degradation mechanism governing the behaviour of the coating. A few studies attempted to explain the pitting initiation stage but omitted mechanistic details about pit growth and propagation [149, 157]. In their study, Wang et al. proposed that corrosive media penetrated the porous coating and resulted in pitting in places where defects were present. Anodic dissolution occurred on exposed α-Mg matrix, while cathodic hydrogen evolution occurred on exposed second phase intermetallics [149]. The theory proposed by Wang et al. provided only cursory commentary about the pitting process and failed to examine the mechanisms governing pit growth and propagation following the initial pitting event. Further research is required in order to elucidate the reaction mechanism occurring on the surface of corroding coated specimens.
Chapter 4 Friction Stir Welding

Friction stir welding is a solid-state process that was first invented by the Welding Institute in 1991 for aluminum joining [3]. The applicability of this methodology was later expanded and was also used for joining of magnesium alloys as it overcame the challenges associated with traditional fusion welding techniques, such as cracks and porosity that significantly weaken the mechanical properties of the weld [1, 2]. The process involves plunging a rotating tool (consisting of a narrow pin and a wider shoulder) and traversing it across the interface between the metals to be joined. A schematic representation of the process in the butt-weld configuration is shown in Figure 4-1. The tool serves two main purposes during the welding process: heating and motion of the material. The heating is accomplished by friction between the tool and the work piece, as well as plastic deformation of the material [158]. The localized heating softens the material and the tool rotation combined with translation causes material flow. During this solid state process the material experiences severe local plastic deformation at elevated temperatures resulting in a recrystallized grain structure [158].

![Figure 4-1 Schematic of friction stir welding in a butt-weld configuration. Reproduced from [160].](image_url)

In addition to the seam weld configuration that is illustrated in Figure 4-1, friction stir welding can be used to produce spot joints as well by plunging and retracting the rotating tool in the same location. There are three main steps in the friction stir spot welding process as outlined in Figure 4-2 below. In the first step a rotating pin is plunged into an overlapping sheet assembly. Both the
rotation speed and the plunge depth are set by the operator. Once the pin achieves the specified plunge depth, the tool continues to rotate within the metal while maintaining its vertical position. The duration of the second step can be controlled by the operator, and it is known as the dwell time. When the weld is complete the tool is removed. The microstructure of the joint can be controlled by altering both process parameters of rotational speed and the dwell time.

**Figure 4-2 Schematic of FSSW [160]**

### 4.1 Friction Stir Spot Welding Zones

The thermomechanical nature of the welding operation modifies the microstructure of the Mg-alloy base metal, resulting in the formation of three distinct microstructural regions that are determined by their radial distance from the joint centerline. The innermost region is called the stir zone (SZ), immediately adjacent to it is the thermo-mechanically affected zone (TMAZ), which is followed by the heat affected zone (HAZ), as seen in Figure 4-3. The size of the zones and the microstructure depend on the choice of the welding process parameters.
Figure 4-3 Schematic of the zones present in a FSSW joint, along with typical microstructures observed in the (A) SZ, (B) TMAZ, (C) HAZ, and (D) base metal regions in FSSW welds made in AZ31. Micrographs are adapted from [161].

The microstructure in the stir zone (Figure 4-3 (A)) results from dynamic recrystallization, which is a recrystallization process occurring while the material is in motion. Heat generation during the friction stir spot welding results from a combination of friction and viscous dissipation as the tool rotates. FSSW is typically regarded as a solid-state joining process. It has been recently suggested that the process is characterized by local melting of a thin 10-20 µm thick layer in the stir zone material located close to the periphery of the rotating pin [162]. Following the formation of the locally melted film, the material’s viscosity decreases, and the temperature falls, and the locally melted film then re-solidifies. Local melting and subsequent solidification cycles continue
through the length of the dwell time in friction stir spot welding [162]. It is important to stress that melting occurs only locally in the form of thin liquid films near the surface of the rotating tool, and the remainder of the materials in the SZ region is solid. This solid material in the SZ is in a state of superplasticity due to the thermo-mechanical input that is caused by the welding operation. The material flow is accommodated by grain boundary sliding that has been well documented for magnesium alloys subjected to high strain rates at elevated temperatures [163, 164]. The resulting microstructure of the stir zone comprises recrystallized $\alpha$-matrix super saturated solid solution grains, with excess aluminum due to second phase particle dissolution.

The TMAZ (located immediately adjacent to the SZ) comprises partially recrystallized $\alpha$-Mg grains that are elongated in the direction of material flow (circumferentially and upwards from the bottom sheet), see Figure 4-3 (B) [165]. The HAZ comprises reheated $\alpha$-Mg grains and exhibits grain growth relative to the base material (BM), see Figure 4-3 (C) and (D).

### 4.2 Thermal Cycle of the Stir Zone

The thermal cycle of the SZ has been thoroughly studied by North et al. [166, 167]. Figure 4-4 shows a typical temperature output produced during friction stir spot welding of AZ31 for a rotation speed of 3000 rev min$^{-1}$ and a dwell time of 4 sec. As the tool plunged into the overlapping metal sheet assembly, the axial force increased rapidly. Upon initial contact with the specimen, surface cracking (of the base metal) accompanied by debris formation occurred directly underneath the rotating pin [160]. As plunging continued, the applied pressure increased ultimately leading local melting of the base metal that resulted in the formation of a thin liquid film at the interface with the rotating tool. When the system reached the conditions required liquid film formation, the axial force began to decrease (see point F1 in Figure 4-4). The reduction in axial force occurred because the local liquid films acted as a lubricant at the interface between the rotating pin and the adjacent plasticized material [160]. The axial force increased again when the tool shoulder surface came into contact and compressed the material extruded from the keyhole. The axial force increased until liquid films were able to form again. From that point onwards, the axial force decreased until the end of the welding operation.

The temperature measured in the stir zone increased rapidly during the plunging period as a result of heat generated through viscous dissipation [162]. The peak temperature was achieved shortly
after the dwell period began (less than 1 sec). The peak temperatures at the pin and shoulder were 515 and 553 °C respectively [167]. The heating rate at the tool pin was 311 °C/sec [167].

The peak temperatures at the pin of the welding tool increased when the rotational speed was increased from 1000 to 3000 rev min⁻¹, see Figure 4-5 [166]. The above observation was independent from the plunging rate used during the welding operation. At a rotational speed greater than 1000 rev min⁻¹, the temperature in the stir zone exceeded the eutectic temperature (437 °C) of the alloy. This observation is important since this condition leads to eutectic melting of β-Mg₁₇Al₁₂ particles as discussed in Section 4.4.2. The temperature difference was caused by the marked differences in the heating rates from varying the rotational speed of the welding tool.
Chapter 4: Friction Stir Welding

The highest temperature attained in the stir zones of magnesium alloy FSSW joints is ultimately limited by either the solidus temperature of the alloy or the melting temperatures of secondary intermetallic phases contained in the base metal [159, 167-169]. Gerlich et al. suggested that the plasticized material immediately adjacent to the tool was melted when the stir zone exceeded the solidus temperature [159]. This local melting resulted in a significant decrease in the viscosity of the material, reduced the heat generation rate, and prevented a further temperature increase. When the temperature of the stir zone decreased again, the liquid film solidified, causing an increase in the viscosity and heat generation rate.

4.3 Effect on Microstructure

4.3.1 Grain Size

The effect of friction stir welding on the grain size of magnesium alloys has been previously investigated in literature [6, 108, 170-174]. It is commonly accepted that the friction stir welding operation results in grain refinement of the stir zone [6, 170-174]. This statement is not entirely accurate, as refinement is a relative term that is entirely determined by the grain size of the base metal. When the initial grain size of the base metal was very fine, the grains in the SZ region became larger than those present in the base metal as has been previously reported by Kish et al. [108]. A better way to examine the influence of FSSW on the grain size of magnesium alloys would be to consider the mechanisms governing grain growth and refinement.
Sun et al. reported that the resultant grain size in the stir zone was related to the balance between high temperature recovery mechanisms which promoted grain growth, and intense plastic deformation which promoted grain refinement [166]. An increase in the rotational speed of the tool increased the temperature in the stir zone (as discussed in Section 4.2), and thus resulted in enhanced recovery and increased grain size [166]. It is important to note that changes in the rotational speed of the tool resulted in only minor differences in the grain size in the stir zone [166]. Statistically significant differences existed only between stir zones produced using 1000 and 3000 rev min\(^{-1}\), where the average grain sizes were 3.0 ± 1.6 and 8.0 ± 3.1 respectively [166]. Contrary to previously reported data [175], grain growth did not occur in the SZ region when the weld cooled to room temperature following tool extraction [166].

The grain size of the TMAZ and HAZ regions depend on the initial grain size of the base metal and the process parameters used to produce the joint. The grain size of the TMAZ is coarser than that of the SZ as the material in the TMAZ undergoes less deformation during the welding process [171]. The grain size of the HAZ is coarser than the initial grain size of the base metal, as the region is produced as a result of thermal input in the absence of mechanical deformation. The heat dissipating from the joint induces some grain growth and stress relaxation [170].

4.3.2 Grain Orientation

Wrought AZ31 sheet exhibits strong texture having a preferred (0002) grain orientation on the rolled surface with the c-axis parallel to the normal direction (ND) [37, 112, 113]. Compressive and shear deformation results in reorientation of the grains. Grains in the stir zone have their basal c-axis perpendicular to the ND [176]. The basal planes in the stir zone experienced a 90° rotation compared to the initial rolled texture [177]. The thermo-mechanically affected zone exhibited a gradual transition between the stir zone orientation to the base metal with the c-axis of the basal grains tilted at 30° clockwise to the ND. The heat affected zone showed a similar texture to that found in the base metal. The texture was more diffuse than the one in the base metal as the zone experiences heating but no deformation [176]. The final orientation of the grains is markedly dependent on the relative contribution of shear and compressive loadings within the weldment, as a result grain orientation shows a distribution that depends on the location within the weld zone [178].
4.3.3 Residual Stress

The FSW process introduces residual stresses and internal strain in welded joints via several different mechanisms [179-181]. When the tool penetrates into the sheet metal, it induces severe plastic deformation that results in compressive stresses in the plane normal to the tool centerline and tensile stresses in the direction parallel to the axis of the rotating tool. Material surrounding the welding spot is deformed elastically, and the incompatibility between the deformed material in the weld zone and surrounding bulk material creates elastic residual stresses that are tensile in the radial direction and compressive normal to the axis of the rotating tool [181]. Residual stresses are also produced as a result of contraction when the joint cools to room temperature. Local heating during FSSW creates a temperature gradient wherein the different zones (SZ, TMAZ and HAZ) cool and contract at different rates. These incompatibilities led Woo et al. to conclude that the different weld regions in FSW joints made in AZ31 sheet had quite distinct residual stress states [179-181]. The residual stress sharply decreased near the SZ boundary indicating that the SZ was in a state of compression, while the surrounding material, which had higher residual stress values, was in tension. The highest residual stress values (up to 150 MPa) were present in the TMAZ region [179].

4.4 Intermetallic Dissolution During Friction Stir Spot Welding

4.4.1 β-Mg_{17}Al_{12}

Friction stir welding of magnesium alloys has been shown to induce the dissolution of β-Mg_{17}Al_{12} intermetallics in the stir zone region [160, 171, 174]. The dissolution of these intermetallics during the welding operation is governed by the diffusion of the aluminum atoms in the α-matrix (Mg). This diffusional process can be divided into two stages separated by eutectic melting (437 °C). Prior to reaching the eutectic temperature, solid state diffusion is the determining factor. Once the SZ zone temperature exceeds the eutectic temperature (437 °C), the dissolution of the second-phase particles will be governed by liquid state diffusion [168, 169, 182].

The dissolution of liquid films has been previously described in literature [160, 169]. The relationship between the half thickness \(B_o\) of a plate-shaped liquid droplet and the time \(t\) available for dissolution is determined by equation (4.1), where \(k_l\) is the driving force for solute diffusion, and \(D_{Al \text{ in Mg}, \text{T}}\) is the diffusion coefficient of aluminum in magnesium at temperature \(T\). The complete derivation of equation (4.1) is shown in Appendix A.
The driving force for solute diffusion was previously described by Yamamoto et al. using equation (4.2) [169].

\[
B_O = \frac{k_l}{\sqrt{\pi}} \sqrt{D_{Al \text{ in } Mg,T} \cdot t}
\]  

(4.1)

where:

- \(C_{T_2}^{\alpha/\text{liq}}\) corresponds to the maximum solubility limit of Al in the \(\alpha\)-Mg phase (13 wt.% Al) at the eutectic temperature (\(T_2 = 437 ^\circ C\))

- \(C_{T_2}^{\text{liq}/\alpha}\) represents the eutectic composition (33 wt.% Al) of the two phases (\(\alpha\)-Mg + \(\beta\)-Mg\(_{17}\)Al\(_{12}\)) present in the melted film at the eutectic temperature (\(T_2 = 437 ^\circ C\))

- \(C_{T_1}^{\alpha/\beta}\) corresponds to the solute concentration (3 wt.% Al) in the \(\alpha\)-Mg phase at room temperature (\(T_1 = 25 ^\circ C\)).

In the case of Mg\(_{17}\)Al\(_{12}\) dissolution in AZ31, the resulting driving force for Al diffusion, has a value of \(k_l = 1\).

As seen from equation (4.1) the dissolution of \(\beta\)-Mg\(_{17}\)Al\(_{12}\) in AZ31B friction stir welds is dependent on the time (t), and the diffusion coefficient (\(D_{Al \text{ in } Mg,T}\)) of solute atoms (Al) in the adjacent matrix (\(\alpha\)-Mg). The diffusion coefficient at a given temperature (T) can be calculated from the Arrhenius expression given in equation (4.3), where, \(D_o\) is \(1.53 \times 10^{-5} \text{ m}^2/\text{sec}\), \(Q_{\text{diff}}\) is the activation energy for diffusion of Al atoms in Mg (125 kJ/mol), and R is the universal gas constant \((8.314 \times 10^{-3} \text{ kJ/(mol·K)})\) [160, 168, 183].
\[ D = D_0 \exp \left( -\frac{Q_{\text{diff}}}{RT(t)} \right) \]  

(4.3)

The heating rate caused by the welding operation varies greatly depending on the selected welding conditions. The dissolution of β-Mg\textsubscript{17}Al\textsubscript{12} particles occurs in two stages (solid and liquid state diffusion). Since the diffusion of Al is significantly slower in the solid than in the liquid state, the dissolution of second phase particles during the initial stage, when the temperature is ramping up, can be assumed to be negligible. The dissolution process is then governed only by the time interval of liquid state diffusion, starting from the instant the stir zone temperature exceeds 437 °C until the point when the welding operation is complete.

4.4.2 γ-Al\textsubscript{8}Mn\textsubscript{5}

The dissolution of Al-Mn particles as during the friction stir welding operation is not as well documented. γ-Al\textsubscript{8}Mn\textsubscript{5} phase is thermodynamically more stable than β-Mg\textsubscript{17}Al\textsubscript{12} intermetallic phase due to its higher melting temperature (989 °C), as shown by the equilibrium phase diagram (Figure 2-5). The maximum temperature measured during friction stir spot welding of AZ31 using a rotational speed of 3000 rev min\textsuperscript{-1} was 562 °C, which is well below the melting temperature of γ-Al\textsubscript{8}Mn\textsubscript{5} intermetallics [166]. This argument can be extended to all types of Al-Mn phases that could be present in the Mg-alloy, since even Al\textsubscript{6}Mn, the least thermodynamically stable phase, will remain solid up to a temperature of 658 °C [184]. Even if the temperature in the stir zone falls below the melting point of Al-Mn intermetallics, their dissolution can occur through solid state diffusion. The kinetics of precipitate dissolution via solid state diffusion have been previously described by Whelan [185]. The complete dissolution of a spherical solid particle with radius, Ro, is described by a similar relation to that shown in equation (4.1), as shown in equation (4.5).

\[ R_0 = \frac{k_s}{\sqrt{\pi}} \sqrt{D_{\text{Al in Mg,T}} \cdot t} \]  

(4.5)
Chapter 4: Friction Stir Welding

The terms in equation (4.5) are identical to those in equation (4.1) with the exception of the driving force for solid state diffusion, \( k_s \), which differs slightly from the driving force for dissolution of liquid films. In the case of solid-state diffusion, the driving force, \( k_s \), can be estimated using equation (4.6) [185]:

\[
k_s = 2 \left[ \frac{C^\alpha_{T_2}/\text{liq} - C^\alpha_{T_1}/\beta}{C_p - C^\alpha_{T_2}/\text{liq}} \right]
\]

(4.6)

where \( C^\alpha_{T_2}/\text{liq} \) and \( C^\alpha_{T_1}/\beta \) are as described previously, and \( C_p \) corresponds to the concentration of the solute in the particle (60 wt.% Al in the case of Al\(_8\)Mn\(_5\)). In the case of Al\(_8\)Mn\(_5\) dissolution in AZ31, the resulting driving force for Al diffusion has a value of \( k_s = 0.42 \).

At present, there is no detailed documentation of the dissolution process responsible for \( \gamma \)-Al\(_8\)Mn\(_5\) intermetallic dissolution. It would be expected that only a partial dissolution of \( \gamma \)-Al\(_8\)Mn\(_5\) particles would occur as a result of the welding operation.

In addition to particle dissolution, particles remaining in the solid state during the welding process may fracture leading to their size refinement. Particle fragmentation and refinement depend on the parameters employed during joining. When examining friction stir welded Al-alloy 2024-T351, Al\(_2\)Cu particles were most refined in the stir zone region, when the mechanical conditions were most intense [186]. It can be expected then that both the length of the welding operation (dwell time) and the intensity of the rotational speed setting will influence the size and distribution of the \( \gamma \)-Al\(_8\)Mn\(_5\) particles in the stir zone.

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Chapter 5 Corrosion of Friction Stir Welded Magnesium Alloys

5.1 Research Progress on the Corrosion of Behaviour of FSW Joints Made in Mg Alloys

5.1.1 Corrosion Morphology

Several researchers have attempted to understand the effect of friction stir welding on the corrosion behaviour of magnesium joints through the examination of corrosion morphology [9, 11, 187]. The results of their studies are summarized in Table 5-1. Examination of AM50 FSW joints after 4 hours of salt spray testing (0.86M NaCl) revealed pitting and filament corrosion in the BM region (Table 5-1) [187]. The corrosion attack appeared to be uniformly distributed in the base metal [187]. Pitting and filament corrosion appeared in the SZ region as well, but unlike the BM region, the attack occurred primarily along surface irregularities that were created by the interaction between the welding tool and the work piece. The change in corrosion morphology was attributed to the redistribution of β-Mg$_{17}$Al$_{12}$ intermetallics in the SZ region. Though not immediately clear from the image in Table 5-1, the authors report that the SZ region exhibited higher corrosion resistance than the TMAZ, HAZ and BM regions. This conclusion was primarily based on potentiodynamic polarization results obtained for individual weld regions [187]. The authors concluded that friction stir welding of AM50 produced a SZ region with improved corrosion resistance properties due to second phase redistribution and grain refinement [187].

In a recent publication, Zhang et al. disagreed with the mechanism detailed above by suggesting that surface contamination had a significantly greater effect on the corrosion behaviour of FSW welds than the underlying microstructural differences occurring between various weld regions [9]. To support this proposition, their study examined the corrosion behaviour of AZ31 FSW joints with three different surface conditions using salt spray testing [9]. Samples in the as-welded condition preferentially pitted in the base metal near the SZ/BM interface, and only a few minor pits were visible in the SZ region (see Table 5-1). Specimens that were abraded following the welding procedure exhibited a markedly different corrosion morphology. The corrosion attack appeared uniformly distributed across all the weld regions that were exposed to corrosive media. The mode of attacked differed as well, as it changed from pitting corrosion to filament corrosion.
Samples that were acid cleaned following the welding procedure, exhibited both pitting and filament corrosion. Some preferential pitting of the BM was apparent but to a lesser degree than that of specimens in the as-welded condition. The differences between the three samples were explained by the presence of surface contamination introduced into the sheet metal during the rolling stage. Specimens in the as-welded condition had contaminants (noble impurity metals like Fe, and Cu) on the surface of the BM region that promoted enhanced pitting attack. These contaminants were not present on the surface of the SZ region since they were mixed into the weld nugget, and so the SZ region appeared to be more corrosion resistant. Abrasion of the samples removed the surface contamination and so samples in the abraded condition exhibited a uniform corrosion attack across all regions exposed to the corrosive media. The mode of attack changed to filament corrosion due to the absence of noble impurities on the surface. Acid cleaning partially removed the contaminants present on the surface of the base metal leading to a mix between the two modes of attack.

While the corrosion morphology supported the proposition made by the authors, additional work is required to prove this hypothesis definitively. Examination of welds made in a base metal without surface contamination would elucidate the role of these contaminants on the overall corrosion resistance of the joint. Such experimental conditions can be achieved by grinding the base metal prior to welding.

*James et al.* who also examined the corrosion behaviour of friction stir welded AZ31 reported a different observation [11]. In their studies, AZ31 exhibited enhanced pitting at the interface between the SZ and the BM regions (see Table 5-1). The location of pitting coincided with the TMAZ region. Though not specifically reported it was observed from the corrosion morphology images in the manuscript that the SZ and the BM regions exhibited filament corrosion. The localized corrosion attack in the TMAZ region was related to the ennoblement of the SZ region. The authors suggested that the SZ exhibited enhanced corrosion resistance properties due to its dynamically recrystallized grain structure, and the dissolution of $\beta$-$\text{Mg}_{17}\text{Al}_{12}$. While the authors identified possible causes for their observations, the relative contribution from changes in each type of microstructural feature has not been discussed. Additional work is required to determine the exact mechanism leading to SZ ennoblement.
### Table 5-1 Corrosion morphology of magnesium FSW/FSSW joints exposed to chloride containing environments. Images were modified from respective publications.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Top Surface</th>
<th>Cross-sectional Surface</th>
<th>Location of Attack</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM50 FSW joint after salt spray testing (0.86M NaCl / 4 hours).</td>
<td><img src="image1.png" alt="Image" /></td>
<td>--</td>
<td>Pitting and filament corrosion attack occurred uniformly in the BM, while the corrosion in the SZ region took place along surface irregularities.</td>
<td>[187]</td>
</tr>
<tr>
<td>AZ31 FSW joint in the as-welded condition after salt spray testing (0.86M NaCl / 24 hours).</td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td>Preferential pitting of the BM near the BM/SZ interface. Only light pitting took place in the SZ region.</td>
<td>[9]</td>
</tr>
<tr>
<td>AZ31 FSW joint that was abraded before salt spray testing (0.86M NaCl / 24 hours) began.</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td>Corrosion morphology of the BM was indistinguishable from that of the SZ region. Preferential attack was not observed. Filament corrosion was the dominant mode of corrosion.</td>
<td>[9]</td>
</tr>
<tr>
<td>AZ31 FSW joint that was acid cleaned (10 wt.% H2SO4/ 20 sec) before salt spray testing (0.86M NaCl / 24 hours) began.</td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td>Both filament and pitting corrosion were present in the SZ and BM regions. Some preferential pitting of the BM was apparent but to a lesser degree than that of specimens in the as-welded condition.</td>
<td>[9]</td>
</tr>
<tr>
<td>AZ31 FSSW joint that was exposed to corrosive environment (0.086M NaCl / 4 hours).</td>
<td>--</td>
<td>--</td>
<td>Severe pitting attack occurred at the interface between the SZ and the BM. The location coincided with the TMAZ region. The SZ and the BM (away from the TMAZ) exhibited filament corrosion.</td>
<td>[11]</td>
</tr>
</tbody>
</table>
5.1.2 Electrochemical Properties of Various Weld Regions

The corrosion resistance of friction stir welded joints made in magnesium alloys has been the focus of many research projects [7, 8, 11, 12, 187-195]. A summary of the corrosion resistance properties of friction stir welded joints and their respective base metals is presented in Table 5-2. There was no clear relation between the corrosion potentials ($E_{\text{corr}}$) of the SZ and the BM regions that could be extended to all magnesium alloys. For AZ31 no consistent trend regarding the effect of friction stir welding on its corrosion potential was observed. Independent investigations by Chen et al. and Kannan et al. reported the SZ region to be consistently more cathodic than the base metal [7, 8]. This effect was not seen by Kish et al. who suggested that in the absence of surface contamination on the BM, friction stir welding did not influence the electrochemical properties of AZ31B [9, 108]. Further work is required to identify the reason for the discrepancy between these studies. No consistent trend was also observed for the effect of friction stir welding on the corrosion potential of AM50 alloys [187, 191]. For WE43 (Mg-4Y-3Nd), the SZ region was consistently more cathodic than the base metal [193, 194], and for pure magnesium and Mg-5Al, the SZ was more anodic than the BM region [189, 190].

A much more consistent trend was revealed when the corrosion current density ($i_{\text{corr}}$) of the SZ was compared to the $i_{\text{corr}}$ of the BM. With the exception of two studies ([9, 108]), the $i_{\text{corr}}$ of the SZ region was lower than that of the BM region in all friction stir welded joints made in alloy materials [7, 8, 187, 190, 191, 193, 194]. The same trend was confirmed through mass loss testing [192, 193]. Only in pure magnesium, the SZ region exhibited higher $i_{\text{corr}}$ values than that of the BM [189].

Explaining definitively why this trend did not occur in studies [9] and [108] is challenging. It is possible that the observed discrepancy is related to the initial microstructure of the BM, and/or to the way the metal sheets were joined. Unfortunately, the experimental information provided in the manuscripts is not detailed enough to assess the validity of this hypothesis.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Electrolyte</th>
<th>Method</th>
<th>Region</th>
<th>$E_{\text{corr}}$ (V SCE)</th>
<th>$i_{\text{corr}}$ (µA/cm²)</th>
<th>$R_p$ (Ωcm²)</th>
<th>Reason for Improved Corrosion Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (99.99%)</td>
<td>Hank's Solution²</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.565</td>
<td>423</td>
<td>--</td>
<td>Reduced corrosion resistance due to grain refinement</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BM</td>
<td>-1.541</td>
<td>349.8</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>AZ31B</td>
<td>0.6 M NaCl</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.472</td>
<td>1</td>
<td>3243</td>
<td>Grain refinement</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HAZ</td>
<td>-1.547</td>
<td>15.3</td>
<td>724</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BM</td>
<td>-1.5</td>
<td>5.53</td>
<td>1568</td>
<td></td>
</tr>
<tr>
<td>AZ31B-H24 (As-welded)</td>
<td>0.6 M NaCl</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.59</td>
<td>200</td>
<td>--</td>
<td>Tafel extrapolation of the cathodic branch showed the SZ to have superior corrosion resistance properties when contaminants were found in the BM. In absence of contaminants no effect was reported.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BM</td>
<td>-1.57</td>
<td>9,000</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>AZ31B-H24 (Abraded)</td>
<td>0.6 M NaCl</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.59</td>
<td>300</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BM</td>
<td>-1.59</td>
<td>300</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>AZ31B-H24</td>
<td>0.6 M NaCl</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.59</td>
<td>126</td>
<td>--</td>
<td>The changes in electrochemical properties somewhat correlated with changes in grain size. A SVET study that was carried out in the same manuscript that microstructural variation only mattered during the corrosion initiation stage.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BM</td>
<td>-1.60</td>
<td>67</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>AZ31B-O</td>
<td>0.6 M NaCl</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.59</td>
<td>133</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BM</td>
<td>-1.59</td>
<td>179</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>AZ31B</td>
<td>SBF³</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.62</td>
<td>190</td>
<td>--</td>
<td>2nd phase dissolution</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BM</td>
<td>-1.645</td>
<td>210</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Mg-5Al</td>
<td>0.01M NaCl</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.445</td>
<td>0.5</td>
<td>--</td>
<td>Grain refinement Intermetallics refinement</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BM</td>
<td>-1.345</td>
<td>0.8</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

¹Testing methods: PDP – potentiodynamic polarization, and MCP – Microcapillary Polarization  
²Hank’s solution - 8 g/L NaCl, 0.35 g/L NaHCO₃, 0.4 g/L KCl, 0.06 g/L K₂HPO₄·3H₂O, 0.1 g/L MgCl₂·6H₂O, 0.1 g/L CaCl₂, 0.1 g/L MgSO₄·7H₂O, and 0.048 g/L NaHPO₄  
³Simulated body fluid (SBF) solution - 8.035 g/L NaCl, 0.355 g/L NaHCO₃, 0.225 g/L KCl, 0.231 g/L K₂HPO₄·3H₂O, 0.311 g/L MgCl₂·6H₂O, 0.292 g/L CaCl₂, 0.072 g/L Na₂SO₄, and 6.118 g/L Tris (HOCH₂)₂CNH₂.

Table 5-2 Corrosion resistance properties of friction stir welded magnesium and magnesium alloys

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<table>
<thead>
<tr>
<th>Alloy</th>
<th>Electrolyte</th>
<th>Method</th>
<th>Region</th>
<th>$E_{\text{corr}}$ (V_SCE)</th>
<th>$i_{\text{corr}}$ (µA cm$^{-2}$)</th>
<th>$R_p$ (Ω cm$^2$)</th>
<th>$CR$ (µg cm$^{-2}$ hr$^{-1}$)</th>
<th>Cause for Improved Corrosion Resistance</th>
<th>Year</th>
<th>Ref.</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM50</td>
<td>0.6 M NaCl + Mg(OH)$_2$ Sat</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.496</td>
<td>15.84</td>
<td>6.58</td>
<td>--</td>
<td>2nd phase redistribution</td>
<td>2013</td>
<td>[191]</td>
<td>Ben-Hamu</td>
</tr>
<tr>
<td>AM50</td>
<td>0.6 M NaCl</td>
<td>PDP</td>
<td>TMAZ</td>
<td>-1.473</td>
<td>17.14</td>
<td>4.85</td>
<td>--</td>
<td>Grain refinement</td>
<td>2009</td>
<td>[187]</td>
<td>Zeng et al.</td>
</tr>
<tr>
<td>AM50</td>
<td>0.6 M NaCl</td>
<td>MCP</td>
<td>TMAZ</td>
<td>-1.574</td>
<td>9.7</td>
<td>--</td>
<td>--</td>
<td>Grain refinement</td>
<td>2009</td>
<td>[187]</td>
<td>Zeng et al.</td>
</tr>
<tr>
<td>AM50</td>
<td>0.6 M NaCl</td>
<td>MCP</td>
<td>HAZ</td>
<td>-1.588</td>
<td>6.2</td>
<td>--</td>
<td>--</td>
<td>Grain refinement</td>
<td>2009</td>
<td>[187]</td>
<td>Zeng et al.</td>
</tr>
<tr>
<td>AM50</td>
<td>0.6 M NaCl</td>
<td>MCP</td>
<td>BM</td>
<td>-1.534</td>
<td>36.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2017</td>
<td>[192]</td>
<td>Liu et al.</td>
</tr>
<tr>
<td>ZK60</td>
<td>0.6 M NaCl</td>
<td>ML (108 hrs)</td>
<td>SZ</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>54.6</td>
<td>2nd phase redistribution</td>
<td>2017</td>
<td>[192]</td>
<td>Liu et al.</td>
</tr>
<tr>
<td>ZK60</td>
<td>0.6 M NaCl</td>
<td>ML (120 hrs)</td>
<td>BM</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>96.3</td>
<td>Grain refinement</td>
<td>2017</td>
<td>[192]</td>
<td>Liu et al.</td>
</tr>
<tr>
<td>WE43 (Mg-4Y-3Nd)</td>
<td>SBF$^2$</td>
<td>PDP</td>
<td>SZ</td>
<td>-1.677</td>
<td>198</td>
<td>--</td>
<td>--</td>
<td>Homogenization of the alloy</td>
<td>2016</td>
<td>[193]</td>
<td>Cao et al.</td>
</tr>
<tr>
<td>WE43 (Mg-4Y-3Nd)</td>
<td>SBF$^2$</td>
<td>PDP</td>
<td>BM</td>
<td>-1.713</td>
<td>268</td>
<td>--</td>
<td>--</td>
<td>Grain refinement</td>
<td>2012</td>
<td>[194]</td>
<td>Argade et al.</td>
</tr>
</tbody>
</table>

1Testing methods: PDP – potentiodynamic polarization, MCP – Microcapillary Polarization, and ML (hrs) – mass loss (X hours)
2Simulated body fluid (SBF) solution - 8.035 g/L NaCl, 0.355 g/L NaHCO$_3$, 0.225 g/L KCl, 0.231 g/L K$_2$HPO$_4$·3H$_2$O, 0.311 g/L MgCl$_2$·6H$_2$O, 0.292 g/L CaCl$_2$, 0.072 g/L Na$_2$SO$_4$, and 6.118 g/L Tris (HOCH$_2$)$_2$CNH$_2$. 

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While the electrochemical interaction between the SZ and the BM has been thoroughly studied, the cause for the improved corrosion resistance exhibited by the weld nugget remains largely unknown. Various studies have suggested that the microstructural evolution occurring during welding was responsible for the increased corrosion resistance of the SZ (see Table 5-2), but the principal microstructural feature responsible for this improvement has not been clearly identified. Grain refinement and second phase redistribution are among the most common explanations for the enhancement in the corrosion resistive properties of the SZ region [8, 187, 190-195]. Unfortunately, these explanations lacked sufficient scientific basis as the role of these microstructural changes have not been clearly outlined. The effect of grain refinement on the corrosion resistance of magnesium alloys remains unknown and a mechanistic explanation describing the role of grain boundaries is still missing (see Section 3.2.3.1). It is also interesting to note that in the case of pure magnesium, grain refinement was cited as the cause for reduced corrosion resistance of the weld nugget [189]. When second phase redistribution was cited, the connection between the microstructural changes occurring during the welding process and the electrochemical properties of various weld regions was not discussed [187, 191, 192]. To the best of the authors knowledge, no attempt was made to systematically evaluate the effect of microstructural evolution on the corrosion of FSSW joints in magnesium and its alloys.

5.1.3 Interaction Between Weld Regions

A different approach to understand the effect of friction stir welding on the corrosion behaviour of joints involved correlating the electrochemical properties of the individual weld zones to the overall corrosion behaviour of the joint [11, 12, 188]. The overall corrosion behaviour of the joint, resulting from electrochemical interaction of the various weld regions that are exposed to corrosive media, can be visualized using a scanning reference electrode technique (SRET) or a scanning vibrating electrode technique (SVET). In both techniques a passive probe is scanned in close proximity to the specimen to map out the electrochemical activity occurring on the specimen.

The SRET is used to indicate local anodic and cathodic sites on the surface of a corroding specimen. It is important to note that SRET does not measure the potential variation on the surface, but instead responds to potential/current variation in a solution [12]. The basis of this technique relies on the current flow through the solution from the local anode to the local cathode, where
both sites are separated by a finite distance [196]. This current flow and the resulting potential variation can be measured by scanning a passive probe with a fine tip in close proximity (~10 µm) to the surface [11]. The first SRET investigation examining the corrosion behaviour of AZ31 FSSW joints was published by James et al. [11].

In their work, the local potential distribution of AZ31 FSSW was examined using SRET, an example of his experimental output is presented in Figure 5-1. An optical image of the 3000 rev min\(^{-1}\) and 1 sec dwell time etched sample is shown in Figure 5-1(a) and the result from the SRET output for that weld is shown in Figure 5-1(b). The SRET image in Figure 5-1(b) is a 2-dimensional contour graph using various colours to represent relative potential values. The red and yellow regions represent noble potential regions (SZ), while the active potential regions are blue and purple which cover the BM. The green boundary between the noble and active area can be described as the TMAZ and HAZ regions. The overlay in Figure 5-1(c) shows the correlation of the SRET data to the etched regions in the optical image of the corresponding welded region.

It is clearly evident that the noble region aligned with the SZ region, which is in agreement with previously reported polarization data [7, 8, 193, 194]. The results of D. Miklas showed a noble behaviour of the weld regardless of the rotational speed of the tool chosen during the welding process [12]. While the size of the noble zone has changed the overall trend has stayed consistent, and in all cases the heaviest attack was seen in the TMAZ region [12].

![Figure 5-1](image.png)

**Figure 5-1** (a) Microstructure of FSSW weld (3000 rev min\(^{-1}\), 1 sec dwell time), (b) SRET, and (c) SRET overlaid on optical image. Adapted from [188].

It is important to note that in both SRET investigations the potential difference between the SZ and the BM was on the order of several hundreds of millivolts [11, 12]. The magnitude of the potential difference in the solution is unusually high and requires further elucidation. The potential drop in the solution above a galvanically coupled interface is usually on a scale of tens of
millivolts in most naturally occurring corrosive environments. Further discussion examining the possible causes responsible for the presence of a potential drop of this magnitude is given in Section 11.4.

Though it is possible to map the current flow distribution on the sample of a corroding specimen using SRET, this measurement is prone to low signal to noise ratio (especially in electrolytes with high solution conductivity) [197]. This challenge can be resolved by scanning a vibrating electrode above the surface of the specimen (~150 µm away) in order to increase the signal-to-noise ratio [198]. In SVET the voltage difference between the two extreme points along the line of vibration (typically 30 µm apart) is measured with a lock-in amplifier [198, 199]. The current density in the direction of vibration is then calculated using equation 5.1 [197]:

\[ \Delta V = -i\rho\Delta r \]  

Where \( \Delta V \) is the potential difference, \( i \) is the current density, \( \rho \) is solution resistivity, and \( \Delta r \) is the amplitude of the vibration (i.e. the distance between the points at which the measurement was taken). From a practical point of view, \( \rho\Delta r \) is viewed as a proportionality factor that is determined during the calibration phase before testing commences [70, 197]. The vibration of the electrode improves the signal-to-noise ratio by reducing the capacitive impedance of the probe tip [199]. The effect of local changes in the electrolyte chemistry are minimized as well by the mixing action of the vibrating electrode [199].

*Kish et al.* conducted a SVET study to spatially resolve the magnitude of the cathodic and anodic currents across the SZ region of an AZ31B-O FSW joint that was exposed to 0.86M NaCl solution [108]. A series of current density distribution maps that were obtained during their investigation are shown in Figure 5-2 and Figure 5-3. The maps depicted in Figure 5-2, showcase the current density distribution during the initial stages of exposure (0-180 minutes), while the maps in Figure 5-3 highlight the current density distribution that occurred during a later stage of the corrosion process (240-360 minutes).

Localized corrosion attack initiated in the BM region, as evidenced from the red sites (anodic current) seen in Figure 5-2 (a). Upon further exposure (60 minutes) the anodic sites propagated across the SZ region Figure 5-2 (c). As the site of active dissolution traversed across the corroding sample, the filament tracks that were produced by the corrosion attack acted as local cathodes, as
can be seen from the areas in Figure 5-2 (d) and (e). It is interesting to note, that a small cathodic region in the center of the SZ was present in all SVET measurements. The authors concluded that it would be expected that this cathodic site would have little direct effect on the sites where corrosion initiated first. No attempts to explain the nature of the cathodic site or its effect on the overall corrosion behaviour of the joint were reported [108].

Figure 5-2 False-color distribution maps of normal current density (i,) above the surface of a welded AZ31B-O joint sample freely corroding in aerated 0.86 M NaCl. Data were obtained from SVET scans initiated after (a) 0 min, (b) 30 min, (c) 60 min, (d) 120 min and (e) 180 min immersion [108].
A large local anode appeared within the SZ region after an exposure time of 240 minutes (Figure 5-3 (a)). This large anode remained in the SZ region for 1 hour as it swept from left to right. At exposure times exceeding 330 minutes (Figure 5-3 (d) and (e)), the local anode remained in the BM metal region. Based on the SVET results presented in Figure 5-2 and Figure 5-3, the authors suggested that the overall corrosion behaviour of the joint is governed by the cathodic activity of the corroded surface [108]. In their model, welding had an effect on the corrosion resistance of various weld regions only during the initial stages of exposure. The SZ exhibited slower surface film breakdown kinetics than the BM, leading to the initial localize corrosion far away from the SZ region (Figure 5-2 (a)). Once this initial corrosion attack took place, the corrosion behaviour was no longer governed by the underlying microstructure of the two regions, rather it was governed by the cathodic activity of the corrosion product.

While the SVET study provided an interesting perspective regarding the current distribution on the surface of a corroding AZ31B-O FSW joint, a number of shortcomings are evident and require further investigation. The authors ignored the cathodic site present in the SZ region in all of their SVET measurements. Its nature and effect on the overall corrosion behaviour of the joint must be examined and explained within the corrosion mechanism proposed by the authors. The cause for the difference in the surface film breakdown kinetics between the SZ and the BM remains unknown as well. The authors briefly mentioned that this phenomenon could occur due to the slight differences in grain size that are present between the two regions, but as discussed in Section 3.2.3.1 the exact influence of changes in grain size on the corrosion behaviour of the weld is unknown.
Figure 5-3 False-color distribution maps of normal current density ($i_z$) above the surface of a welded AZ31B-O joint sample freely corroding in aerated 0.86 M NaCl. Data were obtained from SVET scans initiated after (a) 240 min., (b) 270 min., (c) 300 min., (d) 330 min. and (e) 360 min. immersion [108].

5.1.4 Empirical Relationships

Attempts were also made to develop empirical relationships that predicted the corrosion rate of friction stir welded magnesium alloys in a corrosive environment. This aspect of research was primarily carried out by Dhanapal et al., and their research accounts for most of the publications with this approach [1]. For example, they examined the corrosion rate of friction stir welded AZ61A in a salt spray test [1]. Based on their results they developed a parametric expression able
to predict the corrosion rate of friction stir welded AZ61A in a salt spray test, as shown in equation 5.2 (below).

\[
CR \text{ [mm/year]} = 9.48 - 1.89 \{\text{pH}\} - 0.88 \{t\} + 0.82 \{\text{Cl}^-\} + 1.60 \{\text{pH}\}^2 + 1.27 \{\text{Cl}^-\}^2
\]

(5.2)

Where the variables are scaling factors that are based on the chloride concentration, spraying time, and pH as given below:

- \(\{t\} = \left(\text{t}_{\text{spray}} - 5\right)/2.38\), \(\text{t}_{\text{spray}}\) - spraying time [hours] \((1 \leq \text{t}_{\text{spray}} \leq 9)\)
- \(\{\text{Cl}^-\} = ([\text{Cl}^-] - 0.6)/0.24\), \([\text{Cl}^-]\) - Concentration of Cl\(^-\) ion [M] \((0.2 \leq [\text{Cl}^-] \leq 1)\)
- \(\{\text{pH}\} = (\text{pH} - 7)/2.38\) \((3 \leq \text{pH} \leq 11)\)

The corrosion rate decreased with increasing spraying time due to the formation of a pseudo-passive film. An increase in pH reduced the corrosion rate due to the stabilization of the Mg(OH)\(_2\) film and removal of micro galvanic couples with \(\beta\)-particle caused by their dissolution. Lastly, increasing the chloride concentration led to higher corrosion rates due to its aggressive nature.

Like other publications in the field, the work by Dhanapal et al. failed to elucidate the connection between the microstructural evolution occurring during friction stir welding to the corrosion behaviour of the welded structure [1]. Little attention is given to this approach in the present work as the authors did not study the localized corrosion phenomenon occurring at the surface of the weld, but instead based their conclusions on the overall mass lost during the test. If magnesium alloys were to be utilized in an industrial application, localized corrosion phenomena must be considered, as even a relatively small mass loss may significantly affect the mechanical integrity of a welded structure.

### 5.2 Objectives of This Work

The present work aims at gaining sufficient theoretical knowledge linking corrosion, microstructure and welding process parameters to optimize FSSW design that will enable the use of magnesium alloys in structural applications in the transportation sector. To pursue this overarching goal a number of objectives have been identified:

1. To develop and optimize testing methodologies capable of characterizing both the individual properties of weld regions, and the overall influence of these regions on the corrosion resistance of the joint. A microcapillary polarization apparatus for
electrochemical characterization of friction stir welded joints will be developed and optimized for investigation of joints made in magnesium alloys.

2. To develop a fundamental understanding for the variation of corrosion behavior in the weld zone by evaluating the various corrosion mechanisms and governing reactions at the surface of the weld. To explore the relative contribution of variables, that are affected by the welding process, with respect to the overall corrosion behavior. It is proposed to isolate four separate microstructural features as explained below.

- **Residual stress** – As discussed in Section 4.3.3, FSSW process introduces tensile residual stress in the vicinity of the boundary between the thermo-mechanically affected zone and the stir zone. The presence of tensile residual stress can significantly reduce the corrosion resistance of magnesium alloys [109]. The influence of residual stress on the corrosion behavior of FSSW joints is unknown and may affect the respective corrosion potentials of the SZ and TMAZ regions. In the work herein, the influence of residual stress on the electrochemical characteristics of FSSW joints will be investigated using a combination of microcapillary polarization, stress relief heat-treatment and micro-hardness testing.

- **Grain size** – While differences in the electrochemical properties of various weld regions have been attributed to changes in grain size (see Section 5.1), a specific model describing the governing mechanism remains absent. The effect of grain refinement and/or growth on the corrosion resistance of various weld regions will be investigated via electrochemical characterization (microcapillary polarization) and grain size analysis.

- **Grain orientation** – The corrosion behaviour of magnesium alloys has been previously shown to be significantly affected by changes in grain orientation and texture [113]. Since the welding process creates a preferred grain orientation (see Section 4.3.2), it is possible that these changes will alter the corrosion behavior of the joint. The influence of grain orientation on the electrochemical properties of weld regions will be investigated through the use of microcapillary polarization in conjunction with electron backscattered diffraction (EBSD).

- **Second phase dissolution** – The dissolution, refinement and redistribution of second phase precipitates has been identified as a possible cause for variations in the electrochemical properties of various weld regions (see discussion in Section 5.1).
While some evidence has been given to support this proposition, a detailed model describing the relative contribution of this factor, and the interactions occurring at the surface of the weld, is still missing. The influence of second phase dissolution will be assessed by establishing a model that uses mixed potential theory to relate the electrochemical properties of a weld region to its microstructure. To produce this model, the electrochemical properties of each constituent phase will be characterized individually, while the microstructure of each weld region is analyzed using scanning electron microscopy (SEM) and nuclear magnetic resonance spectroscopy (NMR).

3. To determine if the mechanisms governing the corrosion behaviour of joints made between two identical alloys (similar welds) are applicable for joints made between two different magnesium alloys (dissimilar welds). The present work will examine the corrosion behaviour of a dissimilar AZ31/AZ80 friction stir welded joint through mass loss testing. A model describing the mechanism governing its degradation behavior will be developed based on SRET measurements, in-situ observations, and examination of the corrosion morphology.

4. To develop a corrosion protection strategy for similar and dissimilar FSW joints that is based on the corrosion mechanisms determined in objective 2 and 3. The feasibility of PEO coatings as a corrosion protection strategy will be evaluated by mass loss testing and corrosion morphology examination. To optimize the corrosion resistance properties of the coating, the effect of process parameters will be examined using a statistical analysis of the voltage-time response (produced during the oxidation process), complemented by microstructural characterization and mass loss testing measurements.
Chapter 6 Experimental Procedure

6.1 Materials

6.1.1 Alloy Used to Produce Similar Welds

The material used to produce similar AZ31 FSW and FSSW joints was a wrought magnesium AZ31B alloy in the H24 heat-treated condition. The alloy was supplied by M & B Mag Ltd. in the form of a 1.6 mm thick sheet (121.9 cm x 91.5 cm). Prior to welding, for both FSW and FSSW joints, the metal sheet was cut with a hydraulic shear into smaller more manageable pieces. FSW coupons were rectangular (5 cm x 15 cm), while the coupons used for FSSW joints were square (2.5 cm x 2.5 cm). Chemical composition of the alloy was analyzed using electro thermal vaporization – inductively coupled plasma optical emission spectrometry (ETV-ICP-OES) at the Beauchemin group at Queens University. The setup used in this investigation consisted of a lateral view ICP-OES instrument (Arcos from Spectro Analytical Instruments) that was coupled to an ETV system (ETV 4000C from Spectral Systems). Six specimens were measured and the mean composition, and the standard deviation were recorded. The composition of the alloy along with the corresponding ASTM standard are given in Table 6-1. Both Al and Zn concentrations in the alloy were found to exceed the concentration specified in the ASTM standard. This deviation from the standard could alter the microstructure of the alloy leading to a greater number of Mg$_{17}$Al$_{12}$ and Mg$_{17}$(Al,Zn)$_{12}$ intermetallics (as discussed in Section 2.2). The presence and morphology can impact the corrosion behaviour of the alloy, for more discussion refer to Sections 3.2.1.1-2.

6.1.2 Alloy Used to Produce Dissimilar Welds

The dissimilar FSW joints examined in this investigation were made from AZ31B and AZ80A. Both alloys were supplied by TH Magnesium Inc. in the form of a 5 mm thick plate that was 61 cm long and 15.25 cm wide. Prior to welding, each plate was cut lengthwise along its center axis. The chemical composition of the alloy was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES) at Element Materials Technology. A Perkin-Elmer Optima 3000 inductively coupled plasma-atomic emission spectrometer was used for all measurements. The composition of the alloys along with the corresponding ASTM standards are given in Table 6-2. Only one set of measurements for each alloy was performed and so standard deviations are not available. The composition of both alloys complied with the appropriate standards with the
exception of Si concentration in AZ80 (0.2 measured vs. 0.1 specified). This deviation is expected to have a negligible effect on the microstructure and corrosion behaviour of the alloy.
<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Other</th>
<th>Mg</th>
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</thead>
<tbody>
<tr>
<td>ASTM B90-15 Standard [200]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETV-ICP-OES</td>
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<td>0.18±0.02</td>
<td>1.65±0.09</td>
<td>0.027±0.003</td>
<td>&lt;0.001</td>
<td>0.0034±0.0004</td>
<td>0.0039±0.0001</td>
<td>0.39</td>
<td>Remainder</td>
</tr>
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Table 6-1 Composition of AZ31B used for similar FSW and FSSW joints

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<tr>
<th></th>
<th>Al</th>
<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Other</th>
<th>Mg</th>
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</thead>
<tbody>
<tr>
<td>AZ31B [wt. %]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM B90-15 Standard [200]</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>ICP-AES</td>
<td>2.67</td>
<td>0.32</td>
<td>0.77</td>
<td>&lt;0.005</td>
<td>0.004</td>
<td>&lt;0.002</td>
<td>0.01</td>
<td>&lt;0.02</td>
<td>Remainder</td>
</tr>
</tbody>
</table>

AZ80A [wt. %]

<table>
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<tr>
<th></th>
<th>Al</th>
<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Si</th>
<th>Other</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM B91-17 Standard [201]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICP-AES</td>
<td>8.77</td>
<td>0.19</td>
<td>0.44</td>
<td>&lt;0.005</td>
<td>&lt;0.003</td>
<td>&lt;0.002</td>
<td>0.02</td>
<td>&lt;0.02</td>
<td>Remainder</td>
</tr>
</tbody>
</table>

Table 6-2 Composition of AZ31 and AZ80 used for dissimilar FSW joints
6.1.3 Preparation of AZ31 Phase Constituents

6.1.3.1 $\beta$-Mg$_{17}$Al$_{12}$ Specimens

Bulk $\beta$-Mg$_{17}$Al$_{12}$ ingots were prepared following a methodology that is described elsewhere (10). The work was carried out by Professor Stephan Mathieu at the University of Lorraine. The specimens were synthesized by inductively melting high purity Mg (99.95%, Alfa Aesar 43297) and Al (99.95%, Alfa Aesar 42826). To prevent oxidation, the melting process was carried out in an argon atmosphere that was purified using a getter. Once complete mixing was achieved an ingot was cast. The ingot then was melted and recast to ensure full homogenization. The sample was confirmed to contain only a single phase by XRD analysis shown in Figure 6-1. The present investigation used a Rigaku® MiniFlex 600 X-ray diffractometer (XRD) using Cu K$_{\alpha}$ radiation ($\lambda = 1.5418$ Å). The scans were performed over the diffraction angle ($2\theta$) range from 10° to 90° in 0.02° steps with a 1 sec step duration. The composition of the sample was also examined by ICP-AES (Optima 7300 DV ICP AES) at the Analest facility at the University of Toronto. The sample comprised 43.9 at.% Al and 56.1 at.% Mg, in agreement with the composition predicted from the Al-Mg phase diagram (Figure 2-2 (a)).

![XRD analysis of a single phase Mg$_{17}$Al$_{12}$ sample. For reference a standard from the inorganic chemistry structure database (ICSD) is included as well (card number 01-076-2702).](image-url)
6.1.3.2 Preparation of $\gamma$-Al$_8$Mn$_5$ Specimens

A bulk $\gamma$-Al$_8$Mn$_5$ specimen was prepared from high purity Al (99.9999%, Alfa Aesar 44326) and Mn (99.98%, Alfa Aesar 36215) metal slugs using an Edmund Bühler GmbH vacuum arc melter, using the following procedure:

1. 0.441 g of Al slugs and 0.508 g of Mn flakes were weighted using a Mettler Toledo XS204 scale.
2. Each material was kept in a separate scintillation vial until melting commenced.
3. The arc melter was turned on and the base plate was unscrewed.
4. To remove the oxide build-up from previous users, the base plate was lightly abraded with a “1200 fine” grit SiC paper. Rinsed with isopropanol (ACS Reagent, Caledon 8600-1-40) and dried under a gentle stream of air.
5. Raw materials were loaded into the crucible well, first the Al slugs and then the Mn flakes. Once done, the base plate was returned to its original position, and secured in place with a screw.
6. Before melting, the melting chamber was evacuated down to approximately 0.1 mbar using a roughing pump and then back filled to atmospheric pressure using high purity argon (99.9999%, Linde). Step 6 was repeated 5 times to remove as much oxygen from the melting chamber as possible.
7. After multiple vacuum Ar filling cycles, the melting chamber was filled with high purity argon again to produce a pressure of 1 bar prior to melting.
8. The electrode power was turned on, and the current level knob was set to 6.
9. A plasma arc between the electrode and the base plate was created by touching the electrode to the ignition pin.
10. Once the plasma arc was ignited the current level was reduced to a level of 3.5, and the arc was moved over the crucible well that contained the raw materials. The arc was circled over the raw material for 25 sec to mix the material and homogenize the
composition.

