INFLUENCE OF MICROSTRUCTURE ON THE CORROSION BEHAVIOUR OF MAGNESIUM ALLOYS

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>EDX/EDS</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscattered diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron micro-diffraction</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transform</td>
</tr>
<tr>
<td>SKPFM</td>
<td>Scanning Kelvin probe force microscopy</td>
</tr>
<tr>
<td>PIPS</td>
<td>Precision ion beam polishing system</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction analysis</td>
</tr>
<tr>
<td>TRC</td>
<td>Twin roll cast</td>
</tr>
<tr>
<td>MCTRC</td>
<td>Melt-conditioned twin roll cast</td>
</tr>
<tr>
<td>MCAST</td>
<td>Melt-conditioning via advanced shear technology</td>
</tr>
<tr>
<td>FSW</td>
<td>Friction stir welding</td>
</tr>
<tr>
<td>FSZ</td>
<td>Friction stir zone</td>
</tr>
<tr>
<td>TMAZ</td>
<td>Thermo-mechanically affected zone</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat affected zone</td>
</tr>
<tr>
<td>WN</td>
<td>Weld nugget</td>
</tr>
<tr>
<td>NDE</td>
<td>Negative difference effect</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution rate</td>
</tr>
<tr>
<td>$E_{corr}$</td>
<td>Free corrosion potential</td>
</tr>
<tr>
<td>$E_{pit}$</td>
<td>Pitting potential</td>
</tr>
<tr>
<td>$I_{corr}$</td>
<td>Corrosion current density</td>
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Influence of microstructure on the corrosion behaviour of magnesium alloys

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The University of Manchester
For the Degree of Doctor of Philosophy
(Dated: 09th of September 2011)

Abstract

The influence of microstructure on the corrosion behaviour of magnesium alloys has been investigated using advanced microscopy approaches including optical microscopy, SEM, TEM and SKP FM with a focus on the effect of melt-conditioned twin roll casting (MCTRC) and friction stir welding (FSW) on the resultant microstructure of magnesium alloys.

The microstructure characterization revealed that intense shearing, generated through the advanced shear technology, resulted in grain refinement and a uniform distribution of the β-phase and reduced micro-porosity in the MCTRC Mg-Al alloys, of which were attributed to the enhanced heterogeneous nucleation, which resulted in a highly refined grain structure. The TRC Mg-Al alloys displayed a coarse grained microstructure, with a random distribution of grain sizes. Deformation features like twinning, localized shear, microporosity and centre-line segregation were some of the commonly observed defects in the TRC alloys. The general microstructure of the AZ series Mg-Al alloys was composed of α-Mg grains, the β-phase, rosette-shaped $\text{Al}_8\text{Mn}_5$ intermetallic particles and β-precipitates.

The MCTRC Mg-Al alloys showed improved corrosion resistance owing to the reduced grain size and the β-phase network acting as a corrosion barrier, thereby retarding the corrosion process. The TRC Mg-Al alloys exhibited higher susceptibility to galvanic corrosion due to the coarse and random distribution of grain sizes, and segregation. The corrosion testing results showed different corrosion morphologies, including filiform-like and spherical channel-like along with overall general corrosion. However, galvanic corrosion, initiating at localized sites due to $\text{Al}_8\text{Mn}_5$ intermetallic particles and the Si/Fe impurities accounted for a major deterioration in the performance of the Mg-Al alloys. The polarization curves revealed no evidence of passivation, suggesting that the alloy surface was continuously attacked. SKP FM results indicated that the micro-constituents, namely $\text{Al}_8\text{Mn}_5$ intermetallic particles and the β-phase exhibited higher nobility relative to the α-Mg matrix, suggesting formation of micro-galvanic couples at localized sites leading to the initiation of galvanic corrosion.

The AM60 and AZ91 Mg-Al alloys, subjected to FSW, revealed that the traverse speed had a direct influence on the weld zone microstructure, where the size of the friction stir/weld nugget zone decreased with increase in the traverse speed and the increase in the rate of deformation, led to widening of the friction stir zone, below the shoulder. The weld microstructure displayed a prominent friction stir zone, with an ultrafine grain structure of an average grain size ranging from 2-10 µm. The localized increase in temperatures, in the TMAZ, due to the lower tool rotation rates and traverse speeds, which rise above the eutectic melting point (430°C), showed evidence of partial melting followed by re-solidification of the β-phase and evidence of liquation below the shoulder regions in the TMAZ. The morphology of the β-phase clearly revealed solute segregation, inconsistent with the β-phase observed in the parent alloy microstructure.

The polarization curves obtained from the weld zones in the FSW AM60 alloy showed an improved corrosion resistance compared with the parent metal zone. SKP FM results revealed that the α-Mg matrix in the friction stir zone showed higher surface potential values compared with the parent alloy microstructure, due to the dissolution of the β-phase, suggesting higher nobility. However, the polarization behaviour of the AZ91 alloys did not show a significant difference in the corrosion resistance in the weld zones due to the higher volume fraction of the β-phase in the AZ91 alloys. The immersion testing results revealed higher susceptibility to corrosion in the transition zone due to the flash formation and the banded microstructure leading to failure of the weld zone.
DECLARATION

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

Surajkumar Pawar
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Dedicated to my mother…

My family, for their encouragement…

My daughter, Rajgauri, for her innocence, faith and kindness…

My wife, Yogita…

For her endless love and support…

It would have been just impossible, without you…
Magnesium alloys have a unique combination of high strength to weight ratio and low density, making the alloys an excellent choice for automobile and aerospace applications. Additional properties, including exceptional dimensional stability, high damping capacity, and high recycle ability, good castability, excellent stiffness, etc. are attracting enormous attention from industry. However, low creep resistance, low stability at elevated temperatures, low formability, low ductility and poor corrosion resistance are some of the major setbacks for magnesium and its alloys being used in the industry. With lightweighting being a major focus of current materials research, magnesium alloys are a promising candidate for exploitation in the automobile sector in order to reduce greenhouse gas emissions and, consequently, the carbon footprint [1].

Figure 1.1 summarizes the breakdown of the usage of magnesium in the western world, in 1999. The major uses of magnesium are in aluminium alloys (43%), die casting (36%) and steel desulphurisation (11%). The estimated world demand for magnesium in 2007 was approximately 711 ktonnes and there are good reasons to anticipate that demand will increase very significantly in the near future, particularly in the die casting sector. The major reason for this predicted growth is that the increasingly stringent regulation of emissions from vehicles and rising petrol costs, due to which the car manufacturers are striving to improve the fuel efficiency of their vehicles. Ultra light weighting is one of the solutions and the way to achieve this is to use more magnesium. According to the
research performed by Norsk Hydro, that almost 50% of the magnesium is recycled, there is an average savings of the emissions over the life cycle of a passenger motor vehicle of about 50 kg of CO$_2$ per kg of magnesium used [256, 257]. Research and development to improve various properties in magnesium alloys have resulted in an overwhelming increase in the last decade [171-173]. Some common applications of magnesium alloys including, micro-electronics, automobile, aerospace, to name a few, are illustrated in Fig. 1.2, and the increase in the magnesium applications has been encouraging and the driving force to intensify the efforts in improving the quality of magnesium research.

Magnesium production is a capital-intensive process and largely depends on the price. China has emerged as one of the main magnesium producing countries, contributing ~75% of the world’s production [258], and the magnesium prices have been driven by the low priced supply of the metal from China. Western producers are faced with creating value through either reducing costs or developing products and services with a high added value. In addition, with the closure of nearly all of Europe’s primary magnesium production facilities by the end of 2002 and the removal of the European Commission’s antidumping duty on magnesium from China in April 2003, Europe has become an attractive market for Chinese magnesium.

Nearly 95% of the primary magnesium output of China is produced using the Pidgeon process [259], invented in the 1940s in Canada [260]. Magnesium production is energy intensive, and environmental issues play a significant role in driving the demand for magnesium, magnesium alloys, components and products. The global magnesium production chain should therefore be considered on a life cycle basis to evaluate its environmental impacts over the life cycle of magnesium products. The Pidgeon process being a thermal process is highly endothermic and operates at elevated temperatures (1200°C). The main disadvantages of thermal processes include the relatively high cost of the reducing agents, ferrosilicon and (particularly) aluminium and the batch operation required by the vacuum that causes lower productivity and results in air ingress leading to a loss of magnesium [261].
1.1 Need of alloy development

Although a great variety of applications can be envisaged for magnesium alloys, the actual use is limited due to their poor overall corrosion resistance. Hence, the corrosion performance of magnesium alloys has evoked great interest during the last few years. A major step for improving the corrosion resistance of magnesium alloys was the introduction of high purity alloys. Alloying can further improve the general corrosion behaviour, but it does not change the galvanic corrosion problems if magnesium is in contact with a different metal in the presence of an electrolyte. Appropriate casting methods can serve as an option to improve the microstructure, leading to a refined microstructure and improved performance through enhanced mechanical and corrosion properties of magnesium alloys.