11. At the end of each melting cycle, the electrode power was switched off and the ingot in the crucible was flipped using the electrode.

12. Each ingot was melted three times (2 flips) by repeating steps 8 to 10.

13. Once the three melting cycles were complete, the power was shut off, the chamber was opened and the \(\gamma\)-Al\(_8\)Mn\(_5\) ingot was kept in a sample holder that was placed in a desiccator.

The composition of the Al\(_8\)Mn\(_5\) was confirmed through XRD using the same operational parameters that are described in Section 6.1.3.1. The XRD spectra along with the relevant standards is presented in Figure 6-2. The spectra showed close agreement between the standard measured and the standard spectra for Al\(_8\)Mn\(_5\). Only one peak did not fit the Al\(_8\)Mn\(_5\) phase, and it was attributed to the \(\kappa\)-Al\(_2\)O\(_3\) phase that was likely created due to aluminum oxidation during the synthesis process.

Energy dispersive x-ray spectroscopy (Hitachi SU3500) was used to confirm the elemental composition of the sample. The sample comprised 64.0 at.% Al and 36.0 at.% Mn, in agreement with the composition predicted from the Al-Mn phase diagram (Figure 2-5 (a)).

![Figure 6-2 XRD analysis of a single phase Al\(_8\)Mn\(_5\) sample. For reference standards from the inorganic chemistry structure database (ICSD) are included as well (Al\(_8\)Mn\(_5\): card number 00-032-0021 | \(\kappa\)-Al\(_2\)O\(_3\): card number 00-052-0803).](image-url)
6.2 Friction Stir Welding

6.2.1 Spot Welds

All spot welds examined in this investigation were made using a Friction Stir Link linear displacement benchtop StirSpot™ welding unit shown in Figure 6-3. The unit comprised two servomotors that powered the motion of the welding tool. A rotary servomotor capable of producing 28 Nm allowed the tool to rotate at rotational speeds up to 3000 rev min⁻¹. A linear servomotor capable of producing 12 kN of normal axial force was used to plunge the rotating tool into the overlapping sheet assembly.

![Figure 6-3 Friction Stir Link benchtop welding unit. Modified from [202]](image)

All joints were welded using a “flat shoulder” tool. The tool comprised a flat shoulder (10 mm diameter), and a 2.2 mm long pin that had an M4 metric thread. The tool was machined at the mechanical engineering machine shop at the University of Toronto. The tool was made from H13
tool steel that was heat treated to achieve hardness values ranging from 46 to 48 on a Rockwell C scale. The following heat treatment cycle was used:

1. The steel was preheated to 850 °C using a heating rate of 220 °C/hr.
2. The temperature was then rapidly increased to austenize the steel at 1025 °C for 30 minutes.
3. The austenized steel was air cooled to 60 °C before tempering.
4. Two 2-hour tempering stages with intermediate cooling to room temperature were carried out at 585 °C.
5. Following tempering, the tool was cooled to room temperature and its hardness was verified using a hardness indenter.

Once manufactured, the tool was coated with a protective ZrN coating using physical vapour deposition (PVD). The coating was branded as Alpha™ and was deposited by Surface Solutions Inc. The coating had a thickness of 2-5 µm. A schematic of the tool along with an optical image are shown in Figure 6-4.

![Figure 6-4 FSSW welding tool: (a) schematic view, and (b) optical image.](image)

A modified sample holder was designed during the project to reduce the relative motion of the overlapping metal sheets during the welding operation (see drawing in Appendix B1). The new sample holder provided greater grip than the one supplied by the original manufacturer. In the new
setup, an overlapping sheet assembly was clamped between two carbon steel plates as shown in the schematic in Figure 6-5 (a). For clarity an optical image is included as well (Figure 6-5 (b)).

![Schematic and optical image of modified sample holder.](image)

**Figure 6-5 Modified sample holder: (a) schematic view, and (b) optical image.**

Following the modification of the sample holder, the distance \(d_{\text{travel}}\) between the starting position of the welding tool and the top surface of the metal sheet assembly had to be measured. To determine this distance, two AZ31B metal sheets (as described in Section 6.1.1) were placed into the sample holder and the welding tool was lowered using the continuous movement function. When the distance between the tip of the tool and the top surface of the metal sheet assembly was less than 5 cm, the motion of the tool was halted, and the distance traveled by the tool \(d_1\) was recorded. The remaining distance between the tip of the tool and the top surface of the metal sheet assembly \(d_2\) was then measured with callipers. The two distances were added together \((d_1 + d_2)\) to determine \(d_{\text{travel}}\). The pounce position \(d_{\text{pounce}}\) (the position at which the welding operation begins), was determined by subtracting 3 mm from \(d_{\text{travel}}\). The pounce position was recorded in the software operating the welding machine, this comprised the calibration.

The welding apparatus described above was used to produce spot welds in the following manner:

1. Unless otherwise specified, prior to welding both sides of the AZ31B coupons were abraded with a 600-grit silicon carbide (SiC) paper (LECO 810-229-PRM) on a Buehler MetaServ\textsuperscript® 250 grinder. The grinding was carried out to remove the Rust-Ban 392 (Esso Imperial Oil\textsuperscript®) coating that was present on the as-received material.
2. Before placing the samples into the sample holder, the emergency stop button was activated to ensure the safety of the operator during set up.

3. Ground coupons were placed into the sample holder in an overlapping sheet configuration. The bolts holding the two steel plates of the sample holder were tightened with a torque wrench set to 15.8 Nm.

4. Once the samples were secured in the sample holder, the emergency stop button was deactivated to allow operation of the welding machine.

5. The speed of the tool as it moves from its starting position towards the pounce position was controlled by setting a pounce speed = 25 mm/s.

6. The tool was set to move at a plunging rate of 2.5 mm/s starting from the pounce position and until the shoulder of the welding tool penetrated the upper sheet by 0.2 mm.

7. The plunge depth consisted of the 3 mm that separated \( d_{\text{pounce}} \) from \( d_{\text{travel}} \), the length of the pin (2.2 mm), and the shoulder penetration depth (0.2 mm). The plunge depth in this investigation was set to be 5.4 mm.

8. The rotational speed of the tool and the welding time were varied to examine the effect of these parameters on the microstructural evolution occurring during the welding operation and its subsequent effect on the corrosion resistance of the weld.

9. Once the welding operation was complete, the tool is retracted at a specified speed. In this investigation the retraction speed was set at 35 mm/s. A summary of the welding parameters is given in Table 6-3.

10. The welding parameters were entered into the “welding schedule” section using the touch pad on the control panel of the machine. Both linear and rotational parameters were loaded into the system by pressing the “linear download” and “rotary download” buttons.

11. Once the parameters were loaded, welding was initiated by pressing the “initiate run” button. Samples were left clamped for 3 min after the completion of each weld to allow complete heat dissipation into the clamp.
12. The emergency red button was then pressed and the welded sample was removed from the sample holder. After each welding operation, the penetration depth of the tool was measured with calipers. Samples with a shoulder penetration depth that differed from 0.20 by ± 0.05 mm were not used in the study. A sample FSSW joint made using a rotational speed of 3000 rev min\(^{-1}\) and dwell time of 1 sec is shown in Figure 6-6.

13. After each welding operation the welding tool was cleaned with a 30% HCl (36.5%, Caledon 6025-1) solution. The tool was kept in the solution until all of the magnesium that adhered to the tool was dissolved. The tool was then removed from the solution, rinsed with Type I Milli-Q\textsuperscript{®} water and dried under a gentle stream of compressed air.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance from the origin until the surface of the metal ((d_{travel}))</td>
<td>98.7 mm</td>
</tr>
<tr>
<td>Pounce position ((d_{pounce}))</td>
<td>95.7 mm</td>
</tr>
<tr>
<td>Pounce speed</td>
<td>25 mm/sec</td>
</tr>
<tr>
<td>Plunge rate</td>
<td>2.5 mm/sec</td>
</tr>
<tr>
<td>Plunge depth</td>
<td>5.4 mm</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>1000-3000 rev min(^{-1})</td>
</tr>
<tr>
<td>Dwell time</td>
<td>1000-4000 msec</td>
</tr>
<tr>
<td>Retract speed</td>
<td>35 mm/s</td>
</tr>
</tbody>
</table>

**Table 6-3 Summary of FSSW welding parameters used in this investigation**
6.2.2 Seam Welds

6.2.2.1 Similar Welds

Seam lap welds were produced on AZ31B magnesium alloy at the University of Waterloo. A refurbished milling machine was used to join the overlapping metal sheets. The joints were produced using various transverse velocities ranging from 45 to 355 mm/min; the rotational speed was kept constant at 1400 rev min$^{-1}$. The same welding tool as the one used for spot welds was used for seam welding. Welding was carried out without a tilt of the welding tool. A sample FSW lap joint welded using a traverse speed of 355 mm/min and a tool rotational speed of 1400 rev min$^{-1}$ is shown in Figure 6-7.

Figure 6-6 FSSW joint made using a rotational speed of 3000 rev min$^{-1}$ and dwell time of 1 sec.

Figure 6-7 Similar FSW lap joint made using a traverse speed of 355 mm/min and a tool rotational speed of 1400 rev min$^{-1}$. 
6.2.2.2 Dissimilar Welds

Friction stir welding of dissimilar alloys AZ31 and AZ80 was conducted using a butt welding configuration with a refurbished milling machine at the University of Waterloo. The AZ80 was placed on the advancing side and AZ31 on the retreating side of the joint. The tool was rotated in the counter clockwise direction at 900 rev min⁻¹ and joints were made using a transverse speed of 90 mm/min. During all welding operations, the tool was positioned at a 2.5° tilt angle. The tool employed during FSW had a flat shoulder with standard M6 metric thread. The pin was modified into a three-flat geometry, which has three 0.5 mm deep flat spots positioned every 120° around the pin. The tool had a shoulder diameter of 15 mm and was made from H13 die steel, heat treated to 46–48 hardness on a Rockwell C scale. A sample dissimilar joint is shown in Figure 6-8.

![Figure 6-8 Dissimilar AZ31/AZ80 FSW butt joint made using a traverse speed of 90 mm/min and a tool rotational speed of 900 rev min⁻¹.](image)

6.2.3 Welding Flash Evolution Study

To better understand the microstructure present within the welding flash and its subsequent effect on the corrosion performance of the weld, a study examining the material flow process involved in flash generation was conducted. The welding process was considered as a combination of two main stages: plunging and dwelling. During the plunging period, a rotating tool is penetrated at a constant vertical velocity into the base metal until a specified plunge depth is reached. During the dwell period, the vertical position of the tool is
maintained, while rotating at a constant speed. The material flow during each welding stage was investigated by examining partially completed welds taken from different points of the welding process. This investigation produced a flash evolution sequence that described the generation of welding flash from its first appearance to the final shape on a complete joint.

To evaluate the changes in the flash shape during the plunging portion of the process, samples were prepared at 3000 rev min\(^{-1}\) with plunge depth varying from 5.00 mm to 5.40 mm. The welding process was stopped abruptly, without dwelling, once the desired plunge was achieved. The second set of samples was prepared by plunging to a constant depth of 5.40 mm. For this set, the dwell time was varied between 0.2 and 4 sec. In order to allow complete heat dissipation into the clamp, all samples were left clamped for three minutes following the process. Once welded, shoulder penetration into the base metal was measured by subtracting the thickness of the base metal from the thickness measured on the complete joints underneath the shoulder.

### 6.2.4 Tungsten Carbide Tracing Test

To confirm the location and boundaries of the stir zone in the welded specimens, a tracer material was used. A suitable tracer material should not react with the base metal, should not alter the material flow, and should be easily examinable by common imaging methods. In his work, Horie found tungsten carbide (WC) as a suitable tracer material for imaging material flow in FSSW joints made in AZ alloys [167]. In this investigation, WC (99%, Sigma-Aldrich 241881) tracer was introduced into the base metal by packing WC powder (average particle size < 2 μm) into 1 mm deep drilled holes (1 mm diameter) as seen in Figure 6-9. The powder was introduced in four symmetrical spots located on the circumference of a circle having a diameter of 80% of the diameter of the rotating tool shoulder. The holes were placed in the upper sheet of the base metal. To identify the precise location of these holes the welding tool was lowered onto the clamped base metal sheets to produce a small indent that represented the tool strike location. A circle having a 4 mm radius centered on
the strike location was drawn on the sample denoting the radial location for the drilled holes. WC distribution was detected using the backscatter electron (BSE) mode of scanning electron microscopy through the atomic number contrast. The bright region in the observed planar macrostructures shows the presence of WC.

Figure 6-9 Location and alignment of WC powder tracer material to investigate material flow during FSSW welding. All dimensions in the figure are given in mm.

6.2.5 Force and Temperature Output During Friction Stir Spot Welding

The force and temperature output during friction stir spot welding of AZ31B has been previously measured. The measurements were conducted by Dr. Adrian P. Gerlich and Yuhuan Yin at the University of Toronto in 2010 [160]. The same welding machine as that described in Section 6.2.1 was used for these measurements. In this case, the experimental setup was modified to measure the force output during welding. The axial load and torque were measured using a JR3 six-axis load cell, which was coupled to a data acquisition system.

The thermal cycle in the SZ region during the welding operation was also previously measured by Gerlich by embedding a 0.25 mm diameter K-type thermocouple in the welding tool. The thermocouple was located 1.3 mm away from the tool shoulder. The thermocouple was in direct contact with the dynamically recrystallized material formed during the spot welding operation. Complete discussion of this experimental setup can be found in Dr. Gerlich’s PhD thesis [160].
6.3 Characterization Methods

6.3.1 Sample Preparation

To characterize the microstructure and/or electrochemical properties of welded specimens, they were sectioned, embedded in epoxy, and ground to a final surface finish of \( \frac{1}{4} \mu \text{m} \) as outlined below.

6.3.1.1 Sectioning

For FSSW joints, samples were cut along the centerline of the weld. For FSW joints, samples were cut perpendicular to the weldment at a distance of at least 5 cm away from the beginning of the weld to ensure the microstructure of the weld was representative of steady state welding. In both cases a Struers Accutom-2 diamond saw was used. To prevent microstructural changes in the weld zone, the blade was water-cooled, and cutting was done in a slow manner using a rotational speed of 180 rev min\(^{-1}\) and 1.25 bar of loading pressure. An example of a sectioned FSSW joint is shown in Figure 6-10.

![Figure 6-10 Sectioned FSSW joint.](image)

6.3.1.2 Mounting in Epoxy

Sectioned specimens were embedded in a 2-part Buehler EpoxyCure™ 2 epoxy, such that the sectioned surface remained exposed. Prior to mounting in epoxy, sectioned specimens were degreased with acetone (ACS Reagent, Caledon 1200-1-40), and dried under a gentle stream of compressed air. A specimen was placed in a 1 inch in diameter mold that was greased by applying
a thin layer of high vacuum grease (DOW Corning) to the inner surface of the mold. In a hexagonal tray, 16 grams of EpoxyCure™ 2 Resin (Buehler 20-3430) were mixed with 4 grams of EpoxyCure™ 2 Hardener (Buehler 20-3432). The epoxy was mixed for two minutes using a 3 ml syringe (BD 309657). Once mixed the epoxy was poured into the mold and left to cure for 12 hours. At the end of the curing period, the samples were sonicated in isopropanol (ACS Reagent, Caledon 8600-1-40) to remove the high vacuum grease from the epoxy. Examples of a FSSW, and FSW joints mounted in epoxy are shown in Figure 6-11 (a) and (b) respectively.

Figure 6-11 (a) FSSW, and (b) FSW joints mounted in epoxy.

6.3.1.3 Grinding and Polishing

Once cured, the samples were ground on a series of progressively finer SiC papers to produce a final surface finish of “1200 fine” as outlined below. Unless indicated otherwise, every grinding step described in the present investigation was carried out on Buehler MetaServ® 250 Grinder-Polisher machine, using a rotational speed of 300 rev min⁻¹. Specimens embedded in epoxy were progressively ground on the following SiC papers:

- 320 grit (LECO 810-225-PRM),
- 400 grit (LECO 810-227-PRM),
- 600 grit (LECO 810-229-PRM),
- 1200 grit (LECO 810-034-100), and
- “1200 fine” grit (LECO 810-036-500).
Ground samples were polished to a final surface finish of ¼ µm using diamond paste. The polishing was carried out on a Buehler MetaServ® Grinder-Polisher machine using the sequence of progressive steps outlined in Table 6-4. In each polishing step a water free diamond extender was used (Al-Blue Lube, LECO, 810-946-020-HAZ). At the end of each polishing step the specimen was rinsed with isopropanol (ACS Reagent, Caledon 8600-1-40), and dried with compressed air. The sample was then examined under a stereoscopic microscope (Tasco K1030), using a magnification of 3x, to ensure even polishing before proceeding to polish with a finer diamond paste. Once a final surface finish of ¼ µm was obtained the sample was sonicated in isopropanol to remove any remaining diamond paste from the surface and then dried with compressed air. If a sample was not used immediately after polishing, it was stored in a desiccator.

<table>
<thead>
<tr>
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</thead>
<tbody>
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<td>810-915</td>
<td>Imperial Blue</td>
<td>LECO</td>
<td>810-545-010</td>
</tr>
<tr>
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<td>Micro</td>
<td>MM 197</td>
<td>Imperial Blue</td>
<td>LECO</td>
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<tr>
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<tr>
<td>3 µm</td>
<td>LECO</td>
<td>810-872</td>
<td>Imperial Blue</td>
<td>LECO</td>
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</tr>
<tr>
<td>1 µm</td>
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<td>810-870</td>
<td>Cameo Grey</td>
<td>LECO</td>
<td>812-352</td>
</tr>
<tr>
<td>¼ µm</td>
<td>Micro</td>
<td>MM 182</td>
<td>Imperial Blue</td>
<td>LECO</td>
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<td></td>
<td>Metallurgical Ltd.</td>
<td></td>
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</tbody>
</table>

Table 6-4 Sequence of polishing steps used to polish magnesium alloys.
6.3.2 Etching and Grain Size Measurements

6.3.2.1 Etching

For AZ31, an etchant comprising 1 ml nitric acid (68%, Caledon 7525-1), 1 ml acetic acid (99.7%, ACP Chemicals Inc. A-0300), 1 g oxalic acid (98%, Bio Basic Canada Inc. OD0400), and 150 ml of Type I Milli-Q® water was used.

To reveal the microstructure of samples made of AZ80, polished samples (see Section 6.3.1.3) were etched with an acetic glycol etchant for 4 sec. The etchant comprised 20 ml acetic acid (99.7%, ACP Chemicals Inc. A-0300), 1 ml concentrated nitric acid (68%, Caledon 7525-1), 60 ml ethylene glycol (Certified grade, Fisher Scientific E178-1) and 20 ml of water.

Polished samples (see Section 6.3.1.3) were immersed facing up into the etchant solution that was gently agitated for a duration ranging between 20 and 40 sec at room temperature. Once the sample was etched, it was washed thoroughly with water followed by ethanol (95%, Commercial Alcohols Inc. P016EA95) and dried immediately. The microstructure revealed by the etchant was imaged using a metallographic inverted microscope (Jenaphot 2000).

6.3.2.2 Grain Size Measurements

Grain size was determined from the micrographs of the etched samples using the line intercept method, adapted from ASTM E112-13 standard in which ten lines, 230 mm long, were examined [204]. An example of a micrograph used to measure the grain size in the SZ region of a FSSW joint made in AZ31B using 3000 rev min⁻¹ and a dwell time of 1 sec is shown in Figure 6-12.
6.3.3 Microhardness Profiling

Vicker’s microhardness traverse tests across sample cross-sections indicated the microstructural changes produced during joining and subsequent heat-treatment processes. To produce a specimen for microhardness testing, completed joints were first sectioned (as per Section 6.3.1.1) and then ground and polished (as per Section 6.3.1.3). Microhardness testing was performed using a Buehler MicroMet 5100 series machine using an applied test load of 50 gf and a dwell time of 15 sec. Each microhardness profile comprised 35 individual measurements and all indentations were spaced apart sufficiently to avoid the effect of strain fields produced by adjacent indentations.

6.3.4 Electron backscatter diffraction

Electron backscatter diffraction was used to evaluate the effect of FSSW on the grain orientation of AZ31B. Samples polished to a final surface finish of 1 µm (prepared using the protocol in Section 6.3.1) were further polished using colloidal silica in a propylene glycol media. The final polishing step and all EBSD measurements were carried out by Chris Butcher at the Canadian Centre for Electron Microscopy (CCEM) at McMaster University. The grain orientation of the SZ and BM regions were examined on both the rolling and cross-sectional surfaces as shown schematically in

Figure 6-12 Micrograph depicting the SZ microstructure of a FSSW joint made in AZ31B using 3000 rev min\(^{-1}\) and 1 sec of dwell. The white bar represents 50 µm.
Figure 6-13. The data collection was carried out on a JEOL JSM-7000F SEM using an accelerating voltage of 20kV, a high current probe (10-11 nA), and a sample tilt of 70°.

![Figure 6-13 Cross-sectional schematic of a FSSW joint indicating the locations examined in this investigation.](image)

6.3.5 Second Phase Particle Distribution Measurements

The electrochemical properties of the stir zone region were correlated with the presence and/or dissolution of second phase precipitates. The composition, size, and distribution of second phase particles present in a stir zone produced in joints made using different welding conditions were analyzed using high resolution microscopy coupled with elemental analysis.

6.3.5.1 Electron Microscopy

Following the sample preparation steps described in Section 6.3.1, samples used for microstructural examination in SEM were ion milled in two stages using a Hitachi IM4000 ion mill. The first step of ion milling was adapted from literature; milling was carried at a sample tilt of 80° with no eccentricity with the sample rotated at a rotation speed of 25 rev/min for 30 minutes [205]. An accelerating voltage of 3 kV and a discharge voltage of 1.5 kV were used. In this step any surface
scratches resulting from mechanical polishing were removed by the milling action. The second step of ion milling was done to produce a relief etch on the surface of the sample to improve the visibility of the various phases present. The second step of ion milling was carried at a sample tilt of 60° with eccentricity of 4 mm, the sample was rotated at a rotation speed of 25 rev/min for 10 minutes.

Images were captured using a Hitachi SU8230 UHR-SEM with an accelerating voltage of 5 kV to reduce interaction with the sample. Elemental analysis was performed using an energy dispersive x-ray spectroscopy (EDX) detector. Each weld region was investigated using four magnifications (300X, 1,000X, 10,000X, and 50,000X), and unless otherwise stated at least eight micrographs were examined in each region and magnification. The micrographs were analyzed using image processing software to measure the size and area fractions of second phase particles in the micrograph. The data acquired from all magnifications was normalized to a surface area of 1 mm², and the area fractions associated with second phase particles were determined.

6.3.5.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

In order to complement the findings obtained from analytical microscopy, the volume fraction of β-Mg₁₇Al₁₂ in the stir zone was assessed using nuclear magnetic resonance (NMR) spectroscopy following a protocol previously reported by Celotto and Bastow [206]. NMR measurements examine the surface of a fine powder and thus examine a much greater area than that possible in a high-resolution SEM investigation. Stir zone specimens were extracted from completed weldments using a series of sectioning and grinding steps as detailed in Figure 6-14. Specimens in the as-welded condition were sectioned with a diamond saw to remove the base metal and the HAZ, yielding a 12 mm x 12 mm coupon that contained the SZ region (Figure 6-14 (a)). The top and bottom surfaces of the sectioned specimens were then ground on a 240 grit SiC paper (LECO 810-223-PRM) using a MetaServ® 250 Grinder-Polisher machine to produce an overall thickness of 1.4 mm as shown in Figure 6-14 (b). To remove the TMAZ material from specimen, samples were ground by hand (240 grit SiC paper), while continuously cooled with a gentle stream of cold water (Figure 6-14 (c)). The
Chapter 6: Experimental Procedure

The final specimen had a ring shape that had an inner diameter of 3 mm and an outer diameter of 6 mm. The specimen was considered to contain only SZ material.

![Diagram](Image)

**Figure 6-14 SZ extraction for NMR measurements.** (a) Diamond saw sectioning, (b) machine grinding to reduce thickness, (c) hand grinding to remove the TMAZ region.

Extracted SZ specimens were then ground by hand using 240 grit SiC paper that was submerged in 1 L of Type I Milli-Q® water in a 2.6 L rectangular Pyrex® dish. Caution was given to the cleanliness of the experiment to minimize contamination. The dish was properly cleaned beforehand, and nitrile gloves (Microflex Supreno® SE SU-690-L) were worn during the hand grinding stage. The water was filtered using gravity fed filtration. A funnel and a P8 grade filter paper (Fisherbrand™ 09-795F) were used to separate the powder from the water, P8 grade filter paper can be used to remove 20 µm and larger particles. Following the filtration process the filter paper was placed in a desiccator to dry overnight. Once dry, the powder was scraped off the paper with a polyethylene spatula and stored in a 2 ml micro tube (Sarstedt 72.694.006) until future use. Each specimen yielded approximately 200 mg of powder. SiC does not produce an NMR signal that interferes with the aluminum signal measured using this technique, so any trace SiC powder introduced during the grinding process is inert and does not interfere with the measurement. NMR spectra for $^{27}$Al were
obtained using an Agilent DD2-600 with a magnetic field of 9.4T which operated at 104.2 MHz. The spectra were acquired by the application of a phase-cycled single pulse followed by data acquisition. The operating frequency was selected to be at the halfway point between the matrix and precipitate peak positions. To ensure complete excitation of the $^{27}$Al nuclei in both the matrix and precipitate, a pulse length of 2 μs was selected. The $^{27}$Al shifts were referenced to $^{27}$Al in an aqueous solution of Al(H$_2$O)$_3^+$ as the zero shift point.

### 6.3.6 White Light Profilometry

The average surface roughness ($R_a$) of the top surfaces of PEO coated samples were analyzed using white light profilometry (Zygo white light profilometer). Profilometry relies on white light scattering to study surface contours and roughness. This technique falls within the coherence scanning interferometry class of measurements, and it probes the surface through interference fringes. Through fringe localization and subsequent analysis of the data, information regarding the topography of the sample can be obtained. In the current investigation MetroPro® software was used to record and analyze the topographical characteristics of PEO-coated samples.

Coated samples were placed onto the specimen holder that was raised with an air pump to avoid vibrations during the measurement. The sample holder was then tilted until fringes could be observed on the monitor. Before the measurement, the brightness on the monitor was adjusted to ~97%. Once the measurement was complete a two-dimensional contour plot depicting the topography of the sample was obtained, and $R_a$ was given in the software dialog. Five separate areas of 3 mm × 4 mm were analyzed for each processing condition.
6.4 Corrosion Measurements

Corrosion evaluation of friction stir welded specimens was carried out in Cl⁻ or ClO₄⁻ containing environments. Unless otherwise specified, the experiments detailed in this work were conducted in fully aerated solutions. It is also worth noting that carbonates may be present in the solution, as they have not been purposely removed by scrubbing any CO₂ that could originate from exposure to air.

6.4.1 Mass Loss Testing

6.4.1.1 Background

Mass loss testing is a common industrial method for evaluation of corrosion resistance as described in the ASTM G31 standard [207]. In this technique, specimens are exposed to a corrosive medium and the corrosion rate is determined from the weight of the material that dissolved during a fixed time exposure. The mass lost is determined by finding the difference between the weight of the specimen before testing and the weight of the specimen following the exposure to the corrosive media and removal of corrosion products. In the case of magnesium alloys, corrosion products are removed with a chromic acid solution as described in the ASTM G1 standard [208]. The corrosion rate is then determined by normalizing the change in mass to the exposed surface area of the specimen and the time of the exposure.

*Bland et al.* analyzed and compared the corrosion rates acquired through mass loss testing for commercially pure magnesium and AZ31B magnesium alloy [209]. The study concluded that corrosion rates from mass loss measurements can be just as indicative of the true corrosion rate as those derived through the use of common electrochemical techniques. The use of corrosion rates measured by mass loss testing for industrial design remains a challenge due to large scattering of the reported values. For example, the reported corrosion rates obtained through mass loss testing for AZ31 in 0.6M NaCl can range between 2.57 and 209.50 mm · year⁻¹ [106, 210]. The wide range of corrosion rates measured through mass loss testing is a result of the high sensitivity of the corrosion
resistance of magnesium to slight variations in composition and microstructure. Another factor contributing to the variability of the apparent corrosion rate is the sensitivity of the experimental technique to specific set up details as discussed below.

The data on corrosion rates between various published articles should be compared with caution, as slight differences in the experimental procedures used to evaluate the corrosion rate can be overlooked. Often the exact details of the experimental procedure are vague or incomplete, leaving gaps in the information provided by the manuscript. Currently there is no specification for the immersion time that is required to properly evaluate the corrosion rate of a magnesium test coupon. As a result, corrosion rates are measured for a variety of exposure times ranging between several hours and a few weeks [176, 211]. Pardo et al. has shown that the estimated corrosion rate for magnesium alloy depends on the time used to expose the coupons to corrosive media [210]. The corrosion rate exhibited by a specimen stabilizes with increasing exposure time, and thus long exposure times are recommended for accurate determination of the corrosion rates. The downside of this approach is the long experiment time that is associated with the method. Therefore, a meaningful comparisons of corrosion rates from experiments should be done only for similar exposure times.

Another potential reason for the variation in observed corrosion rates was suggested by Kirkland et al. who claimed that the ratio between the volume of electrolyte and the exposed surface area of the samples can affect the measurement [212]. If insufficient volume of electrolyte is used in the experiment, the pH and ionic chemistry of the environment would change during the exposure period as a result of the corrosion reaction. A higher pH of the solution would stabilize the quasi-passive behaviour of magnesium and result in a reduction in the corrosion rate. A critical ratio of 50 mL/cm$^2$ was identified as a suitable specimen surface area to electrolyte volume ratio for testing of magnesium alloys [212].
## 6.4.1.2 Protocol for Mass Loss Testing of FSSW Joints

Multiple samples were fabricated for each weld examined in the investigation and then sectioned into 4 quarters approximately 8 mm × 8 mm in size using the parameters detailed in Section 6.3.1.1. Two pieces of each weld were reserved for metallographic examination of the weld structure and the remaining two pieces were used in immersion testing. For comparison, bulk base metal samples of AZ31 in the same format were also prepared. All samples were progressively ground with 600, 1200 and “1200 fine” grit SiC grinding paper (as outlined in Section 6.3.1.3). After being cleaned with isopropanol (ACS Reagent, Caledon 8600-1-40) and Type I Milli-Q® water and dried by warm air, specific areas of each sample were masked using AMERCOAT® 90HS epoxy.

Figure 6-15 (a) and (b) show schematically the plane and cross sections of a prepared sample and Figure 6-15 (c) and (d) show the corresponding optical images. Samples areas were measured by capturing digital images optically then analyzing them using “Image J” software. Prior to immersion testing, each sample was weighed three times and the mean recorded.

![Diagram](image)

**Figure 6-15 Schematic of (a) plan view and (b) cross section of a FSSW weld along with the corresponding optical images (c) plan, (d) cross section.**

A—bottom of pin hole surface, B—edge of key hole, C—shoulder penetration surface, D—outer edge of shoulder, E—inner edge of shoulder, F—upper sheet surface, G—hook, and H—mating surface of two sheets.
The relative corrosion performance of welded specimens from the base metal was evaluated through immersion testing adapted from ASTM G31-12a [207]. Immersion testing of the samples in NaCl electrolyte provides an accelerated method to evaluate the corrosion resistance of the welds in a manner that is similar to their service environment. If FSSW welding was to be applied in the automotive industry, the welds may be exposed to highly concentrated NaCl environment resulting from deicing salts used on roadways. Twenty individual test cells were fabricated from polymethyl methacrylate and placed within a 2.6 L rectangular Pyrex® tray containing approximately 1.8 L of 0.086M NaCl (ACS Reagent, BioShop® SOD002.205) solution (pH= 5.5, κ=8.3 mS/cm) held at 25 °C using an external water bath (Polytherm type PY4(L) water bath by Science/Electronics. The surface of the Pyrex® tray was sealed with Parafilm® to minimize evaporation although hydrogen generated from the corrosion process could be discharged. The specimens were exposed to the corrosive environment for 120 hours. At least four samples of each welding condition along with control base metal samples were tested. A ratio of at least 90 mL/cm² was maintained in the present investigation, which is much higher than the critical ratio of 50 mL/cm² that was identified by Kirkland et al. [212]. To accommodate a large number of samples additional rectangular Pyrex® trays were used when needed.

To remove the residual corrosion product attached to the sample surface, a chromic acid solution was used which was comprised of 100 g/l CrO₃ (99.9%, Sigma-Aldrich 232653), and 5 g/l AgNO₃ (99.9999%, Sigma-Aldrich 204390) in Type I Milli-Q® water. The composition of the cleaning solution was based on a solution described in ASTM G1-03 [208]. In order to ensure the efficacy of the cleaning process, both a base metal and a corroded FSSW sample were immersed in the dichromic acid solution for 3, 6 and 9 minutes, rinsed in Type I Milli-Q® water, air dried, and the change in mass with time recorded as shown in Table 6-5. The cleaning solution could completely remove the base metal surface oxide within 3 minutes of immersion and no further attack (weight loss) was observed with time. This solution was equally effective on FSSW welds and all subsequent tests adopted the 3 minutes immersion procedure with the solution to clean samples.
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### Table 6-5 Cleaning test results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area (mm²)</th>
<th>Original Mass (mg)</th>
<th>Immersion Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corroded base metal</td>
<td>133.92</td>
<td>377.2</td>
<td>376.7</td>
</tr>
<tr>
<td>Corroded weld</td>
<td>153.25</td>
<td>471.1</td>
<td>465.4</td>
</tr>
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</table>

The corrosion rate ($CR_{AW}$) was calculated as the change in mass divided by the total area of the sample ($A_{Total}$) and the exposure time ($t_{ML}$) see equation (6.1).

$$CR_{AW} = \frac{(m_i - m_f)}{A_{Total} \times t_{ML}}$$  (6.1)

### 6.4.1.3 Protocol for Mass Loss Testing of Dissimilar FSW Joints

Dissimilar FSW specimens were larger than the FSSW corrosion samples described in Section 6.4.1.2, that necessitated immersion tests to be carried out in larger glassware having a larger volume. Similarly to FSSW coupons, prior to testing, the surface of each sample was partially masked using AMERCOAT® 90HS epoxy so that only the top and bottom surfaces of the coupon were exposed. The samples were then placed in individual beakers containing 600 ml of 0.086M NaCl solution held at 25 °C using an external water bath. A ratio of at least 100 mL/cm² was maintained in all cases. The surface of the beaker was sealed with Parafilm® to minimize evaporation. All test specimens were immersed for 120 hours and at least three samples of each specimen type were tested.
6.4.1.4 Protocol for Mass Loss Testing of PEO Coated Specimens

The protocol applied to PEO coated samples (detailed in Section 6.5) was similar to the one applied for dissimilar FSW joints. In both cases, samples were placed in individual beakers containing 600 ml of 0.086M NaCl solution held at 25 °C using an external water bath. The main difference between the two protocols was related to the approach used to calculate the corrosion rate. In the case of PEO-coated samples, treatment in chromic acid would remove the corrosion product as well as the un-corroded PEO coating, resulting in overestimated values for the corrosion rate experienced by the specimen. An adjustment was required to compensate for the dissolved PEO coating when the corrosion rate was calculated. A series of “as-coated” samples were treated in chromic acid solution to determine the mass loss \((m_i - m_c)\) associated with the dissolution of the PEO coating. The area density of the coating \((\rho_A)\) was calculated by dividing the mass of removed coating by the total area of specimen, see equation (6.2). Three specimens of each coating were examined, and the average area density was recorded.

\[
\rho_A = \frac{[m_i - m_c]}{A_{Total}} \tag{6.2}
\]

Prior to cleaning, all corroded coated samples were imaged, and the un-corroded area of the coating \((A_{UC})\) was measured using digital software. To calculate the corrosion rate associated with PEO coated samples \((CR_{PEO})\), only the mass lost during exposure to the corrosive medium must be considered. As such, the total change in mass \((m_i - m_f)\) was compensated by the mass of the un-corroded coating \((\rho_A \times A_{UC})\). The resulting change in mass was then divided by the total area of the specimen and the exposure time as given by equation (6.3).

\[
CR_{PEO} = \frac{[m_i - m_f + (\rho_A \times A_{UC})]}{A_{Total} \times t_{ML}} \tag{6.3}
\]
6.4.2 Short Term Immersion Testing

To identify the microstructural zones of the weld, the samples were immersed in 0.086 M NaCl solution kept at a constant temperature of 30 °C using a water bath. The solution was agitated with a magnetic stir bar at 260 rev min⁻¹. Lastly, the weld surface was oriented facing downwards to assist dissolution of corrosion product into the electrolyte solution. The schematic is shown in Figure 6-16. Samples were ultrasonically cleaned in Type I Milli-Q® water, rinsed with isopropanol (ACS Reagent, Caledon 8600-1-40), and dried under an air stream. Images were captured using an optical microscope (Olympus SZ-PT) which helped to map the different zones of the weld, providing points of interest for microcapillary polarization measurements.

![Figure 6-16 Immersion set up: (a) schematic, (b) image, and (c) PTFE sample holder.](image)

6.4.3 Anodic Polarization

6.4.3.1 Anodic Polarization of Base Magnesium Alloys

Polarization of bulk specimens of the base metal alloys AZ31 and AZ80 was conducted to determine the difference in corrosion potential of the base metal compared to various weld regions produced during the welding operation. Coupons were cut from the bulk sheet, ground and polished to a final finish of 1 μm (Section 6.3.1.3). These coupons were attached to copper wires to produce electrodes.
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The desired testing area, approximately 1 cm², was exposed while all other areas were masked using AMERCOAT® 90HS epoxy. The samples were rinsed with isopropanol (ACS Reagent, Caledon 8600-1-40) before polarization. Potentiodynamic polarization was conducted at room temperature in 0.1 M NaClO₄ (ACS reagent, 98%, Sigma-Aldrich 410241) (pH= 6.3) in a three-electrode cell using an IviumStat electrochemical interface. The counter electrode consisted of a platinum mesh, while the reference electrode was an Ag/AgCl electrode in 3 M KCl (Cole-Parmer® RK-05990-60). The samples were allowed to equilibrate for one hour in the solution prior to polarization. Samples were polarized from -1.70 V_SCE to -1.3 V_SCE using a scan rate of 0.166 mV/sec. The results were normalized to the exposed planar surface area estimated by using ImageJ imaging software. The corrosion potential and current were determined via Tafel extrapolation. At least three samples were measured, and the mean and standard deviation were recorded.

6.4.3.2 Anodic and Cathodic Polarization of AZ31B Phase Constituents

The electrochemical properties of the individual constituent phases present in AZ31B were examined in 0.1M NaClO₄ (ACS reagent, 98%, Sigma-Aldrich 410241) in order to gain insight into the effect of second phase particle size and distribution on the corrosion resistance of welded samples. The behaviour of the alloy was modelled using mixed potential theory with high purity magnesium (99.998%, Sigma-Aldrich 474754) as a simplified matrix material, and β-Mg₁₇Al₁₂ and γ-Al₈Mn₅ phases as second phase intermetallics.

Test coupons were cut from the bulk specimen and ground to a final surface finish of “1200 fine” grit using the procedure outlined in Section 6.3.1.3. The coupons were joined to copper wires to produce electrodes. The desired area, in the range of 0.06-0.20 cm², was exposed while all other areas were masked using Amercoat® 90HS epoxy. The samples were degreased with isopropanol (ACS Reagent, Caledon 8600-1-40) before polarization. Potentiodynamic polarization was conducted at room temperature in 0.1M NaClO₄ in a three-electrode cell to determine the corrosion potential and current using an IviumStat electrochemical interface. The counter electrode consisted
of platinum mesh while the reference electrode was an Ag/AgCl electrode filled with 3M KCl (Cole-Parmer® RK-05990-60). The samples were allowed to equilibrate for an hour in solution prior to polarization. A scan rate of 0.166 mV/sec was used for all experiments described in this investigation. The results were normalized to the exposed surfaced area and analyzed using Image J software. The corrosion potential and current were found by Tafel extrapolation.

Potentiostatic polarization with a step size of 10 mV and a holding time of 60 minutes was carried out to obtain Tafel slope values with improved accuracy. Both anodic and cathodic polarizations were performed on the matrix material (high purity magnesium), while only cathodic polarization was performed on the intermetallic specimens.

6.4.4 Microcapillary Anodic Polarization

6.4.4.1 Background

Common electrochemical methods used to examine the general corrosion of metal alloys use specimens with a surface area in the mm²-cm² range. As a result, the information retrieved from the sample is average data integrated over the entire area, and as such does not differentiate between the different phases and microstructures present on the surface [213]. Since the surface characteristics affect the corrosion behaviour and often lead to localized corrosion, a technique that will isolate and test specific regions with better spatial resolution is highly desirable. Magnesium friction stir spot welds were examined using the SRET by both James and Miklas to evaluate the local potential distribution across weld zones [12, 188]. However, one of the disadvantages of the SRET scanning method is that it is difficult to produce a polarization curve that dynamically links a broad range of potentials to electrochemical kinetic data while mapping [214]. As such, kinetic information of the local dissolution process, hydrogen evolution rate, etc. cannot be measured.

Corrosion of specific microstructural features can be effectively studied by decreasing the size of the exposed area through the use of microcapillary polarization. The MCP test is based on the use
of a small glass capillary to limit the area of interest on the sample. The capillary is filled with the environment of interest (electrolyte), a reference (Ag-AgCl) electrode, and a counter electrode (Pt wire), while the exposed area at the bottom of the capillary acts as the working electrode, as seen in Figure 6-17. This three electrode “micro” cell enables common electrochemical techniques to be performed on the area of interest, such as potentiostatic, potentiodynamic measurements, galvanostatic measurements, and cyclic voltammetry [214]. Currents associated with the localized cell can be measured directly. Frequently, the cell is attached to a microscope that allows precise placement of the capillary tip on the area of interest [213-215].

![Figure 6-17 Microcapillary polarization apparatus.](image)

The diameter of the capillary typically varies in size from 1 to 1000 µm and is typically produced by heating and pulling borosilicate tubes when they reach their glass transition temperature. The tip of the cell is covered with a thin layer of silicone type sealant, which is chosen based on two main material properties. Its hydrophobic behaviour prevents leakage of the electrolyte from the cell and avoids the formation of a crevice under the seal. Second, its high elasticity permits measurements on rough and extremely curved surfaces [214].
There are some limitations associated with the technique that were previously described in the literature [216, 217]. Due to the small area of the capillary tip, ohmic resistance ($R_\Omega$) becomes a consideration. Birbilis et al. showed that $R_\Omega$ is inversely proportional to the square of the tip diameter [216]. Thus, when the experiment requires a small tip diameter or the use of an electrolyte with low conductivity, it is important to calculate the ohmic resistance and account for the ohmic drop. The scanning rate has the same importance as it exhibits in common electrochemical techniques. Often the scanning rate is altered to reduce the measurement time to prevent leakage or corrosion byproducts from clogging the tip of the capillary.

The fine tip of the capillary affects the transfer of species to and from the electrode surface; thus, the limiting current of the reaction will depend on the diameter of the capillary [216, 217]. Another problem caused by poor mass transfer is the accumulation of corrosion byproducts at the end of the capillary, if the corrosion products are voluminous these by-products can block the opening. To address this problem, a bigger capillary tip can be chosen to increase dissolution of corrosion products into the bulk solution. Alternatively, a capillary with a circulating electrolyte can be chosen, as demonstrated by Sakairi et al. [218]. The design allowed increased mass transport of protons to the surface of the electrode while transporting corrosion byproducts back into the bulk solution [217].

6.4.4.2 Apparatus Design

A literature survey was conducted to facilitate the design of the apparatus and to identify the most important parameters governing the accuracy of a microcapillary polarization setup. Suter et al. suggested the quality of the seal between the capillary and the sample is a critical factor for the microcell technique [214]. To improve the quality of the seal, a holding micropipette (Origio Humagen Pipets) was chosen as a capillary for this investigation. Holding pipettes are commonly used to hold or immobilize egg cells; however, they possess multiple attractive features for their use in the microcapillary polarization technique. Holding micropipettes have a flat polished opening.
with a large ratio of outer to inner diameter that allows for a greater contact area with the sample as seen in Figure 6-18 (b), thereby improving the seal between the capillary and the working electrode. The typical width of a stir zone or the TMAZ typically ranges on the order of hundreds of microns, a capillary with an inner diameter of 30 μm was chosen for this investigation (Origio Humagen Pipets MPH-XLG-0) in order to successfully isolate each weld zone.

A thin silicone coating was deposited on the tip of the capillary to ensure a proper seal between the capillary and the sample. The silicone coating was produced by dissolving 5 grams of silicone rubber compound (RS 555-558) in 30 ml of xylene (ACS Reagent, Caledon 9800-1-40) to reduce the viscosity of the silicone rubber compound and thereby reducing the thickness of the coating. The silicone rubber compound and the xylene were placed in a 50 mL centrifugal tube (FroggaBio TB50-
25). The tube was shaken until all the silicone rubber was dissolved and no solids were observed in the tube. For easier handling 1.5 mL of dissolved silicone solution was transferred into a 2 ml micro tube (Sarstedt 72.694.006). The 50 mL centrifugal tube was then closed immediately to prevent xylene evaporation. The capillary was connected to a compressed argon tank to allow a gentle stream of argon to pass through the capillary throughout the entire process to avoid clogging. The capillary was then dipped into the micro tube containing the dissolved silicone solution and left for 30 minutes for initial drying. The micro tube was discarded. This process was repeated two more times to yield a three-layer silicone coating on the capillary. After the final coating, the silicone was allowed to dry for 24 hours before the capillary was used. Once the coating dried the capillary was tightened into a custom machined polycarbonate cell (CAD drawing available in appendix B2) as seen in Figure 6-18 (a).

To further increase the quality of the seal, samples were mounted on a sample holder and leveled with a four-point contact calibration system on a Newport 2-axis tilt stage [188]. Once the sample is leveled the polycarbonate cell is placed in the cell holder and is positioned above the sample. To allow exact positioning of the microcapillary above a site of interest the cell holder was mounted on an x-y-z brushless servomotor translation stage (Zaber XYZ-T-LSM050A). When the capillary was placed above a site of interest it was lowered down and pressed against the sample to create a seal.

Hydrogen gas accumulation resulting from the corrosion of the sample is a common challenge of microcapillary polarization of magnesium alloys. The gas accumulation at the bottom results in increased resistance across the capillary and poor signal. As a result, the time for polarization is limited and faster scanning rates are typically applied that result in less accurate reading of corrosion current and potential. The selection of electrolyte for microcapillary polarization of magnesium alloys should be done carefully. Two properties of the electrolyte are specifically important: a highly conductive electrolyte will improve the reading but is likely to cause accelerated corrosion attack, while a mildly corrosive electrolyte typically has low conductivity. Krawiec et al. suggested the use of NaClO₄ as the electrolyte for microcapillary polarization of AZ91 magnesium alloy [52]. It has
been shown that the perchlorate (ClO$_4^-$) anions tend to complex less with the surface metal atoms as compared to chloride anions (Cl$^-$) [120]. As a result, perchlorate ions are less corrosive than chloride anions but still cause localized pitting corrosion on magnesium alloys [52]. The chosen electrolyte for this investigation was 0.1M sodium perchlorate (NaClO$_4$) (ACS reagent, 98%, Sigma-Aldrich 410241) which enabled sufficient conductivity, while reducing the corrosion rates, preventing tip blockage from corrosion products and hydrogen, and allowing longer time periods for investigation.

Both the capillary and polycarbonate cell were filled with the 0.1M NaClO$_4$ electrolyte, and both the platinum mesh electrode along with the 3 M silver / silver chloride (Ag/AgCl) micro reference electrode (CH Instruments CHI111) were placed inside the capillary cell. The sample was then polarized using an IviumStat electrochemical interface. The polarization was terminated early if the capillary was clogged and/or the contact was lost. The choice of a potentiostat for this technique is a topic that is commonly explored in literature, Suter et al. suggested that the potentiostat should have input resistance that is 100 times greater than that of the sample, and that the current sensitivity should be at least 10 times lower that the passive current [214]. The typical resistance in this set up is in the range of MΩ and passive currents of tens of pA, the IviumStat has an input impedance of 1T Ω and current sensitivity of +/- 1pA providing the required resolution.

The tested area was imaged using a Hitachi SU3500 scanning electron microscope. In this investigation post corrosion testing spots were imaged at a tilt angle of 60° to increase topographical contrast. The images were taken with the tilt compensation mode to account for the distortion of the image. The contact area was analyzed using the software Image J to find the actual planar area of the electrode. Normalized graphs of potential versus current density were plotted. Corrosion potential, $E_{corr}$, and corrosion current density, $i_{corr}$, were found using Tafel extrapolation.

Figure 6-19 shows an SEM micrograph of typical corroded spot post microcapillary polarization testing. The image shows an isolated corroded area, confirming no leaks of electrolyte from underneath the silicone coating on the capillary. The radius of the examined area was measured to be approximately 20 μm, while the nominal inner radius of the capillary was measured to be roughly
15 μm. It is suggested that the silicon gasket deposited on the capillary is deformed when it is pressed against the sample and allowing a slightly greater exposed area.

![Image](image1.png)

**Figure 6-19 Post-microcapillary polarization corroded spot**

To confirm the accuracy of the microcapillary polarization apparatus, the polarization output generated when testing AZ31B base metal by MCP was compared to that generated through bulk anodic polarization experiments. Figure 6-20 shows the reproducibility for both bulk and microcapillary polarization of the base metal. Both methods produced similar outputs, with greater deviation in-between the trials observed in microcapillary measurements. The increased variability of the potentiodynamic polarization output was attributed to the local inhomogeneous nature of the alloy.
Figure 6-20 Bulk and microcapillary polarization curves for AZ31B in 0.1 M NaClO$_4$ solution at 25 °C.

6.4.4.3 Experimental Protocol

The following section provides a step by step protocol for microcapillary polarization measurements:

1. Test specimens were sectioned and mounted in epoxy following the steps described in Section 6.3.1.1 and 6.3.1.2 respectively.
2. Three equally spaced holes (every 120°), 4.8 mm in diameter, were drilled on the perimeter of the hardened epoxy. The holes were used for plastic screws that fixed the sample to the sample holder.
3. Another hole (1.6 mm diameter) was drilled into the base metal. This hole was used to friction fit a copper led wire for the working electrode.
4. The specimen was then polished to a final surface finish of 1 µm following the steps described in Section 6.3.1.
5. Following the polishing step, the specimen was sonicated in isopropanol (ACS Reagent, Caledon 8600-1-40), and dried under an air stream.

6. The 1.6 mm diameter copper lead wire was pushed into the hole in the base metal to produce intimate physical contact between the alloy and the copper lead and establish an electrical connection. The electrical connection was verified using a digital ohm-meter (Fluke 73 Multimeter). Changes to the positioning of the wire were made until the resistance was lower than 0.2 Ω.

7. AMERCOAT® 90HS epoxy was applied to the wire and base metal near the point of contact to completely isolate the wire from the system. The gap between the two metal sheets was covered with AMERCOAT® 90HS epoxy as well to prevent solution from coming in contact with the copper wire. An example of a microcapillary polarization sample is shown in Figure 6-21.

8. The sample was then placed onto the sample holder and it was fixed in place using three plastic screws.

9. The sample was leveled using a four-point calibration system. The system consisted of a digital ohm-meter that was connected to the sample surface as the working electrode and a calibration probe that was connected as the counter electrode. The probe was mounted onto the x-y-z translation stage and its exact coordinates in the 3D space that can be determined
from the Zaber Module software that controlled the translation stage. The system was used to determine vertical positioning of any point on the surface of the specimen. The calibration probe was lowered to the surface of the specimen until a contact was registered with an ohm-meter. The vertical position of the point was defined as the vertical distance the calibration probe had to travel from its origin until it just touched the surface.

10. The X axis of the 2 axis Newport tilt stage was adjusted to produce a configuration in which two points (X1 and X2 in Figure 6-22) lying along the horizontal axis on opposing sides of the specimen had the same vertical position.

11. The procedure in step 10 was carried to level the Y axis through points Y1 and Y2.

12. Once leveling was complete, the calibration probe was demounted from the translation stage and the microcapillary polarization cell was mounted instead.

13. The capillary was moved above the specimen using the translation stage. Once it reached a site of interest, the capillary was lowered slowly until it touched the surface of the specimen. Contact between the capillary and the surface of the specimen could be determined using a magnifying glass. Noting the position of the optical contact, the capillary was moved another 100 µm down to ensure a proper seal between the capillary and the surface of the specimen. This overcompensation is likely responsible for the slight indentation seen in Figure 6-19.

14. The microcapillary was then filled with electrolyte solution using a 34-gauge flexible nonmetallic syringe needle (World Precision Instruments Inc. MF34G-5) that was long enough to reach the bottom of the capillary. Special care was given to ensure that no bubbles were formed on the metal interface or within the capillary.

15. Once the capillary was full, the rest of the polycarbonate cell was filled with electrolyte solution with the counter and reference electrodes placed into their respective slots.

16. The sample was allowed a minimum of 30 minutes to equilibrate and reach a steady open cell potential. The sample was then polarized from a potential that is rounded to the nearest
50 mV below the recorded open cell potential to a potential that is 100 mV more noble than $E_{\text{corr}}$.