Besides the galvanic corrosion problems related to magnesium, the low stability at elevated temperatures is a further serious problem, limiting the use of magnesium especially for power train applications. Creep resistance is a major requirement for use of magnesium in automotive powertrain components that are currently constructed of aluminium or cast iron. Some magnesium alloys are commercially available in the market e.g. MRI, modified AE and AJ alloy systems [3, 4], which contain mostly aluminium for good castability and strontium, calcium and/or rare earth elements for improved high temperature stability. For automotive applications, it is important that the development of new casting alloys addresses creep resistance and cost effectiveness [4], Mg-Al-Si, Mg-Al-RE, Mg-Al-Ca, Mg-Al-Sr and quaternary combinations of them are very promising new systems for high pressure die casting. However, calcium, strontium and rare earth additions are also studied for gravity or low pressure castings [5]. These new alloys have high temperature properties comparable with common aluminium alloys.

Automotive applications also require good ductility for many components, especially energy absorbed in the case of an accident is a very crucial issue. One direction in the alloy and process development for wrought alloys is to optimise the energy absorption of the material [7]. Nevertheless, other components require preferentially higher strength than ductility. Thus, alloy development has resulted in various requirements, as shown in Fig.
1.3, and alloy groups can be identified to provide particular properties, including specific strength, ductility, creep resistance, etc. Figure 1.3 also presents an overview of the different technologies employed for alloy production in order to enhance the current use of magnesium alloys for various applications.

1.2 Focus of research

Mechanical properties including creep resistance, ductility, stability at elevated temperatures, as well as corrosion performance, largely depend on the "microstructure" of the alloy. Investigations of magnesium alloys have led to metallurgical understanding and consequent ability to control the microstructure to improve the mechanical properties and in turn corrosion performance of the alloys. The research undertaken here is an endeavour to supplement relevant information to the existing database of magnesium alloys on microstructure development of magnesium alloys achieved by modifying the twin roll casting process using melt-conditioning and the influence of such processing on the corrosion behaviour of the resultant alloys.

Developments in casting techniques have always been a topic of interest, leading to quality improvements in the microstructure of alloys, in particular, the last two decades have witnessed breakthroughs leading to refinement of microstructure, defect reduction, etc. Casting methodologies including die-casting, thixo-forming, squeeze casting, semi-solid state forming (combination of casting and forging), new rheo-casting process, rheo-die-casting also called thixo-casting, injection molding, etc., are some of the approaches used to improve the properties of cast magnesium alloys. The twin roll casting (TRC) process combines casting and hot rolling in a single step, providing an economic and promising route to strip casting. However, the strip casting is characterized with a coarse and non-uniform microstructure with centre-line segregation.

In order to eliminate the defects from the TRC process, thereby producing a highly refined and a uniform microstructure, Fan and co-workers at BCAST, Brunel University, designed a casting process that involves intensive shearing of the liquid melt to foster solidification
at the casting stage rather than during rolling. The melt conditioned twin roll casting (MCTRC) process, involves MCAST i.e. melt-conditioning using advanced shear technology, aims at achieving a highly refined microstructure through enhanced heterogeneous nucleation under intensive forced convection, prior to twin roll casting. The main objective of the MCTRC process is largely grain refinement in magnesium alloys with reduced microporosity, improved mechanical properties, extended life and better corrosion resistance. Figure 1.4 presents the development in the coarse grained microstructure of AZ91 magnesium alloys produced by the conventional casting to the homogeneous and highly refined microstructure produced by the MCTRC process.

Microstructure characterization of the as-cast TRC and MCTRC AZ series magnesium alloys was thoroughly undertaken to understand the developments in the microstructure leading to the distribution of β-phase, Al-Mn intermetallic particles, refinement in the grain structure, and defects including porosity, microsegregation, centreline segregation, etc. The metallographic specimens of the AZ31 magnesium alloys were also examined after downstream processing, in order to understand the influence of the microstructure on their corrosion behaviour. Friction stir welding (FSW) is a novel solid state joining method that has been successfully employed for aluminium alloys, magnesium alloys as well as dissimilar alloy groups, etc. The friction stir welding process shows microstructure modification, specifically in the friction stir/weld nugget zone, due to friction and frictional heat, during the joining process. The microstructures in the respective weld zones are characterized by the material flow and the associated temperatures, which largely depend on the FSW parameters. The influence of the FSW parameters on the microstructure and the corrosion behaviour of the FSW AZ91 and the FSW AM60 magnesium alloys is undertaken in the research. The alloy specimens were butt welded by friction stir welding at The Welding Institute (TWI), UK.

In spite of the relatively good mechanical properties achieved, it is well known that magnesium alloys remain highly susceptible to corrosion. The composition, distribution and volume of the β-phase and the micro-constituents in the α-Mg matrix determine the susceptibility to corrosion. The corrosion studies were supported by the investigations
conducted using scanning Kelvin probe force microscopy (SKPFM). The SKPFM results further enhanced the understanding of the corrosion behaviour of the micro-constituent phases in the microstructure of the tested magnesium alloys. The corrosion studies were conducted in 3.5% NaCl solution for different time intervals to study the initiation and propagation of the corrosion front.

1.3 Layout of the thesis

The contents of the major sections in the thesis are briefly summarized as follows:

The Literature Review presented in Chapter 2 is mainly focused on the general aspects of magnesium and magnesium alloys, related to the microstructure development. In particular, it presents an overview of the cast Mg-Al system, the solidification aspects and the microstructures of magnesium alloys. The basic principles of twin roll casting, advantages and limitations of the process, melt-conditioned twin roll casting process, the MCAST process and the expected improvements in the microstructure are discussed. The friction stir welding process, including principles, advantages and limitations of the FSW process are presented with a focus on the microstructure modification due to the FSW parameters. The corrosion of magnesium and magnesium alloys, electrochemical aspects, types of corrosion and the factors affecting corrosion are mainly discussed, focusing on the influence of microstructure on the corrosion behaviour. The experimental techniques employed for microstructure characterization and the corrosion studies conducted in the research are elaborately discussed in Chapter 3.

Microstructure investigation of the TRC and MCTRC magnesium alloys in as-cast and as-rolled conditions is addressed in Chapter 4. The investigation was conducted with a primary focus on the influence of processing on the microstructure, in turn the corrosion behaviour of the magnesium alloys with respect to the two casting processes. Chapter 5 focuses on the corrosion studies conducted on the as cast TRC and MCTRC magnesium alloys including the scanning Kelvin probe force microscopy investigation and electrochemical measurements and immersion testing results. Microstructure characterization of friction stir welded magnesium alloys and their corrosion behaviour
have been discussed in Chapter 6. The main focus was to understand the effect of the welding speeds on the microstructure evolution in the FSW magnesium alloys.

Summary of the results and the suggestions for future work on the areas which need extended research are finally documented in Chapter 7.
Fig. 1.1 Breakdown of the usage of magnesium in the western world [6].
Fig. 1.2 Some industrial applications of magnesium alloys.
Fig. 1.3 Directions of alloy development to improve the performance of magnesium components [174].
Fig. 1.4 AZ91 magnesium alloy specimens showing the development in microstructure from conventional casting to MCTRC processing.
CHAPTER 2

LITERATURE SURVEY

2.1 Introduction

Magnesium is widely used for industrial applications, in the cast form, where die-cast alloys dominate the spectrum as they exhibit good castability. However, magnesium demonstrating poor workability, as a consequence of the hexagonal close packed (hcp) crystal structure, which limits the amount of plastic deformation tolerated.

Die-cast magnesium alloys find a wide range of applications, particularly in automobile industry for the following reasons:

- Magnesium has a low specific heat per unit volume which means that magnesium cools quickly, allowing faster cycle times.
- High gate pressures are possible because of the low density.