17. If another measurement on the same sample was required, the capillary was emptied before lifting it of the surface. The sample and the capillary were then rinsed in Type I Milli-Q® water and dried thoroughly before another measurement could take place.

![Diagram](chart.png)

Figure 6-22 Schematic showing locations of 2 pairs of contact points used for establishing the planarity of the stage relative to the microcapillary used in the microcapillary polarization apparatus.

6.4.5 Scanning Reference Electrode Technique

6.4.5.1 Background

Local variations of potential/current on the surface of a specimen can be measured using a scanning reference electrode in close vicinity to the surface. This technique has proven to be a useful method to obtain high special resolution for investigating the localized corrosion behaviour of a metal [188]. If the potential variations can be measured on the surface of the specimen, local anodic and cathodic regions can be identified. James performed SRET studies on FSSW AZ31 magnesium alloys. He concluded that the best results for a 10µm Pt tip were achieved at a scanning speed of 2 µm/s, a probe height of 10 µm above the surface, in a test solution of 0.086 M NaCl, as shown schematically in Figure 6-23 [188]. The surface of the specimen was mapped using line scans spaced 250 µm apart and the resultant data was plotted as a two-dimensional color map [188] linked to the gradients measured in potential.
6.4.5.2 SRET Measurement of Welded Specimens

The experimental procedure used in this study for producing SRET measurements was modified from James et al. [188]. For SRET measurements of a welded specimen the following steps were carried out:

1. SRET samples were prepared following steps 1-7 outlined in Section 6.4.4.3 for microcapillary measurements.
2. The sample was then placed onto the SRET cell (CAD drawing available in appendix B3) and fixed in place using three plastic screws. An image of an assembled SRET apparatus is shown in Figure 6-24.
3. The sample was leveled using the four-point calibration system that is described in steps 9-11 in section 6.4.4.3.

4. Once leveling was complete, the calibration probe was demounted from the translation stage and replaced with the SRET probe. The SRET probe was a 10 µm diameter platinum wire that was encapsulated in a glass tube (CH Instruments CHI116).

5. An ohm-meter was connected to the sample surface as the working electrode and to the SRET tip as the counter electrode. The SRET probe was moved to a position above the metal specimen, but away from the area that will be measured. The probe was lowered slowly until electrical contact was established. From this point, the probe was lifted 10 µm above the surface, and this vertical position was maintained throughout duration of the measurement.
6. The set up was connected to an IviumStat® potentiostat with the sample acting as the working electrode, the SRET probe being the reference electrode, and the platinum mesh acting as the counter electrode.

7. The probe was moved to the top left corner of the area to be measured and its x-y coordinates were recorded (using the Zaber Console software that operated the translation stage).

8. The probe was moved back to the base metal, and 60 mL of 0.086 M NaCl electrolyte solution (ACS Reagent, BioShop® SOD002.205) was poured into the cell.

9. Prior to scanning, the open cell potential (E_{OCP}) was monitored above the base material until the system stabilized at a resting potential of approximately -0.9 V. The stabilization period took approximately 1 h; no visible corrosion was present at this point.

10. The probe was moved back to the coordinates recorded in step 7, and the potentiostat was set up to record the open cell potential at a frequency of 1 Hz, until the measurement was terminated by the operator.

11. The SRET probe was then scanned at a horizontal scanning rate (SR_x) to the right for a distance of S_x.

12. Once the line scan was complete, the probe travelled downwards at a vertical scanning rate (SR_Y) for a distance of S_Y.

13. The probe was then scanned to the left at a scanning speed of SR_x for the same distance it travelled in the previous line (S_x).

14. Steps 11-13 were repeated to produce a specified number of lines (N_L). At the end of the measurement the probe was moved back to the starting its starting position using a scanning speed of 1500 µm/sec. The path of a SRET probe is shown schematically in Figure 6-25.
15. The scanning parameters depended on the size of the scanned area and the nature of the specimen. The parameters used in this work are summarized in Table 6-6.

<table>
<thead>
<tr>
<th>Area of Interest</th>
<th>SRx [µm/sec]</th>
<th>Sx [µm]</th>
<th>SRY [µm/sec]</th>
<th>SY [µm]</th>
<th>Nl</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSSW SZ</td>
<td>2</td>
<td>3250</td>
<td>1500</td>
<td>250</td>
<td>11</td>
</tr>
<tr>
<td>Welding Flash</td>
<td>1</td>
<td>1250</td>
<td>1500</td>
<td>250</td>
<td>6</td>
</tr>
<tr>
<td>AZ31/AZ80 SZ</td>
<td>2</td>
<td>3500</td>
<td>1500</td>
<td>100</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 6-6 SRET scanning parameters

16. All scanning operations were controlled using the Zaber Console software that operated the translation stage. A customized code was written in C language to produce SRET scans. To run the code the Zaber Console software was opened and COM1 Binary was selected for the “Serial Port” drop down menu. In the scripts tab, “Scripts Editor” was clicked prompting a command that allows code import into software. To import the code simply copy and paste the code in Appendix C1 into the window and click “run script”. The script
Chapter 6: Experimental Procedure

will prompt the user to input SRET scanning parameters. At the end of the query the software will begin the scan.

17. At the end of the scan the output from the IviumStat® was exported as a .txt file.

18. An algorithm was programmed in R to correlate the X-Y position of the SRET probe determined from the input parameters with the measured open cell potential from the IviumStat®. The code is detailed in Appendix C2.

19. To use the code the user is required to specify several variables:
   - `setwd("Enter the address of the folder containing the file to be analyzed")`
   - `Filename=Enter the file name in a "file name.txt" format`
   - `NofLines= Enter the desired number of lines (NL)`
   - `ScanDistance= Enter the desired horizontal scanning distance (SX)`
   - `ScanSpeed= Enter the desired horizontal scanning rate (SRx)`
   - `YDistance= Enter the desired vertical scanning distance ((NL-1)x SY)`

Note that in the work detailed in this investigation the time it took to complete the vertical movement was shorter than the interval between potential measurements, and so the vertical scanning rate (SRy) was not needed for the code.

20. Execution of the code in R outputs a .txt file that contained a two dimensional array correlating the position of the probe (x,y) and the open cell potential recorded at that spot.

21. The data in this file were imported into Sigma Plot software to produce a two-dimensional contour plot depicting the potential distribution profile on the surface of the specimen.

6.4.5.3 SRET Measurement of PEO Coated Specimens

To illustrate the changes in open cell potential distribution during breakdown of PEO coatings, several SRET scans were conducted. The samples for this study were embedded in epoxy such that their coated surface was exposed. The setup of the apparatus followed the same steps as outlined in Section 6.4.5.2. To accelerate degradation the concentration of the electrolyte was increased to 0.86 M NaCl.
Chapter 6: Experimental Procedure

Once the first pit in the sample appeared, the probe was brought near the corroding site, and an area scan was initiated. The area scan was composed of a collection of line scans (150 µm apart) to produce a potential contour plot, corresponding to an area of 2000 x 1350 µm. A scanning speed of 1 µm/sec was used. During this investigation, a series of scans were performed over the same area to illustrate the changes in open cell potential distribution as a function of time. Each scan lasted approximately 6 hours, and a new scan was started immediately after the previous one was completed. A total of eight scans were performed. After the SRET scans, the data sets from the IviumStat® potentiostat were analyzed in the same fashion as described in Section 6.4.5.2.

6.5 Plasma Electrolytic Oxidation

6.5.1 PEO Coating Synthesis on Base Metal Specimens

Prior to coating, the surfaces of all the samples were ground to a final surface finish of “1200 fine” with SiC grinding paper (using the process described in 6.3.1.3). After grinding, the samples were cleaned with isopropanol (ACS Reagent, Caledon 8600-1-40) and Type I Milli-Q® water and air dried. Electroplater’s tape (3M S-10258) was used to mask the sample partially and leave an exposed area of 6 cm² to avoid any waterline effect at the air-electrolyte interface. PEO coating was conducted inside a double-walled beaker (Ace Glass Inc.) containing 480 mL of coating electrolyte. The double-walled beaker allowed temperature control of the electrolyte by circulating water, from an external water bath, between the walls. The electrolyte inside the beaker was stirred by a magnetic stir bar spinning at a constant rate of 450 rev min⁻¹. The sample piece was positioned in the centre of the beaker, surrounded by a nickel mesh cathode wound in a cylindrical shape. The configuration of the apparatus is shown in Figure 6-26.
Chapter 6: Experimental Procedure

**Figure 6-26 PEO coating setup**

A Xantrex® 600-1 power supply with a voltage mode transient response of 1 ms was used to control the voltage and current. The power supply also exports an analog signal indicating the instantaneous voltage, which was recorded at a rate of 100 samples/second (100Hz) with a Measurement Computing® USB1608G data acquisition (DAQ) system. For higher speed recordings, a GW Instek® GDS-122 oscilloscope was used to measure the voltage directly from the electrode connection points. The oscilloscope has a maximum recording speed of 100 million data points per second (100 MHz), but it can only store and transmit 6000 data points in each reading. Therefore, the oscilloscope was used to study the detailed waveform of the voltage transient, and the DAQ was used to sample the voltages for the entire duration of PEO processing. Two groups of samples were produced by varying the process parameters. One group was coated by varying the deposition current density between 5 mA/cm² and 40 mA/cm², all at a fixed temperature of 25 ± 1 °C. A second group was produced by varying the bath temperature between 18 °C and 40 °C (±1 °C) at a fixed current density of 10mA/cm². All samples were coated for 30 minutes, with the exception of the sample produced by applying a current density of 5 mA/cm², which was coated for 60 minutes. The electrolyte contained the following composition: 40 g/L sodium hydroxide (ACS Reagent, BioShop SHY700.1), 50 g/L sodium metasilicate (Sigma-Aldrich 307815), 30 g/L sodium tetraborate (99%, Sigma-Aldrich 221732), 10 g/L sodium citrate (98%, Sigma-Aldrich C3674), and 10 g/L
polyethylene glycol (as PEG1000) (Sigma-Aldrich P3515). The electrolyte composition was adopted from previous work reported by Zhu et al. [153].

Once a sample was coated, the electroplater’s tape was removed, and the sample was cleaned using Type I Milli-Q® water and dried with warm air. Specimens were stored in a desiccator prior to further analysis.

6.5.2 PEO Coating Synthesis on Welded Specimens

Welded specimens were coated following the same procedure as described in Section 6.5.1. The only difference in the experimental methodology was the configuration of the sample and the configuration of the electroplater’s tape. For FSSW joints, the specimens were coated in the as-welded condition. Electroplater’s tape was applied to one of the corners, as shown in Figure 6-27 (left). A small area was left exposed to enable an electrical connection to the power supply. For dissimilar seam welds, specimens were cut perpendicularly to the weld (4.5 cm x 1 cm). Electroplater’s tape was applied such that the base metal 1 cm away from the SZ region was exposed, ensuring that the exposed areas of each of the dissimilar alloys were equal (see Figure 6-27 (right)). In all cases the ratio between the volume of the electrolyte and the area of the specimen was kept at a minimum of 40 ml/cm².

![Figure 6-27 Sample configuration for PEO coating of welded specimens](image-url)
6.5.3 PEO Coating Characterization

The top and cross-sectional surfaces of the coated specimens were analyzed by optical imaging and SEM. The test coupons were cross sectioned at the interface between the coating and the uncoated base metal using the procedure described in Section 6.3.1.1. The resulting section (coated portion of the coupon) was cut again along the center line. One half was kept for top surface analysis, and the other was embedded in epoxy for cross-sectional examination.

The samples embedded in epoxy for SEM cross-sectional examination were progressively ground to a final surface finish of 1/4 µm using diamond paste following the methodology described in Section 6.3.1.3. The samples were then ion milled using a Hitachi® IM4000 apparatus. Ion milling was performed at a sample tilt angle of 87° with no eccentricity. The sample was rotated at a speed of 25 rev min\(^{-1}\) for 30 minutes. Accelerating voltage of 4.5 kV and a discharge voltage of 1.5 kV were used with an argon gas flow of 0.10 cm\(^3\)/min. Prior to imaging, the specimens were carbon coated to reduce charging arising from the insulating nature of the oxide. Images were captured using a Hitachi® SU3500 variable pressure SEM at an accelerating voltage of 5 kV and a working distance of 6 mm. This apparatus configuration reduced the interaction between the beam and the sample.

The elemental composition of the coating was determined by EDX. The crystal structure and phase composition of the coatings was investigated using a Rigaku® MiniFlex 600 X-ray diffractometer (XRD) using Cu K\(_{\alpha}\) radiation (\(\lambda = 1.5418 \text{ Å}\)). The scans were performed over the diffraction angle (2\(\theta\)) range from 10° to 90° in 0.02° steps with a 1 sec step duration.
Chapter 7 Electrochemical Characterization of Individual Weld Regions in Friction Stir Welded AZ31B-H24


7.1 Introduction

As discussed in Chapter 5, preliminary results by James and Miklas have shown cathodic behavior of the weld with respect to the base material in the AZ31 magnesium alloy friction stir spot weldments [11, 12, 188]. SRET was used to generate a potential distribution map on a cross-section of a FSSW weldment. The results showed a potential gradient that existed across the weldment in which the stir zone was noble to both the TMAZ and the BM regions, while the TMAZ was noble to the base metal alone [11]. Optical observations showed localized corrosion attack of the TMAZ region; however, the mechanism(s) responsible for this behaviour is yet to be understood. The measurement of the electrochemical response of each individual zone is essential to investigating the mechanism(s) responsible for preferential corrosion attack on the TMAZ. Polarization measurements of each individual weld zone in AZ31 FSSW can provide the thermodynamic driving force for corrosion to occur as a function of the evolution of the microstructure through variations in the welding process.
As discussed in Section 6.4.4.1, common electrochemical methods to investigate the corrosion behaviour of a material are usually based on large scale experiments with exposed areas in the mm²-cm² range. Microcapillary polarization is a well-established technique to investigate localized corrosion behaviour of various samples, where isolation of specific areas is challenging due to size restrictions [52, 88, 214-216, 219, 220]. The basis of the technique relies on isolating the desired area by pressing a capillary onto the surface of the sample. The capillary then acts as a corrosion cell. It is filled with electrolyte solution and connected to reference and counter electrodes to allow electrochemical control of the investigated surface. In this configuration, common large-scale electrochemical investigations can be performed on the μm² scale (which is suitable for investigating the electrochemical properties of individual weld regions or phases).

The aim of this chapter is to establish an experimental methodology for microcapillary polarization of FSSW welds made in AZ31 magnesium alloy and to investigate the corrosion rates of isolated weld zones using the microcapillary polarization technique. This technique will be applied to examine the effect of dwell time (between 1 and 4 sec) on the corrosion resistance of AZ31B FSSW joints made using a tool rotational speed of 3000 rev min⁻¹. A comparison between the electrochemical properties of individual weld regions in spot and seam welds will also be conducted.

### 7.2 Tungsten Carbide Tracing Test

In order to confirm the location and boundaries of the stir zone in the welded specimens, WC was used to trace the material flow during welding following the experimental procedure described in Section 6.2.4. Figure 7-1 displays the tungsten carbide (WC) tracer (bright area) distributed in the weld nugget region for welds produced at 3000 rev min⁻¹ both 1 and 4 sec of dwell time. The WC tracer was mixed from underneath the shoulder into the weld nugget region by the motion of the tool shoulder and the pin. As such it can be concluded that the stir zone is marked by the WC tracer in both welding conditions. A disadvantage of the WC tracer technique is that large quantities of
powder are required to mark large areas within the weldment, and the time required for the tracer to travel from underneath the shoulder peripheries into the weld nugget has to be considered as well. It is evident from Figure 7-1 that an increase in dwell time resulted in a larger stir zone; these results are in agreement with previous work done by Yin et al. [165]. The results confirm that in both cases the stir zone is present 200 μm below the shoulder penetration surface and 200 μm away from the edge of the key hole.

![Figure 7-1 SEM images in BSE mode of FSSW samples made with WC as a tracer, using a rotational speed of 3000 rev min\(^{-1}\) for: (a) 1 sec dwell, and (b) 4 sec dwell time.](image)

### 7.3 Bulk Polarization of AZ31B in 0.1M NaClO\(_4\)

The corrosion potential \(E_{corr} = -1.467 \text{ V SCE} \pm 6 \text{ mV}\), and corrosion current density \(i_{corr} = 10.5 \pm 0.35 \mu\text{A/cm}^2\) of the base metal, AZ31B, in 0.1M NaClO\(_4\) were found through Tafel extrapolation of the bulk polarization curves (the experimental procedure is described in Section 6.4.3.1 and repeatability of the output can be seen in Appendix D1) shown in Figure 7-2. Wang et al. reported the corrosion potential and corrosion current density for AZ31B in 0.1 M NaCl as -1.524 V\(_{SCE}\) and 18 \(\mu\text{A/cm}^2\) respectively [85]. AZ31 showed a more noble corrosion potential and lower corrosion
current density in this work than the values measured by Wang et al. as the test solution contained perchlorate anions instead of chloride ions [85]. In both cases the concentration of the anions in solution was kept constant. The breakdown potential, $E_b$, is observed around $-1.35 \text{ V}_{\text{SCE}}$, and signified the point where the quasi passive film that was formed as a result of exposure to the corrosive media is locally compromised. The reported breakdown potential for AZ31 in 0.1M NaCl was more active as well ($E_b = -1.46 \text{ V}_{\text{SCE}}$) [85]. Perchlorate ions tend to complex less with the metal atoms at the surface of the electrode as compared to chloride anions. Pitting initiates due to adsorption of chloride anions to the surface of the electrode, and local disruption of the passive film. It is evident that the lower tendency for complexation exhibited by the perchlorate anions resulted in more noble nobler corrosion and breakdown potentials as compared to that observed in chloride anions.

Figure 7-2 Bulk and microcapillary polarization curves for AZ31B base metal in 0.1M $\text{NaClO}_4$ solution at 25°C. This figure originally appeared as Figure 6-20 and has been included again for clarity.
7.4 Microcapillary Polarization

Polarization curves produced from bulk and microcapillary polarization of the base metal were compared to confirm the validity of the output produced by the microcapillary polarization apparatus. Figure 7-2 shows the degree of reproducibility for both bulk and microcapillary polarization measurements (the output of individual trials is given in Appendix G1) of the base metal. Both methods produced similar results with excellent reproducibility within each method and between methodologies, confirming that microcapillary measurements could serve as an excellent analogue to bulk polarization measurements. A slightly greater deviation between the trials was observed in microcapillary measurements. The increased variability of the potentiodynamic polarization output was attributed to the inhomogeneous nature of the alloy linked to the extent of the surface area for which the electrochemical response was being recorded.

Microcapillary polarization was carried out to investigate the corrosion behavior of isolated weld zones. Corrosion potential, \( E_{\text{corr}} \), and corrosion current density, \( i_{\text{corr}} \), were found using Tafel extrapolation. Three zones (SZ, TMAZ, and BM) were tested on each sample, and each zone was measured on at least three different samples. The location of the measurement was determined based on the results obtained from tungsten carbide tracer testing. The stir zone was measured 200 μm below the shoulder penetration surface and 200 μm away from the edge of the key hole as shown in Figure 7-3. The TMAZ was measured 200 μm away from the hook region towards the base metal. The base metal was measured a minimum of 2 cm away from the key hole.
Figure 7-3 Schematic of a cross section of a FSSW weld along with locations for potentiodynamic polarization

Figure 7-4 shows an SEM micrograph of a typical corroded spot post microcapillary polarization testing on the TMAZ region of a weldment made with 3000 rev min$^{-1}$ and 1 sec dwell time. SEM imaging is nominally conducted at a tilt angle of 15°; in this investigation post corrosion testing spots were imaged at a tilt angle of 60° to increase topographical contrast. The images were taken with the tilt compensation mode to account for the distortion of the image. The image shows an isolated corroded area, confirming no leaks of electrolyte from underneath the silicone coating lined on the capillary. The radius of the examined area was measured to be 20 μm, while the nominal inner radius of the capillary was measured to be 15 μm. It is suggested that the silicon gasket deposited on the capillary is deformed when it is pressed against the sample and thus allowed a slightly greater exposed area.
Chapter 7: Electrochemical Characterization of Individual Weld Regions in Friction Stir Welded AZ31B-H24

Figure 7-4 Post microcapillary polarization corroded spot on the TMAZ region of a weldment made with 3000 rev min⁻¹ and 1 sec dwell. This figure originally appeared as Figure 6-19 and has been included again for clarity.

Figure 7-5 shows representative microcapillary polarization curves for the three zones of interest: stir zone, TMAZ, and BM. The output of individual polarization tests for the TMAZ and the SZ regions, can be seen in Appendix H2 and H8 respectively. The stir zone is noble to both the base metal and the TMAZ, while the latter two show a similar corrosion response.
Figure 7-5 Representative microcapillary polarization curves produced for the stir zone, TMAZ, and base metal on a FSSW weldment made with 3000 rev min\(^{-1}\) and 1 sec dwell time

The corrosion potential and corrosion current density, found by Tafel extrapolation, as a function of dwell time at a constant tool rotational speed of 3000 rev min\(^{-1}\) are summarized in Table 7-1. The polarization results for the base metal coincide well with the results reported previously for bulk polarization of AZ31 in 0.1M NaClO\(_4\). It is evident that the stir zone is noble to both the TMAZ and base metal in agreement with results reported by James et al. [11]. The main difference lies in the corrosion behaviour of the TMAZ region. While SRET output suggested that the TMAZ is noble to the base metal, microcapillary polarization showed similar electrochemical behavior between the base metal and the TMAZ. It is proposed that the noble region seen in the SRET measurements by James et al. (see Section 5.1.3 for complete discussion), result from a potential field caused by the presence of the noble stir zone forming a macrogalvanic cell with the base metal and the TMAZ [11]. The macrogalvanic cell formed between the noble stir zone and the active TMAZ/BM resulted
in localized corrosion at the boundary between the zones causing intense attack at the weld nugget periphery.

<table>
<thead>
<tr>
<th>Region</th>
<th>3000 rev min(^{-1}) – 1 Sec Dwell Time</th>
<th>3000 rev min(^{-1}) – 4 Sec Dwell Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_{\text{corr}}) [V SCE +/– mV]</td>
<td>(i_{\text{corr}}) [(\mu\text{A/cm}^2)]</td>
</tr>
<tr>
<td>SZ</td>
<td>-1.411 +/– 4</td>
<td>2.6 +/– 0.2</td>
</tr>
<tr>
<td>TMAZ</td>
<td>-1.463 +/– 9</td>
<td>9.6 +/– 0.6</td>
</tr>
<tr>
<td>BM</td>
<td>-1.468 +/– 5</td>
<td>10.5 +/– 0.2</td>
</tr>
</tbody>
</table>

Table 7-1 Corrosion potentials and currents of various weld zones of weldments made with a tool rotational speed of 3000 rev min\(^{-1}\) and dwell times of 1, and 4 sec. Individual polarization curves can be found in Appendices G and H.

The ennoblement of the SZ was likely related to the microstructural transformation that occurred during the welding cycle. As mentioned in Section 4.1, the stir zone comprises recrystallized \(\alpha\)-matrix super saturated solid solution grains, with the excess aluminum dissolved in the magnesium matrix due to the stirring and elevated temperatures associated with the process. The individual effect of each microstructural feature will be examined in following chapters.

To produce a meaningful comparison between the results presented herein and those reported in literature comparison metrics should be defined. The effect of FSSW on the electrochemical properties of AZ31 can be evaluated by examining the change in the corrosion potential of SZ region relatively to that of the BM \((E_{\text{corr,SZ}} - E_{\text{corr,BM}})\). A positive change would indicate that the SZ became more noble and its corrosion resistance properties likely increased. Similarly, a negative change would indicate that the SZ became more active than the BM and it will likely exhibit poorer corrosion resistance properties than the BM. Corrosion current density can also provide insight into the effect of friction stir welding on the electrochemical properties of AZ31B. Unlike the corrosion potential, where the change is estimated by direct subtraction, the change in corrosion current...
density is better assessed when it is examined as a ratio ($i_{\text{corr}, \text{SZ}}/i_{\text{corr}, \text{BM}}$). Magnesium is highly sensitive to the testing methodology with reported corrosion rates in 0.6M NaCl exhibiting a scatter of two orders of magnitude [106, 210]. When the change in the corrosion current density is assessed as a ratio the differences stemming from the testing methodology are not considered and the effect of welding can be evaluated directly. A ratio that is smaller than unity would indicate a reduction in the corrosion rate of the SZ as compared to the base metal, while a ratio higher than unity would signify that the corrosion susceptibility of the SZ increased.

The metrics describing the change in the corrosion potential and corrosion current density of the SZ were calculated using the electrochemical properties detailed in Table 7-1. These metrics were then plotted against data from other investigations that was previously published in literature, see Figure 7-6. In all cases the corrosion current density of the SZ was lower than that of the BM and the ratio between the two ($(i_{\text{corr}, \text{SZ}}/i_{\text{corr}, \text{BM}})$ was lower than unity. This observation held true for all alloys and testing environments that were examined in this comparison. The corrosion potential of the SZ increased with the exception of two data points (Vuong et al. and Ben-Hamu et al. [190, 191]). As a general trend, most points were located within the upper left quadrant of the graph (labeled as region 1), suggesting that the welding operation increased the corrosion resistance of the SZ as compared to the BM. The discrepancy between the trend observed by Vuong et al. and the trend that was reported here is likely related to the sample preparation methodology [190]. Vuong et al. were able to measure the corrosion potential of the SZ region by cutting out a 1 cm x 1cm specimen from FSW joint and polarizing its top surface [190]. The welding tool used in their investigation had a pin height of 0.5 mm and it is likely that the SZ region was rather thin. The authors indicate that all electrodes were ground to a final surface finish of 1000 grit using SiC grinding paper. It is quite possible that the SZ was partially removed and instead of polarizing an electrode having a SZ microstructure, their electrodes contained a combination of SZ, TMAZ, HAZ, and/or BM microstructures. The authors did not report that the microstructure of the electrodes was assessed
prior to electrochemical testing. A cross-sectional micrograph showing the thickness of the SZ was not provided either. Unfortunately, Ben-Hamu et al. did not describe the experimental procedure that allowed measurements of individual weld zones and so there is insufficient information to conduct a critical assessment that would explain the discrepancy between their results and the work herein [191].

![Figure 7-6 Effect of friction stir welding on the electrochemical properties of magnesium alloys – comparison of the work herein to that published in literature [7, 8, 187, 190, 191, 193, 194]](image)

It is worth noting that Zeng et al. who used bulk polarization to study the corrosion behavior of friction stir welded AM50 magnesium alloy in 3.5 wt.% NaCl solutions, also showed lower corrosion rates present in the stir zone as compared to the rest of the sample [187]. In the same study, the authors also used microcapillary polarization to measure the individual electrochemical response of various weld regions. Surprisingly, in their investigation the corrosion potential of the TMAZ
was shown to be more noble as compared to the corrosion potential measured in the stir zone. The discrepancy between the results in this work and those reported by Zeng et al. was likely caused by the improper identification of the various weld regions present in complete joints. In the case of the FSW joints made in AM50, microcapillary polarization of the TMAZ was carried out on the top surface of the joint near the outer edge of the shoulder. Unfortunately, this classification is inaccurate as the material in that location came in direct contact with the shoulder of the welding tool which induced dynamic recrystallization leading to a SZ microstructure. The accuracy of the microcapillary polarization results produced by Zeng et al. is also subject to criticism as there was a poor agreement between the results produced by microcapillary and bulk polarization when the electrochemical properties of the BM and SZ regions were compared [187].

Dwell time had no significant effect on the electrochemical response of the stir zone and the TMAZ for a tool rotational speed of 3000 rev min⁻¹. In both cases it is believed that the microstructural evolution in the SZ was responsible for its ennoblement. The main effect of the dwell time on the corrosion behaviour of the weld is in the generation of a greater noble area, as it has been demonstrated that increased dwell times resulted in a larger stir zone. A larger stir zone will cause an increased corrosion attack due to the greater cathode/ anode area ratio in the galvanic cell.

7.5 Seam welds

The potentiodynamic polarization behaviour of the SZ and the TMAZ regions in spot versus seam welds are compared in Figure 7-7 (note that welds made using a dwell time of 4 sec are used as a baseline for spot welds). Individual polarization runs obtained for FSW joints are given in Appendix I. A summary of the electrochemical properties obtained for each weld region is given in Table 7-2. It is evident from in Figure 7-7 that the SZ region in seam welds was noble to the adjacent TMAZ region. A comparison between the polarization response obtained for spot and seam welds revealed that no significant difference existed in the corrosion behavior between the two types of weldments.
Both processes resulted in the formation of a noble SZ region that will form a macrogalvanic cell of \(-55\) mV with the active TMAZ and the base metal. It is likely that ennoblement of the SZ region in both cases occurred through a similar mechanism.

![Microcapillary Polarization of the SZ and TMAZ](image)

**Figure 7-7** Microcapillary polarization of the SZ and TMAZ in FSW and FSSW made with a rotational speed of 3000 rev min\(^{-1}\) and a dwell time of 4 sec.

In both cases, the increased corrosion potential in the stir zone compared to the TMAZ and the BM regions was attributed to the microstructural transformations occurring during the welding process. The individual effect of changes in each of the microstructural features affected by the welding process will be explored in subsequent chapters of this thesis.
Table 7-2 Summary of corrosion current and potentials found in seam, and spot welds. The values for the spot weld correspond to a joint made with a rotational speed of 3000 rev min\(^{-1}\) and 4 sec dwell time. Individual polarization curves can be found in Appendices H and I.

### 7.6 Summary

The present investigation examined the corrosion behaviour of friction stir welded AZ31B-H24 using WC tracer testing and microcapillary polarization. A number of conclusions are drawn as detailed below:

1. The use of tungsten carbide as a tracer successfully revealed the shape, location and effect of dwell time on the stir zone in FSSW made in the AZ31B magnesium alloy.

2. The stir zone was found to be noble to both the TMAZ and the base metal due to microstructural evolution occurring during the welding process.

3. Dwell time has shown to have little effect on the corrosion potential and current of the stir zone and TMAZ at a rotation speed of 3000 rev min\(^{-1}\).

4. Friction stir welding had a similar effect of the corrosion potential and corrosion current density of AZ31 in both spot and seam weld configuration. In both cases, the corrosion resistance properties of the SZ region were superior to those exhibited by the TMAZ and BM regions.

5. Localized attack of the TMAZ was a result of the macrogalvanic cell that was formed between the SZ and the TMAZ/BM and its proximity to the noble SZ.
Chapter 8 Effect of Grain Size and Residual Stress on the Corrosion Resistance of Friction Stir Spot Welded AZ31B

This work was published in Materials and Corrosion in 2014 and reproduced with permission. “Savguira, Y., North, T. H., and Thorpe, S. J. “Effect of grain size and residual stress on the corrosion resistance of friction stir spot welded AZ31B joints,” Materials and Corrosion 67 (10), 1068-1074, 2014.”

8.1 Introduction

The electrochemical properties of various weld regions in friction stir spot welded AZ31B have been explored in the previous chapter. The results determined that the SZ region exhibited corrosion resistance properties that were superior to those exhibited by either the TMAZ or the BM regions as evidenced by the ennoblement of the corrosion potential and a lower corrosion current density. The electrochemical properties of the TMAZ and the BM regions were insignificantly different from each other. The presence of a galvanic couple between the noble SZ region and the active TMAZ was determined to be the leading mechanism causing accelerated pitting attack at the interface between the two regions. It was proposed that the ennoblement of the SZ region occurred due to the microstructural transformation induced by welding.

The present chapter aims to begin to examine what microstructural changes in the SZ region could lead to the observed changes in electrochemical behaviour, specifically the role of grain size and residual stress/strain in this ennoblement mechanism. The first objective focuses on the development of a heat treatment procedure that can relieve the residual stress without inducing grain growth in the material. The electrochemical properties of as-welded and stress relieved joints are then compared to assess the effect of residual stress on the corrosion resistance of the weld. Finally, the
effect of grain size is evaluated by cross comparing the electrochemical properties of weld regions with different grain size.

8.2 Microstructure in As-Welded Joints

Optical micrographs (obtained using the experimental procedure detailed in Section 6.3.2.1) of an as-welded joint made in AZ31B-H24 sheet are shown in Figure 8-1. The grain size was determined in accordance with the methodology outlined in Section 6.3.2.2. The base metal comprised a mix of fine and coarse grained α-Mg (2.3-4.5 µm) and evidence of deformation twinning. Similar observations have been reported by other investigators [30, 108, 221, 222]. The stir zone was comprised of fine, dynamically recrystallized grains having an average grain size of 5.1 ± 0.6 µm in close agreement with previous observations by Chowdhury et al. (their average grain size was 5.4 ± 2.2 µm in friction stir processed AZ31 [222]). The recrystallized grains in the TMAZ had an average grain size of 7.6 ± 1.6 µm and were larger than those in the SZ and BM regions. Equiaxed grains formed as a result of partial recrystallization in the HAZ region had an average grain size of 3.0 ± 0.4 µm. Partially recrystallized grains were formed due to energy dissipation into the adjoining sheet during the welding operation. Finally, the average grain size in the HAZ region was only marginally larger than in the base metal.
Vickers microhardness measurements were made across sample cross-sections to examine the microstructural changes produced during the welding operation. The complete experimental procedure is provided in Section 6.3.3. These microhardness measurements were obtained by traversing from the keyhole periphery into the base metal at a distance of 700 µm below the shoulder penetration surface as shown in Figure 8-2. Each microhardness profile comprised 35 individual measurements and all indentations were spaced to avoid the effect of strain fields produced by adjacent indentations.
Chapter 8: Effect of Grain Size and Residual Stress on the Corrosion Resistance of Friction Stir Spot Welded AZ31B

Figure 8-2 Cross-sectional schematic of a FSSW joint indicating the locations used for microcapillary polarization testing. A—bottom of pin hole surface, B—key hole periphery, C—shoulder penetration surface, D—welding flash, E—welding hook, and F—mating surface of two sheets.

Figure 8-3 shows the average microhardness profile produced when traversing a joint in the as-welded condition (3000 rev min$^{-1}$ and 1 sec dwell). The average was computed from three independent hardness profiles that were obtained from different welded samples, and the error bars indicate one standard deviation. The hardness profile in Figure 8-3 is similar to that found previously by Chowdhury et al. in [222]. The microhardness in the SZ region was lower than that of an as-received AZ31B due to dynamic recrystallization and the changes in phase composition that occurred during the FSSW welding operation (60 HV versus 71 HV).

The HAZ region extended from 2 to 11 mm from the keyhole periphery as shown in Figure 8-3. Lower microhardness values were measured in the HAZ region due to partial recrystallization and grain growth during the joining operation. The microhardness of the HAZ region gradually increased with distance from the keyhole periphery, from 58HV to 71HV at the outer edge of the HAZ. The lowest microhardness values in the HAZ region were found at the TMAZ/HAZ boundary, since this particular location was subjected to the highest temperatures within the HAZ region.
Chapter 8: Effect of Grain Size and Residual Stress on the Corrosion Resistance of Friction Stir Spot Welded AZ31B

The hardness in the TMAZ is determined by a combination of mechanical deformation and thermal energy input during joining. The former increases the dislocation density in the material and promotes increased hardness; the latter induces partial recrystallization, which promotes softening. The highest microhardness values in the TMAZ region were found close to the SZ/TMAZ boundary as shown in Figure 8-3. The highest hardness occurred at this location, since material immediately adjacent to the stir zone boundary was subjected to a combination of through-thickness, radial and circumferential compressive deformation. Shibayanagi et al. have already confirmed that material located within 500 microns of the stir zone boundary experiences this mode of deformation during the FSSW welding operation [178].

![Figure 8-3 Average microhardness profile measured across a FSSW joint made in AZ31B using a tool rotational speed of 3000 rev min$^{-1}$ and 1 sec dwell. The profile was obtained for a line located 700 µm below the shoulder penetration surface.](image-url)
8.3 Stress Relieving Heat-Treatment

To examine the effect of residual stress on the corrosion of FSSW joints made in AZ31B, welded specimens were subjected to stress relieving heat-treatments. A heat-treatment that promotes recovery without recrystallization and/or grain coarsening is required to isolate the influence of the residual stress on the corrosion behaviour of the joint. Such heat-treatment conditions can be determined using the experimental approach described by Malheiros et al. [223]. Their investigation examined the changes in microhardness values when test samples were given different annealing heat-treatments. When the heat-treatment temperature increased, a regime that promoted recovery without recrystallization and/or grain coarsening, together with a small reduction in microhardness values could be observed. However, when higher annealing temperatures were applied, recrystallization, precipitation or coarsening occurred leading to significant changes in measured microhardness values.

In the present study, changes in the microhardness of AZ31 joints were determined following heat-treatments for 30 minutes at temperatures ranging between 373K and 523K. It is worth noting that since AZ31B-H24 sheet is a hot-rolled sheet alloy, dissolution of $\beta$-Mg$_{17}$Al$_{12}$ particles occurs during the rolling process and the $\alpha$-Mg matrix has a higher aluminum concentration than that indicated in the Mg-Al phase diagram. Consequently, a heat-treatment cycle, which induces recovery without recrystallization, avoids grain growth and precipitation of second-phase particles, can produce samples that allow a direct comparison of the corrosion resistance properties of as-welded and stress-relieved AZ31B joints. Heat-treated joints in this study were designated with the prefix HT followed by its heat-treatment temperature in kelvin. For example, samples heat-treated at 373K are referred to as HT373.

Figure 8-4 shows the effect of heat-treatment temperature on the microhardness values in different regions in AZ31 friction stir spot welds. To ensure that a direct comparison for each weld region
can be made between as-welded and heat-treated joints, it was important to select regions that can be repeatedly identified. The microhardness values for both the stir zone and base metal were relatively constant and the average hardness measurements in the region were plotted in Figure 8-4. The hardness values measured in the TMAZ region showed variation and so only the highest hardness values in the TMAZ region were indicated in Figure 8-4. Also, the HAZ microhardness values were steadily increasing as the location of the measurement was situated closer to the base metal. To allow a direct comparison only the hardness values measured in the region immediately adjacent to the TMAZ/HAZ boundary were recorded in Figure 8-4.

![Figure 8-4](image)

Figure 8-4 The effect of annealing temperature on the microhardness of various weld regions in FSSW joints made in AZ31

It is apparent from Figure 8-4 that heat-treatment at 373K produced a small decrease in microhardness in the TMAZ and BM regions, due to recovery and stress relaxation. However, the microhardness of the SZ and HAZ regions were unchanged. When the heat-treatment temperature increased to 473 K, higher microhardness values were observed due to the precipitation of second-
Chapter 8: Effect of Grain Size and Residual Stress on the Corrosion Resistance of Friction Stir Spot Welded AZ31B

phase $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ particles. Increasing the heat-treatment temperature above 473 K markedly decreased microhardness values as a result of grain and precipitate coarsening.

The results in Figure 8-4 imply that heat-treatment at 373K for 30 minutes induces recovery without recrystallization in the different regions in AZ31B joints. The influence of heat-treatment on average grain size was investigated in order to provide support for this proposal. Table 8-1 compares the average grain size values in different weld regions in as-welded and heat-treated joints. The SZ, TMAZ and HAZ regions in both as-welded and heat-treated joints exhibited a recrystallized microstructure arising from the thermomechanical input of the welding operation. The grains present in these regions were equiaxed and their grain size is reported as an average calculated from the line intercept method. The error measurement represents one standard deviation. In direct contrast, the base metal exhibited a highly textured structured comprising a mix of fine and coarse grains produced by the welding process, as a result the grain size of this region was reported as a range. It is evident that negligible grain growth occurred when test samples were heat-treated at 373K for 30 minutes for all of the weld zones examined.

<table>
<thead>
<tr>
<th>Region</th>
<th>As-welded</th>
<th>HT373</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>2.3-4.5 µm</td>
<td>2.4-4.7 µm</td>
</tr>
<tr>
<td>HAZ</td>
<td>3.0 ± 0.4 µm</td>
<td>3.2 ± 0.4 µm</td>
</tr>
<tr>
<td>TMAZ</td>
<td>7.6 ± 1.6 µm</td>
<td>7.9 ± 1.6 µm</td>
</tr>
<tr>
<td>SZ</td>
<td>5.1 ± 0.6 µm</td>
<td>4.8 ± 0.6 µm</td>
</tr>
</tbody>
</table>

Table 8-1 Average grain size of various weld regions; in as-welded joints and heat-treated (at 373K) samples (HT373)
8.4 Electrochemical Characterization

The electrochemical behaviour of individual regions (SZ, TMAZ and HAZ) in completed joints were analyzed using microcapillary polarization (Section 6.4.4.3). Individual microcapillary polarization scans were obtained for all weld regions (SZ, TMAZ and HAZ) and the base metal (repeatability of the experimental results is shown in Appendices H and J). Each weld region was measured on at least three different samples to ensure reproducibility. The locations for the polarization measurements were determined from microhardness traverses made across the weld samples. In all cases, the SZ region was located immediately adjacent to the keyhole, while the TMAZ region was adjacent to the stir zone boundary as illustrated schematically in Figure 8-2. The HAZ region was adjacent to the TMAZ boundary and when the base metal was examined, this was carried out at a distance of 1.1 cm away from the joint centerline as determined by microhardness values (see Figure 8-3). The polarization output describing the influence of grain size and residual stress on the corrosion properties of different regions in AZ31B joints is shown in Figure 8-5 (the reproducibility of the measurements for samples in the as-welded and heat-treated conditions is shown in Appendices H and J respectively).
Figure 8-5 Microcapillary polarization curves obtained for (a) stir zone, (b) TMAZ, (c) HAZ, and (d) base metal regions in as-welded (AW) and heat-treated (373K) joints.

The polarization curves for both as-welded and heat-treated joints revealed similar trends. The SZ region was found to be noble with respect to the more active TMAZ, HAZ and BM regions. The noble behaviour of the stir zone as compared to the other weld regions is similar to that reported in Chapter 7. It is important to note that the electrochemical behaviour of the various weld regions did not change as a result of the stress relieving heat-treatment. As such it can be concluded that residual stress did not play a significant role in the corrosion behaviour of friction stir welds made in AZ31B-H24 sheet. The electrochemical characteristics of individual regions in as-welded and heat-treated
joints were evaluated using Tafel extrapolation to estimate the corrosion potential and corrosion current densities associated with different regions. Three measurements were performed on different specimens for each weld region, and the average values and the standard deviations were calculated. Table 8-2 compares the electrochemical characteristics for the various regions in as-welded and heat-treated samples.

<table>
<thead>
<tr>
<th>Region</th>
<th>E_{corr} (V_{SCE} ± mV)</th>
<th>i_{corr} (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-welded</td>
<td>HT373</td>
</tr>
<tr>
<td>SZ</td>
<td>-1.406 ± 4</td>
<td>-1.411 ± 6</td>
</tr>
<tr>
<td>TMAZ</td>
<td>-1.463 ± 9</td>
<td>-1.468 ± 4</td>
</tr>
<tr>
<td>HAZ</td>
<td>-1.468 ± 2</td>
<td>-1.470 ± 5</td>
</tr>
<tr>
<td>BM</td>
<td>-1.468 ± 5</td>
<td>-1.469 ± 2</td>
</tr>
</tbody>
</table>

Table 8-2 Corrosion potentials and currents of various weld regions in as-welded and HT373 joints

The corrosion potentials and corrosion current densities of individual regions were not significantly different between as-welded and HT373 joints, providing support for the conclusion that residual stress did not affect corrosion resistance properties. These findings contradict those reported Aghion et al., who suggested that introduction of internal stresses into AZ80 resulted in a reduction in its corrosion resistance [109]. Two possible explanations could be responsible for the above discrepancy. In Aghion’s study the extrusion process used to introduce the residual stress into the material also increased the iron impurity content in the metal (from 0.0019 wt.% to 0.0271 wt.%), and the effect of each of these factors on the corrosion resistance of AZ80 was not evaluated individually [109]. As discussed in Section 3.2.1.4, iron can significantly reduce the corrosion resistance of magnesium alloys when it is present in concentrations that exceed its tolerance limit in the system (0.006 wt.% Fe in AZ80) [43]. The iron content in the alloy following extrusion was greater than the tolerance level, and therefore its corrosion resistance decreased. Since the individual
effect of changes in residual stress and iron content was not examined, it is possible that the observed variation in the corrosion resistance of AZ80 was related only to the compositional variation. In the present study, changes in residual stress were induced through a heat treatment cycle that relieved the residual stress without inducing any additional microstructural or compositional changes, thus allowing the investigation of only the effect of residual stress on corrosion. The present findings provide additional insight into Aghion’s investigation by elucidating the role of residual stress in the corrosion of magnesium alloys. It is most likely that the reduction in the corrosion resistance of AZ80 was caused by the iron impurities that were introduced into the system and not by residual stress. The above discussion ignores the effect of the magnitude of the residual stress on the corrosion behaviour of the alloy. The present study has shown that the magnitude of the residual stress induced by the welding operation was not sufficiently high enough to cause measurable changes in the electrochemical properties of AZ31. It is possible that the residual stress in Aghion’s investigation was much higher than the magnitude of the residual stress in the present investigation, which lead to a more pronounced effect on the corrosion resistance of the alloy. The residual stress in the present investigation was not quantified and so direct comparisons with literature are not possible. Quantification of the residual stress in the TMAZ is challenging due to the relatively small size (~300 µm in width).

The electrochemical characteristics of the TMAZ, HAZ and BM regions were not statistically different despite having different average grain sizes. For example, although the TMAZ had a grain size twice as great as that in the HAZ and in the BM, the electrochemical properties were not significantly different. The results herein indicated that grain size did not affect the corrosion resistance of the AZ31B alloy. Before this conclusion can be drawn, it is important to ensure that the effect of grain size was isolated, and that the analysis was independent from contributions caused by changes in second phase precipitates (see discussion in Section 3.2.3.1). To address this, the area fractions of second phase particles in the TMAZ and BM regions were compared. The area fractions
were measured by analyzing SEM micrographs, as described in Section 6.5.3.1. The area fraction of $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ particles was not statistically different between the TMAZ (0.09%±0.02%) and the BM (0.10%±0.02%) regions. Some variation in the area fraction of Al-Mn intermetallics existed between the two regions (TMAZ: 0.44%±0.02%, BM:0.68%±0.08%), but this variation was not significant enough to produce measurable changes in the electrochemical properties of the alloy. It follows that the effect of grain size was successfully isolated in the present study, and conclusions regarding its effect on the corrosion resistance of magnesium could be drawn. Based on the experimental evidence it is concluded that grain size does not affect the corrosion resistance of AZ31B within the range of grain sizes examined in this investigation. This conclusion is in agreement with previous observations made by *Kish et al.* who suggested that no significant correlation existed between grain size and electrochemical kinetics of AZ31 in a sodium chloride environment (see Section 3.2.3.1 for complete discussion) [108].

To expand the comparison between the results presented herein and those reported in literature, a plot correlating the corrosion current density of AZ31B to its grain size was prepared (Figure 8-6). The plot was produced by plotting the electrochemical properties summarized in Table 3-6 and Table 8-2 versus the respective grain size of the specimen. It is evident from the figure that the literature data spans several orders of magnitude of grain sizes, necessitating the use of a log scale on the x-axis. The log scale representation was chosen to enhance clarity, and not on the basis that a logarithmic and/or semilogarithmic relationship was expected to exist between the two variables. Finally, it is important to note that the corrosion current density was plotted against the grain size and not versus the reciprocal of the square root of the grain size as suggested by *Ralston et al.*, as the model proposed in their publication stipulates that if a relationship was to exist it would occur in passivating materials that exhibit corrosion current densities that are lower than 10 $\mu$A/cm$^2$[224]. Most of the published work that focuses on the corrosion behavior of magnesium alloys has been carried out in 0.6M NaCl, in this environment magnesium is not passive and its corrosion current
density greatly exceeds the 10 µA/cm² that was specified in the model. On this basis it was determined that the model proposed by Ralston et al. did not apply in the present case [224]. To the best of the authors knowledge, there are no published mathematical models correlating between grain size and the corrosion rate of magnesium. As such, the electrochemical properties of the alloy were plotted directly against the grain size.

The correlation between the corrosion current density of AZ31B and its grain size is shown in Figure 8-6. Attempts to fit the points plotted in Figure 8-6 as a single data set did not produce a statistically meaningful correlation. The corrosion rates measured in this study were significantly lower than the literature values in Figure 8-6. This difference was related to the electrolyte chemistry that was used to assess the corrosion resistance of specimens. The specimens in the present study were tested in 0.1M NaClO₄, which is significantly less aggressive than the 0.6M NaCl was used in the other studies (see Section 6.4.4.2 for the discussion of electrolyte selection). The trends in the data plotted in Figure 8-6 were different as well. Aung et al. and Jang et al. reported that the corrosion current density of the AZ31B increased with increasing grain size [106, 107]; however as already discussed in Section 3.2.3.1, this dependence was likely related to changes in size and distribution of second phase intermetallics and not to the grain size itself. The present study successfully isolated the effect of grain size from the effect of other microstructural features, and as result a different trend was observed. Overall, it is evident that changes (on the scale examined herein) in both residual stress and grain size caused by the welding operation did not influence the corrosion behaviour of the various weld regions.
Figure 8-6 Effect of grain size on the corrosion current density of AZ31B. The plot presents a comparison between the work reported herein and that reported in literature [106-108].

The results in the present study contradict those suggesting that the noble behaviour of the stir zone was attributed to grain size reduction [8, 194]. The above discrepancy exists as the authors of these investigations did not separate the effect of grain size reduction from the effect of changes in size and distribution of second phase precipitates. In both studies, the relation between grain size and the corrosion resistance of the weld was provided as a hypothesis and a mechanistic model explaining the phenomena was missing. The present study refutes this hypothesis, by demonstrating that changes in grain size did not influence the corrosion resistance of the joint.

In order to estimate the corrosion rate accurately via Tafel extrapolation, at least one branch of the polarization curve should exhibit Tafel behaviour over a decade of current; see Bland et al. [209].
One of the challenges associated with microcapillary polarization involves capillary clogging by gas evolution on the surface of the working electrode. This is particularly true when examining magnesium alloys that evolve hydrogen on either branch of the polarization curve. A wider scanning range means that more gas can accumulate and clog the capillary. As a result, the present investigation examined only a narrow window of potentials near $E_{\text{corr}}$. Although the measurements obtained from microcapillary polarization span a relatively short range of currents, the data obtained from the tests can still yield reasonable estimates of the corrosion potential and corrosion current density, as previously shown by comparing microcapillary polarization output to that produced by polarizing bulk specimens (see Section 7.3).

### 8.5 Summary

The present chapter evaluated the influence of microstructural evolution caused by the welding operation on the corrosion resistance of a completed joint, and in particular the role of variations in grain size and residual stress on the electrochemical properties of the joint in order to provide insight into the ennoblement of the SZ relative to the TMAZ, HAZ and BM regions. Microcapillary polarization of stress relieved (heat-treated) and as-welded joins indicated that changes in residual stress did not significantly influence the electrochemical behaviour of AZ31B joints. Comparison of different weld regions showed no correlation between the grain size and the electrochemical characteristics within the range of grain sizes examined. It can be concluded that the microstructural variations in grain size and residual stress on the scale caused by the welding operation did not alter the corrosion resistance of FSSW joints.
Chapter 9 Effect of Grain Orientation on the Corrosion Resistance of FSSW Joints Made in AZ31B

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9.1 Introduction

The macrogalvanic couple formed between the noble SZ and the active BM has been identified as the cause for localized pitting observed within the TMAZ region (see Chapter 7). The cause for the ennoblement of the SZ was hypothesized to be related to the microstructural evolution that occurred during the welding process. Chapter 8 assessed the effects of grain size and residual stress on the corrosion resistance of the joint and concluded that the changes in grain size and residual stress produced by the welding process were not sufficiently large to cause a variation in the electrochemical properties of the SZ. As discussed in Section 4.3.2, friction stir welding has been shown to alter the grain orientation of the BM. To date, the variation in electrochemical activity arising from changes in grain orientation upon FSSW has not been examined and could be another important factor in the ennoblement observed in the SZ. The objective of this chapter is to quantify the effect of grain orientation on the corrosion behaviour of a FSSW joint.

The corrosion resistance of unwelded magnesium and its alloys has been shown to drastically vary as a result of grain orientation [37, 112, 113]. As mentioned in Section 3.2.3.3, Song et al. have shown that the theoretical dissolution rate of the basal closed packed planes is almost twenty times lower than on other planes [113]. The variation in the electrochemical activity of different crystallographic planes was correlated to their surface energy. Experimentally, it has been reported that the rolling surface of AZ31 exhibited a strong basal texture and lower corrosion rates than those
found for the cross-sectional surfaces containing primarily prismatic planes (see Table 3-7 for summary of experimental findings) [37, 112, 113]. Consequently, if the grains in the SZ are reoriented away from the basal texture, such reorientation would alter the electrochemical properties of the stir zone and ultimately would affect the magnitude of the galvanic couple between the SZ and BM regions.

The aim of this chapter is to validate this proposition, as well as to examine the individual influence of changes in grain orientation on the overall electrochemical characteristics of the stir zone. The present investigation deconvolutes the effects of grain orientation from other microstructural changes that occur during the welding process through the use of microcapillary polarization (experimental procedure in Section 6.4.4.3) in conjunction with EBSD (experimental procedure in Section 6.3.4). The grain orientation and electrochemical properties of the SZ and BM regions were examined on both the rolling and cross-sectional surfaces as shown schematically in Figure 6-13.