Magnesium does not stick to the die in the same way as aluminium. Therefore, casting magnesium into thin sheets is relatively easy, which aids design of complex applications such as instrument panels, transfer cases, steering wheels and side mirror brackets [175]. As an engineering material in the automotive industry, magnesium alloys are mostly utilized in structural components shielded from the exterior environment, for example dashboard, steering wheel and gearbox housing.
2.1.1 Physical metallurgy of magnesium

Magnesium has a hexagonal unit cell with axes $a_1 = a_2 \neq c$ and angles $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, with lattice parameters of $a=0.3202$ nm and $c=0.5199$ nm (3). Due to the high $c/a$ ratio, at ambient temperatures, plastic deformation in the magnesium crystal occurs predominantly by slip on the basal plane (0001) and in the close-packed $<11-20>$ directions. Secondary slip occurs in the $<11-20>$ directions on the $\{10-10\}$ vertical faces, and by twinning on the pyramidal $\{10-12\}$ planes, as shown in Fig. 2.2. Deformation at room temperature therefore involves twinning also (initially $\{10-12\} <10-12>$), especially when a compressive stress acts parallel to the basal plane. However, at elevated temperatures, pyramidal $\{10-11\}$ and prismatic $\{11-22\}$ slip planes become more active. Because slip in magnesium only occurs in the basal plane and, therefore, there are only two independent slip systems, polycrystalline magnesium is relatively brittle, as shown in Fig. 2.3 [5].

2.1.2 Solid solution hardening of magnesium

Forming a substitutional solid solution by alloying generally increases the strength and decreases the ductility of the host metal. Alloying with aluminium, however, increases the ductility as well as the hardness of magnesium alloys. The reason for this apparent anomaly is unknown, although it is probably due to the activation of prismatic slip as well as basal slip, which increases the number of independent slip systems to greater than five. It has been suggested that alloying with aluminium activates prismatic slip by changing the axial ratio. However, in reality, aluminium increases the $c/a$ ratio and this is likely to reduce the likelihood of slip on $\{10-10\}$. Its also been suggested that the prismatic stacking fault energy (SFE) is about seven times larger than the stacking fault energy of the basal plane and, therefore, cross slip does not occur. Additionally, alloying with aluminium will reduce the stacking fault energy sufficiently, but there is no experimental evidence for this. The most likely explanation is that alloying reduces the Peierl’s stress on the prismatic planes, while increasing it on the basal plane. Thus, there is solution softening on the prismatic planes and five operating slip systems [5].
2.1.3 Physical and chemical properties of magnesium

Magnesium is available commercially with purity greater than 99.8%, however, it is rarely used without alloying with other metals for engineering applications [6]. With a density of 1.74 g/cm$^3$, magnesium is the lightest structural metal with a silvery white appearance. The density of magnesium is two-thirds that of aluminium and one-quarter of the density of steel. It is a divalent metal, with a melting point of 650°C and a boiling point of 1107°C. Supplies of magnesium are practically unlimited. Sea water contains 0.13% magnesium, which means that one km$^3$ of sea water contains 1.3 million tonnes of magnesium. Magnesium is also widespread in the Earth’s crust in various ores, the most common of which are dolomite (MgCO$_3$·CaCO$_3$) and magnesite (MgCO$_3$).

The standard electrode potential with reference to standard hydrogen electrode at 25°C is -2.363 V and the specific heat at 20°C is 0.245 cal/g/°C. The corrosion resistance of magnesium and its alloys is dependent on film formation in the medium to which they are exposed. The rate of formation, dissolution, or chemical change of the film varies with the medium, and also with the metallic alloying agents are impurities present in the magnesium [3].

2.2 Magnesium-aluminum system

The Mg-Al binary system is the origin of some of the oldest and most commonly used cast magnesium alloys. Alloys, including AZ91, AM50 and AM60, still constitute a large portion of all magnesium alloy casting [7]. Figure 2.4 shows the Mg-Al phase diagram [8]. The maximum solubility of aluminium in magnesium ranges from about 2.1 wt. % at 25°C to 12.6 wt. % at the eutectic temperature of 437°C. The eutectic composition is 32.3 wt. % is between α-Mg and the β-Mg$_{17}$Al$_{12}$ phase [9]. Mg-Al alloys are heat treatable, although solutionizing and aging of Mg-Al magnesium alloys do not have the effectiveness as β-Mg$_{17}$Al$_{12}$ precipitate is formed in an incoherent manner [6].
Mg-Al binary alloys generally possess good castability and, typically, good mechanical properties. However, commercial magnesium alloys are rarely binary alloys, with most ternary and quaternary alloys employed with additions of zinc, manganese, rare earth metals, and silicon. These additions improve specific properties in order to make the alloys more suitable for casting; however, they also complicate the solidification behaviour of the alloys [3].