Figure 9-1 Cross-sectional schematic of a FSSW joint indicating the locations examined in this investigation. This figure originally appeared as Figure 6-13 and has been included again for clarity.
9.2 Microstructural and Electrochemical Characterization

Figure 9-2 shows the inverse pole figure maps obtained for the SZ and BM regions in both RS and CS orientations. The colors in Figure 9-2 correspond to the stereographic triangle in the center of the figure. The BM-RS region exhibited a strong basal (0001) texture, indicating that the c-axes of the grain was normal to the surface of the metal sheet. Such strong texturing was produced by the rolling process and has been previously observed in literature [37, 112, 113]. The texture in the SZ-RS region was different, as the grains experienced a rotation of about 20°-40° rotation from their original (0001) basal orientation towards the prismatic (1210) and (0110) orientation as shown in Figure 9-3. Such a change in grain orientation was caused by the intense compressive and shear deformation that occurred during the welding operation, which is in agreement with previously reported observations [176, 177].

Figure 9-2 Inverse pole figure maps obtained from the SZ and BM regions on the rolling and cross-sectional surfaces. Grain size distribution from examined areas is included as well.
Chapter 9: Effect of Grain Orientation on the Corrosion Resistance of FSSW Joints Made in AZ31B

The BM-CS region consisted primarily of grains in the $(\overline{1}2\overline{1}0)$ and $(01\overline{1}0)$ orientation (Figure 9-2). Although the BM-CS region contained grains of both prismatic orientations, grains exhibited a $(\overline{1}2\overline{1}0)$ preferential orientation (Figure 9-3). Such a preferential orientation was not observed in the SZ-CS region, as both the $(\overline{1}2\overline{1}0)$ and the $(01\overline{1}0)$ orientations were equally present. It is interesting to note that even though the texture in the BM-CS and the SZ-CS regions varied, it is unlikely that this difference would influence the electrochemical properties of these regions, as the $(\overline{1}2\overline{1}0)$ and the $(01\overline{1}0)$ planes were shown to have very similar surface energies [113]. The variation in the electrochemical properties measured for BM-CS and SZ-CS regions can therefore be attributed to microstructural changes independent from grain orientation, while the variation between BM-RS and SZ-RS was also influenced by grain orientation. In this manner, the individual effect of grain reorientation can be examined.

**Figure 9-3 Inverse pole figure plots for SZ and BM regions on the rolling and cross-sectional surfaces.**

Figure 9-4 shows the normalized grain size distribution obtained from EBSD measurements for both RS and CS surfaces of the BM and SZ regions. It can be seen that the grain size distributions on the rolling and cross-sectional surfaces of the base metal had no statistical difference (Figure 9-4 (a)).
In direct contrast, the grain size distributions in the SZ regions of the two surfaces examined in this investigation were different. The grains on the rolling surface were congregated around a single value, while the grains on the cross-sectional surface exhibited a bimodal distribution (Figure 9-4 (b)). It is important to note that even though an apparent difference in the grain size distribution was present, its effect on the electrochemical properties on the SZ is expected to be minimal (see Chapter 8).

Figure 9-4 Grain size distribution of (a) BM, and (b) SZ regions obtained from EBSD measurements.

To examine the influence of grain orientation on the electrochemical properties of the SZ region, it must be first adequately isolated so that the output produced during electrochemical testing reflects the corrosion resistance properties of the SZ alone and with no contribution from the TMAZ. The
results in Chapter 8 have shown that the width of SZ produced using a rotational speed of 3000 rev min\(^{-1}\) and 1 sec of dwell time is approximately 800 µm on either side of the keyhole. The relatively small dimensions of the weld region, and the absence of a clearly visible boundary between different weld regions hinder the use of selective masking and/or physical extraction to isolate the SZ region. Challenges associated with electrochemical testing of small features can be addressed with the use of microcapillary polarization technique capable of conducting common electrochemical experiments on areas on the micron scale.

![Figure 9-5 Influence of grain orientation on the output of microcapillary polarization testing obtained for (a) base metal and, (b) stir zone regions in FSSW joints. For comparison purposes plots showing the effect of friction stir welding on the electrochemical properties of AZ31B on the (c) rolling and the (d) cross-sectional surfaces were included as well.](image-url)
The polarization output produced for the SZ and BM regions is compared in Figure 9-5 (repeatability of the experimental results is shown in Appendices G and H). The electrochemical characteristics of each individual testing spot were evaluated using Tafel extrapolation to estimate the corrosion potential and corrosion current density associated with its microstructure. Table 9-1 compares the electrochemical characteristics of the BM (Figure 9-5 (a)) and SZ (Figure 9-5 (b)) regions on both the rolling and cross-sectional surfaces. The validity of the experimental approach was further confirmed by comparing the corrosion potential and current measured from microcapillary polarization with those measured from polarization of bulk base metal specimens (see experimental procedure in Section 6.4.3.1). The corrosion potential and current measured from bulk base metal specimens in the RS (\(E_{\text{corr}} = -1.401 \pm 7 \text{V}_{\text{SCE}}, \ i_{\text{corr}} = 8 \mu\text{A/cm}^2\)) and CS (\(E_{\text{corr}} = -1.468 \pm 4 \text{V}_{\text{SCE}}, \ i_{\text{corr}} = 10 \mu\text{A/cm}^2\)) orientation were similar to those obtained from microcapillary polarization.

<table>
<thead>
<tr>
<th>Region</th>
<th>(E_{\text{corr}} (\text{V}_{\text{SCE}} \pm \text{mV}))</th>
<th>(i_{\text{corr}} (\mu\text{A/cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RS</td>
<td>CS</td>
</tr>
<tr>
<td>SZ</td>
<td>-1.359 ± 2</td>
<td>-1.406 ± 4</td>
</tr>
<tr>
<td>BM</td>
<td>-1.402 ± 7</td>
<td>-1.468 ± 5</td>
</tr>
</tbody>
</table>

Table 9-1 Influence of grain orientation on the corrosion potentials and currents of the SZ and BM regions

For both surfaces examined in this investigation, the stir zone exhibited a more noble corrosion potential and a lower current density than the base metal on the same surface (Figure 9-5 (c and d)). The RS had better corrosion resistance properties than the CS for both regions examined in this investigation, in agreement with the results summarized in Section 3.2.3.3. The enhanced performance of the RS was attributed to the preferential basal orientation of the grains that had a higher activation energy for dissolution due to its densely packed structure [113]. The difference between the RS and CS was not the same for the BM and SZ regions. The corrosion potential of BM-RS increased by 67 mV, while its corrosion current density was reduced by 21%. Meanwhile
the corrosion potential of SZ-RS increased by 52 mV, while its corrosion current density was reduced by only 15%. The reduced increment in the corrosion resistance properties of the SZ was attributed to weaker basal texturing arising from the rotation of the grains. If the welds were to be implemented in an industrial application then the top surface of the joint would be exposed to corrosive media and not the cross-sectional surface as previously examined in chapters 7 and 8. As such, the influence of grain orientation should be considered and it is likely that the true galvanic couple governing the corrosion behaviour of the joint is smaller than what was estimated from studies done on the cross-sectional surfaces.

The results discussed in this chapter were compared with existing literature to further elucidate the effect of grain orientation on the corrosion resistance properties of AZ31B base metal. Where applicable, the corrosion rate determined through mass loss testing was converted to equivalent corrosion current density using the expression in equation (9.1):

\[
i_{\text{corr}} \left[ \frac{\mu A}{cm^2} \right] = \frac{CR_{\text{AW}} \left[ \frac{g}{cm^2 \cdot hr} \right] \cdot \frac{1}{3600 \frac{hr}{sec}} \cdot n \cdot F \left[ \frac{C}{mol} \right]}{M \left[ \frac{g}{mol} \right]} \cdot 10^6 \frac{\mu A}{A}
\]

(9.1)

where \( CR_{\text{AW}} \) is the corrosion rate obtained from mass loss testing as defined by equation (6.1), \( n \) is the number of electrons transferred (\( n = 2 \) as per equation (3.1)), \( F \) is Faraday’s constant (96,500 C/mol), and \( M \) is the molar mass (\( M_{\text{Mg}} = 24.305 \ g/mol \)) [225]. The corrosion rates reported in the present investigation cannot be compared directly to those reported in other studies due to differences in the corrosive environment in which they were obtained. Microcapillary polarization experiments yielded much lower corrosion rates as they were carried out in 0.1M NaClO₄, an electrolyte that is significantly less corrosive than the 0.6M NaCl or 0.86M NaCl that was used by
others [112, 113]. To draw a meaningful connection to literature, the analysis should be based on relative changes in the corrosion current density and not by comparison of absolute values. The ratio between the corrosion current density of the cross-sectional and rolling surfaces ($\frac{i_{corrBM-CS}}{i_{corrBM-RS}}$) was computed and compared to the results of others.

The corrosion rates associated with basal and prismatic planes were compared and plotted in Figure 9-6. In all cases the close packed basal planes exhibited lower corrosion rates than the prismatic planes. The results reported in the present investigation ($\frac{i_{corrBM-CS}}{i_{corrBM-RS}} = 1.23$) were close to those reported by Xin et al. ($\frac{i_{corrBM-CS}}{i_{corrBM-RS}} = 1.95$) [112]. Song et al. reported a much greater difference between the corrosion rates of CS and RS ($\frac{i_{corrBM-CS}}{i_{corrBM-RS}} = 10.11$) [113]. A possible explanation for such a large discrepancy could be related to experimental procedure used by Song et al. [113]. In their study, the equilibration period prior to testing was significantly shorter (5 minutes) than the equilibration periods used by Xin et al. and the work herein (≥ 30 minutes) [112, 113]. It is likely that the corrosion rates measured by Song et al. were collected under non-equilibrium conditions and therefore differ from the exposure conditions used [113]. It is also worth noting that in a follow up study by the same investigators, the effect of grain orientation was examined by comparing the polarization resistance (obtained through electrochemical impedance spectroscopy) for the two surfaces [37]. If the Tafel slopes of the cross-sectional and rolling surfaces are considered to be similar, then the ratio between the current corrosion current densities will be inversely proportional to the ratio of the respective polarization resistances, see expression 9.2. In Song’s follow up manuscript the ratio between the polarization resistances ($\frac{R_{PBMS-RS}}{R_{PBMS-CS}} = 1.53$), which is much closer to the 1.23 that was reported herein [37].

$$\frac{i_{corrBM-CS}}{i_{corrBM-RS}} = \frac{R_{PBMS-RS}}{R_{PBMS-CS}}$$  \hspace{1cm} (9.2)
Figure 9-6 Effect of grain orientation on the corrosion resistance of AZ31B base metal. The figure compares the data from this chapter to that published elsewhere [112, 113]

By combining the data presented in this chapter with the data in Chapter 7 and 8, another step can be made towards elucidating the mechanism causing the ennoblement of the SZ region. In chapter 8, grain size and residual stress variation were shown to have a negligible effect on the electrochemical properties of the SZ region. The work presented in this chapter showed only minor changes were obtained in the corrosion rate (~15%) with changes in grain orientation. The changes in size and distribution of second phase precipitates remain the only microstructural feature whose effect on the corrosion properties of FSSW joints has yet to be examined. Detailed analysis of the effect of second phase particle dissolution on the corrosion of friction stir spot welded AZ31B is presented in the next chapter (Chapter 10).
9.3 Summary

The corrosion resistance of AZ31B has been shown to depend on the crystallographic orientation of its grains. Surfaces with a strong basal texture exhibited improved corrosion resistance properties due to lower surface energies associated with their close packed structure. Grain orientation was found to affect the corrosion behaviour of FSSW joints, as the grains on the top surface of the SZ region were rotated during the welding operation. As a result, it can be concluded that the galvanic couple formed between the base metal and the stir zone is actually smaller than estimated from studies conducted on the cross-sectional surface.
Chapter 10 The Effect of Second Phase Particle Dissolution on the Corrosion of Friction Stir Spot Welded AZ31B


10.1 Introduction

The studies in chapters 8 and 9 attempted to relate the microstructural evolution occurring during friction stir welding to the increased corrosion resistance of the SZ region; however, the principal microstructural feature responsible for this improvement remains unknown. Changes in grain size, grain orientation and residual stress have been shown to have a minimal influence on the electrochemical properties of the SZ region. One of the proposed causes for the ennoblement of the SZ identified in the literature review in Section 5.1.2 was changes in second phase particle type and distribution [187, 191, 192]. Based on the literature examined, it was noted that the $i_{corr}$ of the SZ region was lower than that of the BM region in all friction stir welded joints made in alloy materials [7, 8, 187, 190, 191, 193, 194]. Only in pure magnesium did the SZ region exhibit higher $i_{corr}$ values than that of the BM [189]. These observations supported the proposition that the ennoblement of the SZ was related to changes in size, type and/or distribution of second phase precipitates. It is important to note, that while this hypothesis supports the experimental findings in the literature, a direct relationship between particle dissolution kinetics and the electrochemical properties of the SZ region has yet to be established.
The present chapter aims to fill this knowledge gap by establishing a direct connection between the process parameters used when producing friction stir welded joints, the size, type and/or distribution of second phase precipitates, and their influence on the electrochemical properties of the SZ region in AZ31B FSSW joints. The influence of process parameters is evaluated through temperature measurements during the welding operation and correlated with corrosion potential and corrosion current density values from the stir zone determined using microcapillary polarization.

10.2 Effect of Process Parameters on the Thermal Cycle of the Stir Zone

Figure 10-1 (a) shows a typical temperature output produced during friction stir spot welding of AZ31 for a rotation speed of 3000 rev min\(^{-1}\) and a dwell time of 4 sec. The temperature was recorded following the experimental procedure outlined in Section 6.2.5 and the repeatability of the experimental results is shown in Appendix M. As the tool was plunged into the overlapping metal sheet assembly, the axial force rapidly increased until the end of the plunging period. The axial force then decreased during the dwell period until the tool was withdrawn from the metal. The temperature measured in the stir zone increased rapidly during the plunging period. The peak temperature was achieved shortly after the dwell period began (less than 1 sec). The peak temperature measured during the welding operation was 552°C.
Chapter 10: The Effect of Second Phase Particle Dissolution on the Corrosion of Friction Stir Spot Welded AZ31B

Figure 10-1 Tool force and temperature obtained during friction stir spot welding of AZ31B base material using (a) 3000 rev min$^{-1}$ and (b) 1000 rev min$^{-1}$. In both cases a dwell time of 4 sec was used.

A series of joints were produced using rotational speeds varying between 1000 and 3000 rev min$^{-1}$ to investigate the influence of tool rotational speed on the peak temperature attained during the welding operation. The temperature output produced during each welding condition was measured at least twice, and the average peak temperatures (obtained during the first 4 sec) are summarized in Table 10-1. The uncertainty values presented in the table represent one standard deviation.
Chapter 10: The Effect of Second Phase Particle Dissolution on the Corrosion of Friction Stir Spot Welded AZ31B

<table>
<thead>
<tr>
<th>Rotational Speed $R_s$ [rev min$^{-1}$]</th>
<th>Dwell Time $t_d$ [sec]</th>
<th>Stir Zone Peak Temperature Following 4 Sec Dwell [°C]</th>
<th>Diffusion Time $t_{diff}$ [sec]</th>
<th>Mg$<em>{17}$Al$</em>{12}$ Liquid Film Half Thickness $B_o$ [nm]</th>
<th>Al$_3$Mn$_5$ Particle Dissolution Radius $R_o$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000$^a$</td>
<td>1</td>
<td>414 ± 5</td>
<td>0</td>
<td>&lt;1$^b$</td>
<td>&lt;1</td>
</tr>
<tr>
<td>1500</td>
<td>1</td>
<td>510 ± 0</td>
<td>0.29</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>2250</td>
<td>1</td>
<td>548 ± 6</td>
<td>0.73</td>
<td>66</td>
<td>30</td>
</tr>
<tr>
<td>2250</td>
<td>2</td>
<td>548 ± 6</td>
<td>1.73</td>
<td>293</td>
<td>120</td>
</tr>
<tr>
<td>3000</td>
<td>1</td>
<td>552 ± 1</td>
<td>0.95</td>
<td>153</td>
<td>65</td>
</tr>
<tr>
<td>3000</td>
<td>4</td>
<td>552 ± 1</td>
<td>3.95</td>
<td>1,200</td>
<td>505</td>
</tr>
</tbody>
</table>

$^a$ Only one measurement was conducted using a rotational speed of 1000 rev min$^{-1}$; the peak temperature following 4 seconds of dwell and the uncertainty value associated with the measurement were determined from the results published in [166].

$^b$ Dissolution by solid state diffusion, particle radius calculated via equation (4.5).

Table 10-1 Influence of rotational speed and dwell time on dissolution of second phase particles. The uncertainty given in the table represents one standard deviation. Repeatability of the experimental results is shown in Appendix M.

The peak temperatures measured at the pin of the welding tool increased from 413.7 to 552 °C when the rotational speed increased from 1000 to 3000 rev min$^{-1}$ (see Figure 10-1 (a) and (b)). When using rotational speeds of 1500 rev min$^{-1}$ and above, the stir zone temperatures measured during the welding operation exceeded the eutectic temperature (437 °C) of the Mg-alloy. In contrast, the temperature in the stir zone did not exceed 437 °C when a rotational speed of 1000 rev min$^{-1}$ was used during the welding operation. This temperature difference was caused by the marked differences in the heating rates when different rotational speeds were used. Examination of the heating cycle in joints produced using high ($\geq$1500 rev min$^{-1}$) and low (1000 rev min$^{-1}$) rotational speeds revealed differences in the temperature profiles measured during the welding operation. High rotational speeds resulted in rapid heating of the stir zone until the temperature plateaued at its peak.
(see Figure 10-1 (a)); such a plateau was not observed in the SZ regions of joints made using low rotational speeds (Figure 10-1 (b)). Consequently, the duration of the welding operation provided insufficient time for the stir zone temperature to reach the eutectic temperature. This is further confirmed by comparing the measured peak temperatures using low rotational speed settings with the solidus or eutectic temperature for AZ31. Welds produced using the lower tool rotational speed settings did not reach the highest temperature that can be achieved during the friction stir welding operation. The highest temperature attained in the stir zones of Mg-alloy FSSW joints is ultimately limited by either the solidus temperature of the alloy or the melting temperatures of secondary intermetallic phases contained in the base metal [159, 167-169]. As mentioned in Section 4.2, Gerlich et al. suggested that the plasticized material immediately adjacent to the tool was melted when the stir zone exceeded the solidus temperature [159]. Local melting resulted in a significant decrease in material viscosity, reduced the heat generation rate, and prevented any further temperature increase. When the stir zone temperature decreased again, the liquid film solidified causing an increase in the viscosity and heat generation rate.

10.3 Intermetallic Dissolution During Friction Stir Spot Welding

Relating particle dissolution kinetics and the electrochemical properties of the SZ region requires a model that describes the dissolution kinetics of intermetallic particles during the thermal history of the SZ region. When the dissolution of second-phase particles is predicted, this output can be correlated with the electrochemical properties of the SZ region.

10.3.1 \( \beta\)-Mg\(_{17}\)Al\(_{12}\) Intermetallics

As discussed in Section 4.4.1, the dissolution of \( \beta\)-Mg\(_{17}\)Al\(_{12}\) particles occurs in two stages (solid and liquid state diffusion). Since the diffusion of Al is significantly slower in the solid state than in the liquid state, the dissolution of second phase particles during the initial stage when the temperature is ramping up can be assumed to be negligible. The dissolution process is then governed only by the
time interval of liquid state diffusion, starting from the instant the stir zone temperature exceeds 437 °C until the point when the welding operation is complete. The diffusion time ($t_{\text{diff}}$) (the time during which the dissolution of $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ particles occurs) when the temperature exceeds 437 °C can be determined from the temperature output, as shown by the example given in Figure 10-2.

![Figure 10-2](image)

**Figure 10-2** Diffusion time ($t_{\text{diff}}$) available for dissolution of $\text{Mg}_{17}\text{Al}_{12}$ during friction stir spot welding of AZ31B base material (3000 rev min$^{-1}$ and 1 sec dwell).

For all welding conditions examined in this investigation, the diffusion time was calculated from the temperature output. This diffusion time was used to estimate the half thickness ($B_o$) of a plate-shaped liquid droplet that would dissolve during the welding operation. It is important to note that before $B_o$ can be estimated, the function that describes the changes in the temperature ($T(t)$) over the diffusion time period ($t_{\text{diff}}$) must be determined. In the present investigation $T(t)$ was approximated by fitting the temperature output from $t_i$ and until $t_f$ (as shown in Figure 10-2). Earlier work by Gerlich and Yamamoto utilized only the peak temperature in the estimation of $B_o$ [160, 169]. In the
The investigation herein, $B_o$ was calculated by modifying equation (4.1) to account for the temperature changes of the stir zone as shown in equation (10.1).

\[
B_o(t_{diff}) = \int_{t_i=0}^{t_f=t_{diff}} \frac{k_i}{\sqrt{\pi}} \sqrt{D_o \exp \left[ - \frac{Q_{diff}}{RT(t)} \right]} \cdot t \, dt
\]  

Table 10-1 shows the influence of rotational speed and dwell time on $t_{diff}$ and $B_o$ (a sample calculation is shown in Appendix N). It is evident that the degree of dissolution of second phase particles is greatly dependent on the welding conditions used to complete each joint.

10.3.2 $\gamma$-Al$_8$Mn$_5$ Intermetallics

By modifying equation (4.5) using a similar approach to that shown in equation (10.1), the maximum radius of Al$_8$Mn$_5$ particles that would fully dissolve was calculated. The estimates obtained in the present investigation were tabulated as a function of the welding setting used to produce the joint, see Table 10-1. It is interesting to note that even at the most intense welding conditions (3000 rev min$^{-1}$ and 4 sec dwell), the largest particle that would dissolve has a radius of 505 nm. This particle size is about an order of magnitude smaller than some of the particles reported to be present in AZ31 base metal [32]. As such, it can be concluded that the FSSW joining operation will always cause only partial dissolution of Al-Mn particles, leading to a SZ microstructure that comprises $\alpha$-Mg matrix, some $\gamma$-Al$_8$Mn$_5$ particles, and almost no $\beta$-Mg$_17$Al$_12$ particles as has been shown in previous work [10].

10.4 Second Phase Particle Distribution Measurements

To confirm the effect of the rotational speed of the welding tool and the dwell time on the extent of second phase particle dissolution, the size and distribution of intermetallics present in the stir zone were analyzed. The size and distribution of particles in the stir zone in these joints were analyzed using SEM imaging, as described in Section 6.5.3.1. Representative micrographs of the particle
distribution in SZ regions produced using varying parameter settings are shown in Figure 10-3 (a). For comparison purposes, the microstructure of the BM was included as well. Micrographs captured at various magnifications were analyzed using image processing software and a histogram depicting the size distribution profile of the particles in the region was generated (Figure 10-3 (b)). The histogram in Figure 10-3 (b) shows the effect of welding conditions on the size and distribution of \( \beta-\text{Mg}_{17}\text{Al}_{12} \) particles in the SZ, TMAZ and BM regions. The overall area fractions of each second phase particle present in stir zone regions welded using varying operating conditions are summarized in Table 10-2.
Figure 10-3 (a) Representative micrographs (50,000X magnification) of SZ regions produced using varying process settings. The microstructure of the base metal is included for reference as well. (b) A histogram depicting the effect of welding conditions on the size and distribution of $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ particles in the SZ, TMAZ and BM regions.
The information presented in Table 10-2 confirms that significant changes in the second phase particle dissolution occurred during friction stir welding. Most of the $\beta$-Mg$_{17}$Al$_{12}$ particles in the stir zone were dissolved, independent of the welding parameters used. The present findings confirm previous observations that were reported for friction stir processed AZ31 by Cristobal et al. [10]. These results are also in general agreement with the theoretical values computed using equation (10.1), see Table 10-1. The average $\beta$-Mg$_{17}$Al$_{12}$ particle diameter in the as-received base metal was $19 \pm 5$ nm (with diameters ranging from 11 to 32 nm). The theoretical thickness of a film that would fully dissolve in welds produced using a rotational speed of 1500 rev min$^{-1}$ is 14 nm. Consequently, almost all of the $\beta$-Mg$_{17}$Al$_{12}$ particles would be expected to dissolve when a rotational speed of 1500 rev min$^{-1}$ is used. Figure 10-3 (b) shows that minor amounts of $\beta$-phase particles were found in the SZ region of joints made using a tool rotational speed of 1500 rev min$^{-1}$. It is likely that larger $\beta$-Mg$_{17}$Al$_{12}$ particles in the as-received base material were unable to fully dissolve during the joining operation. The use of faster rotational speed and/or longer dwell time was calculated to yield dissolution of particles with diameters greater than the diameter of the second phase particles present in the as-received metal (Table 10-1), and so it would be expected that virtually all $\beta$-Mg$_{17}$Al$_{12}$ particles would dissolve. This is confirmed in Figure 10-3 (b) as the number of $\beta$-phase particles that remained in the stir zone region decreased even further.

<table>
<thead>
<tr>
<th>Region</th>
<th>Al-Mn</th>
<th>Mg$<em>{17}$Al$</em>{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ (3000 rev min$^{-1}$ – 4 Sec Dwell)</td>
<td>0.28%±0.02%</td>
<td>0.001%±0.002%</td>
</tr>
<tr>
<td>SZ (2250 rev min$^{-1}$ – 1 Sec Dwell)</td>
<td>0.32%±0.02%</td>
<td>0.004%±0.004%</td>
</tr>
<tr>
<td>SZ (1500 rev min$^{-1}$ – 1 Sec Dwell)</td>
<td>0.35%±0.02%</td>
<td>0.005%±0.007%</td>
</tr>
<tr>
<td>TMAZ (3000 rev min$^{-1}$ – 4 Sec Dwell)</td>
<td>0.44%±0.02%</td>
<td>0.09%±0.02%</td>
</tr>
<tr>
<td>BM</td>
<td>0.68%±0.08%</td>
<td>0.10%±0.02%</td>
</tr>
</tbody>
</table>

Table 10-2 Area fraction of secondary phase particles in various FSSW regions. The uncertainty given in the table represents one standard error.
In direct contrast, as predicted from the theoretical calculations (Table 10-1) only partial dissolution of $\gamma$-Al$_8$Mn$_5$ particles occurred during joining, and the extent of dissolution was dependent on the welding conditions applied. An increase in tool rotational speed from 1500 to 2250 rev min$^{-1}$ had no statistically significant effect on the area fraction of Al-Mn particles in the SZ region. However, increasing both the tool rotational speed from 1500 to 3000 rev min$^{-1}$ and prolonging the dwell period from 1 to 4 seconds resulted in a smaller area fraction of Al-Mn particles, which was statistically significant. The variation in the area fraction of $\beta$-Mg$_{17}$Al$_{12}$ particles in TMAZ and BM regions was negligible. However, the area fraction of Al-Mn particles in the BM region was greater than that observed in the TMAZ region.

In addition to particle dissolution, changes in the size distribution of second phase precipitates can be caused by particle fragmentation during the welding process. Such fragmentation has been previously observed when examining friction stir welded Al-alloy 2024-T351 [186]. It is important to note that based on size distribution measured for $\beta$-Mg$_{17}$Al$_{12}$ intermetallics (Figure 10-3 (c)), the very small size of the particles should preclude any significant particle fracturing during plastic flow of the material. Although particle fragmentation can occur in larger Al-Mn particles, the present study did not specifically isolate the effect of fragmentation from particle refinement by partial dissolution.

While it is possible to estimate the size and distribution of second phase particles using SEM microscopy, this estimation is based on a relatively small sampling of the test specimen. It is assumed that the examined area is representative of the entire volume of the test sample. With this in mind, it is important to confirm that the findings obtained from SEM microscopy are representative of the entire volume by using the technique of nuclear magnetic resonance (NMR). It is possible to use NMR spectroscopy of $^{27}$Al to determine the fraction of aluminum atoms in the specimen that are bound in the $\beta$-Mg$_{17}$Al$_{12}$ phase [206]. NMR analysis produces a spectrum for a specific atomic species where each peak position is associated with a specific phase since the
technique is highly sensitive to the atomic environment of the nuclei in the material. The area under each peak is proportional to the number of nuclei that are detected during the measurement in a particular phase. As such, it is possible to determine the phases and their relative fractions in a given specimen. It is worth noting that $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ intermetallics do not have any polymorphs, and that Zn incorporation into the $\beta$ phase ($\beta$-$\text{Mg}_{17}(\text{Al,Zn})_{12}$) does not change its crystal structure. As such it can be concluded that the NMR measurements herein are uniquely suited to identify the $\beta$ phase as the sole second phase in which Al atoms are found outside of being in solid solution within the $\alpha$-matrix phase or Al-Mn intermetallics.

In the present investigation, NMR was used to measure the fraction of aluminum that is associated with the $\alpha$-Mg solid solution, and the fraction of aluminum that is associated with the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase in accordance with the procedure outlined in Section 6.3.5.2. The phase composition of the base metal was compared to that of the stir zone produced using a tool rotation speed of 3000 rev min$^{-1}$ and a dwell time of 4 sec. Only one welding condition was examined using NMR, since the stir zone region produced using lower rotational speeds and/or dwell times was relatively small, which made specimen preparation extremely difficult.

The spectra obtained from NMR analysis is shown in Figure 10-4. Figure 10-4 (a) is the NMR signal derived from a sample of pure Mg that contains no Al and represents a baseline. Figure 10-4 (b) shows the peak position (~1250 ppm) obtained from a synthesized pure $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ single phase specimen. The NMR spectrum collected for AZ31 base metal (Figure 10-4 (c)) exhibited two peaks which are related to the presence of aluminum in $\alpha$-Mg solid solution and the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase. The peak positioned at 1952 ppm is associated with the solid solution while the peak positioned at 1400 is associated with the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$. It is interesting to note that there is a shift between the precipitate peak position in the base metal (Figure 10-4 (c)) and the precipitate peak position obtained from the synthesized pure $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ single phase specimen (Figure 10-4 (b)). This shift is likely caused by the presence of zinc in $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ in AZ31 that commonly exists as $\beta$-$\text{Mg}_{17}(\text{Al,Zn})_{12}$ [28, 206].
Based on the ratio of the areas under each peak, it was determined that 91.2% of the aluminum in the BM of the alloy was present in solid solution; the rest was associated with $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase. In contrast, the spectra obtained from the SZ material (Figure 10-4 (d)) exhibited only one peak, suggesting that complete dissolution of $\beta$ phase precipitates had occurred as a result of the welding operation. This observation is in agreement with the conclusions drawn from the SEM investigation confirming that microscopic image analysis is a suitable technique for measuring the size distribution of second phase particles in different test samples. It is important to note that the aluminum that is associated with Al-Mn particles was not considered in the NMR analysis. Its magnetic properties result in very significant peak broadening and so the signal could not easily be separated from the background.

![Figure 10-4](image)

**Figure 10-4** $^{27}\text{Al}$ NMR spectra from (a) high purity magnesium, (b) single phase $\beta$-$\text{Mg}_{17}\text{Al}_{12}$, (c) as-received, (d) friction stir processed AZ31 magnesium alloy.
10.5 Effect of Process Parameters on the Electrochemical Properties of the Stir Zone

As discussed previously, changes in rotational speed and dwell time had a pronounced effect on the diffusion of aluminum atoms through the α-Mg matrix, a mechanism that governs the dissolution of β-Mg₁₇Al₁₂ and γ-Al₈Mn₅ during joining. Microcapillary polarization was used to examine the influence of particle dissolution on the corrosion behaviour of the stir zone produced using different rotational speed settings (1000 to 3000 rev min⁻¹) and dwell times (1 to 4 sec). Detailed experimental procedure is given in Section 6.4.4.3). Each polarization experiment was conducted in 0.1M NaClO₄ electrolyte and was repeated on three replicate samples to ensure the results obtained during the investigation were reproducible.

Representative curves obtained during the potentiodynamic polarization are presented in Figure 10-5 (repeatability of the experimental results is shown in Appendix H). The corrosion current density was determined from polarization curves via Tafel extrapolation of the anodic branch. Table 10-3 summarizes the average corrosion potential and current density values obtained from polarization testing; the uncertainty indicated in the table represents one standard deviation.
Table 10-3 Influence of rotational speed on the corrosion potential and current density of the stir zone regions in FSSW made in AZ31. The uncertainty given in the table represents one standard deviation.

<table>
<thead>
<tr>
<th>Rotational Speed [rev min⁻¹]</th>
<th>Dwell Time [sec]</th>
<th>$E_{corr}$ [V SCE]</th>
<th>$i_{corr}$ [$\mu$A/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Metal</td>
<td>--</td>
<td>-1.472 ± 2.5 mV</td>
<td>13.3 ± 2.9</td>
</tr>
<tr>
<td>1000</td>
<td>1</td>
<td>-1.457 ± 4.7 mV</td>
<td>9.5 ± 0.9</td>
</tr>
<tr>
<td>1500</td>
<td>1</td>
<td>-1.430 ± 4.6 mV</td>
<td>4.0 ± 0.5</td>
</tr>
<tr>
<td>2250</td>
<td>1</td>
<td>-1.421 ± 2.5 mV</td>
<td>3.1 ± 0.2</td>
</tr>
<tr>
<td>2250</td>
<td>2</td>
<td>-1.406 ± 0.7 mV</td>
<td>2.5 ± 0.6</td>
</tr>
<tr>
<td>3000</td>
<td>1</td>
<td>-1.411 ± 4.2 mV</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>3000</td>
<td>4</td>
<td>-1.408 ± 3.9 mV</td>
<td>2.8 ± 0.6</td>
</tr>
</tbody>
</table>
Figure 10-5 The influence of (a) rotational speed of the tool, and (b) dwell time on the potentiodynamic polarization response of the SZ region in 0.1M NaClO₄.
For a constant dwell time of 1 sec, the corrosion potential of the stir zone increased when the rotational speed of the welding tool increased from 1000 to 3000 rev min\(^{-1}\) (Figure 10-5 (a)). For all welding conditions, the corrosion potentials measured in the stir zone region were higher than those measured in the Mg-alloy base metal. The corrosion current density of the stir zone region was lower than that of the base metal. When the rotational speed of the welding tool increased from 1000 to 3000 rev min\(^{-1}\), the corrosion current density of the stir zone decreased from 9.5 to 2.6 µA/cm\(^2\). The results presented in Table 10-3 suggest that a strong correlation exists between the tool rotational speed and the corrosion resistance of the SZ region.

Increasing the dwell time from 1 to 2 sec increased the corrosion potential of the stir zone region in joints produced using a rotational speed of 2250 rev min\(^{-1}\); however, there was no statistically significant effect on the corrosion current density (Figure 10-5 (b)). No significant changes in stir zone region corrosion potential were observed in joints made using a rotational speed of 3000 rev min\(^{-1}\) and dwell times of 1 to 4 sec. The dependence of the corrosion potential and current density values on the tool rotational speed and dwell time setting confirmed that altering the welding parameters modified both SZ microstructure and the corrosion resistance of completed joints.

To further illustrate the effect of dissolution of second phase particles on the electrochemical behaviour of the stir zone regions in FSSW joints, Figure 6 relates the corrosion potential and current density values with the diffusion time available for particle dissolution. When the time available for diffusion increased, this ennobled the corrosion potential (Figure 6(a)) and reduced the corrosion current density (Figure 6(b)) of the stir zone.
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Figure 10-6 Influence of particle dissolution on the corrosion (a) potential and (b) current density of the stir zone region in AZ31B FSSW joints. The upper and lower limits show a 95% confidence interval represented as two pooled standard deviations.

In effect, when the time available for diffusion increased sufficiently to allow dissolution of $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ intermetallics, this resulted in more Al in the $\alpha$-Mg matrix and less microgalvanic coupling between the noble intermetallics phases and the active matrix. Changes in the electrochemical behaviour of the stir zone were most pronounced for diffusion times less than 0.7 sec. When the diffusion time was further increased, there was negligible change in corrosion potential and current density values. The above observation suggests that a certain diffusion time limit existed during which nearly all of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ intermetallics present in the base material dissolved. Once these intermetallic particles dissolved, no further change in the electrochemical properties of the stir zone would occur.

It is important to note that varying process parameters also altered the cathode-to-anode ratio, as it has already been shown that the stir zone dimensions were affected by the selection of different tool rotational speed and dwell time settings [12]. Both the cathode-to-anode ratio and the potential difference between coupled phases are important parameters governing the corrosion behaviour of the galvanic couple. It would be expected that an increase in rotational speed or dwell time would increase the dissolution of $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ intermetallics, and consequently increase the corrosion
potential of the stir zone. Ultimately, an increase in the corrosion potential of the stir zone region will increase the magnitude of the galvanic couple it forms with the active base metal, leading to an increased susceptibility to corrosion. It is likely that the true effect of welding parameters on the corrosion behaviour of the joint is caused by a combination of changes in the size of the noble region and its individual corrosion potential and current.

The influence of welding on the corrosion of AZ31B reported in the present study differs from that reported by Zhang et al. [9]. As mentioned in Section 5.1, their study of AZ31B FSW joints concluded that the microstructural evolution caused by the welding process had no effect on the corrosion resistance of AZ31B. Instead, the corrosion behaviour of the joints was governed by the presence of surface contaminants in the BM region. The authors suggested that the contaminants on the surface of the alloy impacted the corrosion resistance of the alloy via two discreet mechanisms [9]. The first mechanism described the ennoblement of the SZ region through the introduction of impurities that were stirred in during the welding process. The second mechanism described a reduction in the corrosion resistance of the BM region due to the presence of surface contamination that introduced additional cathodic sites. The combined effect of the two was responsible for the corrosion attack that was observed in the periphery of the joint observed in samples in the as-welded condition. Unfortunately, the authors did not attempt to examine the corrosion behaviour of joints made in specimens without surface contamination to confirm their theory. In the present investigation, the effect of impurities can be considered negligible as BM coupons were abraded prior to welding to remove the anti-corrosive coating applied by the manufacturer thus eliminating the source for contamination. SEM examination of completed joints did not find any experimental evidence to suggest that iron was introduced into the SZ region as a result of tool wear. Finally, any increase in iron concentration in the SZ as a result of particle dissolution can be ruled out as well. Of the secondary phases present in the alloy, only Al-Mn intermetallics can act as an iron sink and it already has been shown that these particles do not fully dissolve during the welding operation.
It is interesting to note that the effect of fusion welding on the corrosion resistance of AZ31B has also been linked to changes in the phase constituents present in the base metal [226, 227]. Bland et al. reported that the fusion zone in tungsten inert gas weldments made in AZ31B exhibited lower corrosion resistance properties than the adjacent heat affected zone and the base metal [226]. When exposed to a corrosive environment, preferential dissolution of the fusion zone occurred due to its galvanic coupling with the surrounding base metal. Similar observations were also reported by Ben Hamu et al. [227]. Even though the two welding techniques had the opposite effect on the corrosion resistance properties of the weld nugget, the mechanism responsible for the change in the electrochemical properties was the same. In both cases, the corrosion resistance of the weldment was governed by the precipitation and/or dissolution of second phase intermetallics.

10.6 Estimating Corrosion Behaviour using Mixed Potential Theory

Mixed potential theory calculations can be used to correlate changes in stir zone microstructural constituents with observed changes in its corrosion potential and current. The polarization current density of a multiphase specimen can be expressed as a weighted sum of the polarization current densities of each of its constituent phases. In Mg-alloy AZ31 the polarization current ($I_{AZ31}$) can be determined using equation (10.2):

$$I_{AZ31} = f_{\alpha-Mg} I_{\alpha-Mg} + f_{\beta-Mg_{17}Al_{12}} I_{\beta-Mg_{17}Al_{12}} + f_{Al_8Mn_5} I_{Al_8Mn_5}$$  (10.2)

where $I_{\alpha-Mg}$, $I_{\beta-Mg_{17}Al_{12}}$, and $I_{Al_8Mn_5}$ are the polarization currents of the major phase constituents present in AZ31, and $f_{\alpha-Mg}$, $f_{\beta-Mg_{17}Al_{12}}$, and $f_{Al_8Mn_5}$ are their respective area fractions of the specimen surface. High purity magnesium was selected as a simplified representation of the matrix material, and the second phases present in the alloys were approximated from single phase $\beta-Mg_{17}Al_{12}$ and $\gamma-Al_8Mn_5$ specimens. The corrosion potential was considered to be the potential at which the current approached zero on the polarization curve (in 0.1M NaClO₄), while the corrosion
current density was determined using Tafel extrapolation of the anodic branch. Representative curves produced during potentiodynamic polarization testing (Section 6.4.3.2) are presented in Figure 10-7 (the reproducibility of the measurement is shown in Appendix E). For reference, the potentiodynamic polarization curve of AZ31 in 0.1M NaClO₄ was included as well (Figure 10-7 (b)).

Figure 10-7 Sample potentiodynamic polarization outputs of (a) high purity magnesium, (b) AZ31, (c) Mg₁₇Al₁₂ and (d) Al₈Mn₅ in 0.1M NaClO₄.

The Tafel slopes for high purity Mg, β-Mg₁₇Al₁₂ and γ-Al₈Mn₅ were determined from potentiostatic polarization measurements, see the description in Section 6.4.3.2. In the case of pure Mg, both anodic and cathodic Tafel slopes were examined. Only the cathodic branch was analyzed for the passivating intermetallic phases. Figure 10-8 shows typical potentiostatic polarization curves obtained for pure Mg, β-Mg₁₇Al₁₂ and γ-Al₈Mn₅ in 0.1M NaClO₄ (the reproducibility of the
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measurement is shown in Appendix F). Each measurement was repeated three times for each condition and the average and standard deviation values are summarized in Table 10-4. The error indicated in Table 10-4 is one standard deviation.

**Figure 10-8** Sample potentiostatic polarization outputs of (a) high purity magnesium in the anodic direction, and (b) high purity magnesium, (c) Mg$_{17}$Al$_{12}$ and (d) Al$_8$Mn$_5$ in the cathodic direction. All experiments were carried out in 0.1M NaClO$_4$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ [V SCE]</th>
<th>$i_{corr}$ [µA/cm$^2$]</th>
<th>$\beta_a$ [mV/decade]</th>
<th>$\beta_c$ [mV/decade]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Magnesium</td>
<td>-1.906 ± 4 mV</td>
<td>11.7 ± 1.5</td>
<td>185 ± 13</td>
<td>320 ± 10</td>
</tr>
<tr>
<td>$\beta$-Mg$<em>{17}$Al$</em>{12}$</td>
<td>-1.253 ± 8 mV</td>
<td>6.2 ± 1.7</td>
<td>--</td>
<td>140 ± 0</td>
</tr>
<tr>
<td>$\gamma$-Al$_8$Mn$_5$</td>
<td>-1.259 ± 8 mV</td>
<td>2.7 ± 0.6</td>
<td>--</td>
<td>139 ± 4</td>
</tr>
<tr>
<td>AZ31</td>
<td>-1.469 ± 3 mV</td>
<td>10.3 ± 0.2</td>
<td>101 ± 17</td>
<td>128 ± 3</td>
</tr>
</tbody>
</table>

**Table 10-4** Electrochemical properties of high purity magnesium, $\beta$-Mg$_{17}$Al$_{12}$, $\gamma$-Al$_8$Mn$_5$, and AZ31 in 0.1M NaClO$_4$ solution. The uncertainty given in the table represents one standard deviation.
The corrosion potentials of β-Mg$_{17}$Al$_{12}$ and γ-Al$_8$Mn$_5$ were higher than the corrosion potential of pure Mg and Mg-alloy AZ31. In AZ31, alloying produced a significant increase in its corrosion potential as compared to pure Mg, in agreement with observations reported by McNutly et al. [228]. Little difference was observed between the Tafel slopes of β-Mg$_{17}$Al$_{12}$ and γ-Al$_8$Mn$_5$. The Tafel slopes measured for pure Mg were much higher than those measured for β-Mg$_{17}$Al$_{12}$ and γ-Al$_8$Mn$_5$, in agreement with published literature [49, 229].

The corrosion potential and current can be estimated using mixed potential theory when the relative area fractions and the electrochemical properties of each of the different phase constituents are known, and the law of superposition applies. The calculations herein were based two-dimensional exposed cross-sectional area of phase constituents (as determined from SEM imaging) and did not account for their electrochemically active surface area or any volume three-dimensional based area measurements. It was also assumed that the anodic reaction occurred only on the metal matrix and that the cathodic reaction occurred only on second phase intermetallic particles. As a simplification, the effects of corrosion product build up and/or surface film formation, as well as any IR drop in the solution were ignored. Figure 10-9 (a) presents a simplified mixed potential theory model that aims to estimate the corrosion potential and corrosion current density for a base metal specimen in 0.1M NaClO$_4$. 

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Figure 10-9 (a) Mixed potential theory model estimating the corrosion behaviour of AZ31 base metal specimen in 0.1M NaClO₄, where the anodic area comprised all exposed α-Mg matrix. (b) Modified mixed potential theory where only discreet sites on the α-Mg matrix are anodic and the rest of the exposed area acts as a cathode. (c) Modified mixed potential theory where only discreet sites on the α-Mg matrix are anodic and the rest of the exposed area is inert. The anodic areas in (b) and (c) were adjusted such that the estimated corrosion current values would match those obtained from experimental observations.

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The corrosion potential and corrosion current were estimated from the mixed potential theory model for the BM, TMAZ and each of the SZ regions for which particle counts were performed. Note that the mixed potential calculations were carried out for samples having a total area of 1 cm$^2$, under this condition the current (I [$\mu$A]) is equal to the current density (i [$\mu$A/cm$^2$]). The results are summarized and compared to experimental values in Table 10-5. When the corrosion current is compared across the various weld regions, a trend similar to that observed from the experimental values emerges. The corrosion current was lower in the stir zone region, and the stir zone that was produced with the fastest rotational speed and longest dwell time had the greatest corrosion resistance. Unlike the corrosion current, the trend observed for the estimated corrosion potential in the various weld regions did not match the trend that was observed experimentally.

<table>
<thead>
<tr>
<th></th>
<th>Base Metal</th>
<th>TMAZ</th>
<th>SZ: 1500 rev min$^{-1}$ 1 Sec Dwell</th>
<th>SZ: 2250 rev min$^{-1}$ 1 Sec Dwell</th>
<th>SZ: 3000 rev min$^{-1}$ 4 Sec Dwell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{corr}$ [V$_{SCE}$]</td>
<td>Measured</td>
<td>-1.469</td>
<td>-1.464</td>
<td>-1.430</td>
<td>-1.421</td>
</tr>
<tr>
<td></td>
<td>Estimated</td>
<td>-1.75</td>
<td>-1.76</td>
<td>-1.78</td>
<td>-1.79</td>
</tr>
<tr>
<td>$i_{corr}$ [$\mu$A/cm$^2$]</td>
<td>Measured</td>
<td>10.3</td>
<td>9.2</td>
<td>4.0</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Estimated</td>
<td>80</td>
<td>70</td>
<td>55</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 10-5 Comparison between measured and estimated corrosion potential and current for various regions in a friction stir spot weldment. Estimates based on mixed potential theory for the scenario of Figure 10-9 (a).

Using this simplified model, the magnitude of the corrosion potential and current estimates were approximately an order of magnitude greater than those determined experimentally. The deviation between predicted and experimental results can be partially attributed to the use of high purity magnesium as a matrix metal. The $\alpha$-Mg solid solution phase exhibits greater corrosion resistance. 
than high purity magnesium [82, 230], and so it would be expected that the coupling between the active $\alpha$-Mg phase and the noble second phase particles would yield lower corrosion rates than those predicted in this investigation. However, it is unlikely that the use of a simplified metal matrix is solely responsible for the deviation between predicted values and experimental results. Instead, it is probable that the model was incomplete and required adjustment.

The model described in Figure 10-9 (a) assumes that anodic dissolution occurred uniformly across the entire surface of the $\alpha$-Mg matrix. This assumption does not accurately describe the electrochemical behaviour of magnesium, as it is well known that Mg is prone to localized corrosion [51, 98, 231]. It is likely that only a small fraction of the $\alpha$-Mg matrix (where the oxide is compromised) is actively dissolving while the rest is either cathodic or inert. The anodic area fraction ($f_{\text{anode}}$) in a magnesium alloy, whose corrosion behaviour is governed by microgalvanic coupling between noble intermetallics and the active matrix, is related to the size and distribution of these particles along with the potential distribution around them. Several attempts have been made to model the potential distribution around noble particles that are embedded in the matrix, with some of the early work being done on the electrochemical behaviour of aluminum [232, 233]. More recently this model was applied to a magnesium alloy system in an attempt to explain the effect of intermetallic particle size and spacing on the corrosion of Mg-Al alloys [234]. Application of the model to the work herein did not produce meaningful results, as the $f_{\text{anode}}$ predicted by the model was determined to be larger than unity. It is important to note that the model was originally developed for application in an aluminum alloy system (Al-Li-Cu) and it describes a passivating system, a condition that does not reflect the magnesium alloy in the present investigation [232].

Even though $f_{\text{anode}}$ could not be determined from theoretical calculations it is possible to estimate its value by modifying the $\alpha$-Mg matrix area fraction in the mixed potential theory model such that it yields a corrosion current that matched that observed experimentally. The rest of the exposed magnesium matrix (that is not actively dissolving) can then act as a cathode or is inert, modified
mixed potential theory models depicting this behaviour are shown in Figure 10-9 (b) and (c) respectively. The models described in Figure 10-9 (b) and (c) represent the two extremities that can occur on a surface of a corroding magnesium specimen. In reality, local variation in the electrolyte chemistry and/or oxide structure might lead to the presence of both cathodic and inert regions on the $\alpha$-Mg matrix that is not actively corroding. The present work examined these two extremities as well as several scenarios where the area ratio between the cathodic and the inert regions was varied. In a similar fashion to the approach taken for the model described in Figure 10-9 (a), the corrosion potential in each scenario was determined from the model for the weld regions examined in this investigation as summarized in Table 10-6. Following this modification, the predicted corrosion potentials were much closer to those observed experimentally for all scenarios considered. When the $\alpha$-Mg matrix that was not actively dissolving was assumed to act as a cathode, the trend between the regions matched the trend observed experimentally. The potential of the SZ region was higher than that of the BM and the TMAZ regions, and the potential of the stir zone increased with increasing particle dissolution. The similarity between the theoretical and experimental trends became less pronounced when the ratio between the cathodic and inert areas on the $\alpha$-Mg matrix that was not actively dissolving decreased. The best match to experimental results was obtained when it was assumed that 75% of the $\alpha$-Mg matrix that is not actively corroding acted as a cathode and 25% was inert as shown in Table 10-6. The model cannot predict the exact fraction but shows that the experimentally observed behaviour lies between fractional bounds of the matrix being cathodic and/or inert.

For all cases, only a small fraction of the area was associated with the anodic reaction while the rest of the metal matrix was supporting the cathodic reaction or was inert. The anodic dissolution reaction would likely occur locally at the dissimilar interface between the matrix and the second phase particle. Examination of the $f_{\text{anode}}$ that would be associated with each region revealed that $f_{\text{anode}}$ that was required to support the anodic reaction in the SZ region (for any of the welding parameters)
was lower than that of the BM or the TMAZ regions, see Table 10-6. Comparison of the required $f_{\text{anode}}$ between the various SZ regions examined in the study have shown that $f_{\text{anode}}$ decreased with increasing second phase particle dissolution. The anodic reaction is expected to preferentially occur at the interface between the two phases and if there are less particles there would be less locations where coupled localized corrosion would take place.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Base Metal</th>
<th>TMAZ</th>
<th>SZ: 1500 rev min$^{-1}$ 1 Sec Dwell</th>
<th>SZ: 2250 rev min$^{-1}$ 1 Sec Dwell</th>
<th>SZ: 3000 rev min$^{-1}$ 4 Sec Dwell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured $E_{\text{corr}}$ [V$_{\text{SCE}}$]</td>
<td>-1.469</td>
<td>-1.464</td>
<td>-1.430</td>
<td>-1.421</td>
<td>-1.408</td>
</tr>
<tr>
<td>Estimated $E_{\text{corr}}$ when 100% of the α-Mg matrix that is not dissolving acts as a cathode [V$_{\text{SCE}}$]</td>
<td>-1.600</td>
<td>-1.610</td>
<td>-1.580</td>
<td>-1.560</td>
<td>-1.550</td>
</tr>
<tr>
<td>Estimated $E_{\text{corr}}$ when 75% of the α-Mg matrix that is not dissolving acts as cathode and 25% is inert [V$_{\text{SCE}}$]</td>
<td>-1.605</td>
<td>-1.620</td>
<td>-1.585</td>
<td>-1.570</td>
<td>-1.560</td>
</tr>
<tr>
<td>Estimated $E_{\text{corr}}$ when 50% of the α-Mg matrix that is not dissolving acts as cathode and 50% is inert [V$_{\text{SCE}}$]</td>
<td>-1.610</td>
<td>-1.625</td>
<td>-1.600</td>
<td>-1.585</td>
<td>-1.575</td>
</tr>
<tr>
<td>Estimated $E_{\text{corr}}$ when 25% of the α-Mg matrix that is not dissolving acts as cathode and 75% is inert [V$_{\text{SCE}}$]</td>
<td>-1.615</td>
<td>-1.630</td>
<td>-1.610</td>
<td>-1.600</td>
<td>-1.595</td>
</tr>
<tr>
<td>Estimated $E_{\text{corr}}$ when 100% of the α-Mg matrix that is not dissolving is inert [V$_{\text{SCE}}$]</td>
<td>-1.625</td>
<td>-1.640</td>
<td>-1.625</td>
<td>-1.615</td>
<td>-1.61</td>
</tr>
<tr>
<td>Estimated Anodic Area Fraction [%]</td>
<td>1.8-2.6</td>
<td>2.0-2.8</td>
<td>0.6-1.0</td>
<td>0.4-0.7</td>
<td>0.3-0.6</td>
</tr>
</tbody>
</table>

Table 10-6 Comparison between measured and estimated corrosion potentials for various regions in a friction stir spot weldment. Several scenarios were examined in which the area ratios of α-Mg acting as anodic, cathodic, and inert sites were varied. The anodic area was adjusted such that the estimated corrosion current values would match those obtained from experimental observations as shown in Figure 10-9 (b) and (c).
Discussion of corrosion mechanisms occurring through microgalvanic coupling in high purity magnesium and AZ31 has been previously reported in literature [51, 98, 231]. In these mechanisms the anodic reaction occurred on a small fraction of the exposed magnesium matrix, while the hydrogen evolution reaction was supported by the cathodic activity of noble intermetallic particles and the corrosion product present on the surface [98]. The cathodic reaction on the corrosion product was driven by the catalytic activity of impurity enrichment that has been shown to occur on the surface of corroding magnesium specimens [98]. Typically, noble metal enrichment is explained through incongruent dissolution and/or replating [69, 72, 98, 123]. It is possible that the corrosion of AZ31B FSSW joints is also influenced by the presence of impurity enrichment, but this has not been considered in the present model. Further studies are required to determine the mechanisms governing any impurity enrichment process and any subsequent partitioning of the current in a controlled and systematic fashion. Specifically, it is important to determine the influence of microstructural changes on the mechanism(s) governing surface enrichment.

The model herein presents first steps towards relating the effects of welding parameters on the electrochemical properties of the joint. It is acknowledged that the model should be modified as new information is published. Future work should focus on developing a theoretical model describing the potential distribution around noble intermetallic particles in a magnesium matrix. The present study did not consider the effect of particle spacing and their interaction with one another (territory theory), a factor that should be the subject of future studies as well.
10.7 Summary

This work established a correlation between the process parameters during FSSW, second phase particle dissolution, and its effect on the electrochemical properties of the SZ region. A number of conclusions can be derived from the experimental work presented above:

1. Increasing the tool rotation speed above 1500 rev min$^{-1}$ produced temperatures $>437$ °C which promoted rapid dissolution of Mg$_{17}$Al$_{12}$ second phase intermetallics.

2. Intermetallic particle dissolution has been assessed through a SEM investigation that was coupled with NMR. The microstructure of the SZ region exhibited complete dissolution of β-Mg$_{17}$Al$_{12}$ particles, and only partial dissolution of γ-Al$_8$Mn$_5$ intermetallics.

3. A direct correlation between the diffusion time available for particle dissolution ($t_{\text{diff}}$), and the corrosion potential ($E_{\text{corr}}$) and current density ($i_{\text{corr}}$) has been established.

4. Diffusion times beyond 1 sec did not alter the electrochemical properties of the SZ as near-complete dissolution of β-Mg$_{17}$Al$_{12}$ particles was achieved.

5. The electrochemical properties of high purity Mg, β-Mg$_{17}$Al$_{12}$ and γ-Al$_8$Mn$_5$ have been assessed.

6. A mixed potential theory model correlating changes in second phase particle size and distribution to the corrosion behaviour of friction stir spot welded AZ31 was constructed. The model suggested that the anodic reaction took place only on discreet sites located in the α-Mg matrix coupled to the precipitate distribution, while the cathodic reaction occurred predominantly on adjacent second phase intermetallics. The α-Mg matrix that was not dissolving anodically consisted of either additional local cathodic sites and/or inert regions.
Chapter 11 Mass Loss Testing in Magnesium AZ31B Friction Stir Spot Welds

This work was published in Corrosion in 2014 and reproduced with permission. Liu contributed to mass loss testing and Miklas aided with SRET measurements. "Savguira, Y., Liu, W., D. J. Miklas, North, T. H., and Thorpe, S. J. “Mass loss testing in magnesium AZ31 friction stir spot welds,” Corrosion 70 (8), 858-866, 2014.”

11.1 Introduction

Chapter 10 identified second phase precipitate dissolution as the principal cause for the ennoblement of the SZ region during friction stir welding. It has also been demonstrated that the choice of welding parameters affected the diffusion time available for intermetallic dissolution ($t_{\text{diff}}$), which then influenced the corrosion potential and corrosion current density of the stir zone region. While the connection between welding parameters and the electrochemical characteristics of the SZ has been established, the effect of these parameters on the overall corrosion properties of the entire welded joint remains unknown. If this welding technique was used in industrial practice, it is essential to understand how the various processing conditions may affect the service life of the weld.

The objective of this chapter is to examine the overall corrosion behaviour of friction stir welded AZ31B when all the microstructural regions induced by the welding process are exposed to a chloride containing environment. Where Chapters 7-10 of this thesis focused on the effect of welding on the electrochemical properties of individual weld regions, the present work will focus on the combined effect of the coupling between the noble SZ and the active TMAZ, HAZ and BM regions. Specific attention is given to the role of FSSW parameters on the morphology, the location, and the extent of corrosive attack in AZ31B FSSW joints. This chapter seeks to establish a
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correlation between the nature of the attack and the microstructural evolution caused by the welding process.

The effect of welding parameter on the corrosion resistance of FSSW joints made in AZ31B can be evaluated by mass loss testing combined with SRET measurements. Detailed information on the experimental procedure can be found in Section 6.4.1.2 and Section 6.5.4.2 respectively. See Table 11-1 for a summary of the various welding conditions used in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Rotation speed [rev min⁻¹]</th>
<th>Dwell time [sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>A4</td>
<td>1000</td>
<td>4</td>
</tr>
<tr>
<td>D1</td>
<td>3000</td>
<td>1</td>
</tr>
<tr>
<td>D4</td>
<td>3000</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 11-1 Sample identification and welding parameters

11.2 Influence of Welding Parameters on Corrosion Rate

The average corrosion rate in 0.086M NaCl was calculated from the mass loss data per unit area per unit time after cleaning in a dichromate solution and is given in Figure 11-1. The error bars represent 95% confidence as gathered from multiple measurements. The scatter in the experimental results varied between 5 and 9%, in accordance with ASTM G31-12a (+/-10%) [207]. The corrosion rate was observed to increase with increasing tool rotation speed for a constant dwell time of either 1 or 4 sec. The corrosion rate also increased with increasing dwell time for a constant tool rotation rate of either 1000 or 3000 rev min⁻¹. The corrosion rate was observed to vary more than 25% with changes in the welding conditions. The lowest corrosion rate was observed for the welding conditions of 1000 rev min⁻¹ and 1 sec dwell time and the highest corrosion rate was obtained at 3000 rev min⁻¹ at a dwell time of 4 sec. The welding process significantly altered the corrosion rate...
of the AZ31B H24 magnesium alloy with welded specimens having increased corrosion rates (as much as 40%) when compared to base metal specimens (un-welded) under identical exposure conditions. The work herein represents the first time that the corrosion of complete FSSW joints made in magnesium alloy was examined by means of mass loss testing. Other mass loss testing studies examined the corrosion resistance of individual weld regions and did not account for the coupling between the SZ and the BM [192, 193]. A summary of these results can be found in Section 5.1.2. Since this study was the first of its kind, comparison of the results presented in this investigation to literature can only be done on the basis of the corrosion rate measured for BM specimens. It is important to note that the comparison must be done between specimens that were exposed to similar electrolytes, as changes in concentration of chloride ions can have a dramatic effect on the corrosion rate (see Section 3.3.1 for complete discussion on the effect of [Cl\textsuperscript{-}] on the corrosion rate of AZ31). Liao et al. reported that the corrosion rate of AZ31B in 0.1M NaCl following a 7-day exposure was 0.014 mg-cm\textsuperscript{-2}·hr\textsuperscript{-1}, a value that was close to the corrosion rate of 0.020 mg-cm\textsuperscript{-2}·hr\textsuperscript{-1} that was reported herein [211].

![Figure 11-1](image)

**Figure 11-1** Effect of welding parameters (tool rotational speed and dwell time) on the corrosion rate measured by weight loss in 0.086M NaCl. The times in the legend indicate the dwell time used to produce the joint.
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It is important to note that the results in Figure 11-1 cannot be directly compared to the results presented in Figure 10-6. Chapter 10 (Figure 10-6) examined the effect of welding parameters on the corrosion resistance properties of the SZ region using a microcapillary polarization technique. The measurement provided an insight into the electrochemical properties of an uncoupled SZ material that was exposed to corrosive media. In the present chapter the corrosion rate of the whole weld was examined, and the corrosion rates in Figure 11-1 describe the corrosion behaviour of the joint when all weld regions are coupled and exposed to the electrolyte. The time scale of the two experiments was different as well, as microcapillary polarization takes place over a few hours while mass loss testing is conducted over a much longer time frame of 120 hours. Significant changes in the electrochemical properties of the corroding specimen and the surrounding electrolyte can occur if prolonged exposure times are used. In the present investigation the pH of the solution was measured to increase from 5.5 to 10.1 following the exposure period. Such changes are related to the formation of Mg(OH)$_2$ and are expected to occur during mass loss testing of magnesium alloys.

The timescale of the mass loss experiments and the associated changes in surface condition and electrolyte composition have an important implication on the applicability of the mixed potential theory model that has been developed in Chapter 10. Specifically, if one is interested in estimating the corrosion rate of the TMAZ based on the corrosion behaviour caused by the galvanic coupling between the noble SZ and the active BM, estimates for the corrosion rate of the TMAZ can be made. The mixed potential theory model in Chapter 10 was based on the assumption that the effects of corrosion product build up and/or surface film formation, were negligible. It was also assumed that no local changes in the electrolyte occurred throughout the entire exposure period. Unfortunately, these assumptions are only true under mild corrosion conditions and short exposure periods. As such, the corrosion rate predicted for the TMAZ would only represent the corrosion rate occurring during the initial stages of the corrosion attack. Estimates for the extent of corrosion cease to be accurate once the sample has degraded, and the corroding system changed from that which was used to produce the model.
Changes that could occur when prolonged corrosion periods are employed may be related to local electrolyte composition, and to the anodically induced cathodic activation phenomenon that has been previously reported in literature [5, 235, 236]. In this connection, it has already been reported that Cl\(^-\) enrichment was present in corroded magnesium specimens at the interface between the corrosion product and the metal substrate [237]. In the same study it was specifically noted that this enrichment likely played an important role at breaking the quasi protective film formed on the surface of corroding magnesium specimens. Such changes were not considered in the mixed potential theory model and would likely impact its ability to accurately estimate the corrosion rate in the TMAZ region. Another factor that should be considered is the surface film formed on the surface of corroding specimens. It has previously been shown that corroded magnesium surfaces contained increased levels of impurities caused by incongruent dissolution and/or replating of noble elements onto the surface of the alloy [5, 235, 236]. As such, the level of impurity enrichment on the surface of specimens showing relatively low degree of corrosion attack (i.e. from microcapillary polarization testing) would be different from the level of impurities on the surface of specimens showing severe pitting (i.e. from mass loss testing) and thus deviating from the model proposed in Chapter 10.

Future work is required to examine the changes occurring to the system during prolonged exposure of magnesium to corrosive media. The individual effect of changes in the electrolyte composition and surface properties should be evaluated along with their time dependence so that the model from Chapter 10 could be expanded to apply to cases examining the corrosion behaviour of FSSW joints under long exposure conditions. Finally, any synergistic effects between electrolyte and surface changes should be considered as well.
11.3 Influence of Welding Parameters on Corrosion Morphology

Before discussing the morphology of corrosion attack on welded specimens it is important to define the terminology that will be used in this chapter. The plane and cross-sectional views of the samples used in the present study are shown schematically Figure 11-2 (a) and (b). The corresponding optical images are shown in Figure 11-2 (c) and (d).

Figure 11-2 Schematic of (a) plan view and (b) cross section of a FSSW weld along with the corresponding optical images (c) plan, (d) cross section. This figure originally appeared as Figure 6-15 and has been included again for clarity.

A—bottom of pin hole surface, B—edge of key hole, C—shoulder penetration surface, D—outer edge of shoulder, E—inner edge of shoulder, F—upper sheet surface, G—hook, and H—mating surface of two sheets.

Figure 11-3 illustrates the morphological nature and location of the corrosion attack. The letters that identify the surface of the corrosion attack correspond to the locations defined in Figure 11-2. In samples welded at 1000 rev min⁻¹, the corrosive attack was limited to the upper sheet surface (region F) at a dwell time of 1 sec as seen in Figure 11-3 (a) and consisted largely of patches of dendrite-
like tracks (filaments). With an increase in dwell time from 1 sec to 4 sec, the attack also occurred mainly in region F, but occurred over a much larger area. In addition, at 1000 rev min\(^{-1}\), 4 sec dwell time, some localized pitting attack was also observed at region D (see schematic in Figure 11-2) on the outer edge of the shoulder penetration surface as seen in Figure 11-3 (b) (pointed by the white arrow).

Increasing the tool rotational speed from 1000 to 3000 rev min\(^{-1}\) had a marked effect on the corrosion morphology. For samples welded at 3000 rev min\(^{-1}\) and 1 sec dwell time, corrosion occurred both on the upper sheet surface and in a ring on the shoulder penetration surface at region C, as shown in Figure 11-3 (c). A comparison of Figure 11-3 (a) and Figure 11-3 (c) clearly show the much greater extent of corrosion with increasing tool rotation speed at a constant dwell time. In addition, increasing the dwell time from 1 sec to 4 sec at 3000 rev min\(^{-1}\) also expanded the area fraction and depth of localized attack as seen by comparing Figure 11-3 (c) to Figure 11-3 (d).
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Location and Morphology of Corrosion Attack

1 Second

4 Seconds

Figure 11-3 Influence of different welding procedure on the location and morphology of corrosive attack. Important weld surfaces are labeled with letters that are consistent with the schematic in Figure 11-2: A—bottom of pin hole surface, C—shoulder penetration surface, and F—upper sheet surface.

In order to explain the corrosion morphology observed in the specimens using each of the welding conditions, it is important to consider the effect of welding parameters on the shape and size of the SZ region. Figure 11-4 shows the individual cross-sectional profiles (of unexposed samples) highlighting the microstructural differences along periphery of the shoulder penetration surface as a result of increasing the rotational speed of the welding tool from 1000 rev min⁻¹ to 3000 rev min⁻¹. Figure 11-4 (a) and (b) show the location and size variation of the stir zone as a result of an increased rotational speed of the welding tool. The boundary of the stir zone is outlined by the arrows on the micrographs. The stir zone extended to the outer edge of the shoulder in samples welded with 1000
rev min⁻¹, while in samples welded with 3000 rev min⁻¹ it stopped about 700 μm short of the edge of the shoulder.

Figure 11-4 (c) and (d) show the grain size variation at the periphery of the shoulder penetration surface for samples welded with a rotational speed of 1000 and 3000 rev min⁻¹, respectively. A close examination of the figure revealed uniformly distributed, dynamically recrystallized small grains below the shoulder penetration surface in samples made with a rotational speed of 1000 rev min⁻¹. This microstructure was characteristic of the SZ region. Only a thin layer of dynamically recrystallized grains was present below the shoulder penetration surface in samples welded with a rotational speed of 3000 rev min⁻¹. A region with larger grains, corresponding to the TMAZ, was present directly under the thin layer of dynamically recrystallized grains.

A good correlation exists between the corrosion morphology observed in mass loss samples (Figure 11-3) and microstructural features seen in Figure 11-4. Samples welded with a rotational speed of 1000 rev min⁻¹ did not show corrosion on the shoulder penetration surface as a result of the uniform stir zone region microstructure that is present directly underneath it, while samples made with 3000 rev min⁻¹ showed a distinct corrosion attack in the same region. The corrosion groove on the shoulder penetration surface is aligned with the TMAZ region that lies under the thin layer of dynamically recrystallized grains. Once the thin SZ layer on top of the TMAZ has been damaged it exposes the active TMAZ to the corrosive media, leading to a localized corrosion attack on the shoulder penetration surface.
Figure 11-4 Microstructural cross-sectional profiles showing changes in location and size of the stir zone as a function of rotational speed of the welding tool: a) 1000 rev min$^{-1}$, 4 sec dwell time, and b) 3000 rev min$^{-1}$, 4 sec dwell time. The arrows point at the boundary of the stir zone. Grain size variation at the shoulder penetration surface periphery as a function of rotational speed of the welding tool: c) 1000 rev min$^{-1}$, 4 sec dwell time, and d) 3000 rev min$^{-1}$, 4 sec dwell time. Micrographs are taken at the location indicated by the white rectangle in images a) and b) respectively. Higher magnification images of micrographs c) and d) are shown in e) and f) respectively.
11.4 Effect of Welding Parameters on the Potential Distribution Across the SZ region

The effect of welding parameters on the corrosion of FSSW joints can be further elucidated by examining the connection between the potential distribution on the cross-sectional surface of the weld to its microstructure. James and Miklas used the scanning reference electrode technique to spatially map the potential distribution across sections of the welds made with varying rotational speeds and dwell times [12, 188]. The results from their studies, along with corresponding BSE micrographs of FSSW samples made with WC as a tracer are shown in Figure 11-5. For each welding condition the SRET map was overlaid on top of the BSE image to correlate the local potential variations on the surface of the weld to the underlying microstructural differences in various weld regions.

The SRET testing output showed profoundly different regions in the potential maps when examining friction stir spot welds made using different tool rotational speeds and dwell times. For all conditions, the SZ (marked by WC powder) was found to be noble to the base metal with the potential gradient in the solution on the order of 400 mV. The presence of such a large potential drop was unexpected, and theoretical calculations predicting the electrostatic potential distribution in the solution were carried out for comparison purposes. An analytical expression describing the electrostatic potential distribution in the electrolyte near the surface of the joint was obtained by solving the corresponding Laplace equation (see Appendix O). From the derivation in Appendix O, the potential drop in the electrolyte at a height of 10 μm above the surface of the corroding joint was estimated to be 4.3 mV. The discrepancy between theoretical and experimental observations was likely related to the presence local changes in the electrolyte as changes in pH, and concentration of dissolved gasses (H₂ and O₂) would influence the open cell potential of the Pt probe. For example, during the exposure period the pH near the metal surface rose from 5.5 (pH of the bulk electrolyte measured before exposure) to 10.1 (pH of the bulk electrolyte measured following exposure) as a result of the metal dissolution reaction (as described in equation (3.4)). The preferential dissolution of the BM region increased the pH of the electrolyte near the BM, ultimately leading to the formation of a pH gradient across the SRET surface. Since the electrochemical properties of both, magnesium and platinum (in the scanning probe) are sensitive to pH changes, it is plausible that the potential drop measured during the
SRET scan is caused not only by the microstructural variation in the alloy, but also by the local pH changes in the electrolyte. In effect, the SRET tip acted as a pseudo pH electrode that mapped the pH of the electrolyte near the metal interface. Under these experimental conditions, active potentials correlated with high pH values (blue shades in Figure 11-5), while noble potentials indicated the presence of low pH (red shades in Figure 11-5.). The active potential measured in the BM region indicated that the electrolyte over that region was basic (due to its increased susceptibility to corrosion), while the pH of the electrolyte near the SZ was relatively lower as manifested by the noble potentials measured in that region. Even though SRET testing was not able to resolve the potential variation that occurred due to the difference in the electrochemical activity of the SZ and the BM, the results were still consistent with microcapillary polarization as they confirmed (albeit indirectly) that the SZ exhibited better corrosion resistance properties than the BM.

Increasing the rotational speed of the welding tool from 1000 to 3000 rev min\(^{-1}\) increased the size of the noble region (SZ) as illustrated in Figure 11-5 (a) and (b). This observation was in agreement with Yin et al. who reported that larger SZ regions were formed when higher rotational speeds were used due to increased mechanical mixing and greater heat generation [238]. Increasing the dwell time of the welding process also increased the size of the SZ region as shown in Figure 11-5 (b) and (c).
Figure 11-5 Potential distribution profiles on the surface of friction stir welded AZ31B as a function of process parameters. Corresponding BSE micrographs of FSSW samples made with WC as a tracer, and an overlay correlating the potential distribution to the location of the SZ are included as well. (a) 1000 rev min\(^{-1}\) and 1 sec dwell time (adapted from [12]), (b) 3000 rev min\(^{-1}\) and 1 sec dwell time (adapted from [188]), and (c) 3000 rev min\(^{-1}\) and 4 sec dwell time (adapted from [188]). Potential distribution profiles were obtained using the scanning reference electrode technique in 0.086M NaCl. The scale bars in BSE micrographs corresponds to 2 mm.

Post SRET testing image of a cross section of a FSSW joint made with 3000 rev min\(^{-1}\) and 1 sec dwell time is shown in Figure 11-6. The interface between the noble SZ and the active BM is heavily corroded as a result of a macro-galvanic cell that was formed in the joint. The pitting attack is aligned with the TMAZ/HAZ region in a similar manner as it has been seen in the mass loss samples. At low rotational speeds (Figure 11-5 (a)), the SZ is confined to the very periphery of the pin and shoulder penetration surface; with increasing rotational speeds the SZ expanded along with the size of the TMAZ region as shown in Figure 11-5 (b) and (c), leading to a different corrosion path.
Figure 11-6 Cross section of a FSSW joint made with 3000 rev min\(^{-1}\) and 1 sec dwell time after SRET testing showing pitting of the TMAZ as a result of a macrogalvanic cell formed between the noble SZ and active BM (adapted from [188]).

The use of high rotational speeds and long dwell times affected the corrosion behaviour of FSSW joints through a number of pathways. In terms of corrosion rate, Chapter 10 has already showed that the use of these welding parameters increased the corrosion potential of the SZ region resulting in a stronger galvanic couple. The effect of welding parameters on the intrinsic electrochemical properties of the SZ is clearly evident in samples made using a rotational speed of 1000 rev min\(^{-1}\) with a dwell time of 1 and 4 sec (Figure 11-1). In both specimens, the cathode-to-anode ratio of the galvanic couple between the noble SZ and the active BM was similar. The cathode in this galvanic couple (SZ) was confined to the very peripheries of the pin and shoulder penetration surfaces, and both surfaces exhibited minimal degradation during the exposure period (Figure 11-3). Since the cathode-to-anode ratios of the two specimens were similar, the higher corrosion rate associated with specimens made using a dwell time of 4 sec can be attributed to the intrinsic electrochemical properties of the SZ region. Following the conclusions made in Chapter 10, longer dwell time (4 sec) increased the time available for intermetallic dissolution, and promoted the formation of a SZ region with a higher corrosion potential and lower corrosion current density than those of a SZ region welded using a dwell time of 1 sec.

While the effect of dwell time on the corrosion rate of using a rotational speed of 1000 rev min\(^{-1}\) can be explained by the differences in intrinsic electrochemical properties of the SZ region, the same argument cannot be applied to specimens made with a rotational speed of 3000 rev min\(^{-1}\). Chapter 10 clearly determined that the electrochemical properties of SZ regions made using a rotational speed of 3000 rev min\(^{-1}\) were independent of the dwell time (Figure 10-6). The differences observed in the corrosion rate for specimens welded at 3000 rev min\(^{-1}\) were linked to
the galvanic couple that have formed during the exposure period. Although, initially the cathode-to-anode ratios were similar for the two samples, it has changed noticeably once the thin SZ layer on top of the TMAZ (on the shoulder penetration surface) has been damaged, and the active TMAZ has been exposed to the corrosive media (Figure 11-3). The size of the remaining SZ region in each case was different (see schematic representation in Figure 11-7). Samples welded using a rotational speed of 3000 rev min$^{-1}$ and 4 sec dwell time had a larger SZ region (Figure 11-7 (b)) which resulted in the formation of a stronger galvanic couple and a higher corrosion rate.

![Figure 11-7 Schematic representation of the effect of dwell time on the corrosion morphology of samples welded using a rotational speed of 3000 rev min$^{-1}$ and a dwell time of (a) 1 and (b) 4 sec. Location for galvanic couples that drive the corrosion process are labeled using roman numerals.](image)

Two galvanic couples were responsible for the corrosion morphology observed in samples made using a rotational speed of 3000 rev min$^{-1}$. The corrosion attack on the shoulder penetration surface (labeled as I in Figure 11-7) was driven by the galvanic coupling between the noble SZ and the adjacent TMAZ (active). Localized corrosion also appeared on the upper sheet surface (labeled as F in Figure 11-2 (b)) at the weld periphery. This corrosion attack occurred as a result of SZ formation on the surface (labeled as II in Figure 11-7) that came in contact with the rotating welding tool. The effect of welding parameters on the size of the SZ in that location, and its effect on the corrosion behaviour of the weld will be discussed in further detail in Chapter 12.

The results herein show that the size of the local cathode (SZ) was also related to the selection of welding parameters. Higher rotational speed and longer dwell time produced a larger SZ region which led to a greater cathode-to-anode ratio and a stronger driving force for the galvanic attack occur. In terms of corrosion morphology, the use of higher rotational speeds and longer dwell time broadened and extended the TMAZ near to the shoulder penetration surface. This
microstructural change increased the likelihood that the active TMAZ will be exposed to corrosion attack (in the event that thin SZ layer is compromised), which could compromise the integrity of the weld.

11.5 Summary

The influence of tool rotation speed and dwell time on the microstructure, weight loss, morphology of corrosion attack and potential distribution was investigated in friction stir spot welded joints in AZ31B material. The following conclusions can be drawn:

1. Both rotational speed of the tool and dwell time are important in changing the microstructure within the weld zone and in particular the relative size of the stir zone and TMAZ/HAZ zones.
2. For a constant dwell time, increasing the rotational speed of the tool increased the corrosion rate.
3. For a constant rotational speed of the tool, increasing the dwell time increased the corrosion rate.
4. Changing welding parameters altered the corrosion rate of the joint by influencing the individual electrochemical properties of the SZ (as discussed in Chapter 10), and by altering the geometry of the galvanic couple that has formed in the joint (as discussed in this chapter).
5. The location of the corrosion attack was related to the geometry and the dimensions of the SZ region, which were determined by the welding parameters used to produce it.
Chapter 12 Effect of Welding Flash on the Corrosion of Friction Stir Spot Welded AZ31B


12.1 Introduction

In the previous chapters, the effect of FSSW on the corrosion behaviour of AZ31B focused on the local galvanic cell formed between the noble SZ and the active base metal. However, to understand the overall effect of FSSW on the corrosion behaviour of AZ31B, all the morphological features of the weld have to be decoupled and considered separately.

During the welding process, material is expelled from underneath the rotating pin into the void between the tool shoulder and the base metal. As the tool continues to plunge, this material is squeezed from underneath the shoulder and forms the welding flash. The welding flash is not commonly considered in the research of FSSW, although previous work by Da Silva et al. showed that the formation of a larger secondary flash improved the mechanical interlocking between the lower and upper sheet with higher tool plunge depth [239].

Though it is a standard practice for many industries to remove the welding flash upon completion of the joint, there is no formal requirement to do so [240]. The previous chapter has already alluded that the welding flash may influence the corrosion behaviour of the friction stir welded magnesium alloys. It is therefore important to understand any effect the welding flash may have on the overall corrosion resistance of the weld as to ensure proper corrosion performance of the weld in the absence of its complete removal. The effect of this feature on the corrosion behaviour of the weld has not been previously considered.

The objective of this chapter is to examine the effect of the welding flash on the extent, morphology, and rate of corrosive attack, on FSSW made in AZ31B magnesium alloy exposed to chloride media. Ultimately the goal is to correlate the nature of the attack with the evolution of the microstructure/flash arising from the welding process.
12.2 Flash Evolution Study

To better understand the microstructure present within the flash and its subsequent effect on the corrosion performance of the weld, it is essential to understand the material flow that occurs during flash generation. The welding process can be broken down into two main phases: plunging and dwelling. During the first portion of the process, a rotating tool is plunged at a constant vertical velocity into the base metal until it reaches a depth specified by the operator. In the second stage of the operation, the tool maintains a constant vertical position while rotating at a constant speed. Both the speed and the dwell time can be modified. In this investigation, partially completed welds were taken from different points of the welding process in order to produce a flash evolution sequence that will describe the generation of welding flash from its first appearance to the final shape on a completed joint.

To evaluate the changes in the flash shape during the plunging portion of the process, samples were prepared at 3000 rev min\(^{-1}\) with plunge depth varying from 6.25 mm to 6.65 mm. The welding process was stopped abruptly, without dwelling, once the desired plunge was achieved. The second set of samples was prepared by plunging to a constant depth of 6.65 mm. For this set, the dwell time was varied between 0.2 and 4 seconds. In order to allow complete heat dissipation into the clamp, all samples were left clamped for three minutes following the process. Once welded, shoulder penetration into the base metal was measured by subtracting the thickness of the base metal from the thickness measured on the complete joints underneath the shoulder. All thickness measurements were performed at the four corners of the coupon/weld and the mean was recorded.

Figure 12-1 shows a cross section of a sample welded with a plunge of 6.25 mm and 0 seconds dwell time. The base material was displaced from below the rotating pin into the gap between the rotating shoulder of the tool and the base metal. Similar behaviour was observed by Gerlich et al. [203], who examined hook formation in friction stir spot welds in aluminum alloys with the use of a high-speed camera. At the stage of the process pictured, the shoulder had not plunged into the material, so the thickness of the weld was greater than the thickness of the base metal. The edges of the expelled material did not represent the initial stages of the flash present on complete joints, as the diameter of the expelled material was only 7.7 mm (shorter than the 10 mm diameter of the rotating tool). As the plunging progressed, the gap between the base metal and the shoulder
filled with material expelled by the rotating pin. When the gap was finally filled, the shoulder continued to move down, and material was squeezed from under the shoulder producing the first step in flash generation. At that point, the flash was composed of material that was stirred and heavily deformed. It is expected that this material will share common characteristics with the SZ with minimal TMAZ present since the shoulder had not penetrated the metal sheet and mechanical work was not introduced yet. Only when the shoulder strikes the metal sheet both SZ and the TMAZ can be formed.

It is important to note that the volume of the material that was removed from the keyhole appeared substantially greater than the volume of the material that was expelled during the welding operation. The material displacement occurred as a result of compressive stress occurring during the plunging period. The compressive stress was exerted orthogonally to the pin away from its centerline. As a result, plastic deformation led to increased metal sheet thickness at the weld periphery. Some material was also lost as it adhered to the welding tool and was removed when the tool was withdrawn at the end of the welding operation. Finally, a small portion of the material was expelled by the rotation of the threaded pin of the welding tool in the material.

![Figure 12-1 Cross-sectional view of a weld (3000 rev min⁻¹ / 6.25 mm plunge / 0 sec dwell time)](image)

Table 12-1 outlines the shoulder penetration depth as it changed throughout the welding process, where negative penetration denoted that the shoulder had not struck the metal sheet yet. It was observed that the radius of the expelled material was equal to the radius of the rotating tool at a plunge of 6.40 mm; this point was identified as the origin of flash. The rotating shoulder struck the base metal sheets at a plunge depth of 6.65 mm as can be seen in Table 12-1. The flash
generation consisted of two distinct stages. During the first stage, when the tool plunged between a vertical position of 6.40 mm and 6.65 mm, the expelled material was free to flow from underneath the shoulder to the top surface of the metal sheet. This material is expected to be primarily composed of dynamically recrystallized equiaxed grains. The second stage occurred when the shoulder struck the material and flash was developed during the dwelling period. Both SZ and TMAZ were produced at this stage. Shoulder penetration increased with increasing dwell time up to a final target depth of 0.33 mm. If longer dwell times are allowed, the rate of increase in shoulder penetration depth decreased (Table 12-1). A much smaller increase in shoulder penetration depth was observed when dwell time was increased from 1 to 4 sec as compared to the changes occurred in the first second of dwell.

<table>
<thead>
<tr>
<th>Plunge Depth [mm]</th>
<th>Dwell Time [sec]</th>
<th>Shoulder Penetration [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.25</td>
<td>0</td>
<td>-0.203</td>
</tr>
<tr>
<td>6.35</td>
<td>0</td>
<td>-0.152</td>
</tr>
<tr>
<td>6.40</td>
<td>0</td>
<td>-0.127</td>
</tr>
<tr>
<td>6.45</td>
<td>0</td>
<td>-0.102</td>
</tr>
<tr>
<td>6.55</td>
<td>0</td>
<td>-0.051</td>
</tr>
<tr>
<td>6.65</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6.65</td>
<td>0.2</td>
<td>0.127</td>
</tr>
<tr>
<td>6.65</td>
<td>0.4</td>
<td>0.203</td>
</tr>
<tr>
<td>6.65</td>
<td>0.6</td>
<td>0.254</td>
</tr>
<tr>
<td>6.65</td>
<td>0.8</td>
<td>0.305</td>
</tr>
<tr>
<td>6.65</td>
<td>1</td>
<td>0.330</td>
</tr>
<tr>
<td>6.65</td>
<td>4</td>
<td>0.457</td>
</tr>
</tbody>
</table>

Table 12-1 Shoulder penetration throughout the welding process (3000 rev min⁻¹)

Miklas shown that the material flow that occurred during friction stir welding of AZ31 can be studied by exposing the weld cross sections to corrosive media (0.086M NaCl) for a short period of time (1.5 hours) [12]. These exposure conditions induced filament corrosion on the surface of the specimen, and the corrosion tracks aligned with material flow patterns that were present during
the welding operation. In this chapter, the material flow in the welding flash was examined by immersing welded specimens into 0.86M NaCl solution at 30 °C for 1.5 hours. Detailed information on the experimental procedure can be obtained from Section 6.4.2.

Figure 12-2 shows a series of micrographs documenting the shape of the flash and the instantaneous material flow characteristics occurring during various points of welding (as outlined in Table 12-1). Flash was generated from the point when the gap between the shoulder of the welding tool and the metal sheet was filled with expelled material. Before the shoulder came in contact with the BM (plunge depth from 6.40 mm to 6.65 mm), the flow line in the welding flash were smooth and relatively straight. This flow pattern occurred since the material was allowed to flow unobstructed. When the shoulder of the welding tool came in contact with the BM, a sharp change in material the flow direction occurred. At this point, the size of the welding flash started increasing rapidly as well. The flash grew rapidly during the first 0.4 sec of dwell and then its size remained largely unchanged. When the rotating tool achieved its final plunge depth, only a finite amount of material could be displaced from underneath the tool, therefore no further growth of the flash was observed with further increase in dwell time.
Figure 12-2 Material flow during flash evolution (3000 rev min\(^{-1}\))
12.3 Microstructure

The microstructure of the welding flash was examined to assess its effect on the corrosion properties of the joint. The microstructure of the cross-sectional surface (Figure 12-3) of the welding flash showed the presence of a compact layer of dynamically recrystallized grains near the inner edge of the flash. The layer of dynamically recrystallized equiaxed grains was adjacent to an area of larger grains. A similar microstructure was observed at the periphery of the keyhole in the weld nugget, having a compacted layer of grains, which corresponded to the SZ followed by larger grains associated with the TMAZ. In the case of the weld nugget it has been shown that a local galvanic cell is formed between the noble SZ and the active base metal, causing enhanced corrosion at the SZ periphery (chapters 7-11). The presence of a second SZ and TMAZ regions in the welding flash would suggest that a second local galvanic cell could form in the welding flash, further accelerating the corrosion rate of the joint. The removal of the welding flash would eliminate the second local galvanic couple and reduce the corrosion rate of said joints.

Figure 12-3 Microstructure of the cross-sectional surface of the welding flash in a FSSW made in AZ31B magnesium alloy (dark-field optical microscopy). Joint made using 3000 rev min\(^{-1}\) and 1 sec dwell time.
12.4 WC Tracer Imaging

As shown in Chapter 7, a WC tracer could be used to mark the SZ region in a FSSW joint made in AZ31. In this investigation a similar approach was used to confirm the presence of the SZ in the welding flash region. Figure 12-4 shows the tungsten carbide (WC) tracer (bright area) distribution within the welding flash. The WC tracer was mixed from underneath the shoulder into the welding flash by the motion of the tool shoulder. The above observation is in agreement with prior work done by Su et al. that showed that material located underneath the shoulder at 95% of its diameter was extruded away from the weld nugget to form the flash [162]. The presence of intermixed WC tracer in the flash region confirmed the existence of a SZ within the flash region. The adjacent region was subjected to mechanical deformation and heat input, producing a region that resembled a second TMAZ zone. The region marked by the WC tracer corresponded to the compact region seen in Figure 12-3. The width of the SZ can be characterized by the width of the bright region in Figure 12-4.

Figure 12-4 SEM images in BSE mode of welding flash in FSSW joints made with WC tracer, using 1 sec dwell, (a) 1000 rev min\(^{-1}\), and (b) 3000 rev min\(^{-1}\)

The effect of rotational speed of the tool on the size of the SZ in the welding flash is depicted in Figure 12-4. Both samples were welded using a dwell time of 1 sec, but the rotational speed of the tool was varied from 1000 rev min\(^{-1}\) (Figure 12-4 (a)) to 3000 rev min\(^{-1}\) (Figure 12-4 (b)). The width of the region marked by the WC region was found to increase with the rotational speed of the tool. The same effect was also observed by Su et al. and James et al. [11, 165].
Chapter 12: Effect of Welding Flash on the Corrosion of Friction Stir Spot Welded AZ31B

To further elucidate the effect of welding parameters on the size of the cross-sectional area of the flash and the SZ, the dimensions of the flash (width \([W_f]\), and height \([H_f]\)), and the cross-sectional areas of the flash and SZ were measured. The portion of the flash that was marked by WC tracer was calculated and summarized in Table 12-2. An increase in the dwell time and/or rotational speed resulted in an increase in the cross-sectional area of the flash. The area portion of the SZ as marked by WC tracer increased with an increase in rotational speed for all dwell times. The dwell time played an important role for joints made using a rotational speed of 1000 rev min\(^{-1}\). Only a slight increase in the relative area of the SZ was observed in samples made using a rotational speed of 3000 rev min\(^{-1}\). The relative size of the SZ began to plateau when high rotational speed and dwell time were used, as the size of the tool served as the main limiting factor for further growth of the zone.

<table>
<thead>
<tr>
<th>Joint ID</th>
<th>A1</th>
<th>A4</th>
<th>D1</th>
<th>D4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational speed of the tool [rev min(^{-1})]</td>
<td>1000</td>
<td>3000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dwell time [sec]</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Flash width -- (W_f) [(\mu m)]</td>
<td>1533</td>
<td>1697</td>
<td>1072</td>
<td>1167</td>
</tr>
<tr>
<td>Flash height -- (H_f) [(\mu m)]</td>
<td>905</td>
<td>1003</td>
<td>834</td>
<td>851</td>
</tr>
<tr>
<td>Flash cross section area [(mm^2)]</td>
<td>0.887</td>
<td>0.914</td>
<td>0.895</td>
<td>0.946</td>
</tr>
<tr>
<td>WC tracer area ratio in flash</td>
<td>5.86%</td>
<td>15.10%</td>
<td>22.73%</td>
<td>24.16%</td>
</tr>
</tbody>
</table>

Table 12-2 The effect of welding parameters on the dimensions of the welding flash and relative size of the stir zone

12.5 Mass Loss Testing

The work herein examined the effect of welding flash on the corrosion behaviour of FSSW in AZ31 in two conditions: “as welded” (full flash), and fully removed flash (no flash) as shown in Figure 12-5. The exposure time of the samples to corrosive media was varied between 120 and 480 hours, and the experimental procedure followed the protocol detailed in Section 6.4.1.2. The average corrosion rates in 0.086M NaCl were calculated from the mass loss data per unit area per unit time, after the corrosion product was removed using the dichromate solution. The summary of mass loss corrosion rates for all exposure times and flash conditions is presented in figure 5.
Each condition was tested at least four times, and the standard deviations are shown by the error bars.

Figure 12-5 Schematic of (a) plan view, (b) cross section, and (c) cross section with removed flash of a 3000 rev min⁻¹ FSSW weld along with the corresponding optical images (d) plan, (e) cross section, and (f) cross section of a sample with removed flash. A—bottom of pin hole surface, B—edge of key hole, C—shoulder penetration surface, D—outer edge of shoulder, E—inner edge of shoulder, F—upper sheet surface, G—hook, H—mating surface of two sheets, I—welding flash, Wf—flash width, Hf—flash height.

The corrosion rates calculated for the base metal are in general agreement with the corrosion rates reported by Liao et al. who reported corrosion rates of 0.014 and 0.010 mg·cm⁻²·hr⁻¹ or exposure of AZ31B to 0.1M NaCl for 168 and 336 hours respectively [211]. In this investigation the authors used a slightly more dilute electrolyte (0.086M NaCl) and a different exposure time (120, and 360
hours), nonetheless it is expected that the corrosion rates reported in this manuscript would not vary greatly from the ones reported by Liao et al. [211]. For comparison, the corrosion rates reported by Liao et al. were also plotted in Figure 12-6 [211].

Figure 12-6 shows that welded specimens (with and without flash) displayed lower corrosion resistance than the base metal coupons. The above results are in agreement with the observations from Chapter 11 that suggested that FSSW resulted in accelerated corrosion around the weld nugget. The presence of the welding flash did not affect the corrosion rate of FSSW welds for short exposure times, up to 240 hours in 0.086M NaCl, but the effect became apparent after exposure of 360 hours and 480 hours. The corrosion rate of welded samples with the flash (0.018 ± 0.001 mg·cm⁻²·hr⁻¹) was approximately 20% higher than that of specimens which had the flash removed (0.014 ± 0.001 mg·cm⁻²·hr⁻¹).

![Figure 12-6 Effect of welding flash and exposure time on the corrosion rate of FSSW joints (3000 rev min⁻¹ and 4 sec dwell time) measured by weight loss in 0.086 M NaCl. For comparison the corrosion rates of AZ31B in 0.1M NaCl as reported by Liao et al. were plotted as well [211].](image)

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It is noted that the corrosion rate values for both the base metal and FSSW joints were lower in this experiment than the ones reported in Chapter 11. The difference in the corrosion rate is attributed to the oxide film formed on the surface of the mass loss coupons. The samples in the previous investigation were polished on the same day they were immersed in NaCl solution, while the samples in this investigation were polished prior to the welding procedure and were exposed to the nominal laboratory atmosphere for 7 days. The prolonged exposure of magnesium to the ambient atmosphere has been shown to increase the thickness of its oxide film by about 40% over a course of 7 days (from 4.3 nm to 6.2 nm) [64]. Work by Feliu et al. indicated that the oxide film developed on a polished magnesium alloy surface was relatively compact and uniform, and it increased its corrosion resistance during short exposure (less than 7 days) to sodium chloride media [67, 241]. It is not surprising that the two data sets showed slightly varying corrosion rates for base metal and FSSW joint coupons upon a short exposure of 120 hours.

Examination of the corrosion morphology of corroded samples (Figure 12-7) provided insight into the effect of exposure time on the corrosion behaviour of the weld. The oxide film formed on the coupons prevented localized attack during short exposure times, in agreement with previous observations [242]. Upon longer exposures, the effect of the initial surface condition diminished, and a localization of the corrosion attack was observed around the weld nugget [67]. Figure 12-7 shows that samples that had the welding flash were subjected to a greater degree of localized corrosion attack around the weld.
Figure 12-7 Influence of welding flash and exposure time on the location and morphology of corrosive attack. Important weld surfaces are labeled with letters that are consisted with the schematic in Figure 12-5(b). A—bottom of pin hole surface, C—shoulder penetration surface, F—upper sheet surface, I – welding flash

12.6 Scanning Reference Electrode Technique Analysis

Mass loss testing provides insightful information on the relative corrosion performance of the welds, but it cannot elucidate the underlying corrosion mechanism that causes the variance in corrosion resistance. To address this issue, the results obtained from mass loss testing were coupled with a localized corrosion investigation to explain the effect of welding flash on the overall corrosion behaviour of the joint. SRET investigation followed the procedure outlined in Section 6.4.5.2. The location for SRET measurements is shown schematically in Figure 12-8 (a).
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Figure 12-8 Welding flash schematic: (a) location of SRET, and (b) location of microcapillary polarization. Important weld surfaces are labeled with letters that are consistent with the schematic in Figure 12-5 (b). C—shoulder penetration surface, D—outer edge of the shoulder, E—edge of key hole, F—upper sheet surface, W_f—welding flash width, and H_f—welding flash height.

Previous SRET studies on the corrosion behaviour of a FSSW joint in AZ31B have shown that the SZ is noble to the base metal [11, 12]. A complete discussion of SRET studies on AZ31B FSSW joints is available in Section 5.3.1. The potential distribution mapped by the SRET analysis showed that the noble zone coincided with the regions in the weld nugget marked by WC tracer [11]. A similar approach was taken in the present study to evaluate the possibility of formation of a local galvanic cell in the welding flash. Figure 12-9 (c) shows a collage between the scanned area (Figure 12-9 (a)) and the SRET output (Figure 12-9 (b)). The SRET image in Figure 12-9 (b) is a 2-dimensional contour graph showing the relative potential values. The red and orange regions represent noble potential regions, which correspond to the SZ. The yellow and green regions adjacent to the SZ correspond to the active region, the TMAZ. The SRET results show the formation of a local galvanic cell, which would result in accelerated corrosion of the flash as seen through mass loss testing as discussed in the previous section.

It is important to note that similarly to the SRET measurements in the weld nugget, the potential drop measured between the SZ and the TMAZ is also likely to be influenced by the presence of a local variation in the electrolyte (pH, and dissolved gasses (O_2 and H_2)). For example, following the rational presented in Section 11.4, it can be inferred that the pH of the electrolyte near the SZ was lower than the pH of the electrolyte near the TMAZ. The presence of such pH difference suggest that a galvanic couple is present in the welding flash, where the SZ is noble and the TMAZ is active.
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Figure 12-9 SRET of the welding flash in a FSSW made in AZ31B (3000 rev min⁻¹, 4 sec dwell): (a) post SRET optical micrograph, (b) SRET output, and (c) overlay of potential distribution and optical micrograph

The effect of welding parameters on localized corrosion caused by the presence of a noble SZ in both the welding flash and the weld nugget is analogous. In both cases an increase in rotational speed of the tool, and/or dwell time would increase the size of the area marked by the WC tracer as shown in Chapter 7 for the weld nugget and in Table 12-2 for the welding flash. Changes in rotational speed of the tool, and/or dwell time also affected the intrinsic electrochemical properties as the selection of process parameters was shown to influence intermetallic dissolution (see Chapter 10). Regardless of the location of the SZ, the area marked by the tracer corresponded to a local noble SZ that formed a galvanic couple with the nearby active TMAZ region as shown by SRET studies. An increase in either of the aforementioned welding parameters increased the size and the potential of the local cathodic regions and led to stronger galvanic coupling, and higher corrosion rates.

It is important to note that the galvanic coupling between the noble SZ region and the surrounding active material was similar in samples with or without welding flash, even though the welding flash did not have an HAZ region. In both cases, when the top surface of the joint is exposed to corrosive media during mass loss testing, the noble SZ is coupled with the adjacent TMAZ region leading to the initiation of localized pitting at the weld periphery. As the corrosion process proceeded pitting expanded into the HAZ region that was located immediately beside the TMAZ. The galvanic couple in this advanced corrosion state would be governed by the coupling between the corroding region and the noble SZ regardless of its location (in the nugget or the welding flash). It can be concluded that the SZ in the welding flash was coupled with the HAZ region even though this region was missing in the flash. The presence of the welding flash did not alter the
corrosion mechanism, instead the main effect of its presence on the overall corrosion behaviour of the join was caused by an increase in the overall cathodic area which altered the cathode-to-anode ratio leading to higher corrosion rates.

12.7 Second Phase Particle Distribution Measurements

The dissolution of secondary phase particles was further investigated by examining their size and distribution in the welding flash. For experimental procedure, see Section 6.5.3. Figure 12-10 shows the influence of the welding operation on the microstructure of the welding flash, by comparing the particle size distribution of the TMAZ region with that of the SZ region. Parts (a-d) of the figure provide representative micrographs of both regions, while part (e) provides a distribution profiles for Mg\(_{17}\)Al\(_{12}\) particles present in these regions. For comparison, measurements obtained for the BM, SZ, and TMAZ regions in the weld nugget were included in the figure as well. Examination of the figure revealed that complete dissolution of Mg\(_{17}\)Al\(_{12}\) particles occurred in both stir zone regions, while the number of particles in the TMAZ did not vary significantly from the base metal.
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Figure 12-10 Representative micrographs of the (a,c) TMAZ, and (b,d) SZ regions in the welding flash, along with (e) normalized particle size distribution profiles for Mg_{17}Al_{12} intermetallics
To further examine the influence of the welding operation on the microstructural constituents of the alloy, the area fraction of each secondary phase was calculated, and the results were summarized in Table 12-3. The area fractions of each second phase measured in the SZ region were statistically similar for both the nugget and the welding flash. Statistical similarity was also found when the two TMAZ regions were compared. The above observation further strengthens the proposition that a second SZ/TMAZ regions are present in the welding flash.

<table>
<thead>
<tr>
<th>Secondary Phase</th>
<th>Al-Mn (%)</th>
<th>Mg$<em>{17}$Al$</em>{12}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ Flash</td>
<td>0.322 ± 0.022</td>
<td>0.002 ± 0.003</td>
</tr>
<tr>
<td>SZ Nugget</td>
<td>0.279 ± 0.025</td>
<td>0.001 ± 0.002</td>
</tr>
<tr>
<td>TMAZ Flash</td>
<td>0.457 ± 0.023</td>
<td>0.117 ± 0.012</td>
</tr>
<tr>
<td>TMAZ Nugget</td>
<td>0.437 ± 0.021</td>
<td>0.095 ± 0.015</td>
</tr>
<tr>
<td>BM</td>
<td>0.622 ± 0.081</td>
<td>0.100 ± 0.022</td>
</tr>
</tbody>
</table>

**Table 12-3 Area fraction of secondary phase particles in various FSSW regions. The uncertainty given in the table represents one standard error.**

Area fraction measurements presented in Table 12-3 emphasized the dissolution of Mg$_{17}$Al$_{12}$ particles that was observed in Figure 12-10. The results show that in both cases, flash and nugget, the stir zone exhibited a microstructure that was virtually free of Mg$_{17}$Al$_{12}$ intermetallics. The above observations support previously published findings suggesting that the friction stir welding operation resulted in the dissolution of Mg$_{17}$Al$_{12}$ particles in the stir zone [168, 169]. In a similar manner to intermetallic dissolution in the weld nugget, the welding operation did not result in complete dissolution of all second phase particles present in AZ31B magnesium alloy. While the welding operation resulted in a complete dissolution of Mg$_{17}$Al$_{12}$ particles in the SZ regions, the quantity and the relative area fraction of Al-Mn particles was reduced in the SZ compared to both the TMAZ (flash/nugget) and BM. An extensive discussion of dissolution mechanisms is available in Section 4.4.

### 12.8 Microcapillary Polarization

While the SRET output can visualize the formation of localized galvanic cell, it does not provide an insight into the kinetics present in the corrosion process in the flash. In order to supplement the information gathered from SRET, microcapillary polarization experiments were conducted to
Chapter 12: Effect of Welding Flash on the Corrosion of Friction Stir Spot Welded AZ31B

quantify the corrosion potential and corrosion current density for each weld zone. Both the SZ and the TMAZ in the welding flash were examined (see schematic in Figure 12-8 (b) for the location of the measurement). Figure 12-11 shows the potentiodynamic polarization graphs for various weld zones, located in both the weld and the flash (repeatability of the experimental results is shown in Appendices H and K). It can be seen that the zones in the weld nugget behave in a similar manner to their respective zones in the flash. Each zone was measured on three samples and the corrosion potential and current density were found through Tafel extrapolation.

![Figure 12-11 Microcapillary polarization of various weld zones: potentiodynamic polarization graphs comparing between the weld nugget and the welding flash, extrapolation.](image)

The results from Tafel extrapolation are summarized in Table 12-4. The SZ was found to be noble with respect to the TMAZ, confirming the observations made using the scanning reference electrode technique. The electrochemical characteristics of the SZ in the flash were statistically similar to the electrochemical properties of the SZ region in the weld nugget (Figure 12-11). Similarly, the TMAZ region in both the weld nugget and the flash displays comparable corrosion potential and corrosion current density. The corrosion rates of the SZ in both the flash and the weld nugget were found to be lower than the TMAZ.
Table 12-4 Summary of corrosion current and potentials found in the flash and the weld nugget. The error is given as the standard deviation taken from the average of at least three measurements. Repeatability of the experimental results is shown in Appendices H and K.

Microcapillary polarization measurements confirmed the existence of a noble region in the welding flash corresponding to a second SZ area. The presence of the noble SZ in the welding flash results in the formation of a local galvanic cell, and subsequently results in localized corrosion of the boundary between the TMAZ and the SZ, as seen in Figure 12-12 (a), which shows a cross section of the welding flash of a FSSW joint after a 6 hours exposure to 0.086M NaCl. The figure shows heavy pitting attack along the boundary between the noble (SZ) and the active (TMAZ) regions. As a result, the welding flash would accelerate the corrosion of FSSW joints made in AZ31.
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The resulting corrosion morphology after exposure of 480 hours is shown in Figure 12-12 (b). The TMAZ portion of the welding flash was preferentially attacked, leaving the noble SZ behind. Overall, the presence of the welding flash accelerated the localized corrosion attack around the weld nugget, by forming a secondary local galvanic cell between the active TMAZ and the noble SZ.

The overall corrosion resistance of FSSW joints is governed by the galvanic coupling between the noble SZ regions present in the weld (nugget and the welding flash), and the active TMAZ regions. The ratio between the exposed areas of the two regions determined the degree of localized corrosion attack occurring in the joint. If the welding flash is not removed upon the completion of the weld, then the overall exposed cathodic area is increased resulting in a joint that is more susceptible for localized corrosion as shown in the work herein. Design of specific regulations and guidelines to remove the welding flash is suggested if this technology is to be implemented in an industrial application.