2.2.1 Alloy designations and tempers

The classification of magnesium alloys adopts the method used by the American Society for Testing and Materials (ASTM). The designation system uses the following combination of letters and numbers for identification of the alloys. The first two letters indicate the major alloying elements in the alloy. The letter corresponding to the element shows the quantity of higher element in the alloy system followed by the smaller one, while, if the elemental composition exists in equal quantities, then the alphabetical order is followed.

The letters mean the following, A – aluminium, B – bismuth, C – copper, D – cadmium, E – rare earths, F – iron, H – thorium, K – zirconium, L – lithium, M – manganese, N – nickel, P – lead, Q – silver, R – chromium, S – silicon, T – tin, W – yttrium, Y – antimony and Z – zinc. For example, AZ91D, reveals a magnesium alloy containing aluminium (8.3 – 9.7 wt. %), zinc (0.4 – 1.0 wt. %), D describing the experimental alloy, according to the ASTM standards [4, 5].

2.2.2 Alloying behaviour

Commercial magnesium alloys use alloying elements having maximum equilibrium solubility exceeding 1 at.% in magnesium, namely Al, Zn, Mn, Zr, Li, Ag, Y, Nd, Si, Cu, Ca and Ce. Aluminium and zinc show a profound effect in reducing the lattice parameters of magnesium and simultaneously, raise the critical resolved stress for slip; therefore, such elements are potent solid solution hardners in magnesium. However, aluminium is a less potent precipitation hardener than zinc or neodymium, because it precipitates incoherently
as $\text{Mg}_{17}\text{Al}_{12}$ at grain boundaries rather than as Guinier-Preston zones within the grains. The small grain size has a specially marked hardening effect on magnesium, almost double that in aluminum, for example; the small grain size also improves ductility [6].

Magnesium and its alloys are commonly melted in mild steel crucibles because of their low solubility for iron. The melt surface, however, must be protected by a flux or inert atmosphere. Grain refinement of the cast microstructure can be achieved by treating with $\text{CCl}_6$ (when aluminium is present) or with zirconium (when it is not) prior to casting. The nucleant is expected to be $\text{Al}_4\text{C}_3$, and zirconium itself, in the two cases.

Most magnesium alloy components are produced by high-pressure die casting, using hot chamber machines except for the largest castings (up to 10 kg). The alloys also can be sand-cast if certain precautions are taken, for example, to inhibit reaction with the sand and moisture. Ingots are produced by direct chill casting, either for remelting or as feedstock for wrought products.

### 2.2.2.1 Effect of addition of aluminium

Aluminium is known to improve the corrosion properties of the alloy; it is added to approximately 2-9%, depending on the required composition and desired properties of the alloy. Song et. al., studied the effect of alloying with different amounts of aluminium and zinc on the microstructure of Mg-Al magnesium alloys. The study also encapsulated the effect of solution heat treatment on the microstructure, as shown in Fig. 2.9. The addition of aluminium in quantities of 1%, 5% and 10% resulted in a considerable decrease in the grain size in the original alloy microstructure. Sizable increase in the precipitation of the $\beta$-phase at the grain boundaries was evident in the microstructure as the aluminium content increases from 1% to 10% [11].
2.2.2.2 Effect of addition of zinc

Zinc, is known to increase the tensile properties of the alloy. With approximately 1% addition of zinc, a profound effect on the properties of the AZ series alloys has been observed. Beyond a certain limit it is susceptible to hot cracking as shown in Fig. 2.6 [1] Song et. al., studied the effect of alloying with different amounts of zinc, on the microstructure of magnesium alloys. They also studied the effect of solution heat treatment on the microstructure, as shown in Fig. 2.10. The addition of zinc in quantities of 0.5%, 1% and 2% reveals a considerable decrease in the grain size compared with the original alloy microstructure. Precipitation of Mg$_2$Zn particles is evident in the alloy with 2% zinc. Solution heat treatment showed negligible impact on the microstructure after addition of different quantities of zinc [11].

2.2.2.3 Effect of addition of manganese

Manganese is used as a grain refiner in Mg-Al magnesium alloys, used in the form of Al-60%Mn master alloy splatter, as pure manganese does not show grain refinement. The hexagonal close packed structure of the ε-AlMn phase is crystallographically favourable as a nucleant for magnesium grains. However, if the melt is held for sufficiently long at about 730°C, the ε-AlMn phase transforms to a more stable Al$_8$Mn$_5$ phase which is a less effective nucleant and leads to an increase in the grain size rather than a refinement of grain size, in the nucleation process [12].

Aluminium, in combination with manganese, shows an impact on the grain refinement but a commercial grain refiner, which is reliable and easy to use, is yet to be developed. Figure 2.8 shows the effect of additions of manganese to various alloys on the grain size. AZ31, AZ61 and AZ91 alloys show a rapid decrease in the grain size initially, by addition of 0.1%Mn. However, further addition of manganese does not show a significant refinement in the grain size.
2.3 Casting of magnesium alloys

Although magnesium can be fabricated by virtually all manufacturing techniques [3], majority of the industrial components are manufactured by die-casting methods. Magnesium casting processes may be divided into three groups: sand casting, permanent mold casting, and high-pressure die-casting. Selection of the casting processes is determined by the part geometry, required tolerance, and production quantity; similar to other commonly cast materials. High-pressure die-casting is currently the most commonly used method for casting magnesium alloys.

Since casting is a net shape or near-net shape forming process, work-hardening is not applicable in order to improve the properties of magnesium casting alloys. Therefore, other techniques, such as solid solution strengthening, precipitation hardening, grain refinement, and specially designed heat treatments are used in order to enhance the properties of magnesium alloy castings [10].

2.4 Solidification behaviour and microstructure of (Mg-Al) magnesium alloys

The final microstructure of Mg-Al magnesium alloys is dependent on the nucleation and growth characteristics of both the primary grains and the eutectic [13]. Therefore, alloying elements, grain refiners, and cooling rate during solidification have a major effect on the final microstructure and properties of the cast alloy. Nucleation is typically controlled by the use of grain refiners. Grain refinement in cast magnesium alloys is not as well understood as in cast aluminum alloys [14, 15]. The growth morphologies of both the primary dendrites and the eutectic in the Mg-Al system are highly dependent on the aluminum content and cooling rate [13].

Zirconium has been found to be a satisfactory grain refiner for some magnesium alloys. Alloys based on the Mg-Zn and the Mg-RE (rare earth addition) show very fine grains when zirconium is added. It is the most potent of the various methods, but the mechanism
is not clear. It is thought to relate to the lattice disregistry between zirconium and magnesium, both hexagonally close packed structures, with similar lattice parameters: Zr: $a = 3.23\ \text{Å}$ and $c = 5.14\ \text{Å}$; Mg: $a = 3.20\ \text{Å}$ and $c = 5.20\ \text{Å}$. This suggests that zirconium particles are the nucleant. Although it is the most efficient of the grain refinement systems, it is not universally applied because the effect is poisoned by some alloying elements, particularly aluminium. Therefore, zirconium is not used in the aluminium-containing magnesium alloys [13]. Most Mg-Al alloys are used for high pressure die-casting, and this process has very high cooling rates, which introduces a high driving force for nucleation. This causes increased nucleation and, therefore, creates a large number of primary grains thereby reducing the need for a potent grain refiner.

Recent research has been undertaken in order to determine an improved method of grain refining aluminum-based magnesium alloys. Lee et. al., have shown the effects of aluminum and strontium additions on the grain size of magnesium alloys. It was found that the grain size decreases dramatically with increasing aluminium content of the alloy from 1 wt.% to 5 wt.%, but further additions have no effect. Figure 2.9 shows the grain refining effects of aluminium in Mg-Al alloys. Investigations on the effect of strontium addition on Mg-Al alloys for both Mg-3 wt.% Al and Mg-9 wt.% Al alloys. The results showed that a 0.01-0.1 wt.% Sr addition has a very strong grain refining effect on the 3 wt.% Al alloys as it decreases the average grain size by about 100 μm. In the case of 9 wt.% Al alloy, addition of strontium hardly showed any grain refinement and in most cases no difference was observed [14, 15].

The primary grain morphology and eutectic formation have been shown to have a correlation since the size and shape of the α-Mg primary phase affects the size of the eutectic pockets that form upon solidification. Depending on the alloy composition and the cooling rate, the eutectic has been found to possess four different morphological transitions. Changes in microstructure of the primary phase can be attributed to both increase in the aluminium content of the alloy and increase in the cooling rate. The microstructure of α-Mg phase with 1wt% aluminium addition is globular and with increasing aluminium content to 9 wt.% the globular structure passes through a transition to a highly dendritic structure [7,
The critical concentration for the transition from globular to dendritic is in the range of 4 to 7 wt.% aluminium, depending on the cooling rate. Figure 2.11 shows this transition; the six fold symmetry of the dendrites should be noted. The increase in the cooling rate shows the transition of the on the primary phase from granular to dendritic [15].