Figure 12-11 shows an apparent decrease in the anodic kinetics of the SZ in both the weld nugget and the flash. The dissolution of second phase Mg$_{17}$Al$_{12}$ and Al-Mn intermetallics (see Table 12-3) increased the aluminum content in $\alpha$-Mg matrix, which in turn reduced the anodic kinetics of the region. The above observation is in agreement with previously reported work by Song et al. and Mathieu et al. that examined the effect of aluminum concentration in single phase $\alpha$-Mg samples [81, 82, 230]. A meaningful analysis of the effect of welding on the cathodic kinetics of the SZ and TMAZ in the welding flash was not possible in the present investigation. One of the challenges associated with microcapillary polarization involves capillary clogging by gas evolution on the surface of the working electrode. This is particularly true when examination of the cathodic branch is desired, as hydrogen is rapidly evolved when cathodic overpotentials are applied. Future work should focus on measuring the electrochemical response of isolated weld regions under cathodic polarization. A capillary with a circulating electrolyte can be used to enhance hydrogen gas bubble removal from the corroding surface. Such apparatus would minimize capillary clogging and widen the potential window that can be examined by microcapillary polarization. Sakairi et al. developed a microcapillary polarization apparatus that utilized a two channel microcapillary that enhanced the electrolyte flow near the surface of the corroding specimen [218]. In this design, the first channel was connected to a source of electrolyte, while the other was connected to a vacuum chamber that collected the used electrolyte [218].
use of such apparatus to examine the corrosion resistance of FSSW joints made in magnesium alloys would greatly enhance the research capability of this particular technique.

12.9 Summary

The effect of the welding flash on the corrosion behaviour of FSSW joints was investigated through a combination of various complimentary techniques: mass loss testing, WC tracer, SRET analysis, detailed microscopy and microcapillary polarization. The following conclusions can be drawn:

1. The corrosion rate of FSSW joints made in AZ31 magnesium alloy was sensitive to the presence of welding flash upon prolonged exposure to corrosive media.
2. A noble SZ region and an active TMAZ existed in the welding flash.
3. The welding process resulted in a partial dissolution of Al-Mn and complete dissolution of Mg$_{17}$Al$_{12}$ particles in the SZ region in the welding flash.
4. The ennoblement of the SZ region in the welding flash followed a similar mechanism to that responsible for the ennoblement of the SZ region in the weld nugget, see Chapter 10.
5. The microstructure and electrochemical behaviour of the SZ and TMAZ in the welding flash were similar to their respective regions in the weld nugget when each is measured independently.
6. The presence of a noble and an active region in the flash resulted in the formation of a local galvanic cell, which caused accelerated corrosion attack at the boundary between the SZ and the TMAZ.
7. Complete removal of the welding flash can improve the corrosion resistance of the weld.
Chapter 13 Corrosion Mechanisms in Dissimilar AZ31/AZ80 Friction Stir Welds

This work was published in the Journal of the Electrochemical Society in 2018 and reproduced with permission. “Savguira, Y., North, T. H., and Thorpe, S. J. “Corrosion mechanisms in dissimilar AZ31/AZ80 friction stir welds,” Journal of the Electrochemical Society 165 (2), C1-C10, 2018.”

13.1 Introduction

The work described in chapters 7-12 focused on the effect of welding on the corrosion resistance of FSW joints made between two metals of identical composition (i.e. similar welds). The present chapter expands the focus of this thesis to examine joints between different alloys. Many industrial applications require joining of dissimilar alloys in order to facilitate design criteria such as strength or stiffness. For example, AZ31/AZ80 dissimilar joints could be used to manufacture light-weight magnesium alloy spare wheels to replace the mini-spare steel wheels that are commonly used today. A basic wheel consists of two components: the hub and the rim, both experiencing different loading conditions in such an application. The hub is responsible for supporting the load of the vehicle, and typically experiences considerable compressive and bending stresses. The rim is responsible for distributing the load through the pressurized tire. In the present case, AZ80 is sufficiently strong to support the load of the vehicle, but the high alloying content limits its ductility, making it challenging to form it into a rim. In direct contrast, AZ31 has insufficient strength to be used in the hub structure, but it has much better low temperature formability allowing it to be shaped into a rim [13]. With the use of tailor-welded blanks and friction stir joining technologies it is possible to produce a multi-material optimized spare wheel that utilizes the benefits of each material while avoiding their shortcomings.

If dissimilar FSW magnesium joints were to be used in an industrial application, it is essential to understand the influence of the welding process on their corrosion behaviour. It is currently unknown whether the corrosion behaviour of dissimilar welds is governed by the microstructural changes occurring during the welding operation (as observed in similar welds) and/or by the galvanic coupling of the alloys themselves. In either case, the susceptibility for localized corrosion in the region adjacent to the welded joint must be addressed when dissimilar magnesium alloys are joined during industrial applications.
Chapter 13: Corrosion Mechanisms in Dissimilar AZ31/AZ80 Friction Stir Welds

This investigation was focused on the localized corrosion behaviour of a dissimilar FSW joint made between two magnesium alloys of the same class, AZ31 and AZ80 alloys. The chapter aims to evaluate the corrosion resistance of the dissimilar weld, and to propose a model describing the mechanism(s) governing its degradation behaviour. Corrosion rates were measured through mass loss testing, while the model was developed based on in-situ observations, and examination of the corrosion morphology.

13.2 Microstructure and Corrosion Susceptibility

Figure 13-1 (a) shows a through-thickness cross section of the stir zone formed in a dissimilar FSW weld. There is a clearly defined boundary between AZ31 (on the retreating side of the joint) and AZ80 (on the advancing (left) side of the joint), see Figure 13-1 (b). EDX mapping output (Figure 13-1 (c)) shows the contact region between the higher aluminum content AZ80 and the lower aluminum content AZ31 alloy. Both optical and EDX analysis showed no evidence of inter-diffusion between the dissimilar magnesium alloys. Similar microstructural features in dissimilar AZ80/AZ31 FSW joints were also observed by Liu et al. [243]. The AZ80 material (on the advancing side) directly underneath the rotating shoulder was moved downwards via the pin thread before discharging at the bottom of the rotating pin. This plasticized material flow near the bottom of the pin channeled the AZ80 towards the adjacent AZ31, ultimately producing the large lamella that extended past the weld centerline (Figure 13-1 (b)). The rotation of the welding tool on the retreating size resulted in plasticized AZ31 flow towards the adjacent AZ80. Ultimately, the rapid heating and cooling of the material in the SZ did not provide sufficient time for solid state diffusion, thus limiting the formation of new phases at the interface. As a result, the stir zone comprised a series of fine alternating layers of AZ80 and AZ31.

Figure 13-1 (d) shows the corrosion morphology produced following exposure of the joint cross section to 0.086 M NaCl for a period of 2 hours. The location of the micrograph corresponds with the dashed line rectangle in Figure 13-1 (a). It is apparent that AZ31 corroded preferentially compared to AZ80. The most severe attack occurred at the interface between the dissimilar magnesium alloys. This localization of the corrosion attack suggested that the preferential dissolution of AZ31 was caused by a galvanic couple formed between the two alloys.
Figure 13-1 (a) Cross section of a dissimilar AZ31/AZ80 FSW joint. (b) Magnified optical micrograph of the area shown by the solid line, along with the corresponding (c) aluminum EDX map. (d) Corrosion morphology observed upon exposure of the cross-sectional surface of the joint to 0.086 M NaCl for 120 minutes (corresponding to the area bound by the dashed line). The left-hand side of these images show the advancing side of the dissimilar joint.

13.3 Investigation of the Galvanic Couple

Microcapillary polarization tests were performed on the stir zone material in similar AZ31 and AZ80 joints in order determine the theoretical magnitude of the expected galvanic couple formed between the dissimilar magnesium alloys (repeatability of the experimental results is shown in Appendices H and L). The experimental procedure for the test is detailed in Section 6.4.4.3. The output produced during microcapillary polarization of the stir zone regions in AZ31 and AZ80 similar joints is shown in Figure 13-2. The reproducibility for these measurements is shown in Appendices H and L respectively. Table 13-1 shows the corrosion potential and corrosion current
values determine using Tafel extrapolation. Results are generally considered to be reliable if a Tafel extrapolation of an iR-corrected polarization curve exhibits linearity over an entire decade of current [209]. Achieving such linearity in microcapillary polarization of magnesium alloys is quite challenging due to the limited scanning potential window that is caused by gas evolution and capillary clogging. However, the technique still has its merits as it has been shown to produce reliable data, seen from the agreement between the experimental results in bulk and microcapillary polarization (see Chapter 7).

![Microcapillary polarization curves](image)

**Figure 13-2** Comparison of microcapillary polarization curves obtained in the stir zone of AZ31 and AZ80. The AZ31 FSSW was welded using 3000 rev min⁻¹ and 4 sec dwell, while the AZ80 FSW was welded using 820 rev min⁻¹ and 88 mm/min.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Region</th>
<th>$E_{\text{corr}}$ [V SCE]</th>
<th>$i_{\text{corr}}$ [µA/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31</td>
<td>Stir Zone</td>
<td>-1.408 ± 4 mV</td>
<td>2.8 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>Base Metal</td>
<td>-1.469 ± 3 mV</td>
<td>10.3 ± 0.2</td>
</tr>
<tr>
<td>AZ80</td>
<td>Stir Zone</td>
<td>-1.449 ± 5 mV</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Base Metal</td>
<td>-1.500 ± 1 mV</td>
<td>2.8 ± 0.2</td>
</tr>
</tbody>
</table>

**Table 13-1** Corrosion potentials and currents of stir zone and base metal in similar welds
Chapter 13: Corrosion Mechanisms in Dissimilar AZ31/AZ80 Friction Stir Welds

The results in Table 13-1 confirmed that both the corrosion potential and corrosion current of the stir zone in a similar AZ31 weld were higher (~40 mV and 1.7 μA/cm²) than those in the stir zone of a similar AZ80 weld. FSW welding increased the corrosion potential and decreased the corrosion current in the stir zone in similar welds, regardless of the aluminum content in the magnesium alloy, see Table 13-1. The electrochemical properties of the stir zone in either alloy were correlated to the phase constituents present in the region (experimental procedure given in Section 6.3.5). A summary of the relative area fraction of second phase intermetallics present in both base metal and stir zone regions in AZ31 and AZ80 is given in Table 13-2.

<table>
<thead>
<tr>
<th>Secondary Phase</th>
<th>Ti-Al-Mn</th>
<th>Mg17Al12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Metal AZ31</td>
<td>0.302 ± 0.067 %</td>
<td>Not Detected*</td>
</tr>
<tr>
<td>Stir Zone AZ31</td>
<td>0.121 ± 0.023 %</td>
<td>Not Detected*</td>
</tr>
<tr>
<td>Base Metal AZ80</td>
<td>0.327 ± 0.039 %</td>
<td>0.093 ± 0.009 %</td>
</tr>
<tr>
<td>Stir Zone AZ80</td>
<td>0.206 ± 0.013 %</td>
<td>0.052 ± 0.031 %</td>
</tr>
</tbody>
</table>

* Mg17Al12 particles were not found in AZ31 at the magnifications examined in this chapter. The Mg17Al12 particles in AZ31 are present on a nanoscale as has been shown in section 10.4, and therefore were not included here.

Table 13-2 Area fraction of secondary phase particles in various FSSW regions. The uncertainty given in the table represents one standard error.

As expected, the area fraction of second phase intermetallics in AZ80 was higher than that in AZ31 regardless of the region examined. The difference in the phase constituents between the two alloys was attributed to the greater aluminum content in AZ80 as compared to that of AZ31. It is interesting to note that no β-Mg17Al12 particles were found in AZ31 at the magnifications examined in this investigation (x300 – x1,000). The above is not surprising, as it has already been shown that AZ31 contains β-Mg17Al12 particles that are present only on the nanoscale and as such are not visible at a magnification of 1,000 times (see Section 10.4). It is evident from the information presented in Table 13-2 that the welding operation resulted in a reduction in the overall area fraction of second phase precipitates in the stir zone, regardless of the alloy. While the overall area fraction of second phase particles decreased, the degree of dissolution of each phase varied between the two alloys. Unlike AZ31 that has been previously shown to exhibit complete dissolution of β-Mg17Al12 particles as a result of welding, AZ80 exhibited only a partial dissolution of these particles. The difference is likely related to their size in which they are initially
present in the base metal. The nano sized $\beta$-Mg$_{17}$Al$_{12}$ particles in AZ31 would be expected to dissolve faster than the micron sized particles in AZ80. In both alloys, Al-Mn particles exhibited only partial dissolution; however, a greater fraction of the initial quantity dissolved in AZ31. This is likely due to the lower aluminum content in the $\alpha$-Mg matrix, and the higher concentration gradient enabling the driving force for diffusion.

In both alloys, the stir zone was noble to the base metal due to partial dissolution of $\beta$-Mg$_{17}$Al$_{12}$ and Al-Mn particles in the stir zone region. Previous observations have shown that in similar FSSW welds this promoted localized corrosion in the TMAZ/HAZ regions located between the stir zone and the adjoining base material (see Section 11.5). In direct contrast, corrosive attack in dissimilar FSW joints was most pronounced within the stir zone, at the contact interface between the dissimilar base materials.

The difference in the location most susceptible to localized corrosion in FSW joints is related to the nature of the galvanic couple that governs the corrosion behaviour of the welds. In similar welds, the noble stir zone formed a galvanic couple with the active base metal, causing preferential dissolution at the periphery of the weld nugget. Such galvanic couples exist in dissimilar welds as well, where the friction stir processed material in the stir zone (noble) was coupled to its respective base metal (active). It is interesting to note that the presence of these galvanic couples in the dissimilar weld did not result in localized corrosion at the periphery of the weld nugget as observed in similar welds. Instead, metal dissolution occurred at the dissimilar interface between the two alloys, as the corrosion behaviour of the weld was dominated by the dissimilar coupling and not by the microstructural changes caused by FSW.

The stir zone regions in similar AZ31 joints had a higher corrosion potential and corrosion current values than those found when examining the stir zone regions in AZ80 welds. These results correspond with the electrochemical output during polarization testing of AZ31 and AZ80 in 3.5 wt. % NaCl [84, 210]. As discussed in Section 3.2.1.1, the corrosion resistance of magnesium increases with increasing aluminum content in the $\alpha$-Mg matrix. The AZ80 SZ region exhibited greater corrosion resistance than the AZ31 SZ region due to the greater aluminum content in its $\alpha$-Mg matrix.

In the present study, comparison of the size and distribution of $\beta$-Mg$_{17}$Al$_{12}$ intermetallics between the two alloys (Table 13-2) revealed significant differences. In AZ80, micro-scale $\beta$-Mg$_{17}$Al$_{12}$
intermetallics in AZ80 were found along grain boundaries as seen from optical micrographs of etched specimens (Figure 13-3 (b)). In direct contrast, AZ31 contained only nano-scale $\beta$-Mg$_{17}$Al$_{12}$ intermetallics, as has been shown in a previously published high resolution scanning electron microscopy (HRSEM) investigation (section 10.3). The difference in the corrosion rate and microstructure between the two alloys are consistent with results reported by Padro et al. [84, 210].

![Optical micrographs of etched AZ80 base metal taken at a magnification of (a) 500X and (b) 2,000X. The samples were etched with acetic glycol etchant for 4 sec.](image)

SRET was utilized to investigate the galvanic couple formed in the dissimilar weld examined in this chapter. The detailed experimental procedure is provided in Section 6.4.5.2. The output produced in a linear SRET scan across a dissimilar joint is shown in Figure 13-4 (b). This horizontal scan was performed on a thin layer of AZ80 (the bright region in Figure 13-4 (a)), which was intermingled with AZ31 (the dark region in Figure 13-4 (a)) in the stir zone. The scan shows a step in the OCP, indicating the transition that exists between the two dissimilar metals. The observed potential difference (35 mV) was significantly larger than the theoretical estimation (2 mV) that was obtained by solving the Laplace equation (Appendix O). Although the difference between the experimental and theoretical values was smaller than that in Section 11.4, it is likely that the measurement was still affected by local changes in the electrolyte composition that were present in the near vicinity of the weld surface. These local changes were related to alloy chemistry as the OCP step correlated well with the changes in composition along the line of measurement as shown by EDX (Figure 13-4 (c)).
Figure 13-4 (a) Micrograph of the dissimilar interface that is present in the stir zone region of an AZ31/AZ80 FSW joint along with the output from (b) SRET and (c) EDX linear scans taken from the horizontal traverse indicated by the dashed line.

A SRET potential distribution map overlaid on the joint optical microstructure is shown in Figure 13-5. All potentials are indicated with reference to the potential measured on AZ31 base metal following one hour of equilibration. The SRET scan confirms the formation of a galvanic couple between AZ31 and AZ80. Also, the potential distribution indicates the contours of the intermingled AZ80 layer in AZ31. The above finding further confirms that the corrosion behaviour of dissimilar joints is governed by the formation of a macro-galvanic couple between the dissimilar magnesium alloy materials.
Figure 13-5 Corrosion potential distribution of a through-thickness cross-section in a dissimilar AZ31/AZ80 FSW joint in 0.086 M NaCl. The SRET output is overlaid on the optical micrograph of a welded specimen following exposure to the corrosive medium. All potentials are indicated with reference to the potential measured on AZ31 base metal following one hour of equilibration.

13.4 Corrosion Rate Measurements

Mass loss testing was used to determine the corrosion rates of AZ31, AZ80, along with dissimilar FSW joints made between these magnesium alloys. The experimental procedure followed the protocol outlined in 6.4.1.3. All test samples were exposed for 5 days to 0.086 M NaCl and the average corrosion rate was calculated based on the exposed area, holding time, and mass difference values, see Figure 13-6 (a). The error bars in the figure represent one standard deviation. Each base material had a lower corrosion rate than dissimilar FSW welded samples. Higher aluminum content increased the corrosion resistance of AZ80 compared with AZ31, which is in agreement with the corrosion rates predicted following potentiodynamic polarization, and the discussion in Section 3.2.1.1.
Corrosion morphology after a 5-day exposure to 0.086 M NaCl of a welded specimen: (b) top, and (c) bottom surfaces.

Examination of the corrosion morphology (see Figure 13-6 (b) & (c)) revealed localized attack at the interface between AZ31 and AZ80, suggesting accelerated corrosion attack due to the presence of the galvanic couple formed between the dissimilar magnesium alloys. The most severe corrosion attack occurred along the interface line on the top and bottom surfaces of the dissimilar AZ31/AZ80 joints. Corrosive attack on the bottom surface (Figure 13-6 (c)) was localized at the contact interface between the dissimilar metals, with enhanced dissolution on the AZ31 side. Although corrosion attack on the top surface of the dissimilar joint (Figure 13-6 (b)) was similar in character to that on the bottom surface, the location where the attack occurred was shifted from the joint centerline towards the AZ80 side of the weld. It would be expected that a galvanic couple would create symmetrical corrosion morphologies on the top and bottom surfaces of dissimilar AZ31/AZ80 joints. EDX was employed to investigate the cause for the difference in the location of the corrosion attack between the top and bottom surfaces of the dissimilar joint. The EDX output produced in a traverse across the top surface of a dissimilar AZ31/AZ80 weld is shown in Figure 13-7. It is apparent that AZ31 (the dark region in Figure 13-7) has been displaced by the tool shoulder towards the AZ80 (the bright region in Figure 13-7). A thin layer of AZ31 material is formed near the top surface of the dissimilar joint as a result of high temperature and shear rate that exists beneath the surface of the welding tool shoulder. AZ31 material is displaced from the retreating to the advancing side of the dissimilar joint. Similar behaviour has been observed in dissimilar FSW joints made in aluminum alloy base materials [244]. The thickness of
the AZ31 layer formed on the top surface of the joint decreased with increasing distance from the weld centerline. The displacement of AZ31 material towards the AZ80 side of the joint readily explained the site of localized attack on the upper surface of dissimilar AZ31/AZ80 joints, see Figure 13-6 (b). Severe localized corrosion at the boundary between the thin AZ31 layer and AZ80 promoted formation of pits predominantly in the AZ31 layer.

![Figure 13-7 Aluminum EDX map of a cross section of a FSW joint near the top surface of the weld.](image_url)

When two dissimilar alloys are galvanically coupled, mixed potential theory predicts that the corrosion rate of the more active alloy would accelerate while that of the more noble one would decrease. It is interesting to note that the corrosion morphology observed following mass loss testing did not support this prediction. Instead, the galvanic coupling between AZ31 and AZ80 resulted in preferential dissolution of the more noble material (AZ31). To further investigate this rather unexpected behaviour, welded samples exposed to chloride containing media were monitored for a duration of 48 hours and in situ images at select times were taken. For comparison purposes, uncoupled based metals specimens were exposed to the corrosive media and imaged as well. In order to simplify the geometry of the galvanic couple in the joint, only the bottom surface of the weld was exposed in this experiment. The corrosion morphology observed following mass loss testing suggested that the mechanism governing the corrosion of the joint was similar on both, the top and the bottom, surfaces (Figure 13-6 (b) & (c)). Exposing only the bottom surface simplifies the geometry of the galvanic couple as the dissimilar interface coincides directly with the centerline of the weld. Additionally, there is no need to consider the microstructural changes seen in the stir zone and TMAZ regions, as the microstructural features on the bottom surface that are exposed to corrosive media would correspond to the HAZ and base metal regions.

A series of representative in situ images captured at various times during the exposure period for welded and uncoupled base metal specimens are shown in Figure 13-8 and Figure 13-9 respectively. Initially (time = 0 hours), the hydrogen evolution reaction accompanying the anodic
dissolution reaction, was well distributed on both sides of the dissimilar weld as evidenced by the presence of small hydrogen bubbles on the surface of the specimen. The appearance of the welded specimen did not vary much from the appearance of either of the base metal specimens at the same time point (Figure 13-9). At this early stage of exposure, no preferential sites for the cathodic or anodic reaction could be identified. After 3 hours of exposure, the number of hydrogen bubbles on the AZ31 side of the dissimilar weld decreased. The bubbles that were still present on AZ31 were located at the periphery of filiform corrosion sites that appeared in several spots on the surface of the specimen, and at the dissimilar interface. Their size was noticeably larger than the size of the bubbles observed upon initial exposure. On the AZ80 side, the number of hydrogen bubbles decreased, and their size increased slightly. The distribution of the bubbles was still random, and no visible signs of corrosion were present.

\[\text{Figure 13-8 In situ imaging of dissimilar AZ31/AZ80 FSW joint in 0.086M NaCl.}\]

After 6 hours of exposure, filiform corrosion continued to spread on the AZ31 side, covering most of its area. Only a few hydrogen bubbles remained on AZ31, located near the filiform corrosion sites and at the dissimilar interface. The uncoupled AZ31 specimen also exhibited filiform corrosion, with hydrogen bubbles present at the periphery of the sample and near corroding sites. On the AZ80 side, the number and distribution of bubbles did not change significantly, but their size, specifically near the dissimilar interface, grew. On the uncoupled AZ80 specimen, hydrogen bubbles were distributed randomly on the surface of the specimen. Comparison between the sizes of bubbles formed on the uncoupled AZ80 base metal to that of bubbles present on welded AZ80 revealed an interesting phenomenon. The bubbles at the dissimilar interface, measuring 1.5 mm in diameter, were greater than those on the uncoupled specimen (~1 mm in diameter). In direct
contrast, the bubbles located away from the dissimilar interface (~0.6 mm in diameter) were smaller than those on the uncoupled specimen. The above observation supports the proposition that the cathodic reaction near the interface on AZ80 was accelerated due to the galvanic coupling. The hydrogen evolution reaction up to this point exhibited two opposite trends on either side of the weld. On AZ80, it became significantly more pronounced, while it subsided on the AZ31. Corrosion appeared only on AZ31 in the form of filiform corrosion. No preferential attack was observed at the dissimilar interface at this short exposure time suggesting that the corrosion behaviour of the joint was not yet governed by the galvanic coupling.

After 16 hours of exposure, virtually no hydrogen evolution was observed on AZ31, and its surface was completely covered with filiform corrosion. On the uncoupled AZ31 base metal specimen, filiform corrosion continued to grow, and gas bubbles were located at the periphery of the specimen, near the epoxy-metal interface. The effect of dissimilar coupling was clearly visible from the preferential dissolution of AZ31 along the entire length of the dissimilar interface, and from the heavy pitting that was present as well (marked by the white arrow in Figure 13-8). The largest gas bubbles appeared near the dissimilar interface suggesting that the accelerated dissolution was driven by the faster cathodic kinetics that were present locally. The uncoupled AZ80 base metal specimen also appeared protected. Comparison of the bubble sizes on the coupled and uncoupled AZ80 specimens have shown a similar trend to the one observed at the 6-hour time interval. The bubbles on the uncoupled base metal were smaller than the ones near the dissimilar interface.

As the exposure continued (26 hours), filiform corrosion continued to spread and the pit at the dissimilar interface grew. No hydrogen bubbles were visible on the AZ31 side, while those present on AZ80 continued to grow. It was clear that the anodic reaction proceeded on AZ31, while the cathodic reaction occurred on AZ80. Finally, when the exposure time increased even further (43 hours) the corrosion resistance of both alloys increased due to the presence of the quasi-passive film, and the overall number of bubbles decreased [84]. The reduction in the apparent corrosion rate due to changes to surface film formation that was promoted by prolonged exposure is in agreement with the discussion in Section 3.2.2, and the results presented in Section 12.5. The bubbles that remained on the surface were preferentially located on the AZ80 side, with some preference being given to sites near the dissimilar interface. Similar observations were made on the corresponding uncoupled based metals (Figure 13-9).
Figure 13-9 In situ imaging of dissimilar AZ31 and AZ80 base metal specimens in 0.086M NaCl.
Galvanic coupling between AZ31 and AZ80 resulted in accelerated dissolution of AZ31 despite its higher corrosion potential (Table 13-1). The accelerated anodic reaction on AZ31 was promoted by the increased hydrogen evolution occurring on the surface of AZ80. To gain a greater insight into the mechanism governing this phenomena, active cathodic sites on corroded specimens were examined by SEM and EDX. Cathodic sites on AZ80 were determined from the location of hydrogen gas bubbles on the surface of the specimen at an exposure time of 16 hours. The investigation revealed that each of the cathodic sites identified from the location of the bubbles on the surface of AZ80 coincided with a cluster of Al-Mn intermetallic particles as shown in Figure 13-10.

The composition of the intermetallic phase identified as cathodic sites was determined to be Al₄Mn with trace amounts of iron. While AZ alloys contain several different Al-Mn intermetallics, it is expected that an increase in the Al content of the alloy would increase the proportion of aluminum rich intermetallics [31]. The aluminum to manganese concentration ratio \( R_{Al/Mn} = \frac{\text{wt.\% Al}}{\text{wt.\% Mn}} \) in AZ31 and AZ80 were 8.3 and 46.1, respectively. The greater \( R_{Al/Mn} \) in AZ80 promoted the formation of secondary phase intermetallic particles with higher aluminum content, i.e. Al₄Mn. It is important to note that other Al-Mn intermetallics such as Al₈Mn₅ were identified as active sites for the hydrogen evolution reaction in addition to the Al₄Mn particles identified as cathodic sites in Figure 13-10. The activity of Al₄Mn towards the hydrogen evolution reaction was reported to be lower than that of Al₈Mn₅ particles [97]. *Lunder et al.* examined the electrochemical properties of Al-Mn-Fe phases in a 0.86M NaCl solution that was saturated with Mg(OH)₂ (pH=10.5) [97]. The Al₄Mn phase exhibited a more active corrosion potential (\( E_{\text{corr}} = -1.40 \text{ V}_{\text{SCE}} \)) than the Al₈Mn₅ phase (\( E_{\text{corr}} = -1.25 \text{ V}_{\text{SCE}} \)) [97]. The cathodic kinetics of Al₄Mn phase were about an order of magnitude lower than those of the Al₈Mn₅ phase when both phases were cathodically polarized at a potential of -1.60 V\text{SCE}.

The coupling of the cathodic Al-Mn intermetallic particles to the highly active \(\alpha\)-Mg phase on AZ31 accelerated its anodic dissolution and resulted in greater corrosion rates at the dissimilar interface. Although the cathodic activity of Al₄Mn was lower than Al₈Mn₅, it has been reported to be comparable to that of Mg₁₇Al₁₂ particles [97], and the presence of these particles has already been shown to accelerate the corrosion of the surrounding \(\alpha\)-Mg phase in a variety of alloys [81, 84, 85].
Based on the results obtained in this investigation, a mechanism governing the corrosion behaviour of dissimilar AZ31/AZ80 FSW joints can be proposed. The factors governing the corrosion resistance of individual base metals and the dissimilar joint are summarized schematically in Figure 13-11. When uncoupled AZ31 is exposed to chloride containing solution the anodic reaction occurs on the poorly protected $\alpha$-Mg phase. The cathodic reaction occurs on noble intermetallic particles ($\text{Al-Mn}$ and $\text{Mg}_{17}\text{Al}_{12}$), and on the corrosion products formed on the surface of the specimen [98]. The oxide/hydroxide layer formed in chloride solutions was previously shown to contain increased levels of impurities caused by incongruent dissolution and/or replating of noble elements onto the surface of the alloy [5, 235, 236]. These impurities were suggested to be the cause for the increased cathodic behaviour of the corrosion products that accelerated the dissolution of magnesium and its alloys (see Section 3.2.2 for complete discussion of this mechanism). In AZ31, the oxide formed on the $\alpha$-Mg matrix phase offers poor corrosion resistance, allowing the anodic reaction to proceed. The relatively low aluminum content results in a smaller number of Al-rich intermetallic particles (compared to AZ80), as seen from the particle size distribution profile in Figure 13-12. As a result, a limited number of sites that are able to sustain the cathodic reaction. As such, the anodic kinetics of AZ31 are much faster than its cathodic kinetics, and the corrosion reaction is limited by the number of available catalytic sites to sustain the hydrogen evolution reaction.
Figure 13-11 Schematic of mechanisms governing the corrosion behaviour of base metals and dissimilar welds.

The opposite can be observed for AZ80. Its high aluminum content results in a large number of intermetallic particles (Figure 13-12). Consequentially, when AZ80 is exposed to chloride containing media there are many available catalytic sites to support the hydrogen evolution reaction. In addition to the greater number of intermetallic particles, increased aluminum content also increases the stability of the oxide film formed on the α-Mg matrix phase. As a result, the dissolution rate of the α-Mg matrix in AZ80 is reduced significantly. Contrary to AZ31, the cathodic kinetics of AZ80 are much faster than its anodic kinetics, and so the corrosion rate of AZ80 is limited by the dissolution rate of the α-Mg matrix.
Chapter 13: Corrosion Mechanisms in Dissimilar AZ31/AZ80 Friction Stir Welds

When examining the corrosion behaviour of the dissimilar weld, attention must be given to the phase constituents of each of the alloys. In the present case, considering each alloy as a homogenous material would over simplify the system and yield incorrect estimation of the corrosion behaviour. Considering the corrosion potentials of the two alloys, it would be expected that AZ31 (noble) would be protected by the preferential dissolution of AZ80 (active), which was not observed experimentally. However, if individual phases are considered then experimental observations can be explained theoretically. When AZ31 is welded to AZ80, new catalytic sites on AZ80 (Al-rich intermetallic particles) are introduced into the system. As a result, the cathodic kinetics (which limit the anodic dissolution of α-Mg matrix on AZ31) are accelerated and the overall corrosion rate is increased. Accelerated localized anodic dissolution kinetics on AZ31 as a result of welding, are observed by the preferential dissolution of AZ31 near the dissimilar interface, when coupled with the accelerated cathodic kinetics on AZ80 (as evident by the preferential presence of hydrogen bubbles on the AZ80 side).

It is interesting to note that a comparison of the particle size distribution profiles (Figure 13-12) for intermetallics in both stir zones revealed that the greatest difference was present in quantity of

![Figure 13-12 Particle size distribution profiles for intermetallics present in friction stir welded AZ31 and AZ80.](image-url)
particles with an area ranging between 1 and 10 µm². This correlates well with the intermetallics found in the clusters of particles near the dissimilar interface (Figure 13-10). Ultimately, these particles were determined to be responsible for accelerating the local cathodic kinetics and accelerating the dissolution of AZ31. This observation further supports the proposition that the accelerated corrosion attack at the dissimilar interface was caused by the greater number of catalytic sites able to support the cathodic reaction.

The corrosion mechanism herein constitutes the first attempt to provide a mechanistic explanation for the corrosion behaviour of dissimilar magnesium welds. The corrosion mechanisms summarized in Table 3-4 were developed to describe the factors governing the corrosion of a single magnesium alloy and did not consider a situation where a dissimilar interface could exist. The present work expands on these mechanisms to assess the changes arising from dissimilar joining. For both similar and dissimilar joints, the anodic reaction is considered to occur on unprotected α-Mg phase, while the cathodic reaction occurred on noble intermetallic particles, and on the corrosion products formed on the surface of the specimen. This is also consistent with the mechanism described in Section 10.6 of this thesis.

The present investigation examined the corrosion behaviour of dissimilar AZ31/AZ80 FSW joints. It was evident that dissimilar joining increased the corrosion susceptibility of the weld. Galvanic coupling between the active α-Mg matrix in AZ31 and the noble Al-rich intermetallic particles in AZ80 resulted in localized pitting at the dissimilar interface. If dissimilar welding was to be used in an industrial application, isolation of the galvanic couple from corrosive media would be required to prevent corrosion. Application of a coatings to mask the dissimilar interface could be a viable corrosion mitigation strategy. Further discussion on the development of a PEO process able to produce protective coatings across the dissimilar interface is available in Section 15.2.
13.5 Summary

This work investigated the corrosion behaviour of dissimilar AZ31/AZ80 FSW joints. It is concluded that:

1. There was negligible evidence of inter-diffusion between the dissimilar substrates (AZ31 and AZ80) in the stir zone region of FSW joints. The stir zone microstructure was comprised of fine intermingled layers of AZ31 and AZ80, which were formed due to material flow during the joining operation.

2. Based on mass loss testing, dissimilar AZ31/AZ80 joints exhibited higher corrosion rates than either of the as-received AZ31 and AZ80 substrates.

3. Corrosion of the dissimilar joints was governed by the galvanic coupling between the dissimilar magnesium alloys, not by microstructural changes resulting from the welding operation.

4. A mechanism describing the corrosion behaviour of dissimilar AZ31/AZ80 FSW welds has been proposed. Galvanic coupling between the active $\alpha$-Mg matrix in AZ31 and the noble Al-rich intermetallic particles in AZ80 resulted in enhanced localized corrosion in the form of pitting at the dissimilar interface.
Chapter 14 Plasma Electrolytic Oxidation of Magnesium Alloys

This work was published in Surface and Coating Technology in 2017 and reproduced with permission. Sobrinho aided with early stage sample preparation and Ni assisted with R code development and statistical analysis. His input to the discussion is also greatly appreciated. “Sobrinho, P. H., Savguira, Y., Ni, Q., and Thorpe, S. J. “Statistical analysis of the voltage-time response produced during PEO coating of AZ31B magnesium alloy,” Surface and Coating Technology 315, 530-545, 2017.”

14.1 Introduction

Much of the research investigating PEO coatings on magnesium alloys has been focused on optimization of treatment conditions to improve the corrosion resistance of these coatings [124, 138, 140-144]. A discussion of the relevant advances in the field is given in Section 3.5. Before assessing the feasibility of PEO coatings to act as a corrosion mitigating strategy for friction stir welded magnesium alloys, it is essential to understand the mechanism governing PEO coating formation on magnesium alloys.

The aim of this chapter is to develop a methodology for examining the mechanisms governing PEO treatment of magnesium alloys. In particular, the goal is to develop sufficient theoretical knowledge to relate the process parameters used during PEO treatment to the physical properties of the resulting coatings. The knowledge gained in this chapter will serve as a foundation for PEO coating design for application as a corrosion resistant barrier on friction stir welded AZ31. The corrosion behaviour of PEO coatings produced on base metal and welded magnesium alloys will be examined in Chapter 15.

14.2 Formation Mechanism

To examine the effect of process parameters on coatings produced using a constant applied current, the potential output measured during the treatment process is commonly correlated to the microstructural features of the coating. This potential output usually appears as a gradually increasing line with a number of distinct regions signifying various stages in the development of the coating [146, 153, 245]. While this potential rise is generally representative of the microstructural changes occurring on the surface of the substrate, it does not account for the sporadic nature of the plasma discharges. It would be expected that the potential measured during
the oxidation treatment will fluctuate significantly as a result of the plasma discharges. As such, a greater insight into the oxidation mechanism can be gained by measuring the voltage fluctuations at a much higher frequency (0.1-1000 kHz) to what has been done previously (0.01-1 Hz).

The investigation herein presents a novel approach to examine the mechanisms governing PEO treatment of magnesium alloys. In this approach, a statistical analysis was applied to the instantaneous voltage-time measurements acquired during treatment. Statistical results are complimented with structural analysis techniques (SEM/EDX/XRD), in order to distinguish between the various stages of oxidation and to characterize the type of discharges that occurred during each of those stages. The applicability of the newly developed approach was then demonstrated by examining the effect of select process parameters. Specifically, the effect of applied current density and electrolyte temperature was correlated to the principle discharge mechanisms, and the resulting properties of the synthesized coatings.

14.2.1 PEO Coating Evolution

To examine the coating evolution occurring during the PEO treatment process, a sample was coated with a current density of 10 mA/cm² and a bath temperature of 25 °C. The voltage-time response measured during the oxidation process showed a significant variation in voltage, as represented by the shaded region of Figure 14-1 (a). Such variation occurred due to continuous plasma discharge and passivation events at the surface of the specimen. Zhu et al. also observed some voltage fluctuation; however, their fluctuation was significantly smaller in magnitude due to the low sampling rate used in their study [153]. Interpretation of such a voltage response presents a challenge as the direct V-t plot, moving average (white line in Figure 14-1 (a)), and moving maximum (black line in Figure 14-1 (a)) would lose much of the information that can be extracted from the measurement.

To address this issue, a novel interpretation method was developed (see Appendix C3 for the R code used to process the data). In this method, a V-t curve is first divided into segments of length $\Delta t_{\text{bin}}$ (Figure 14-1 (a)). A sample segment is shown in Figure 14-1 (b), where the dots represent the voltage values as recorded. All the voltage values in each segment are processed into a histogram using a voltage bin size of $\Delta V_{\text{bin}}$ (Figure 14-1 (c)). For each segment, the frequency of appearance of voltage values is normalized against the highest count in each segment, and the
histogram can be represented by a grayscale map of segment $\Delta t_{\text{bin}}$, with voltage as the vertical axis (Figure 14-1 (d)). Then, all the histograms of all the time segments are connected and plotted into a 2-D contour map, where the horizontal axis is time, and the vertical axis is the voltage (bins) (Figure 14-1 (e)). This time-series histogram uses grayscale to represent the frequency $N(V, t)$ of voltage values recorded between $V$ and $V + \Delta V_{\text{bin}}$, in the segment between $t$ and $t + \Delta t_{\text{bin}}$. The 2-D contour map illustrated where the voltage tends to be concentrated at any given time during the PEO coating process. Darker spots represented the voltages that were recorded more frequently in the V-t function.

In visualizing the V-t function by time-series histograms, the choice of $\Delta t_{\text{bin}}$ and $\Delta V_{\text{bin}}$ would affect the final output. A small $\Delta t_{\text{bin}}$ (i.e. more segments) provides better resolution in the time axis, but it increases the noise of the histograms because each segment has fewer data points. Conversely, a large $\Delta t_{\text{bin}}$ can produce histograms with a greater number of data points, but the uncertainty of the time of each segment becomes larger. As for the bin size, $\Delta V_{\text{bin}}$, decreasing the bin size provides better resolution of voltage divisions, but doing so also results in higher noise as the number of data points in each bin is reduced. By balancing the resolution and signal-to-noise ratios in the horizontal and vertical directions, the combination of a 10 second window and a 5 V bin size were found to be optimal in the analysis of V-t spectra.
Figure 14-1 The voltage-time function during the PEO coating. (a) Recorded voltage (grey shade), maximum and average values. (b) Extracted V-t curve in segment Δt_{bin} (10 sec). (c) Voltage histogram of the segment Δt_{bin}. (d) Normalized histogram plotted in grayscale. (e) Normalized time-dependent histogram of voltage. Electrolyte composition: 40 g/L NaOH, 50 g/L Na₂SiO₄, 30 g/L Na₂B₄O₇, 10 g/L C₆H₅O₇Na₃, and 10 g/L PEG1000. Coating conditions: 10 mA/cm² current density and 25 °C bath temperature.

Figure 14-1 (e) offers insight into the statistical distribution of voltages recorded during the treatment process. It is evident from Figure 14-1 (e) that the coating process can be divided into
four distinctive regions, each representing a unique stage (labeled as I-IV in the graph) in the development of the coating. In stage I, the voltage rises steadily for about 1 minute, the voltage fluctuation in this stage was minimal. Stage II, which starts at 1 minute and ends at about 7 minutes, showed a very stable distribution of voltages. The majority of the voltage values measured were concentrated near 75 V, while some were near 100 V. In Stage III, the voltages continued to disperse but they increased gradually to about 150 V. At 16 minutes, the voltage distribution plateaued again, as stage IV. In this final stage, the voltages remained high, with occasional discharges that caused the voltage to suddenly plunge. For stages II and IV, the most frequently occurring voltages can be determined. In this investigation, this voltage is referred to as a characteristic voltage mode ($V_m$), as shown in Figure 14-1 (e).

To further investigate the two steady stages (II and IV), a histogram was produced for each stage, using all the data points collected in that range. The voltage distribution shown in the histogram produced for stage II (Figure 14-2 (a)) exhibited a bimodal distribution pattern. During this stage, the voltage frequently alternated between two distinct values around 75 and 100 V, with the majority of voltage concentrated on the lower level (designated as $V_m$(II)). In stage IV (Figure 14-2 (b)), the voltage varied across a wider range, but the majority of the voltages stayed near 150 V ($V_m$(IV)). There is also a possibility for the presence of a second minor peak at about 100 V, a voltage response that could be associated with the voltage frequency observed during stage II.

![Figure 14-2 Histograms of recorded voltage values in (a) stage II and (b) stage IV. Coating conditions: 10 mA/cm² current density and 25 °C bath temperature.](image)

The distribution of voltage signals in stages II and IV can be examined in detail by recording the high frequencies using an oscilloscope. In this investigation the voltage transients were measured at different sampling frequencies; representative outputs from each stage are given in Figure 14-3.
For comparison purposes, voltage transients obtained at 100 Hz were included as well. The oscilloscope used in this investigation was able to record up to 6,000 points in a single measurement, as such the duration of the measurements at each frequency varied.

Voltage transients recorded at higher sampling rates could reveal more details of the waveforms, as shown in the comparison chart of Figure 14-3. For example, the voltages recorded for stage II (Figure 14-3 (a)) showed a rather stochastic wave pattern. The only extractable information is that all the voltages fall in a steady band between 75 V and 100 V. Signals recorded at 10 kHz revealed that the voltages were actually cyclic, with a period of 10~15 milliseconds. Higher scan rates at 100 kHz can resolve even more details of the wave. It is clear that the cycles were asymmetric, with the voltage rising fast but dropping slowly. By the same means, the detailed waveforms of Stage III and Stage IV could be resolved at 10 kHz and 100 kHz. Stage III, which was sampled at 11 minutes, shows a transition behavior. The voltage wave resembled that of stage II, but another type of wave signified by a larger voltage drop was also evident. For Stage IV, the voltage transient showed a convolution of at least two types of voltage fluctuations. One type was found to bring the voltage down from 150 V to as low as 20 V. This type of transient occurred at a time interval of 100 milliseconds or so. The other type resembled the behavior observed in stage II, where the voltage was cycling between 100 V and 75 V, within the 10~15 cycle range.

It is worth noting, that the voltage distribution from the recordings did not vary with the scan rate employed. For example, the histogram of voltages recorded for Stage II at 100 Hz is compared to that recorded at 10 kHz in Figure 14-4. Both of them showed the characteristic bimodal distribution. That means the voltage modes were indeed originating from the waveforms as depicted by the high-speed recording in Figure 14-3. For stage II, the two voltage modes corresponded to the upper and lower boundary of the waves. A close examination of the wave in the bottom graph of Figure 14-3 (a) showed that the rate of voltage change was the slowest at these extremes, which explains why the voltage values close to them would be recorded at the higher frequencies. For stage IV, another type of bimodal distribution was recorded, which corresponded to the middle graph of Figure 14-3 (c). The major voltage mode corresponded to the top of the wave at around 150 V. The minor voltage mode seemed to correspond to the series of waves at 75~100 V that resembled stage II.
Figure 14.3 Voltage transients measured at different sampling rates (100 Hz via a data acquisition system, 10 kHz and 100 kHz via an oscilloscope) during (a) stage II, (b) stage III, and (c) stage IV.
Chapter 14: Plasma Electrolytic Oxidation of Magnesium Alloys

The cyclic behavior of the voltage in stage II and stage IV was an indication of the mechanisms responsible for PEO coating formation. A rise in the voltage indicated that the surface barrier layer was growing thicker, while a drop in the voltage indicated that the barrier layer broke down and the resistance across the barrier layer decreased. For stage II, the film formation seemed to be a much faster process than film breakdown. This asymmetric behavior with a long breakdown time (about 10 ms) suggests that the local breakdown of the coating film should proceed via a series of progressive events. Dunleavy et al. monitored current transients in the PEO process and reported that the surface barrier film breakdown in PEO processes is composed of a cascade of discharging events, each occurring on a microsecond scale [126]. Therefore, a voltage cycle in Stage II in the present results was likely associated with a cascade of discharging events that resulted in local breakdown of the existing film and formation of a new film at the discharge site. When the voltage reached a critical breakdown voltage of about 100 V, an initial discharge occurred resulting in a series of other discharges near the same site. In a few milliseconds, the voltage was brought down to about 75 V, due to the breach in the surface barrier layer. The voltage then rose, indicating that a surface barrier layer was forming again. The breakdown-reform cycle dominated the entire Stage II, as can be seen in the constant distribution of voltage values in Figure 14-1 (e).

![Image](image-url)

Figure 14-4 Comparison between the voltage histograms (stage II) produced from the voltage values obtained by a data acquisition system at 100 Hz and by an oscilloscope at 10 kHz.
In stage III, which was a transitioning stage between II and IV, the voltage continued to show cyclic behavior (Figure 14-3 (b)). The upper and lower boundaries of the voltage increased from stage II, a change that was correlated to the transitioning behavior in the histogram of Figure 14-1 (e). Occasionally, another type of discharge occurred in stage III (Figure 14-3 (b)), this was represented by a large voltage plunge to as low as 60 V. This type of discharge will become the major type in Stage IV.

The cyclic voltage transient (Figure 14-3 (c)) in stage IV was composed of at least two types of discharge cycles. One of the discharge cycles corresponded to the large voltage drop from 150 V down to about 50 V. This type of discharge was less frequent and occurred more than 100 milliseconds apart. The other type of discharge cycle resembled that present in Stage II, with fluctuations between 100 V and 75 V at a period of ca. 15 milliseconds. The second cycle, which resembled stage II behavior, occurred only on the rising portion of the larger dips, indicating that such cycles only occurred when the film was being reformed. The major discharge occurring at 150 V damaged the existing oxide layer, ultimately exposing the underlying substrate. As the coating grew to reform the oxide layer, it is first governed by the oxidation mechanism prevalent in stage II. When the thickness of the coating was restored the voltage rose to 150 V again, and the cycles begin anew.

To further interpret the physical representation of the voltage transient, it was necessary to look at the morphology of the coating in each stage of development.

**14.2.2 Morphology and Crystal Structures**

It is possible to gain an understanding of the mechanistic steps occurring during the oxidation process by correlating the instantaneous voltage-time output recorded during PEO treatment to the morphological and structural evolution of the coating. A series of samples were prepared by abruptly stopping the coating process at various stages of the oxidation process. Both the top and cross-sectional surfaces of these samples were imaged as shown in Figure 14-5 and Figure 14-6. A subset of the samples was examined using XRD to determine the type of phases in the coating.
Figure 14-5 Top views of PEO coatings produced at different times. Coating conditions: 10 mA/cm² current density and 25 °C bath temperature
In the first minute (stage I), a semi-transparent thin film appeared on the specimen surface (see Figure 14-5 (a)). High magnification cross-sectional imaging (Figure 14-6 (a) right) revealed the presence of a thin uniform compact layer on top of the base metal substrate (indicated by the white arrows). The thickness of this layer was measured to be approximately 0.3 μm. EDX analysis of samples in the middle of stage I (0.5 minutes) revealed that silicon was not present on the surface of the substrate, see EDX spectra in Figure 14-7 and quantitative analysis in Table 14-1. The coating developed during stage I was comprised principally of MgO. Previously published work described a similar thin film formation mechanism in silicate-containing electrolyte, which is analogous to conventional anodization [153, 246]. It is important to note that no sparks were emitted during stage I of the PEO treatment, in contrast to PEO coatings made in phosphate-based solution, as reported by Yagi et al. [245].

At the beginning of stage II (where the voltage profile was flat during 1-7 minutes), a porous layer started to form in different locations on the surface of the substrate. Figure 14-5 (b) shows isolated patches of these porous structure on the substrate surface at 4 minutes. By the end of stage II (7 minutes), the substrate was almost entirely covered with the porous layer except for a few spots, see Figure 14-5 (c). From the cross-sectional view, the isolated spots of coatings observed at 4 minutes (Figure 14-6 (b)) had developed into a near continuous layer by 7 minutes (Figure 14-6 (c)). High magnification images revealed that these coatings contained many spherical pores, which likely originated from water evaporation (Figure 14-6 (b)).
Figure 14-6 Cross-sectional views of PEO coatings produced at different times. Coating conditions: 10 mA/cm$^2$ current density and 25 $^\circ$C bath temperature.
Silicon incorporation into the coating began at the transition between stage I and II as evidenced by the minimal presence of silicon on the surface of samples treated for 1 minute. From this stage onwards, silicon was detected in every PEO coating measured using EDX (Figure 14-7 and Table 14-1). XRD did not detect any crystalline diffraction peaks other than those from magnesium AZ31 (Figure 14-8). It is unknown whether this film was crystalline or amorphous, as the thickness of the coating (<10 μm) and the lack of full substrate coverage were not sufficient to produce strong diffraction signals.

**Figure 14-7** EDX of the top surface of PEO coatings on Mg AZ31 samples treated for different lengths of time.
### Table 14-1 EDX Analysis of PEO treated specimens processed for various durations.

In stage III (7-15 minutes), where the voltage continued to rise from 75 V to 150 V, the coating did not increase in thickness. Instead the uniformity of the coating improved as seen from the cross-sectional view in Figure 14-6 (d). It is likely that at this stage both growth and dissolution of the coating occurred at similar rates, as such promoting uniformity and preventing any measurable increase in thickness. At 11 minutes, the surface was entirely covered with a fine porous layer, although a few spots devoid of this porous layer could still be found by optical and electron microscopy of the top surface as seen in Figure 14-5 (d). Similar to specimens coated for 4 minutes, no crystalline phases associated with the coating were detected by XRD (Figure 14-8). Comparison of the diffraction patterns obtained for the base metal and specimens coated for 4 and 11 minutes revealed that the samples coated for 11 minutes exhibited peak broadening phenomena between 20° and 40°. It has been previously shown that the extremely high energy generated by the plasma discharges promoted polymerization of the silicates and resulted in a glassy phase formation [134, 247]. Similar peak broadening has been previously observed when examining coatings made on AZ91 [248].
Once stage IV was reached, the outer porous layer started to grow thicker, as shown by the increase in coating thickness for specimens treated from 15 (Figure 14-6 (e)) to 30 minutes (Figure 14-6 (f)). The substrate, which was initially polished to a 1200 “fine” finish, had lost its uniformity, as magnesium was continuously consumed to form the coating. The final surface had an ivory-white color, and the top view showed numerous pores of various sizes as shown in Figure 14-5 (f). The sizes of the pores varied dramatically from the micron to the sub-micron range. The presence of crystalline phases in the coating was clearly evident in the XRD spectra (Figure 14-8) after 30 minutes. The coating comprised crystalline Mg$_2$SiO$_4$ and MgO, which is in agreement with previously reported results obtained when examining PEO coatings made on magnesium alloys processed in a silicate-containing electrolyte [144].

14.2.3 Mechanisms of Coating Formation

From the results presented above, the mechanism of coating formation can be elucidated, and a summary of the process is shown schematically in Figure 14-9. First, a compact dense layer developed uniformly on the entire surface under galvanostatic condition as shown in Stage I. This
initial compact layer was formed by the oxidation of the substrate without the deposition of silicate from the solution. The growth of this compact layer increased the resistance of the substrate, resulting in a gradual rise of the potential.

Once the voltage reached 90 V, dielectric breakdown occurred resulting in a cascade of plasma discharge at an imperfection in the oxide layer, and the onset of stage II. As a result of the breakdown, Mg$^{2+}$ ions were released into the electrolyte where they immediately reacted with silicate and hydroxide present in the solution to form a Mg$_2$SiO$_4$ / MgO deposit around the discharge site. These initial plasma discharges were responsible for the patches of porous coating observed in Figure 14-5 (b).

The bimodal distribution of voltages observed in Figure 14-2 (a) and the detailed voltage transient (10 kHz) in Figure 14-3 (a) suggested that the coating in stage II was developed in a steady cyclic process. The top and cross-sectional images revealed that the cycles were manifested by the gradual replacement of the initial compact layer formed in stage I by a new porous layer of material via cascades of discharges. The discharges could occur in isolated spots or as an extension of existing discharging sites. From Figure 14-5 (b), the latter type dominated stage II, possibly because the boundary between the newly formed porous materials and the compact layer formed during stage I was easier to breach by discharge than through the layer itself. The discharging in stage II resulted in the gradual expansion of coating over the entire surface (Figure 14-5 (c)). The rate of new coating formation was much faster than the rate at which the original oxide layer broke down, as such the voltage transient in stage II showed asymmetric waves as shown in Figure 14-3 (a). By the end of stage II, the coating material had covered the entire surface, leaving only very small pores (see Figure 14-5 and 6, at 11 minutes).
Figure 14-9 Schematic of coating formation by plasma electro-oxidation.
In stage III, dielectric breakdown continued to occur at the bottom of these pores. The resulting discharge ejected Mg$^{2+}$ into the solution and formed Mg$_2$SiO$_4$ / MgO deposits that would seal the pore. The closing of the remaining pores resulted in a rise in the voltage in stage III, until the next critical voltage of 150 V was reached (stage IV). This higher breakdown voltage was likely associated with the breakdown of the porous silicate-containing layer, as it had now covered the entire surface of the sample.

The discharges produced during stage IV were likely governed via two distinct mechanisms. One of them proceeded via breakdown of the porous film itself. The most likely sites of breakdown are the bottom surface of large pores. These pores, measuring over tens of microns in diameter (Figure 14-5 (f)), would exhibit a thin barrier layer at the bottom, with a higher probability of dielectric breakdown than anywhere else on the surface. This mechanism happened at a critical breakdown voltage that corresponded to the major voltage mode ($V_m$(IV)) of about 150 V (Figure 14-2 (b)). It accounts for the major dip of voltage from 150 V to below 50 V (Figure 14-3 (c)) and happened about every 100 milliseconds. Another type of discharge likely occurred at the bottom of the voids between the base metal and the bulk oxide coating. These voids were electrically connected to the external electrolyte via cracks that traversed through the film, similar to one seen in Figure 14-6 (f) (marked by the white arrow). The bottom of these voids contained a thin layer of oxide separating the electrolyte from the base metal (Figure 14-6 (f)), which could be subjected to dielectric breakdown. This type of discharge occurred at a critical potential of around 100 V. On the detailed voltage transient in Figure 14-3 (c), this discharge type corresponded to the voltage fluctuation zone between 75 V and 100 V, with a cycle period of about milliseconds. This discharge resembled that governing stage II, possibly by the same mechanism. In both cases, the electrolyte had come in close proximity with the base metal, separated only by a thin barrier layer. It is worth noting that this secondary discharge always occurred on the rising portion of the major discharge cycles (10 kHz voltage transient in Figure 14-3 (c)). The above observation is related to the breakdown and formation cycle of the coating. When a major cascade of discharges (150 V) occurred, the film broke locally which exposed the underlying substrate material. An oxide layer would then re-form on the exposed area following the coating growth mechanism observed in stage II. This led to the minor discharges (100 V) recorded in the voltage transient (10 kHz) in stage IV (Figure 14-3 (c)). The oxide on the discharge site would eventually grow thicker and the resistance would rise (as seen from the voltage rise up to 150 V).
Based on the observation in stage II, the discharge in stage IV also ejected Mg$^{2+}$ ions to form new Mg$_2$SiO$_4$ / MgO deposits, which filled the pores and voids [134, 247]. Rapidly vaporized electrolyte and the newly deposited material would then apply stress on the porous layer of the coating, resulting in the formation of new cracks. The overall result is an increase of coating thickness. The coating time must be long enough to reach stage IV, or the coating thickness will not increase.

The work herein has provided insight into the formation mechanism of the PEO coating on magnesium alloys in silicate solutions. The statistical analysis of voltage transient provided a clear distinction between different stages of development during the PEO process of AZ31 magnesium alloy. In literature, the division of stages was mainly based on visual observation, V-t curve and optical emission [127, 128, 157, 249-251]. Direct analysis of the V-t curve was often complicated by the stochastic response in the signals and clear distinction of the stages of the PEO process was not apparent. The present work has overcome such difficulty and identified the stages with a clear definition. Voltage sampling at a rate of 100 Hz would not recreate the detailed voltage transient, rather it collected sufficient unbiased data points to statistically describe the stages of development.

A comparison between the oxidation mechanism presented herein and those reported in literature was summarized in Table 14-2. While most manuscripts suggest that PEO treatment of magnesium alloys followed a multi-stage mechanism, clear evidence supporting this proposition was largely lacking [127, 128, 157, 249-251]. The V-t curves in these investigations do not exhibit well-defined regions, thus complicating the analysis and the subsequent comparison. For the purpose of this investigation, only samples from literature that showed well-defined stages of oxidation were included in the comparison [153, 245, 246]. Examination of Table 14-2 revealed several similarities between the studies. The number of stages (3 or 4) involved in the PEO treatment process was similar regardless of the choice of substrate material, electrolyte composition, or process parameters used in the study. In all cases, the first stage of treatment was considered to be similar to conventional anodization. It was also commonly accepted that stage II was initiated when the first plasma discharges occurred, and the formation of the outer porous oxide coating began. Finally, it was generally accepted that the final stage (regardless of its number in the sequence) was characterized by increased thickness of the coating porous oxide coating.
Chapter 14: Plasma Electrolytic Oxidation of Magnesium Alloys

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>This Work</th>
<th>Feng et al.[153]</th>
<th>Yagi et al.[245]</th>
<th>Boinet et al.[246]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AZ31B</td>
<td>AZ31B</td>
<td>ACM522 (Alloying elements given in wt.%)</td>
<td>AM60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al:5.3, (Ce + La):2.6, Ca:2.0, Mn:0.2</td>
<td></td>
</tr>
<tr>
<td>Electrolyte</td>
<td>40 g/L NaOH, 50 g/L Na_2SiO_4, 30 g/L Na_2B_4O_7, 10 g/L CaH_2O_3Na_3, 10 g/L PEG1000.</td>
<td>40 g/L NaOH, 50 g/L Na_2SiO_4, 30 g/L Na_2B_4O_7, 10 g/L CaH_2O_3Na_3, 10 g/L PEG1000</td>
<td>140 g/L Na_3PO_4·12H_2O</td>
<td>84 g/L NaOH, 29 g/L KF, 90 g/L Na_3HPO_4·H_2O, 41 g/L NaAlO_2</td>
</tr>
<tr>
<td>Composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrolyte</td>
<td>25 °C</td>
<td>Room Temperature (Methodology for temperature control was not specified)</td>
<td>20 °C</td>
<td>Room Temperature (Methodology for temperature control was not specified)</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applied Current</td>
<td>10 mA/cm^2</td>
<td>10 mA/cm^2</td>
<td>30 mA/cm^2</td>
<td>5-30 mA/cm^2</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treatment Duration</td>
<td>30 minutes</td>
<td>10 minutes</td>
<td>10 minutes</td>
<td>11 minutes</td>
</tr>
<tr>
<td>Mode of Observation</td>
<td>Statistical analysis of the V-t curve recorded at 100 Hz</td>
<td>V-t curve recorded at 0.1 Hz</td>
<td>V-t curve recorded at 1 Hz</td>
<td>V-t curve recorded at 1 Hz</td>
</tr>
<tr>
<td>Number of Stages</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Description of Stage I</td>
<td>Anodization</td>
<td>Anodization</td>
<td>Development of a compact, uniform dense layer (Anodization)</td>
<td>Anodization</td>
</tr>
<tr>
<td>Description of Stage II</td>
<td>Dielectric breakdown leading to plasma discharge and the breakdown of the oxide film formed in stage I. Formation of a porous oxide layer with non-uniform coverage.</td>
<td>Dielectric breakdown leading to plasma discharge and formation of a porous oxide layer with non-uniform coverage. The stage was called “micro-arcing” referencing the work of Boinet et al. [246].</td>
<td>Dielectric breakdown leading to plasma discharge and formation of a porous oxide layer on top of the oxide layer produced in stage I.</td>
<td>Dielectric breakdown leading to plasma discharge and the breakdown of the oxide film formed in stage I. Formation of a porous oxide layer with non-uniform coverage. The stage was called “micro-arcing”.</td>
</tr>
<tr>
<td>V_m(II)</td>
<td>76 V</td>
<td>85 V</td>
<td>150 V</td>
<td>55 V</td>
</tr>
<tr>
<td>Description of Stage III</td>
<td>Plasma discharges leading to increased coverage of the porous oxide layer</td>
<td>The stage was called “arcing” referencing the work of Boinet et al. [246]. No physical description of the process was provided in the manuscript.</td>
<td>Plasma discharges leading to increased coverage of the porous oxide layer</td>
<td>The stage was called “arcing”. The stage was characterized by large discharges which were less frequent and had a longer lifetime than the discharges in stage II.</td>
</tr>
<tr>
<td>Description of Stage IV</td>
<td>Plasma discharges leading to increased thickness of the porous oxide layer</td>
<td>Stage IV was never reached due to the short duration of the PEO treatment</td>
<td>Plasma discharges leading to increased thickness of the porous oxide layer</td>
<td>N/A</td>
</tr>
<tr>
<td>V_m(IV)</td>
<td>150 V</td>
<td>N/A</td>
<td>225 V</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 14-2 Comparison of the PEO coating formation mechanism proposed in this investigation to other published work.
While some parallels could be drawn between the studies summarized in Table 14-2, there existed several discrepancies. The study by Feng et al. reported that PEO treatment of AZ31B occurred in three stages, which differed from the four-stage mechanism proposed herein [153]. The samples prepared by Feng et al. were treated for 10 minutes only, a time that was much shorter than the 15.5 minutes it took to reach stage IV in the present study (when a current density of 10 mA/cm² was applied) [153]. It is likely that the treatment time was insufficient to reach stage IV, and if longer treatment times were used stage IV would be observed from the V-t curve. The observations made by Yagi et al. largely agreed with the present findings [245]. The main discrepancy between the two studies was related to the explanation of the mechanism that governed the porous oxide layer formation in stage II. Yagi et al. suggested that the porous oxide that was formed in stage II grew on top of the dense layer that was formed during the anodization period (stage I) [245]. In the present investigation evidence was provided to support the proposition that the porous oxide layer gradually replaced the initial compact layer formed in stage I via cascades of discharges. It was identified that the discharge occurred primarily at the boundary between the porous material formed in stage II and the compact layer formed during stage I. Similarly to the observations made by Yagi et al., Boinet et al. concluded that PEO treatment of magnesium alloys followed a mechanism with three stages [245, 246]. In the case of the work by Boinet et al., this discrepancy was not related to the duration of the PEO treatment (like it did in Yagi’s work) but instead it was related to incorrect interpretation of the V-t curve [245, 246]. The V-t curve obtained by Boinet et al. had a similar shape to the one presented in this investigation, but in their investigation they grouped stage II and III together and termed it “micro-arcing” [246]. The resulting mechanism consisted of three stages, namely conventional anodizing (stage I), micro-arcing (stage II and stage III), and arching (stage IV) [246]. It is interesting to note, that Boinet et al. noted that using their method of rate data acquisition (1 Hz) and method of analysis, it was difficult to identify the various stages of treatment when the applied current density was lower than 10 mA/cm² [246]. This observation further supports the value proposition of the analysis method presented herein. High frequency (100 Hz) data acquisition coupled with statistical analysis provided clear definition for the stages involved in PEO treatment of magnesium alloys. Another benefit of this technique was that it provided information on the type of discharge occurring at each stage of state of treatment. This information was not provided by any of the studies examined in this comparison.
Specifically, the mechanism of growth of the PEO coating on AZ31 alloy in stage IV, which was the focus of most work in the literature, was clarified. As discussed in Section 3.5.1 (and in Figure 3-11), Hussein et al. and Cheng et al. proposed 5 mechanisms by which the PEO coating could grow by discharges across an existing oxide-based layer [8, 127, 128]. Present evidence suggested that the growth of PEO coating on AZ31 magnesium alloy in silicate-based solution proceeds via two predominant mechanisms (Figure 14-9) resembling only types “C” and “D” discharge in stage IV. Type “C”, which refers to the discharge at the bottom of the micro-pores, was much preferred over the other proposed types because it targeted the thinnest points in the coating. This type of discharge corresponded to the voltage mode near 150 V in stage IV. Type “D” mechanism involved the micro-voids underneath the coating, resulting in a voltage mode near 100 V. Other modes of discharge were theoretically possible, there was no evidence in this work that showed they were responsible for the growth of the PEO coating on AZ31 magnesium alloy in a silicate-based solution.

Further insight into the mechanism governing the formation of the PEO coating can be gained by altering process conditions and examining their effect on the voltage-time response acquired during the oxidation process and the thickness of the resulting coating.

### 14.3 Effect of Process Parameters on Coating Morphology

The analysis method described in Section 14.2 was used to study the effect of varying current density and bath temperature during the coating on the process kinetics and resulting morphology of the coatings. High-speed voltage transient measurements (10 kHz) were not used due to the storage limitation of the oscilloscope employed in this work. By the previous discussion, low speed recording (100 Hz) using DAQ, augmented with statistical analysis, can cover the entire duration of processing while providing a clear distinction between the stages and distribution of the voltages. Therefore, the analysis is based only on the statistical analysis of voltage transients.

#### 14.3.1 Effect of Current Density

The influence of applied current density was evaluated by examining the voltage-time response from coatings produced by applying different current densities ranging between 5 and 40 mA/cm². The corresponding V-t curves and histograms examining the effect of applied current density are shown in Figure 14-10.
Figure 14-10 Influence of applied current density on voltage density-time plots and histograms of voltages sampled in stage II and IV. Samples coated by applying a current density of (a-c) 5 mA/cm$^2$, (d-f) 10 mA/cm$^2$, (g-i) 20 mA/cm$^2$, and (j-l) 40 mA/cm$^2$.

The transition times ($t_i$), characteristic voltage mode ($V_m$) values, and coating thicknesses as a function of current density are summarized in Table 14-3. When the current density was increased from 5 mA/cm$^2$ to 40 mA/cm$^2$, the voltages represented by $V_m$(II) and $V_m$(IV) did not rise, instead the transition times ($t_{II/III}$, $t_{III/IV}$, and $t_{III/IV}$) were almost proportionally shortened. The above observation suggested that the duration of each stage was governed by the amount of charge transferred.
Table 14-3 Transition times (t₁/II), voltage mode (Vₘ) for stages II and IV, and the thickness of the coating films as a function of applied current density. Electrolyte temperature: 25 °C. The errors represent the uncertainty in measurement, except for thickness, which is the standard deviation.

The voltage transient in Figure 14-11 confirmed that the cycle time in stage II decreased from 15 milliseconds at 10 mA/cm², to 10 milliseconds at 20 mA/cm². This means that the discharging rate was faster at a higher current density. Also, with the decrease in the cycle time, both rates of film breakdown and reformation were proportionally shortened. Microscopically, this can be explained as a change in the intensity of individual discharges, assuming that the energy input of each discharge event was proportional to the rate of film breakdown and reformation.

Electron microscopy was employed to correlate the findings from the voltage-time output to the oxidation mechanism proposed in Figure 14-9. Cross-sectional images of the coatings produced...
by varying the applied current density from 5 mA/cm² to 40 mA/cm² are presented in Figure 14-12, and thickness measurements are reported in Table 14-3. It can be seen that thickness of the coatings increased proportionally when the applied current density increased from 5 mA/cm² to 20 mA/cm². Changes in the applied current density did not only influence the thickness of the coating, but also its porosity. Examination of the region near the metal/oxide interface revealed that an increase in the applied current density resulted in a larger number of pores and voids in the region, see Figure 14-12 (c) and (d). The above observation is consistent with previous reports by Rapheal et al. who correlated the increase in porosity as a result of increased current density to a higher gas evolution rate and greater energy release during discharging [252].

![Cross-sectional views of PEO coatings](image)

**Figure 14-12** Cross-sectional views of PEO coatings produced by applying (a) 5, (b) 10, (c) 20, and (d) 40 mA/cm². The temperature of the electrolyte was kept at 25 °C.

The microstructural changes induced by varying the applied current density can be explained by the oxidation mechanism proposed in this work. At higher current densities, the film developed at a proportionally faster rate with an earlier onset of transition between the stages. Consequently, the sample coated by applying higher current densities had undergone a longer oxidation time at stage IV than that coated at lower current densities. Since the last stage was the one responsible for the growth of the porous layer, samples coated by applying 20 mA/cm² were much thicker compared to the samples prepared 5 or 10 mA/cm². Similar observations were noted by Srinivasan et al. who examined the influence of current density on PEO coatings of AM50 [253].

A change in current density also influenced the type and frequency of discharges during the growth of coating in stage IV. This is illustrated in the voltage distribution in Figure 14-10 (c), (f), (i), and (l), and the detailed voltage transient in Figure 14-11. With increased current density, the voltage transient exhibited two types of discharges: one deep fluctuation which occurred every 100 milliseconds, and another series of smaller fluctuation that resembled stage II waves. The first was termed type “C” discharge, and the second was termed type “D” discharge as discussed in Section 3.5.1. In Figure 14-11, the length of the high-frequency limits the data size available,
such that it could not tell whether there was a change in the relative portions of these two types of discharges. On the voltage histograms in Figure 14-10, the rise of a small voltage mode between 80 V and 100 V clearly indicated that the second type of discharge increased with an increase in applied current density. This can now be correlated to the voids near the metal/oxide interface at higher current density. At low current densities the film exhibited relatively fewer electrolyte-filled voids at the metal/oxide interface, which in turn limited the number of sites available for Type “D” discharging. As a result, discharging at the bottom of the micro-pores of the oxide (Type “C”) was the dominant mechanism in treatments produced by applying a low current density. As the current density increased to 20 mA/cm$^2$ and 40 mA/cm$^2$ the number of electrolyte filled voids beneath the coating increased, and the number of sites capable of supporting Type “D” discharge increased as well. In this case, Type “D” discharging occurred more frequently as seen from the growing intensity of the minor peak in Figure 14-10.

14.3.2 Effect of Temperature

The effect of electrolyte temperature was also examined by investigating the voltage-time response acquired during PEO coatings in an electrolyte held at 18, 25 and 40 °C. The corresponding V-t curves and histograms examining the effect of electrolyte temperature are shown in Figure 14-13. When the bath temperature was increased from 18 °C to 40 °C, the V-t curve showed some subtle changes as shown in Figure 14-13. The duration of the two transition times $t_{II/III}$ and $t_{III/IV}$ were longer in specimens prepared with an electrolyte at 40 °C than those measured for specimens prepared using an electrolyte at 18 °C and 25 °C, see Table 14-4. During stages II and IV, the voltage distribution was shifted to lower voltage values (Figure 14-13), marked by the lower characteristic voltage modes measured for these two stages ($V_{m(II)}$ and $V_{m(IV)}$ of Table 14-4).
Figure 14-13 Influence of electrolyte temperature on voltage density-time plots and histograms of voltages sampled in stage II and IV. Samples were coated in an electrolyte held at a constant temperature of (a-c) 18 °C, (d-f) 25 °C, and (g-i) 40 °C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$t_{I/II}$</th>
<th>$t_{II/III}$</th>
<th>$t_{III/IV}$</th>
<th>$V_m$(II)</th>
<th>$V_m$(IV)</th>
<th>Thickness [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[°C]</td>
<td>[minutes]</td>
<td>[minutes]</td>
<td>[minutes]</td>
<td>[V]</td>
<td>[V]</td>
<td>[μm]</td>
</tr>
<tr>
<td>18</td>
<td>0.83 ± 0.02</td>
<td>7.5 ± 0.5</td>
<td>14.8 ± 0.5</td>
<td>82 ± 1</td>
<td>156 ± 2</td>
<td>45.0 ± 7.5</td>
</tr>
<tr>
<td>25</td>
<td>0.83 ± 0.02</td>
<td>6.5 ± 0.5</td>
<td>15.5 ± 0.5</td>
<td>76 ± 1</td>
<td>150 ± 2</td>
<td>43.0 ± 8.7</td>
</tr>
<tr>
<td>40</td>
<td>0.98 ± 0.02</td>
<td>7.0 ± 0.5</td>
<td>18.5 ± 0.5</td>
<td>69 ± 1</td>
<td>146 ± 2</td>
<td>9.5 ± 3.0</td>
</tr>
</tbody>
</table>

Table 14-4 Transition times ($t_i$), voltage mode ($V_m$) for stages II and IV, and the thickness of the coating films as a function of bath temperature. Applied current density: 10 mA/cm². The errors represent the uncertainty in measurement, except for thickness, which is the standard deviation.
In the detailed voltage transient in Figure 14-11 (b), the voltage waves maintained the same frequency in stage II and stage IV, but the upper and lower boundaries of voltage wave shifted downwards. The lower critical breakdown voltages and reformation voltages suggested that the film was less stable at higher temperatures. Another notable change was the rise in the minor voltage mode in stage IV, at about 100 V (Figure 14-13). As previously discussed, this minor peak correlated to discharges that occurred in the voids between the base metal and the bulk oxide coating, which was one of the two mechanisms responsible for the growth of coating in stage IV (Figure 14-9). Cross-sectional views and thickness measurements of the films revealed that as the bath temperature increased, the film thickness decreased (Figure 14-15, Table 14-4). The difference in thickness was most significant between the sample prepared at 25 °C (43μm) and that prepared at 40 °C (9.5μm).

The bath temperature could affect the PEO process and the coating morphology. The critical breakdown potential was lowered, resulting in a shifted voltage distribution. This might be associated with a change in the resistivity or the dielectric constant of the coating as temperature changed, but this theory is yet to be confirmed. The oxide coating formed was less stable at higher temperature as shown by the longer transition times ($t_{II/III}$ and $t_{III/IV}$) and the thinner film produced (Figure 14-15). The difference in thickness seen in Figure 14-15 cannot be explained by the shorter duration of stage IV alone, as the changes in duration of stage IV were much less significant than the change in thickness of the resulting coating. Instead, the thinner PEO coating produced at higher temperatures must have been associated with the rate of growth and dissolution.
of the film. An increase in the temperature of the electrolyte is expected to have a minimal impact on the growth rate, as the temperature at oxidation sites is dominated by the intense heat input caused by the plasma discharge. The dissolution of the coating however is expected to happen across the entire surface of the coating and is dominated by the ambient temperature. As discussed in Section 3.5.1, higher bath temperature would then promote dissolution over growth. The reduction in the coating thickness was caused by the accelerated dissolution rate of the coating, confirming previous recommendations by Li et al. [148].

Figure 14-15 Cross-sectional views of PEO coatings produced in an electrolyte at (a) 18, (b) 25, and (d) 40 °C. The current density used to produce the coatings was kept constant at 10 mA/cm².

Higher dissolution rates induced by the elevated temperature of the electrolyte also accounted for the changes observed in the voltage-time plot. Since the development of the coating is a competition between the growth and dissolution rates, an increase in the dissolution rate resulted in the delay of transition times \( t_{III} \), \( t_{III/IV} \), \( t_{III/IV} \) as a function of increasing temperature (Table 14-4). Changes in the dissolution rate also affected the type of discharging governing the oxidation process in stage IV. Increased dissolution of the coating resulted in a greater exposure of the voids between the oxide and the substrate material to the bulk electrolyte. As such, the number of sites where a discharge underneath the coating (Type “D”) could occur was increased, and a more pronounced minor peak (100 V) was observed in the voltage distribution profile in Figure 14-13.

It is worth noting that the plasma discharges would heat the coating material and electrolyte in the vicinity of discharge sites. This is evident from the fact that higher current densities also lowered the voltages, as can be observed by the left shift of voltage distribution in Figure 14-10 and reduced \( V_m \) in Table 14-3. This influence is similar to the temperature effect. From this, it can also be inferred that higher current density can increase the dissolution of the coating film via this localized heating effect. In the practical application of PEO for corrosion protection of Mg alloys,
increasing the current density can shorten the deposition time, but the temperature must be adequately controlled to prevent detrimental effects to the PEO coating.

### 14.4 Summary

In this work, the evolution of a protective coating produced on magnesium AZ31 alloy by the plasma-electrolytic oxidation method was investigated in detail. The influence of current density and bath temperature on the formation mechanism and morphology of the coatings was examined. A number of conclusions can be derived from the experimental work presented above:

1. A novel method to analyze instantaneous voltage-time output produced during PEO treatment of magnesium has been designed and implemented. Although high-speed recording using an oscilloscope could resolve the detailed voltage waveform, the limited data buffer size and transfer bandwidth of present oscilloscope technology make it impractical for studying the overall PEO process. In contrast, data acquired from a mainstream data acquisition system can be very useful if augmented with statistical analysis. It provides key information about the evolution of the coating as well as descriptors of the overall voltage profiles. This method can be used for research and application of PEO technology, particularly for systems showing sporadic voltage/current transient responses.

2. The voltage-time function during the galvanostatic oxidation process contained four discreet stages of development. A compact layer comprising MgO was formed during the first stage (anodization) of the treatment process. The formation of a thicker coating with silicon incorporation occurred in the second and third stages. PEO coating thickening and crystallization occurred in the final stage.

3. The statistical distribution of voltages at different stages during PEO revealed voltage peaks which were associated with the breakdown of the layers in the coating. The bimodal distribution of voltages in stage II was explained by cascades of discharge at different locations. The distribution in stage IV showed a prominent peak related to the discharges in the deep pores in the oxide coating, accompanied by a secondary discharge voltage associated with the discharge through the micro-voids.

4. Increasing the current density lowered the critical breakdown potentials of coatings produced and increased the rate of discharges. As a result, specimens coated by applying
a higher current density experienced a longer stage IV that led to increased coating thickness.

5. Increasing the temperature of the electrolyte increased the oxide dissolution rate, ultimately yielding coatings with reduced thickness. Increasing the current density also produced a similar effect, by heating the local environment.
Chapter 15 Corrosion Protection of Friction Stir Welded Magnesium Alloys


15.1 PEO Coatings of Friction Stir Welded AZ31B Magnesium Alloy

PEO coatings have been shown to be a suitable technology for improving the corrosion resistance of friction stir welded joints. Preliminary studies have shown that PEO coatings can improve the corrosion resistance of FSW joints in various corrosive media using linear polarization and impedance spectroscopy [8, 152]. While these are valid techniques to assess the improvement in the corrosion resistance associated with the synthesized coating, they should be supplemented by mass loss measurements as it would be more indicative of the exposure to the service environment during application [209].

The present work evaluates the corrosion behaviour of PEO coatings generated on FSSW joints made in AZ31B through mass loss testing. The mechanism of coating degradation is examined through a series SRET scans coupled with *in situ* imaging of the corroded surface.

15.1.1 Corrosion Resistance of PEO Coatings Made on AZ31 FSSW Joints and Bulk Metal Specimens

To determine if PEO coatings can be successfully applied as a corrosion mitigation strategy for friction stir welded AZ31B, the work herein compared the corrosion behaviour of FSSW joints in coated and uncoated conditions using mass loss testing. Matching sets of base metal specimens were tested as well in order to evaluate the role of the underlying microstructure (in different weld region) on the corrosion resistance properties of PEO coatings. Finally, two electrolyte
compositions (with and without PEG) were used in this investigation. As discussed in Section 3.5.2, addition of PEG into the PEO processing electrolyte has been shown to produce coatings with superior corrosion resistance properties. The current investigation examined if the conclusions from studies conducted on PEO-coated AZ31B base metal specimens can be extended to friction stir welded specimens.

Coated samples were produced in a sodium silicate electrolyte with and without the addition of 10 g/L PEG. Detailed explanation of the experimental procedure is given in Sections 6.5.1 and 6.5.2. The top and cross-sectional morphology of the coating produced on base metal specimens is shown in Figure 15-1. The mean thicknesses of the coatings were measured, and the errors are given as one standard deviation. The area fractions of pores were calculated from the top surface micrographs. The addition of PEG did not have a statistically significant effect on the thickness of the coating and its porosity area fraction. Samples produced without PEG were 11.70 ± 3.53 µm in thickness and had 5.00 ± 2.60 % porosity area fraction. Samples produced with PEG present in the electrolyte were 12.30 ± 6.53 µm in thickness and had 9.28 ± 2.90 % porosity area fraction.

![Figure 15-1](image.png)

**Figure 15-1** Top (a-b) and cross-sectional (c-d) morphology of PEO coating on AZ31B specimens processed in a sodium silicate electrolyte with (b, d) and without (a, c) the addition of 10 g/L of PEG electrolyte additive.
The main effect of PEG on the PEO coating characteristics was observed in the composition of the synthesized coatings. EDS analysis revealed that the coatings produced in electrolyte with PEG contained a greater silicate content (~17.5 wt.% Si) as compared to coatings made in an electrolyte without PEG (~14.0 wt.% Si). The above is indicative of greater Mg$_2$SiO$_4$ formation in coatings produced with PEG, in agreement with the findings reported by Zhu et al. [153]. For more details, see discussion in Section 3.5.2.

A series of “as-coated” samples were treated with the chromic acid solution to determine the mass loss ($m_i$-$m_c$) associated with the dissolution of the coating in accordance with the procedure outlined in Section 6.4.1.4. The area densities of the coatings produced on AZ31B with and without the addition of PEG were 4.71 ± 0.18 and 3.90 ± 0.17 mg/cm$^2$ respectively. The increase in area density of the coating is likely associated with the observed changes in coating thickness, compactness and composition. The corrosion rates of the base metal and welded specimens, uncoated and coated, were measured by 5-day mass loss testing in a 0.086 M NaCl solution. See Section 6.4.1.4 for complete experimental procedure. Estimated corrosion rates calculated from equation 6.3 are given in Figure 15-2 for the base metals and welded samples with and without PEO coating.

![Figure 15-2 Comparison of the corrosion rates of the base metal and the welded specimens in uncoated and coated conditions obtained for a 5-day exposure to 0.086M NaCl](image-url)
Figure 15-2 proved the efficacy of PEO for mitigating the corrosion problem associated with FSW magnesium alloys. Without the coating, the welded specimens exhibited significantly higher corrosion rates than the base metal due to the microstructural evolution occurring during the welding process (see detailed discussion of the corrosion mechanisms in chapters 8-10). Once the PEO coating was applied, the corrosion rate decreased significantly (by as much as 50%) and was further decreased by the addition of PEG into the processing electrolyte. No significant difference in the apparent corrosion was observed between welded and base metal specimens for both coating conditions. The corrosion rates measured through mass loss also confirmed the beneficial effect of the PEG additive on the corrosion resistance of AZ31B base metal as previously reported by Zhu et al. [153]. In this work the additive has been found to improve the corrosion resistance of welded specimens as well. The corrosion rates measured in this investigation would be more indicative of the true corrosion attack experienced in an industrial application than those measured by common electrochemical techniques, as they account for possible coating failure.

![Image of corroded specimens](image)

Figure 15-3 Corrosion morphology of a PEO processed (with PEG) base metal and FSSW specimens after 5-day exposure to 0.086M NaCl.
The corrosion morphology of base metal and welded specimens coated in an electrolyte with the addition of 10 g/L of PEG is shown in Figure 15-3. Examination of the corroded specimens revealed that localized breakdown of the coating, and subsequent pitting occurred in both samples. No localized attack was observed in the TMAZ and/or HAZ zone in coated welded specimens as was previously shown for uncoated welded specimens (Figure 11-3). Instead the corrosion morphology of the welded specimens appeared to be similar to the corrosion morphology exhibited by coated base metal specimens. Similar observations were made for PEO coatings produced in electrolytes without any PEG addition. This suggests that the coating was able to overcome the effects of localized corrosion associated with microstructural evolution during the welding process. The corrosion behaviour of coated joints was no longer governed by the underlying microstructure, and instead was governed by the inherit corrosion resistance properties of the coating alone. The results indicate that BM specimens can be used as model specimens to study the corrosion resistance properties of PEO coatings on FSSW joints since the conclusions drawn for BM samples appear to be relevant to welded specimens as well.

15.1.2 PEO Coating Degradation Mechanism

To date, studies examining PEO degradation focused on explaining the pitting initiation stage but omitted mechanistic details about pit growth and propagation (see complete discussion in Section 3.5.2) [150, 158]. As discussed in Section 6.4.5.1, localized degradation mechanisms can be studied using SRET experiments as initially proposed by Isaacs et al. (23). In this investigation, SRET experiments were utilized to monitor changes in the open cell potential distribution on the surface of a corroding PEO coating. The potential distribution around a newly initiated pit was investigated as it was propagating through the sample over intervals of 6 hours. The complete experimental procedure is given in Section 6.4.5.3. The study was conducted on coated BM specimens since it was already concluded in the previous section that they can be used to represent the coating on a welded specimen.

The potential distribution maps obtained from the SRET experiments are given in Figure 15-4. The potentials are shown with reference to the potential measured on the un-corroded PEO coating before the first scan began (1-hour stabilization). The SRET scans showed the evolution of a noble region that shifted within the observed frame during the first 25 hours of exposure to corrosive media. The noble region was originally located in the center of the potential map and slowly drifted leftwise within the scanned region. Beginning from the potential map obtained after the
31st hour of exposure of the sample to the electrolyte no further changes in the potential distribution were observed.

![Figure 15-4 Corrosion potential distribution on the surface of a PEO coating produced on AZ31B magnesium alloy in a sodium silicate electrolyte with the addition of 10 g/L PEG.](image)

To correlate the potential changes measured through the SRET experiment with the observed pit evolution, the potential distribution maps were overlaid on the corresponding *in situ* images of the pit as shown in Figure 15-5. The image showed that the local noble potential measured by the SRET experiment coincided with the center of the pit and shifted to the left as the pit grew. Once the advancing front of the pit moved beyond the SRET frame of observation, the potential distribution on the surface of the specimen remained constant. The coupling between the local noble region and the advancing corroding edge suggested that the growth mechanism of the pit was governed by the cathodic activation. A similar mechanism was observed by Ralston et al. and Kish et al. for the corrosion of pure magnesium and AZ31B (a discussion of the study on AZ31B is given in Section 5.1.3) [106, 253].

As mentioned in Section 3.3.1, the cause for the cathodic activation of magnesium has been a subject of debate in recent years, and one possible explanation is the enrichment of impurities on the corroding magnesium surfaces [68, 72]. Another possible cause for the cathodic behaviour of the corrosion product in the pit could be associated with the local pH increase in the confined area of the pit stemming from the hydrogen evolution reaction accompanying the corrosion process. An increase in the local pH of the solution will stabilize Mg(OH)₂ which would be cathodic to the nearly located corroding interface. As the pit grew and the distance between the corrosion track and the actively corroding interface increased, and the initial spot of corrosion no longer
accelerated the growth of the pit. Further investigation is required to understand the cathodic activation mechanisms occurring at the surface of the corroded region. More insight can be obtained by mapping the local pH variation of the electrochemically active site, and by conducting elemental analysis of the corroding surface to identify possible impurity enrichment.

Figure 15-5 A collage showing the potential distribution on the surface of a PEO coating (top), in situ images of the pit (bottom), and an overlay of the two together (middle). Roman numerals mark the locations of the center of the noble region at any given time interval.

It is also important to note that it is difficult to calculate the theoretical potential distribution in the electrolyte above the corroding pit as the electrochemical properties of the corrosion product inside the pit, and the corroding metal interface are not known. The discussions in Sections 11.4, 12.6, and 13.3 have already shown that the measurement can be strongly affected by local changes in the electrolyte, and thus it is plausible that the electrolyte variation played a significant role in the present measurement as well. At present, it is not possible to differentiate between the relative contribution arising from the electrochemical activity of the pit and that arising from local changes in the electrolyte. Further insight into the results obtained from the SRET measurement could be gained by conducting a modified SRET test that is capable of mapping the potential distribution in the electrolyte, along with any local changes in the pH, and dissolved gas concentrations. Similar experiments were conducted on aluminum joints by Gnedekov et al., who were able to conduct a SVET investigation while mapping the pH on the surface of the specimen [264].
SRET experiment suggested that the corrosion of PEO coatings is governed by cathodic activation, similarly to pure magnesium and AZ31B. It is also important to note that the current SRET apparatus was able to resolve the cathodic region driving the corrosion but was not able to pick the anodic dissolution occurring at the pit coating interface. It is recommended to examine the anodic dissolution using the SVET technique that able to measure the anodic current in the region. For more information about application of the SVET technique to examine the corrosion behaviour of magnesium alloys see discussion in Section 5.1.3.

15.2 Plasma Electrolytic Oxidation Coating of Dissimilar AZ31/AZ80 Friction Stir Welds

15.2.1 Introduction

The work presented in Chapter 13 concluded that dissimilar AZ31/AZ80 FSW joints exhibited increased susceptibility to localized corrosion. It was determined that the coupling between AZ31 and AZ80 near the welded interface increased the number of catalytic sites (Al-rich intermetallic particles) available to support the hydrogen evolution reaction, which accelerated the dissolution of the α-Mg matrix on the AZ31 side. If dissimilar welding of magnesium alloys was to be used in an industrial application, mitigation strategies would be required to enable this technology.

The deleterious effect of the galvanic coupling between the AZ31 and AZ80 in a dissimilar joint might be mitigated by the application of a PEO coating, which has been previously shown to improve both the corrosion and wear resistance of monolithic and friction stir welded magnesium alloys (see discussion in Section 3.5.2 and results in Section 15.1). No prior information is available concerning the application and effectiveness of PEO coatings following dissimilar welding of magnesium alloys. The current section evaluates the feasibility of applying PEO coatings as a corrosion mitigating strategy. The overall corrosion rates of PEO coated base metal and dissimilar AZ31/AZ80 joints were estimated using mass loss testing, while the composition and morphology of the coatings were analyzed using a combination of XRD, electron microscopy, and white light profilometry.

15.2.2 PEO Coated AZ31 and AZ80

The influence of applied current density on PEO coating characteristics on AZ31 and AZ80 has been examined to identify suitable processing conditions for PEO coatings of dissimilar
AZ31/AZ80 joints. PEO coatings were produced on AZ31 and AZ80 substrates using current densities of 10 and 20 mA/cm² (see Section 6.5 for experimental procedure). All coatings were analyzed using a combination of SEM imaging (both upper and cross-sectional surfaces), white light profilometry, and XRD. PEO processing resulted in the formation of an ivory-white porous oxide structure. The roughness of the coatings was measured since it has been previously shown that the roughness was related to the process parameters employed to synthesize the coating, and to the deposition mechanism occurring at the surface of the sample [254-256]. Additionally, a reduction in the surface roughness was correlated to a lower defect concentration and improved corrosion resistance [255, 257]. In this investigation, surface roughness was utilized as an indicator of changes in the oxidation process stemming from changes in composition of the substrate and applied current density.

White light profilometry measurements were used to determine the average surface roughness of the PEO coatings (see Section 6.3.6 for experimental procedure). The output obtained from profilometry is shown in Table 15-1. When the current density remained constant, the choice of substrate (AZ31 or AZ80) did not produce a significant difference in the surface roughness of the PEO coatings. However, higher applied current density increased the average surface roughness of both AZ31 and AZ80 substrates, see Table 15-1. When the applied current density increased, the frequency and density of local plasma micro-discharges increased causing an increase in the number of discharge channels. Consequently, the oxidation rate increased resulting in a more porous and rougher outer layer. Similar observations have been reported by Hwang et al. during PEO coating of AM50 [137].

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>10 mA/cm² [µm]</th>
<th>20 mA/cm² [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31B</td>
<td>8.09 ± 0.21</td>
<td>9.85 ± 0.61</td>
</tr>
<tr>
<td>AZ80A</td>
<td>7.85 ± 0.21</td>
<td>8.89 ± 0.73</td>
</tr>
</tbody>
</table>

Table 15-1 Average surface roughness (Rₐ) values obtained from white light profilometry measurements of PEO coatings produced on AZ31B and AZ80A substrates by applying current densities of 10 mA/cm² and 20 mA/cm². The uncertainty given in the table signifies one standard deviation.

Changing the magnitude of the applied current density not only affected the average roughness of the PEO coating, but it also altered the coating thickness as seen from the back-scattered electron
micrographs in Figure 15-6 (a). All PEO coatings had a bi-layer structure consisting of a relatively thick porous outer layer and a thin denser inner layer. This bilayer structure is consistent with observations that were previously reported in literature [125, 138, 139]. A discussion of the studies examining this bilayer structure can be found in Section 3.5.1.

A representative micrograph of the inner layer of a PEO coating produced on AZ31 by applying a current density of 20 mA/cm² is shown in Figure 15-7. The presence of the bilayer structure in the coating was determined based on BSE imaging. The contrast in BSE images stems from variation in atomic weight and are directly related to variations in chemical composition. EDS examination of the coatings did not show silicon variation through its thickness. It is likely that this variation was still present, but it could not be resolved due to the very small thickness of the inner layer. The influence of processing parameters on the thickness of PEO coatings has typically been reported based on the changes in overall coating thickness [253, 258]. It is also important to examine the changes that occurred to the inner layer, since this layer is typically responsible for the increased wear and corrosion resistance properties due to its dense nature [259, 260].
Figure 15-6 (a) SEM-BSE micrographs showing the effect of applied current density on overall (i,iii), and inner layer (ii,iv) thickness on PEO coatings produced on AZ31. Changes in overall (v,vii), and inner layer (vi,viii) thickness on PEO coatings produced on AZ80 are depicted as well. (b) Graphical representation of changes in overall (i), and inner layer (ii) thickness are also presented.
The changes in the overall and inner layer thicknesses of PEO coatings are presented in Figure 15-6 (b). The error bars in these figures represent one standard deviation. It is apparent that higher current density increased the overall coating thickness for both AZ31 and AZ80 base materials. These observations are in general agreement with the proposition that higher current densities increased the frequency of localized plasma discharges and oxide growth [253, 261, 262]. A mechanistic explanation elucidating the effect of current density on the thickness of PEO coatings is provided in Section 14.2.1. The thickness of the inner oxide layer only increased in AZ80 but not on AZ31. It is worth noting that the influence of applied current density on the thickness of the inner oxide layer is not well understood and further investigation is required.

![SEM micrograph](image)

**Figure 15-7** A representative SEM micrograph of the inner layer of a PEO coating made on AZ31 using an applied current density of 20 mA/cm².

The phase composition of the synthesized PEO coatings was analyzed using XRD. Figure 15-8 shows the XRD spectra produced when examining PEO coatings produced on AZ31 and AZ80 substrates using different current densities. These spectra indicated that the PEO coating comprised two principal phases, namely magnesium oxide (MgO) and forsterite (Mg₂SiO₄). The measured compositions are in agreement with Durdu et al. when examining PEO coatings made on magnesium alloys processed in a silicate-containing electrolyte [144]. The mechanism explaining silicate incorporation into the PEO coating has been published elsewhere [135, 136].
Figure 15-8 XRD spectra for bare AZ31 (a) and AZ80 (b) metal substrate, and PEO coatings produced under different current density.

The ratio between magnesium oxide and magnesium silicate was estimated using the reference intensity ratio (RIR) analysis. The mass ratio (MgO/Mg$_2$SiO$_4$) of PEO coatings on AZ31 decreased from 0.63 (10 mA/cm$^2$) to 0.11 (20 mA/cm$^2$). Similar observations were found when examining PEO coatings on AZ80; in this case the ratio decreased from 0.22 to 0.08. Similar
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changes in the MgO/Mg$_2$SiO$_4$ ratio values were reported by Li et al. when they examined the influence of current density on the composition of PEO coatings produced on Mg-Li alloys [262].

It has been previously reported that the weight fraction of forsterite resulting from the application of a higher current density is associated with the polymerization of silicate ions during the plasma oxidation process. The extremely high energy generated by the plasma discharges promotes polymerization of the silicate and its incorporation into the PEO coating which lead to higher weight fractions of forsterite and lower weight fractions of magnesium oxide [134, 247].

The spectra obtained when examining PEO coated test samples exhibited peak broadening in the range between 20° and 40°, due to the formation of an amorphous phase. The presence of an amorphous phase in PEO coatings has been previously observed by Hoche et al. when examining coatings made on AZ91 [248]. The amorphous characteristics of PEO coatings were closely related to the polymerization of silicates and glassy phase formation. Increased spectral broadening was also apparent when higher current densities were applied.

The MgO/Mg$_2$SiO$_4$ ratio for PEO coatings produced using a current density of 10 mA/cm$^2$ depended on the chemical composition of the metallic substrate. In contrast, this dependence was not observed in PEO coatings made using a current density of 20 mA/cm$^2$. Since the roughness of the coatings was independent of the substrate material, current density can be used as a tunable parameter to overcome the non-uniformity of the PEO coating on the dissimilar joint. Application of 20 mA/cm$^2$ would be expected to yield a more uniform coating (less variation in coating composition) compared to coatings produced using the lower current density.

15.2.3 PEO Coated Dissimilar AZ31/AZ80 FSW Joints

Figure 15-9 shows the PEO coating morphologies in different regions of a dissimilar AZ31-AZ80 joint made using a current density of 20 mA/cm$^2$. PEO coatings produced using current densities of 10 mA/cm$^2$ and 20 mA/cm$^2$ had average surface roughness values of 8.60 ± 0.64 µm and 8.93 ± 0.97 µm. The coating roughness was uniform and did not vary significantly across the stir zone, the TMAZ, or the HAZ regions. It is worth noting that the roughness of the coating produced on welded samples was independent of the applied current density, unlike those on AZ31 and AZ80 (as shown in Table 15-1).
Figure 15-9 Top surface SEM-BSE micrographs showing PEO coating morphology on a dissimilar AZ31-AZ80 FSW joint produced with applied current of 10 mA/cm² and an oxidation period of 30 minutes.
Based on the results obtained from examining the cross-sectional images, the thickness of coatings made using a current density of 10 mA/cm² was not uniform. There was a dramatic change in coating thickness on either side of the joint centerline, see Table 15-2. The coating on AZ80 (on the advancing side of the dissimilar joint) was about three times thicker than the coating formed on AZ31. The PEO coating on AZ31 increased in thickness with distance from the joint centerline, while the coating on AZ80 was thicker in the stir zone region. In contrast, the PEO coatings produced using a current density of 20 mA/cm² were relatively uniform in thickness across all regions in dissimilar AZ31-AZ80 joints.

The difference in coating thickness on samples made using a lower current density of 10 mA/cm² was likely related to the differences in electrochemical activities of AZ31 and AZ80. It is worth noting that the use of higher current density values promoted both growth and dissolution of the PEO coating, see Su et al. [263]. Since the more active AZ31 was welded with the passive AZ80, it would be expected that the welded specimen would experience a non-uniform charge distribution. Consequently, the AZ31 portion of the dissimilar joint will generate a greater number of plasma discharges and increase the dissolution rate of the PEO coating on the AZ31 substrate. As result, there will be reduced coating dissolution on the coated AZ80 substrate, and this will facilitate uneven growth. The differences in PEO coating thickness were most pronounced closest to the interface between the AZ31 and AZ80 substrates, where the difference in charge distribution was greatest. Further from the contact interface, the influence of charge non-uniformity decreased, and the coating thickness became uniform.

Table 15-2 Changes in overall PEO coating thickness deposited on dissimilar AZ31-AZ80 FSW joints and uncoupled base metal samples.

<table>
<thead>
<tr>
<th>Coated Region</th>
<th>10 mA/cm² [µm]</th>
<th>20 mA/cm² [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoupled AZ31 BM</td>
<td>15.3 ± 5.3</td>
<td>48.1 ± 8.8</td>
</tr>
<tr>
<td>AZ31 HAZ</td>
<td>43.5 ± 6.4</td>
<td>24.7 ± 9.0</td>
</tr>
<tr>
<td>AZ31 SZ</td>
<td>24.2 ± 8.2</td>
<td>23.1 ± 6.8</td>
</tr>
<tr>
<td>AZ80 SZ</td>
<td>102.4 ± 9.7</td>
<td>24.3 ± 5.8</td>
</tr>
<tr>
<td>AZ80 HAZ</td>
<td>53.7 ± 11.7</td>
<td>25.9 ± 8.7</td>
</tr>
<tr>
<td>Uncoupled AZ80 BM</td>
<td>22.0 ± 6.5</td>
<td>55.7 ± 11.7</td>
</tr>
</tbody>
</table>
The growth and dissolution rates of PEO coatings were uniform across the entire width of the dissimilar joints when a higher current density of 20 mA/cm² was applied. These observations illustrate the importance of process parameter selection when PEO coatings are made following dissimilar welding. PEO coatings of uniform thickness are produced when all of the parameters of current density, and the relative areas and activities of the dissimilar substrates are taken into consideration.

It is worth noting that the PEO coating thickness on uncoupled AZ31 and AZ80 substrates did not correspond with the thickness of the coatings made on welded samples, for either current density examined in this investigation. When a current density of 10 mA/cm² was applied, the PEO coatings on welded joints were generally thicker. In contrast, the PEO coatings on welded joints were generally thinner than those on the AZ31 and AZ80 substrates, when a higher current density (20 mA/cm²) was applied. In effect, coupling of the dissimilar substrates modified the oxidation process and further research is required to determine the mechanisms governing the coupling effect.

A series of “as-coated” samples were treated with the chromic acid solution to determine the mass loss \( (m_i - m_c) \) associated with the dissolution of the coating in accordance with the procedure outlined in Section 6.4.1.4. The area densities of the coatings produced on AZ31B with and without the addition of PEG were 4.71 ± 0.18 and 3.90 ± 0.17 mg/cm², respectively. The increase in area density of the coating is likely associated with the observed changes in coating thickness, compactness, and composition. The corrosion rates of the base metal and welded specimens, uncoated and coated, were measured by 5-day mass loss testing in a 0.086 M NaCl solution. See Section 6.4.1.4 for the complete experimental procedure. Estimated corrosion rates calculated from equation 6.3 are given in Figure 15-2 for the base metals and welded samples with and without PEO coating.

**15.2.4 Corrosion Resistance of PEO Coated Dissimilar Joints**

Mass loss testing was used to examine the corrosion resistance of the coating applied to base metal and welded specimens. The experimental procedure for this test is described in Section 6.4.1.4. Prior to exposure to corrosive media, the area density of PEO coatings on AZ31 and AZ80 was calculated by treating as-coated samples in the chromic acid solution. The area densities of PEO coatings produced on AZ31 using 10 and 20 mA/cm² were 3.90 ± 0.17 and 4.41 ± 0.35 mg/cm².
respectively. On AZ80, the area densities when applying current densities of 10 and 20 mA/cm$^2$ were $3.84 \pm 0.20$ and $5.21 \pm 0.35$ mg/cm$^2$. Although the thickness of the PEO coatings on uncoupled base metal specimens increased significantly when higher current densities were applied, there was only a small change in area density values. This observation is consistent with the formation of an increasingly porous outer layer when high current densities were applied, see Bala Srinivasan et al.[253].

The corrosion rates of uncoated and PEO-coated AZ31, AZ80 and welded joints were examined via mass loss testing in a 0.086 M NaCl solution. All corrosion rates were determined using equation 6.3. Welded test samples were sectioned exposing identical fractions of AZ31 and AZ80, and the corrosion rate was determined using the mean area density value for PEO coatings on AZ31 and AZ80 substrates produced using the same current density. All calculated corrosion rates are presented in Figure 15-10 and are compared with uncoated AZ31, AZ80, and welded test samples.

Figure 15-10 Mass loss testing output: comparison of the corrosion rates of the base metals and the welded specimen in un-coated and coated conditions
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Figure 15-10 illustrates the effectiveness of PEO coatings in mitigating the corrosion problem arising from dissimilar joining of magnesium alloys. Based on the mass loss testing output, the corrosion rates of dissimilar joints and the AZ31 substrate were reduced by around 63%. It is possible that corrosion protection could be further improved through the selection of more appropriate current density values during processing. Although the PEO coating did not provide increased protection in the case of the AZ80 substrate, this substrate was much less susceptible to corrosion than AZ31. Little has been reported on the corrosion resistance of PEO coatings made on AZ80, especially on their corrosion rate estimated by means of mass loss testing. It is likely that under the deposition conditions used in the present investigation, the surface-film formed had similar corrosion resistance as the native oxide present on AZ80. On this basis, PEO coatings on AZ80 prove to be significantly more effective when they are applied to prevent the exposure of a galvanic couple. Finally, it is interesting to note that an increase in the current density had a varying effect on the corrosion resistance of the coatings depending if they were produced on AZ31 or AZ80. Figure 15-10 shows that changes in current density has an almost negligible effect on the corrosion rate of AZ80, since bare specimens and specimens coated using both process parameters showed no statistical difference in their corrosion rate. As mentioned previously, the coating did not provide additional protection to AZ80, and as a result minor changes to the coating did not alter its corrosion resistance. In direct contrast to AZ80, the coating on AZ31 acted as a barrier to the corrosive medium. The increase in porosity (as a result of higher current density), resulted in a greater number of defects in the coating which lowered the corrosion resistance.

The corrosion morphology of welded samples coated using a current density of 10 mA/cm² exhibited localized corrosion on the AZ31 side of the dissimilar joint, in the location close to the centerline, where a galvanic cell formed, see Figure 15-11 (a). The location of the corrosion attack was similar to that observed for uncoated dissimilar joint samples. This observation suggests that full coverage of the galvanic couple was not obtained when PEO coatings were applied using a current density of 10 mA/cm². Although full coverage of the galvanic couple was not obtained, the corrosion rates of coated samples were still lower than that of the uncoated samples, due to the presence of the PEO coating that reduced the size of the galvanic couple.
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Figure 15-11 Corrosion morphology after a 5-day exposure to 0.086M NaCl of a PEO processed FSW weldment coated at: (a) 10 mA/cm$^2$ and (b) 20 mA/cm$^2$. For comparison purposes (c) images showing the corrosion morphology of uncoated specimens were included as well (Figure 13-6 (b) and (c)). Complete description of the mechanism governing the corrosion behaviour of dissimilar AZ31/AZ80 FSW joints is described in Chapter 13.

Corrosive attack on PEO-coated welded specimens using a current density of 20 mA/cm$^2$ occurred on the AZ31 substrate far from the joint centerline, see Figure 15-11 (b). In this case, the occurrence of coating porosity exposed the active bare metal beneath the coating and promoted localized pitting. The corrosion rates and the morphology of welded test samples coated using higher current densities were similar to those observed when examining non-welded samples. Since corrosive attack occurred far from the dissimilar joint, the mechanism governing corrosion was altered. Corrosion of PEO-coated dissimilar joints was no longer governed by the galvanic couple formed between AZ31 and AZ80, but by the nature of the PEO coating itself. As a result, the calculated corrosion rates found during mass loss testing of welded samples were not statistically different from those found when examining uncoupled AZ31 and AZ80 test samples coated using the same current density, see Figure 15-10. The same trend was not true for welded specimens coated by applying a current a lower current of 10 mA/cm$^2$, where welded specimens showed significantly higher corrosion rates than the coated base metals.

The differences in the corrosion morphology of PEO coatings produced using high and low current densities are likely associated with the marked differences in coating thickness produced on the top surface of the stir zone region in test samples processed using lower current density values, see schematic in Figure 15-12 and Table 15-1. These observations illustrate the importance processing conditions during PEO coating of dissimilar joints.
Figure 15-12 Schematic of the corrosion behaviour of PEO coatings produced by applying a current density of 10 and 20 mA/cm$^2$. 
The corrosion rates found when examining PEO coated samples have greater variability than what would normally be expected in mass loss testing (see the magnitude of the error bars in Figure 15-10). A uniform area density is assumed when the weight of the PEO coating is compensated for that may introduce an uncertainty during estimation. In spite of this, the estimated corrosion rates presented in this study provide a useful insight concerning the marked improvement in corrosion resistance properties resulting from PEO coating of dissimilar weld test samples.

15.3 Summary

This work investigated the corrosion behaviour of PEO coatings produced on friction stir welded magnesium alloys. A number of conclusions can be derived from the experimental work presented above:

1. Mass loss testing is a successful approach to evaluate the corrosion resistance of PEO coatings on monolithic and welded materials.
2. The corrosion resistance of PEO coatings was insensitive to microstructural changes produced during friction stir welding of similar alloys.
3. The addition of PEG as an electrolyte additive had a beneficial effect on the corrosion resistance of PEO coatings produced in a sodium silicate electrolyte on both base metal and welded specimens.
4. PEO coatings drastically improved the corrosion resistance of both base metal and welded specimens, eliminating the deleterious effect of friction stir welding on the corrosion resistance of AZ31B.
5. SRET measurements revealed that PEO coating breakdown was governed by the cathodic activity of the corroded region inside the pit.
6. PEO coatings increased the corrosion resistance properties of AZ31 and dissimilar welded test specimens, while the corrosion resistance properties of AZ80 remained unchanged.
7. PEO coatings of uniform thickness produced using a current density of 20 mA/cm² changed the degradation mechanism governing the corrosion resistance of dissimilar AZ31/AZ80 FSW joints. The corrosion resistance of the welds was no longer affected by the galvanic couple formed between the two alloys, but rather by the inherit imperfections of the PEO coating.
Chapter 16 Conclusions and Future Work

16.1 Conclusions

This dissertation has studied the mechanisms governing the corrosion behaviour of FSW joints made in AZ magnesium alloys and proposed a promising corrosion mitigation strategy. Different aspects of this work are detailed in Chapters 7-15. The findings of each section and their significance have been summarized at the end of each chapter. The overarching conclusions of this work are detailed below:

1. The effect of friction stir welding on the corrosion resistance of AZ31B was studied, by evaluating the individual roles of various metallurgical characteristics (grain size, residual stress, grain orientation, and intermetallic particle dissolution) on the corrosion properties of the joint. The study concluded that the corrosion behaviour of the joint was principally governed by the ennoblement of the SZ region that was caused by the dissolution of second phase intermetallics during the welding process. Changes in grain orientation had a minor effect on the corrosion resistance of the alloy, while other factors like grain size and residual stress showed no correlation with the electrochemical properties of AZ31B.

2. The mechanism responsible for the ennoblement of SZ region as a result of intermetallic dissolution was proposed based on experimental data and theoretical calculations. Particle dissolution in the SZ region enhanced its corrosion resistance properties by eliminating harmful microgalvanic couples between second phase particles and intermetallics, and by increasing the aluminum content in the $\alpha$-Mg matrix. A direct correlation between the diffusion time available for particle dissolution and the resultant corrosion characteristics embodied in $E_{\text{corr}}$ and $i_{\text{corr}}$ has shown that the corrosion resistance properties of the SZ improved when longer diffusion times were available for particle dissolution. This proposition agreed with mixed potential theory-based calculations, correlating changes in second phase particle size and distribution to the corrosion behaviour of friction stir spot welded AZ31. It was determined that corrosion behaviour of friction stir welded AZ31 during initial exposure can be successfully estimated from theoretical calculations.

3. The corrosion resistance of friction stir welded AZ31 (in both spot and seam weld configuration) was governed by the galvanic coupling between the noble SZ region and the active BM. This galvanic coupling resulted in an accelerated pitting attack at the
interface between the two regions (coinciding with the TMAZ). The corrosion rate of the weldment was affected by the cathode-to-anode area ratio that depended on the welding parameters and microstructural evolution in the SZ upon welding. Faster rotational speeds and longer dwell times increased the size of the SZ region and as a result accelerated the rate of the corrosion attack.

4. The welding flash contained a region whose microstructure and electrochemical properties were statistically similar to those exhibited by the SZ in the weld nugget. The presence of the welding flash increased the cathode-to-anode ratio and accelerated localized corrosion in the TMAZ region. Complete removal of the welding flash improve can improve the corrosion resistance of the weld.

5. The mechanism governing the corrosion resistance of similar friction stir welded AZ31B joints did not apply to dissimilar AZ31/AZ80 welds. Instead, the corrosion of dissimilar joints was governed by the galvanic coupling between the dissimilar magnesium alloys, and not by the microstructural changes resulting from the welding operation. Galvanic coupling between the active α-Mg matrix in AZ31 and the noble Al-rich intermetallic particles in AZ80 resulted in enhanced localized corrosion in the form of pitting at the dissimilar interface.

6. A novel method to analyze instantaneous voltage-time output produced during PEO treatment of magnesium has been designed and implemented (in collaboration with Dr. Qing Ni). Based on the analysis, a mechanism describing PEO coating formation was proposed, and the effects of process parameters were evaluated. The oxidation process comprised four distinct oxidation stages that were related to the evolution of the oxide film on the surface of the specimen. The thickness of the coating increased with increasing applied current density due to increased plasma discharge rate. The plasma electrolytic oxidation process was highly sensitive to the temperature of the electrolyte, as increased temperatures enhanced the dissolution rate of the coating and reduced the coating thickness.

7. Application of PEO coatings to friction stir welded specimens is a promising corrosion mitigation strategy for both similar and dissimilar types of joints. In similar welds, PEO coatings were able to mask the galvanic couple formed between the noble SZ region and the active BM. In dissimilar joints, the coating masked the coupling between AZ31 and AZ80. In both cases, coated specimens exhibited significantly lower corrosion rates than
uncoated specimens. The corrosion behaviour of coated specimens was principally governed by the imperfections of the PEO coating, and not by the microstructural changes caused by the welding operation.

16.2 Future Work

While the present thesis was successful at achieving its objectives, additional work can be carried out in order to deepen the understanding of the mechanisms governing the corrosion behaviour of friction stir welded magnesium alloys. Future work is also recommended in the area of PEO coatings and other corrosion mitigating strategies. A summary of areas for future work is given below:

1. The mixed potential theory model that was discussed in this thesis (Chapter 10) represents the first steps towards relating the effects of welding parameters on the electrochemical properties of the joint. It is acknowledged that the model should be modified as new information becomes available. Specifically, a number of aspects should be addressed:
   a. The model should be modified to account for corrosion product build up on the surface of the specimen and any changes in the local composition of the electrolyte. Accounting for these variables and their dependence on exposure time would improve the model, so that it can be applied to scenarios where welded magnesium specimens are exposed to corrosive environment for a prolonged period.
   b. Electrochemical properties of single phase $\alpha$-Mg matrix specimens with varying concentration of aluminum should be measured and used in the model instead of high purity magnesium that was used in the present work.
   c. A model describing the potential distribution around noble intermetallic particles in a magnesium matrix should be developed in order to accurately determine the anodic area fraction of the corroding $\alpha$-Mg matrix.
   d. The present model did not account for the effect of interparticle spacing and their interaction with one another (territory theory). Consideration for this factor should be incorporated into future iterations of the model.

Increasing the accuracy of the model would improve its ability to predict the overall corrosion rate of the joint and thus enable optimization. If the effect of particle size and distribution is better understood, optimized welding procedures and/or post welding
secondary treatments can be designed to reduce the deleterious effect of friction stir welding.

2. The magnitude of the potential drop in the electrolyte measured by SRET greatly exceeded the theoretical estimation that was based on the Laplace equation. It was proposed that local changes in the electrolyte (pH, dissolved H₂ and O₂) on the surface of the corroding weld were responsible for this potential discrepancy. While the proposition was able to explain the results obtained in the investigation herein, it has not been proven experimentally. It is recommended to assess the effect of pH on SRET measurements by monitoring the pH variation on the surface while scanning the probe tip. Similar experiments were conducted on aluminum joints by Gnedekov et al., who were able to conduct a SVET investigation while mapping the pH on the surface of the specimen [264]. It is also recommended to conduct the SRET measurements on welded specimens in a buffered solution such that the effect of pH variation on the measurement can minimized. The role of changes in dissolved H₂ and O₂ in the electrolyte could be assessed using a similar approach. Such an experiment would help to elucidate the contribution arising from the microstructural variation in the weld to the overall potential drop that was measured in this investigation.

3. A novel method to analyze instantaneous voltage-time output produced during PEO treatment of magnesium has been used to study the mechanisms involved in coating growth on monolithic samples. To the best of the author’s knowledge, the coating growth mechanism across a dissimilar interface (such as a dissimilar AZ31/AZ80 FSW joint), has not been explored yet. It is recommended to use the statistical analysis method that was described in this thesis to gain additional insight onto growth mechanisms of PEO coatings across a dissimilar interface.

4. The degradation mechanism of PEO coatings on AZ31 has been examined in Chapter 15. It was proposed that the pit growth mechanism was driven by cathodic activation that likely occurred through impurity enrichment of the corrosion product. While this proposition is plausible, elemental analysis of the corrosion surface is still required to identify if impurity enrichment is actually present in the pit. The role of local pH changes was ignored as well, and it is recommended to map the local pH variation near the
electrochemically active site to gain further insight on into the mechanism that governs PEO coating degradation.
Chapter 17 References


Chapter 17 References


Appendix A: Dissolution of Liquid Films – Theoretical Derivation

The kinetics of precipitate dissolution were previously approximated by Whelan [185]. Whelan’s approach was later modified by Gerlich and Yamamoto et al. to describe the dissolution of liquid films during friction stir welding [160, 169]. This section provides a step-by-step derivation of the general expression reported by Whelan [185].

Dissolution of intermetallic particles occurs through the diffusion of solute atoms in the metal matrix. If the system is simplified and dissolution is considered to occur through one dimensional diffusion, the concentration profile, \( \Delta \rho \) can be described by Equation (A.1).

\[
\Delta \rho(r, t) = (\rho_s - \rho_e) \cdot erf\left(\frac{r - R}{2 \sqrt{D t}}\right)
\]  

(A.1)

where D is the coefficient of diffusion of solute atoms in the matrix. 

Figure A1 Schematic diagram of the solute concentration in the vicinity of a dissolving precipitate, where \( \rho_c \) is the solute concentration in the precipitate that is surrounded by a metal matrix with a uniform solute concentration of \( \rho_e \). When the temperature is raised by \( \Delta T \) the concentration at the interface particle/matrix interface becomes \( \rho_s \). The solid line gives the solute concentration before the temperature was increased and the dashed line gives the solute concentration at time \( t \) after the temperature was increased. \( R_o \) is the initial half thickness or radius of the particle. The picture was reproduced from reference [185].
To ensure mass balance, the flux of solute across the particle/matrix interface must equal the rate of loss of solute from the particle as shown in Equation (A.2).

\[-(\rho_c - \rho_s) \cdot \frac{dR}{dt} = -D \cdot \left( \frac{\partial \Delta \rho}{\partial r} \right)_{r=R}\]  \hspace{1cm} (A.2)

Substituting Equation (A.1) into (A.2) gives Equation (A.3), which can be rearranged to yield Equation (A.8) using the steps outlined below.

\[\frac{dR}{dt} = \frac{D}{\rho_c - \rho_s} \cdot \frac{\partial}{\partial r} \left( (\rho_s - \rho_e) \cdot erf \left( \frac{r - R}{2\sqrt{Dt}} \right) \right)_{r=R}\]  \hspace{1cm} (A.3)

Note: \[\frac{\partial}{\partial r} \left( a \cdot erf \left( \frac{r - x}{y} \right) \right) = -2 \cdot a \cdot e^{-\left(\frac{r-x}{y}\right)^2/\sqrt{\pi} \cdot y} \]  \hspace{1cm} (A.4)

\[\frac{\partial}{\partial r} \left( (\rho_s - \rho_e) \cdot erf \left( \frac{r - R}{2\sqrt{Dt}} \right) \right)_{r=R} = \left( -\frac{2 \cdot (\rho_s - \rho_e) \cdot e^{-\left(\frac{r-R}{2\sqrt{Dt}}\right)^2}}{\sqrt{\pi} \cdot 2\sqrt{Dt}} \right)_{r=R}\]  \hspace{1cm} (A.5)
Where $k$ is the driving force for diffusion as defined in Equation (A.9)

$$k = 2 \left( \frac{\rho_s - \rho_e}{\rho_c - \rho_s} \right)$$

(A.9)

The half thickness or radius of a particle at a specified time $t$, after the temperature was raised can be found by integrating the expression in (A.8) to yield Equation (A.12)
If complete dissolution is considered (R=0) then the largest particle that would fully dissolve after time $t$ will have an initial radius $R_o$ as shown in (A.13). The form of this equation is identical to that given in Equation (4.1) with the exception of the term describing the driving force for diffusion, $k$, which was modified by Gerlich and Yamamoto et al. to describe the dissolution of liquid films [160, 169].

\[ R = R_o - \frac{k}{2} \sqrt{Dt} \]  \hspace{1cm} \text{(A.12)}

\[ R = \int_0^t - \frac{k}{2} \cdot \frac{D}{\sqrt{\pi t}} dt \]  \hspace{1cm} \text{(A.10)}

Note: \[ \int a \cdot \frac{\sqrt{c}}{\sqrt{t}} dt = 2at \sqrt{c} + \text{constant} \]  \hspace{1cm} \text{(A.11)}

\[ R_o' = \frac{k}{2} \cdot \sqrt{Dt} \]  \hspace{1cm} \text{(A.13)}

To describe the driving force for diffusion when dissolution of liquid films is examined, the expression given in (A.9) must be adjusted. The term describing the concentration of the solute in
the particle, $\rho_c$, was changed to the eutectic composition of the two phases present in the melted film at the eutectic temperature, $c_{T_2}^{\text{liq}/\alpha}$. The term describing the composition of the surrounding matrix after the temperature was increased, $\rho_s$, was adjusted as well to represent the maximum solubility limit of the solute in the metal matrix, $c_{T_2}^{\alpha/\text{liq}}$, at the eutectic temperature. Finally, the term describing the solute concentration in the bulk matrix, $\rho_e$, was left unchanged. The resulting expression is that given in Equation (4.2) in Chapter 4 of this thesis.

$$k_1 = 2 \left[ \frac{c_{T_2}^{\alpha/\text{liq}} - c_{T_1}^{\alpha/\beta}}{c_{T_2}^{\text{liq}/\alpha} - c_{T_2}^{\alpha/\text{liq}}} \right]$$
Appendix B: Engineering Drawings for Apparatus Used in This Thesis

B1 – Sample Holder for the Welding Machine

Countersunk for M6
B2 – Microcapillary Cell Drawings

B2.1 Microcapillary Polycarbonate Cell - 3D View

All Parts made of Polycarbonate
B2.2 Microcapillary Polycarbonate Cell - Cross Section

Main eye Sight
Electrode openings
Top Lid
Main Cell
Capillary Opening

10-32 standard port for 1/16” OD tubing

SECTION A-A
SCALE 2 : 1
B2.3 Microcapillary Polycarbonate Cell - Cell Drawing

All dimensions are given in mm.
B2.4 Mounting Device for a Microcapillary Polycarbonate Cell – Cell Holder

All dimensions are given in mm.
B3 – SRET Cell Drawings

B3.1 SRET Cell - 3D View
B3.2 SRET Cell – Cell Drawings

All dimensions are given in inches.
Appendix C: Computer Code Written for This Thesis

C1 – Zaber Code

The code used to control the Zaber system was written in C and it is detailed below:

```c
//template(simple)

// Define Devices
var ConversationX = PortFacade.GetConversation(1);
var ConversationY = PortFacade.GetConversation(2);

// Define Units
var step = 0.047625;
var SpeedConversion = 1/(9.375 * step);

// Input Variables by the User
Output.WriteLine("How far would you like to scan to the right? [um] ");
var line = Input.ReadLine();
var HorizontalDistance_um = Convert.ToInt32(line);
var HorizontalDistance = Convert.ToInt32(HorizontalDistance_um / step);
Output.WriteLine("How many lines would you like to scan? ");
line = Input.ReadLine();
var NumberLines = Convert.ToInt32(line);
Output.WriteLine("What is the spacing between the lines? [um] ");
line = Input.ReadLine();
var Jump_um = Convert.ToInt32(line);
var Jump = Convert.ToInt32(Jump_um / step);
Output.WriteLine("How fast would you like to scan? [um/sec] ");
line = Input.ReadLine();
var SpeedXum = Convert.ToInt32(line);
var SpeedX = Convert.ToInt32(SpeedXum * SpeedConversion);
Output.WriteLine("How fast would you like to move vertically? [um/sec] ");
line = Input.ReadLine();
var SpeedYum = Convert.ToInt32(line);
var SpeedY = Convert.ToInt32(SpeedYum * SpeedConversion);

// Set Speeds
ConversationX.Request(Command.SetTargetSpeed, SpeedX);
ConversationY.Request(Command.SetTargetSpeed, SpeedY);

// Set X axis on a fast travel speed
ConversationX.Request(Command.SetTargetSpeed, SpeedY);

// Return to the origin
ConversationX.Request(Command.MoveAbsolute, OriginX);
ConversationY.Request(Command.MoveAbsolute, OriginY);
```


C2 – SRET Output Analyzer

The code used to analyze the output produced during SRET testing was written in R and it is detailed below:

```r
setwd("Enter the address of the folder containing the file to be analyzed")

Filename= "file name.txt"
NoL>N
Start=1

ScanDistance=Sx
ScanSpeed=SRx
DataRate=1
YDistance= (NL-1)x Sy

Analyze <- function(
  Filename= " file name.txt",
  DataRate=1,
  NoL>N,
  File=FALSE,
  ScanDistance= Sx,
  YDistance= (NL-1)x Sy,
  ScanSpeed= SRx,
  Start=1,
  OCP=-1.35){
  RawData<-read.table(Filename, header=FALSE)

  DataPerLine=round(ScanDistance/ScanSpeed*DataRate)+1
  V<-matrix (nrow=NoL, ncol=DataPerLine)
  for (iRow in 1:NoL){
    V[iRow,]=RawData[(Start+(iRow-1)*DataPerLine):(Start+(iRow)*DataPerLine-1),3]-OCP
  }

  for (iRow in 1:NoL){
    if ( iRow%%2 ==0) V[iRow,]=rev(V[iRow,])
  }
  for (iCol in 1:DataPerLine) V[,iCol]=rev(V[,iCol])
  filled.contour(t(V), col=rev(rainbow(20, end=0.8)))
  #filled.contour(t(V), col=hsv(h=0.5, s=1,v=seq(0.5,1, by=0.01))

  ExportFile=paste("Output", Filename)
  XYZ_Table<-matrix(nrow=DataPerLine*NoL, ncol=3)
  for (iRow in 1:NoL){
    for (iCol in 1:DataPerLine) XYZ_Table [(iCol+(iRow-1)*DataPerLine-1)*ScanDistance,(iRow-1)/(NoL-1)*YDistance, V[iRow, iCol])
  }
  if (File) write.table(XYZ_Table, ExportFile, row.names=FALSE, col.names=FALSE, sep="t")
}

Analyze("file name1.txt", 1, NoL, File=FALSE, ScanDistance=Sx, YDistance= (NL-1)x Sy, ScanSpeed= SRx, Start=1, OCP=-0.9)
```

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C3 – R Code Used to Monitor PEO Coating Formation

The code used to analyze the output produced during PEO coating was written in R and it is detailed below:

```r
# Input format is 2-column, Tab-separated, without headings.
# The first column is time in seconds, and the second column is voltage
# In the below example, the file is "input.txt"
InputFileName = "E:\Directory\Sample.txt"

Data = read.table(InputFileName, header=FALSE)
colnames(Data) = c("Time", "V")

# Parameters
WindowSize = 2000 # Number of data points per period
BinSize = 5 #[V] Bin size for voltage histograms
TimeOffset = 5 #[seconds] The time of start of the experiment
VRange = c(0, 200) #[V] Range of voltage to be considered

# Adjust the time series to start at the beginning of experiment (Time Offset)
Data$Time = Data$Time - TimeOffset
Data = Data[which(Data$Time<0),]

TimeSeries = seq(0, length.out=round(length(Data$Time)/WindowSize),
by = Data$Time[WindowSize+1] - Data$Time[1])
VoltagePoints = seq(VRange[1], VRange[2], by=BinSize)
Result = matrix(0, nrow=length(TimeSeries), ncol=length(VoltagePoints)-1)

for (iSegment in 1:length(TimeSeries)){
  V_Data = Data$V[iSegment * WindowSize - 1:WindowSize]
  V_Data = V_Data [which(V_Data<VRange[2] & V_Data>VRange[1])]
  Histogram = hist(V_Data, breaks=VoltagePoints)
  Result[iSegment, ] = Histogram$count / max(Histogram$count) # Normalize the frequency to 1
}

### The final results are

TimeSeries  # an array of N time points, at the interval defined by WindowSize
VoltagePoints  # an array of M+1 voltage levels, at a separation defined by BinSize
Result  # a matrix of N rows and M columns, where the rows are the time points,
# and the columns are the voltage separation points

### This provides a preview of the results

filled.contour(x = TimeSeries, y = VoltagePoints[1:(length(VoltagePoints)-1)],
z = Result, col=hsv(0.65, seq(0, 1, length.out=22), 1), nlevels=21,
xlab="Time (s)", ylab="Voltage (V)", key.title = "Normalized intensity")
```
Appendix D: Potentiodynamic Polarization of Bulk AZ31 Base Metal Specimens

D1 – AZ31 (CS) in 0.1M NaClO₄

![Graph showing potentiodynamic polarization of AZ31 (CS) in 0.1M NaClO₄.](image)
D2 – AZ31 (RS) in 0.1M NaClO₄
Appendix E: Potentiodynamic Polarization of AZ31 Phase Constituents

E1 – Pure Mg in 0.1M NaClO$_4$
E2 – Mg$_{17}$Al$_{12}$ in 0.1M NaClO$_4$
E3 – Al₈Mn₅ in 0.1M NaClO₄
Appendix F: Potentiostatic Polarization of AZ31 Phase Constituents

F1 – Anodic Polarization of Pure Mg in 0.1M NaClO₄
F2 – Cathodic Polarization of Pure Mg in 0.1 M NaClO₄
F3 – Cathodic Polarization of Mg$_{17}$Al$_{12}$ in 0.1M NaClO$_4$
F4 – Cathodic Polarization of Al₈Mn₅ in 0.1M NaClO₄
Appendix G: Microcapillary Polarization of AZ31 Base Metal

G1 – Microcapillary Polarization of AZ31 (CS) in 0.1M NaClO₄
G2 – Microcapillary Polarization of AZ31 (RS) in 0.1M NaClO₄

MCP - 0.1M NaClO₄ - AZ31 Magnesium Alloy (RS)

Potential [V_RHE] vs. Current Density [mA/cm²]

- Trial 1
- Trial 2
- Trial 3
Appendix H: Microcapillary Polarization of FSSW Joints Made in AZ31B

H1 – Microcapillary Polarization of the HAZ Region (CS) in 0.1M NaClO₄.

*The joint was welded using 3000 rev min⁻¹ and 1 sec dwell.*

![Graph showing microcapillary polarization](image)
H2 – Microcapillary Polarization of the TMAZ Region (CS) in 0.1M NaClO₄.

The joint was welded using 3000 rev min⁻¹ and 1 sec dwell.
H3 – Microcapillary Polarization of the TMAZ Region (CS) in 0.1M NaClO₄.

*The joint was welded using 3000 rev min⁻¹ and 4 sec dwell.*
H4 – Microcapillary Polarization of the SZ Region (CS) in 0.1M NaClO$_4$.

The joint was welded using 1000 rev min$^{-1}$ and 1 sec dwell.
H5 – Microcapillary Polarization of the SZ Region (CS) in 0.1M NaClO4.

The joint was welded using 1500 rev min\(^{-1}\) and 1 sec dwell.
H6 – Microcapillary Polarization of the SZ Region (CS) in 0.1M NaClO₄.

The joint was welded using 2250 rev min⁻¹ and 1 sec dwell.
H7 – Microcapillary Polarization of the SZ Region (CS) in 0.1M NaClO₄.

The joint was welded using 2250 rev min⁻¹ and 2 sec dwell.
H8 – Microcapillary Polarization of the SZ Region (CS) in 0.1M NaClO₄.

The joint was welded using 3000 rev min⁻¹ and 1 sec dwell.
H9 – Microcapillary Polarization of the SZ Region (RS) in 0.1M NaClO₄.

The joint was welded using 3000 rev min⁻¹ and 1 sec dwell.
H10 – Microcapillary Polarization of the SZ Region (CS) in 0.1M NaClO$_4$.

The joint was welded using 3000 rev min$^{-1}$ and 4 sec dwell.
Appendix I: Microcapillary Polarization of FSW Joints Made in AZ31B

I1 – Microcapillary Polarization of the TMAZ Region (CS) in 0.1M NaClO₄.

The joint was welded using a rotational speed of 1400 rev min⁻¹ and a traverse speed of 180 mm min⁻¹.
I2 – Microcapillary Polarization of the SZ Region (CS) in 0.1M NaClO₄.

The joint was welded using a rotational speed of 1400 rev min⁻¹ and a traverse speed of 180 mm min⁻¹.
Appendix J: Microcapillary Polarization of Heat-Treated FSSW Joints Made in AZ31B

J1 – Microcapillary Polarization of a Heat-Treated BM Region (CS) in 0.1M NaClO₄.

The joint was welded using a rotational speed of 3000 rev min⁻¹ and 1 sec dwell.
J2 – Microcapillary Polarization of a Heat-Treated HAZ Region (CS) in 0.1M NaClO₄.

The joint was welded using a rotational speed of 3000 rev min⁻¹ and 1 sec dwell.
J3 – Microcapillary Polarization of a Heat-Treated TMAZ Region (CS) in 0.1M NaClO$_4$.

The joint was welded using a rotational speed of 3000 rev min$^{-1}$ and 1 sec dwell.
J4 – Microcapillary Polarization of a Heat-Treated SZ Region (CS) in 0.1M NaClO$_4$.

The joint was welded using a rotational speed of 3000 rev min$^{-1}$ and 1 sec dwell.
Appendix K: Microcapillary Polarization of the Welding Flash in FSSW Joints Made in AZ31B

K1 – Microcapillary Polarization of the Welding Flash TMAZ Region (CS) in 0.1M NaClO₄.

The joint was welded using a rotational speed of 3000 rev min⁻¹ and 4 sec dwell.
K2 – Microcapillary Polarization of the Welding Flash SZ Region (CS) in 0.1M NaClO₄.

The joint was welded using a rotational speed of 3000 rev min⁻¹ and 4 sec dwell.
Appendix L: Electrochemical Characterization of Friction Stir Welded AZ80

L2 – Bulk Polarization of AZ80 (CS) in 0.1M NaClO₄.
L2 – Microcapillary Polarization of an AZ80 FSW SZ Region (CS) in 0.1M NaClO₄.
Appendix M: Temperature Measurements During Welding

M1 – FSSW Joints Made Using a Rotational Speed of 1000 rev min$^{-1}$.
M2 – FSSW Joints Made Using a Rotational Speed of 1500 rev min$^{-1}$.
M3 – FSSW Joints Made Using a Rotational Speed of 2250 rev min\(^{-1}\).
M4 – FSSW Joints Made Using a Rotational Speed of 3000 rev min\(^{-1}\).
Appendix N: Particle Dissolution (Sample Calculations)

The work detailed below provides a sample calculation for the methodology used to estimate the half thickness of a Mg$_{17}$Al$_{12}$ plate-shaped liquid droplet that would dissolve when a rotational speed of 3000 rev min$^{-1}$ and a dwell time of 1 sec were used.

As detailed in Section 10.3.1, $B_0$ can be estimated using equation 10.1.

\[
B_0(t) = \int_0^{t_{\text{diff}}} \frac{1}{\sqrt{\pi \sqrt{D_o}}} \sqrt{D_o} \exp \left[ -\frac{Q_{\text{diff}}}{RT(t)} \right] \cdot t \, dt
\]  

(10.1)

The function that describes the changes in the temperature ($T(t)$) over the diffusion time ($t_{\text{diff}}$) can be determined from the experimental results. In the present investigation $T(t)$ was approximated by fitting the temperature output from the instant the stir zone temperature exceeded 437 °C and until the point when the welding operation was complete, see figure below for an example.
\[ T(t) = -2.4722t^6 + 32.916t^5 - 172.13t^4 + 447.96t^3 - 605.75t^2 + 397.91t + 726.32 \]  
\text{(N.1)}

\[ B_0(0.95) = \int_{0}^{0.95} \frac{1}{\sqrt{\pi}} \left( 1.53 \cdot 10^{-5} \right) \left( e^{\left( \frac{1.25 \cdot 10^5}{8.314(-2.4722t^6 + 32.916t^5 - 172.13t^4 + 447.96t^3 - 605.75t^2 + 397.91t + 726.32)} \right)} \right) dt \]  
\text{(N.2)}

\[ B_0(0.95) = 1.3536 \times 10^{-7} \text{ m} \]  
\text{(N.3)}

\[ B_0(0.95) = 135.36 \text{ nm} \]  
\text{(N.4)}

The half thickness of a Mg\textsubscript{17}Al\textsubscript{12} plate-shaped liquid droplet that would dissolve when a rotational speed of 3000 rev min\textsuperscript{-1} and a dwell time of 4 sec were used can then be calculated using the calculation below.

\[ B_0(3.95) = \int_{0}^{3.95} \frac{1}{\sqrt{\pi}} \left( 1.53 \cdot 10^{-5} \right) \left( e^{\left( \frac{1.25 \cdot 10^5}{8.314(-2.4722t^6 + 32.916t^5 - 172.13t^4 + 447.96t^3 - 605.75t^2 + 397.91t + 726.32)} \right)} \right) dt \]  
\text{(N.5)}

\[ B_0(3.95) = 1.20152 \times 10^{-6} \text{ m} \]  
\text{(N.6)}

\[ B_0(3.95) = 1.2015 \text{ nm} \]  
\text{(N.7)}
Appendix O: Potential Distribution in the Electrolyte Above a Galvanic Couple

The potential distribution in the electrolyte above a galvanic couple can be estimated by solving the Laplace equation. In the present work the theoretical calculations were simplified by examining a butt-welded geometry (semi-infinite strip), as shown in Figure O1. The model was further simplified by omitting any possible contributions arising from the presence TMAZ region as its electrochemical properties were not statistically different from the BM region.

![Figure O1 Schematic of the simplified weld geometry used to solve the Laplace equation.](image)

The Laplace equation in this work was solved using the semi-infinite strip model. The solution utilizes an approach that was initially reported by Waber et al. [265-267]. Using symmetry, the system can be further simplified to examine only one half of the weld shown the Figure O2. In the present system the potential of the BM was set as zero, and the difference between the corrosion potential of base metal and the SZ was defined as $E_{SZ}$. The SZ is said to have a width of “a” and the BM is said to have a width of “b-a”, where “b” is half of the width of the welded coupon. The conditions described above are shown schematically in the sketches below. The solution focuses on the potential distribution at a distance of 10 µm above the galvanic interface, but the electrostatic potential at any height can be obtained from the expression derived herein by substituting the appropriate value for “y”.
Figure O2 (left) Schematic defining the axis location on a 2D cryosection of the joint in Figure O1. (right) Schematic showing the potential distribution at the surface of the weld.
Laplace Equation

\[ \nabla^2 \varphi = 0 \quad (O.1) \]

\[ \frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} = 0 \quad \{ x, 0 \leq x \leq b \}
\{ y, 0 \leq y \leq \infty \} \quad (O.2) \]

Boundary Conditions

\[ \lim_{y \to \infty} \varphi(x, y) = Finite \quad (O.3) \]

\[ \frac{\partial \varphi(0, y)}{\partial x} = 0 \quad (O.4) \]

\[ \frac{\partial \varphi(b, y)}{\partial x} = 0 \quad (O.5) \]

\[ \varphi(x, 0) = E_a S(x) + i R_p = E_a S(x) + \sigma \frac{\partial \varphi(x, 0)}{\partial y} \frac{\Delta E}{\Delta i} = E_a S(x) + \varpi \frac{\partial \varphi(x, 0)}{\partial y} \quad (O.6) \]

Where \( E_{SZ} \) is the potential difference between the stir zone and the base metal, and \( S(x) \) is a step function as defined in (O.7). The polarization of the electrode is accounted for by the \( iR_p \) term, where \( i \) is the current density and \( R_p \left( \frac{\Delta E}{\Delta i} \right) \) is the polarization resistance of the metal. Since \( i \) can be expressed as \( \sigma \frac{\partial \varphi(x, 0)}{\partial y} \) the expression is then further rearranged in terms of \( \varpi \) (Wagner’s polarization constant), which is defined in (O.8). Finally, \( \frac{\partial \varphi(x, 0)}{\partial y} \) is the potential gradient near the metal-electrolyte interface.

\[ S(x) = \begin{cases} 1, & 0 \leq x \leq a - 0 \\ 0, & a + 0 \leq x \leq b \end{cases} \quad (O.7) \]

\[ \varpi = \sigma \frac{\Delta E}{\Delta i} \quad (O.8) \]
Separation of Variables

\[ \varphi(x, y) = X(x)Y(y) \]  

(O.9)

Then it follows that:

\[ \frac{\partial^2 \varphi}{\partial x^2} = X''Y \]  

(O.10)

\[ \frac{\partial^2 \varphi}{\partial y^2} = XY''' \]  

(O.11)

Substitution of (O.10) and (O.11) into (O.9) yields:

\[ X''Y + XY''' = 0 \]  

(O.12)

\[ \frac{X''}{X} = -\frac{Y''}{Y} \]  

(O.13)

(O.13) can only be true if both are equal to a constant, let it be -\(\lambda\)

\[ \frac{X''}{X} = -\frac{Y''}{Y} = -\lambda \]  

(14)

From (O.14) it is possible to arrange 2 ODEs where (O.15) is dependents only on x and (O.16) depends only on y.

\[ X'' + \lambda X = 0 \]  

(O.15)

\[ Y'' - \lambda Y = 0 \]  

(O.16)

Examine the boundary conditions in equations (O.3) to (O.5), starting with equation (O.3).

\[ \lim_{y \to \infty} \varphi(x, y) = \text{Finite} \]  

(O.17)

\[ \varphi(x, \infty) = \text{Finite} \]  

(O.18)
And by equation (O.9)

\[ \varphi(x, y) = X(x)Y(y) \quad (O.19) \]

Then

\[ \varphi(x, y) = X(x)Y(\infty) \quad (O.20) \]

\[ X(x)Y(\infty) = \text{Finite} \quad (O.21) \]

So, it can be concluded that

\[ Y(\infty) = \text{Finite} \quad (O.22) \]

\[ \frac{\partial \varphi(x, y)}{\partial x} = X'(x)Y(y) \quad (O.23) \]

From equation (O.4) it follows that

\[ \frac{\partial \varphi(0, y)}{\partial x} = X'(0)Y(y) = 0 \quad (O.24) \]

Since

\[ Y(y) \neq 0 \quad (O.25) \]

Then

\[ X'(0) = 0 \quad (O.26) \]
Similarly, from equation (O.5)

\[ \frac{\partial \varphi(b, y)}{\partial x} = X'(b)Y(y) = 0 \]  

(O.27)

\[ X'(b) = 0 \]  

(O.28)

Dealing with the first ODE that is a function of X (equation (O.15))

\[ X'' + \lambda X = 0 \]  

(O.29)

The characteristic equation of this equation is then

\[ r^2 + \lambda = 0 \]  

(O.30)

Where \( r \) is such that

\[ X(x) = C_1 e^{r_1 x} + C_2 e^{r_2 x} \]  

(O.31)

From equation (O.30)

\[ r = \pm i \sqrt{\lambda} \]  

(O.32)

Then

\[ X(x) = C_1 e^{+i \sqrt{\lambda} x} + C_2 e^{-i \sqrt{\lambda} x} \]  

(O.33)

But from Euler’s formula

\[ e^{i \sqrt{\lambda} x} = \cos(\sqrt{\lambda} x) + i \sin(\sqrt{\lambda} x) \]  

(O.34)
So

\[ X(x) = C_1 \cos(\sqrt{\lambda}x) + i \sin(\sqrt{\lambda}x) + C_2 \cos(-\sqrt{\lambda}x) + i \sin(-\sqrt{\lambda}x) \] (O.35)

\[ X(x) = C_1 \cos(\sqrt{\lambda}x) + iC_1 \sin(\sqrt{\lambda}x) + C_2 \cos(\sqrt{\lambda}x) - iC_2 \sin(\sqrt{\lambda}x) \] (O.36)

\[ X(x) = (C_1 + C_2) \cos(\sqrt{\lambda}x) + (C_1 i - C_2 i) \sin(\sqrt{\lambda}x) \] (O.37)

\[ X(x) = C_3 \cos(\sqrt{\lambda}x) + C_4 \sin(\sqrt{\lambda}x) \] (O.38)

\[ X'(x) = -C_3 \sqrt{\lambda} \sin(\sqrt{\lambda}x) + C_4 \sqrt{\lambda} \cos(\sqrt{\lambda}x) \] (O.39)

\[ X'(x) = \sqrt{\lambda}[-C_3 \sin(\sqrt{\lambda}x) + C_4 \cos(\sqrt{\lambda}x)] \] (O.40)

From equation (O.26) we know that

\[ X'(0) = 0 \] (O.41)

\[ X'(0) = \sqrt{\lambda}[-C_3 \sin(0) + C_4 \cos(0)] = 0 \] (O.42)

\[ \sqrt{\lambda}C_4 = 0 \] (O.43)

Since \( \lambda \) is not zero we can conclude that

\[ C_4 = 0 \] (O.44)

Substituting (O.44) into (O.38) we get

\[ X(x) = C_3 \cos(\sqrt{\lambda}x) \] (O.45)

\[ X'(x) = -C_3 \sqrt{\lambda} \sin(\sqrt{\lambda}x) \] (O.46)
From (O.28) we know

\[ X'(b) = 0 \]  
\[ (O.47) \]

\[ X'(c) = -C_3 \sqrt{\lambda} \sin(\sqrt{\lambda} b) = 0 \]  
\[ (O.48) \]

\[ C_3 \sin(\sqrt{\lambda} b) = 0 \]  
\[ (O.49) \]

\[ X(x) \] is not zero it follows that \( C_3 \) is not zero either, so it must be that

\[ \sin(\sqrt{\lambda} b) = 0 \]  
\[ (O.50) \]

\[ \sqrt{\lambda} b = \sin^{-1}(0) \]  
\[ (O.51) \]

\[ \sqrt{\lambda} b = n\pi \]  
\[ (O.52) \]

Where \( n \) is a positive integer \((n=1,2,3...)\)

\[ \lambda_n = \left( \frac{n\pi}{b} \right)^2 \]  
\[ (O.53) \]

\[ X_n(x) = D_n \cos \left( \frac{n\pi}{b} x \right) \]  
\[ (O.54) \]

Dealing with the second ODE that is a function of \( Y \) (equation (O.16))

\[ Y'' - \lambda Y = 0 \]  
\[ (O.55) \]

The characteristic equation of this equation is then

\[ r^2 - \lambda = 0 \]  
\[ (O.56) \]

Where \( r \) is such that

\[ Y(y) = C_1 e^{r_1 y} + C_2 e^{r_2 y} \]  
\[ (O.57) \]
From equation (O.56)

\[ r^2 = \pm \sqrt{\lambda} \]  

(O.58)

Then

\[ Y(y) = C_1 e^{\sqrt{\lambda}y} + C_2 e^{-\sqrt{\lambda}y} \]  

(O.59)

From equation (O.22) we know that

\[ Y(\infty) = \text{Finite} \]  

(O.60)

\[ Y(\infty) = C_1 e^{\sqrt{\lambda}\infty} + C_2 e^{-\sqrt{\lambda}\infty} = \text{Finite} \]  

(O.61)

\[ \frac{C_2}{e^{\sqrt{\lambda}\infty}} = 0 \]  

(O.62)

\[ C_1 e^{\sqrt{\lambda}\infty} \approx C_1 e^\infty = \text{Finite} \]  

(O.63)

\[ C_1 = \frac{\text{Finite}}{e^\infty} = 0 \]  

(O.64)

\[ Y(y) = C_2 e^{-\sqrt{\lambda}y} \]  

(O.65)

\[ Y_n(y) = C_n e^{-\frac{n\pi}{b}y} \]  

(O.66)

The general solutions from (O.54) and (O.66) are

\[ \varphi_n(x, y) = D_n \cos \left( \frac{n\pi}{b} x \right) C_n e^{-\frac{n\pi}{b} y} \]  

(O.67)

\[ \varphi_n(x, y) = \sum_{n=0}^{\infty} A_n \cos \left( \frac{n\pi}{b} x \right) e^{-\frac{n\pi}{b} y} \quad (A_n = D_n C_n) \]  

(O.68)
\[
\frac{\partial \phi(x, y)}{\partial y} = \sum_{n=0}^{\infty} A_n \left( -\frac{n\pi}{b} \right) \cos \left( \frac{n\pi}{b} x \right) e^{-\frac{n\pi}{b} y}
\]

(O.69)

Equation (O.68) can be rewritten as a Fourier series

\[
\phi_n(x, y) = A_0 + \sum_{n=1}^{\infty} A_n \cos \left( \frac{n\pi}{b} x \right) e^{-\frac{n\pi}{b} y}
\]

(O.70)

\[
\phi(x, 0) = A_0 + \sum_{n=1}^{\infty} A_n \cos \left( \frac{n\pi}{b} x \right)
\]

(O.71)

But from equation (O.6) it is known that

\[
\phi(x, 0) = E_{SZ} S(x) + \mathcal{Q} \frac{\partial \phi(x, 0)}{\partial y}
\]

(O.72)

Where (O.72) can be expanded by evaluating (O.69) at \(y=0\)

\[
\frac{\partial \phi(x, 0)}{\partial y} = \sum_{n=0}^{\infty} A_n \left( -\frac{n\pi}{b} \right) \cos \left( \frac{n\pi}{b} x \right)
\]

(O.73)

Substituting (O.71) and (O.73) into (O.72) yields

\[
A_0 + \sum_{n=1}^{\infty} A_n \cos \left( \frac{n\pi}{b} x \right) = E_{SZ} S(x) - \frac{\mathcal{Q}\pi}{b} \sum_{n=0}^{\infty} nA_n \cos \left( \frac{n\pi}{b} x \right)
\]

(O.74)
Multiply by $\cos\left(\frac{m\pi}{b}x\right)$ on both sides of the equation

$$A_0\left(\cos\left(\frac{m\pi}{b}x\right)\right) + \sum_{n=1}^{\infty} A_n\cos\left(\frac{n\pi}{b}x\right)\cos\left(\frac{m\pi}{b}x\right) = E_{SZ}(x)\cos\left(\frac{m\pi}{b}x\right) - \frac{Q\pi}{b}\sum_{n=0}^{\infty} nA_n\cos\left(\frac{n\pi}{b}x\right)\cos\left(\frac{m\pi}{b}x\right)$$

Integrate both sides with respect to x over the defined range of x ($0 \leq x \leq b$)

$$\int_{0}^{b} A_0 \cos\left(\frac{m\pi}{b}x\right)\,dx + \int_{0}^{b} \sum_{n=1}^{\infty} A_n\cos\left(\frac{n\pi}{b}x\right)\cos\left(\frac{m\pi}{b}x\right)\,dx$$

$$= \int_{0}^{a} E_{SZ} \cos\left(\frac{m\pi}{b}x\right)\,dx + \int_{a}^{b} 0 \cos\left(\frac{m\pi}{b}x\right)\,dx$$

$$- \frac{Q\pi}{b} \int_{0}^{b} \sum_{n=0}^{\infty} nA_n\cos\left(\frac{n\pi}{b}x\right)\cos\left(\frac{m\pi}{b}x\right)\,dx$$

For clarity each integral is solved separately, starting with the left-hand side

$$\int_{0}^{b} A_0 \cos\left(\frac{m\pi}{b}x\right)\,dx = A_0\left[\sin\left(\frac{m\pi}{b}x\right)\frac{b}{m}\right]_{0}^{b} = 0 - 0 = 0$$

For $A_n\int_{0}^{b} \cos\left(\frac{n\pi}{b}x\right)\cos\left(\frac{m\pi}{b}x\right)\,dx$ Consider two cases $n=m\neq0$ and $n\neq m$. For $n=m\neq0$,

$$A_n\int_{0}^{b} \cos\left(\frac{n\pi}{b}x\right)\cos\left(\frac{m\pi}{b}x\right)\,dx = A_n\int_{0}^{b} \cos^2\left(\frac{n\pi}{b}x\right)\,dx$$
Since
\[ 1 + \cos(2x) = 2 \cos^2(x) \]  
(O.79)

\[
A_n \int_0^b \cos^2 \left( \frac{n\pi}{b}x \right) dx = A_n \frac{1 + \cos \left( \frac{2n\pi}{b}x \right)}{2} \int_0^b dx
\]  
(O.80)

\[
A_n \int_0^b \frac{1}{2} + \frac{\cos \left( \frac{2n\pi}{b}x \right)}{2} dx = A_n \left[ \frac{1}{2}x + \sin \left( \frac{2n\pi}{b}x \right) \frac{b}{2n\pi} \right]_0^b = \frac{b}{2}A_n
\]  
(O.81)

For all other cases \((n \neq m)\), and remembering that
\[
\int \cos(ax) \cos(bx) \, dx = \frac{\sin((a-b)x)}{2(a-b)} + \frac{\sin((a+b)x)}{2(a+b)} + c
\]  
(O.82)

\[
A_n \int_0^b \cos \left( \frac{n\pi}{b}x \right) \cos \left( \frac{m\pi}{b}x \right) dx = A_n \left[ \frac{\sin \left( \frac{(n-m)\pi x}{b} \right)}{2 \left( \frac{m\pi}{b} - \frac{n\pi}{b} \right)} + \frac{\sin \left( \frac{(n+m)\pi x}{b} \right)}{2 \left( \frac{m\pi}{b} + \frac{n\pi}{b} \right)} \right]_0^b = 0
\]  
(O.83)

Now on the right-hand side the only integral of concern is
\[
\int_0^a E_{SZ} \cos \left( \frac{m\pi}{b}x \right) dx = E_{SZ} \left[ \sin \left( \frac{m\pi}{b}x \right) \frac{b}{m\pi} \right]_0^a = E_{SZ} \frac{b}{m\pi} \sin \left( \frac{m\pi a}{b} \right)
\]  
(O.84)

Similar to (O.78) if \(m=n \neq 0\)

\[
\frac{\varpi}{b} \int_0^b \sum_{n=0}^\infty nA_n \cos \left( \frac{n\pi}{b}x \right) \cos \left( \frac{m\pi}{b}x \right) dx = \frac{\varpi}{b} \int_0^b \sum_{n=0}^\infty nA_n \cos^2 \left( \frac{n\pi}{b}x \right) dx
\]  
(O.85)

\[
\frac{\varpi}{b} \int_0^b \sum_{n=0}^\infty nA_n \cos^2 \left( \frac{n\pi}{b}x \right) dx = \frac{\varpi}{b} \int_0^b \sum_{n=0}^\infty nA_n \left( \frac{1 + \cos \left( \frac{2n\pi}{b}x \right)}{2} \right) dx
\]  
(O.86)
\[
\frac{\varpi \pi}{b} \int_0^b \sum_{n=0}^{\infty} nA_n \left( 1 + \cos \left( \frac{2n\pi}{b} x \right) \right) dx = \frac{\varpi \pi n}{b} A_n \left[ \frac{1}{2} x + \sin \left( \frac{2n\pi}{b} x \right) \right]_0^b
\] (O.87)

\[
\frac{\varpi \pi n}{b} b A_n \frac{b}{2} = A_n \frac{\varpi \pi n}{2}
\] (O.88)

Substitution of (O.77), (O.81), (O.84), and (O.88) into (O.76) yields

\[
\frac{b}{2} A_n = E_{SZ} \frac{b}{m\pi} \sin \left( \frac{m\pi a}{b} \right) - A_n \frac{\varpi \pi n}{2}
\] (O.89)

\[
\frac{b}{2} A_n(1 + \frac{\varpi \pi n}{b}) = E_{SZ} \frac{b}{m\pi} \sin \left( \frac{m\pi a}{b} \right)
\] (O.90)

Solving for \( A_n \) while remembering the \( m=n \) (see (O.78) and (O.85))

\[
A_n = \frac{E_{SZ} \sin \left( \frac{n\pi a}{b} \right)}{n\pi(1 + \frac{\varpi \pi n}{b})}
\] (O.91)

To solve for \( A_0 \), use Fourier coefficient formula

\[
A_0 = \frac{1}{b} \int_0^b f(x) dx
\] (O.92)

Where \( f(x) \) is such that

\[
f(x) = \begin{cases} 
E_{SZ}, & 0 \leq x \leq a \\
0, & a < x \leq b 
\end{cases}
\] (O.93)

\[
A_0 = \frac{1}{b} \left[ \int_0^a E_{SZ} dx + \int_a^b 0 \ dx \right]
\] (O.94)

\[
A_0 = \frac{a}{b} E_{SZ}
\] (O.95)
Substituting (O.91) and (O.95) into (O.70)

\[
\varphi_n(x, y) = \frac{a}{b}E_{SZ} + \frac{2E_{SZ}}{\pi} \sum_{n=1}^{\infty} \frac{e^{-\frac{n\pi y}{b}} \sin \left( \frac{n\pi a}{b} \right) \cos \left( \frac{n\pi x}{b} \right)}{n\pi \left( 1 + \frac{\Omega \pi n}{b} \right)}
\]  

(O.96)

The potential difference that could be measured using a SRET tip that is scanned at a distance of 10 µm can be estimated by evaluating \( \varphi_n(x, y) \) at \( y = 0.01 \) mm for \( x \) between 0 and \( b \). Mathematica software was used to compute the function using an \( n \) value of 1000 which was well above the value required for the convergence of the function. Two scenarios were calculated as described below:

**Spot-Welded Configuration**

If a spot weld was to be produced using the welding tool with a shoulder diameter of 10 mm (as was used in this thesis) the following parameters would apply:

- \( a = 1.3 \) mm
- \( b = 4.1 \) mm
- \( E_{SZ} = 50 \) mV
- \( y = 0.01 \) mm
- \( R_p = 1550 \) \( \Omega \)cm²
- \( \sigma = 9.311 \times 10^{-3} \) S/cm

Note that the widths “\( a \)” and “\( b \)” were chosen such that they match experimental conditions as outlined in the schematic in Figure O3.
Figure O3 Schematic of the top view of a friction stir spot welded SRET specimen.

The potential drop in the electrolyte at a distance of 10 µm above the surface of the weld is plotted in Figure O4.

Figure O4 Potential distribution in the electrolyte at a height of 10 µm above the surface of a corroding FSSW joint (3000 rev min⁻¹ and 4 sec dwell time) in 0.086M NaCl.

The potential difference in this case was about 4.3 mV, significantly lower than the potential variation observed in SRET measurements. To further explore the cause for the discrepancy between experimental and theoretical values, the effect of experimental conditions on the magnitude of the potential drop measured during SRET testing was examined. In particular, the calculations herein investigated the effect of probe height and electrolyte concentration. Figure
O5 below shows the effect of probe height on the magnitude of the potential drop in the electrolyte. It is evident from the figure that as the probe height was increased, the magnitude of the potential drop decreased. The greatest effect of the probe height was observed at heights exceeding 100 µm.

![Effect of Scan Height](image)

**Figure O5** Effect of probe height on the potential drop in the electrolyte above the surface of a corroding FSSW joint (3000 rev min\(^{-1}\) and 4 sec dwell time) in 0.086M NaCl.

The effect of electrolyte concentration is plotted in the Figure O6 below. As the electrolyte concentration increased, the potential drop in the electrolyte decreased. Relatively small changes were predicted to occur if a more concentrated electrolyte (greater than 0.086M NaCl) was used in the experiment. A potential drop of nearly 15 mV was predicted to exist in experiments utilizing a 0.01M NaCl experiments. Neither of the examined experimental parameters can be responsible for a potential drop of hundreds of millivolts as was observed in the SRET experiment. It is plausible that the observed potential drop was caused by local variation in the chemistry of the electrolyte.
Figure O6 Effect of NaCl concentration on the potential drop in the electrolyte at a height of 10 µm above the surface of a corroding FSSW joint (3000 rev min\(^{-1}\) and 4 sec dwell time).