The eutectic in the Mg-Al system is in the form of $\beta$-Mg$_{17}$Al$_{12}$. This eutectic forms in virtually all Mg-Al alloys with as little as 2 wt.% aluminium. A schematic representation of the conventional eutectic formation is presented in Fig. 2.13 (I), with non-conventional eutectic formation shown in Fig. 2.13 (II). Fig. 2.13 (II) shows fully divorced eutectic in A and partially divorced eutectic in B and C. Partially divorced eutectic is present in either the lamellar form (B) or in the form of tiny islands embedded within the $\beta$-phase (C). Although in most commercial alloys, the eutectic is a fully or partially divorced eutectic, it has also been found to form lamellar, fibrous, and granular morphologies. Figure 2.14 shows different morphologies of the $\beta$-Mg$_{17}$Al$_{12}$ eutectic [17]. The relationship between the morphology of the eutectic and the cooling rate of the alloy depend on the concentrations of aluminium and zinc, has been studied by Dahle et. al., with the outcome presented in tabular form in Fig. 2.7.

The lamellar and fibrous eutectic morphologies form in alloys with more than 12 wt.% aluminium. Therefore, these morphologies are not likely to develop in commercial alloys. The eutectic structure has been related to the primary phase morphology. The dendritic and highly dendritic structures are accompanied by the partially and fully divorced eutectics, while the globular and rosette-like primary grains are accompanied by the granular eutectic [15]. This can be attributed to the size and shape of the eutectic pockets formed. A dendritic structure creates smaller pockets of entrapped liquid with a high local aluminium concentration. Globular structures inherently leave large eutectic channels. Smaller pockets of entrapped liquid require reduced undercooling for eutectic nucleation and growth; therefore, divorced eutectics are favored and commonly found in Mg-Al alloys [13].

On heat treatment, the dissolution of the lamellar structure of the eutectic leads to solid solution strengthening [1, 18]. Considering the large freezing range and the low eutectic
volume, Mg-Al alloys can be cast into thin sections. Hence, this advantage increases their susceptibility to banded defects, segregated eutectic, porosity or tears within the microstructure. Recent research has shown that by controlling the casting parameters, the degree of damage caused by the defects can be minimized.

A schematic representation of the solidification sequence of Mg-Al alloys is shown in Fig. 2.12. According to the cooling temperature ranges, precipitation of aluminium-manganese particles on the MgO particles occurs at 642°C followed by nucleation of α-Mg dendrites at 468-642°C and finally formation of the (α+β)eutectic at 431°C [62, 176].

To summarize, commercial AZ series magnesium alloys, have a multi-phase microstructure constituting the α-Mg matrix embedded in the (α+β) eutectic. The eutectic may be in the form of α-eutectic or an (α+β) lamellar aggregate structure. The secondary phase i.e. β-Mg_{17}Al_{12} is observed in the interdendritic spaces in the microstructure. Al_{8}Mn_{5} intermetallic particles are usually found randomly distributed in the microstructure, i.e. within the matrix or found in the (α+β) eutectic. The microstructural features, including the size and the morphology, depend on the casting process involved in the production of magnesium alloys.

### 2.5 Twin roll casting (TRC) process

#### 2.5.1 Introduction

Twin roll strip casting was first conceived by Sir Henry Bessemer in 1856. Since continuous strip casting eliminates several production steps compared with conventional technologies, it has gained importance over the last 40 years. TRC converts molten metals directly into endless coiled strip that is suitable for cold/hot rolling [20]. However, unlike aluminium alloys, TRC of magnesium alloys pose serious challenges including severe oxidation, costs of production, etc. Extensive research has been carried out in optimizing the TRC parameters, evaluating the performance of the resultant TRC magnesium alloys.
and to reduce the cost of production and the complications related to solid state deformation processing [21-25]. Regardless of the efforts, TRC produces a coarse, non-uniform dendritic microstructure with severe defects and poor surface quality [26, 27].

2.5.2 Principles of the TRC process

In the TRC process, molten magnesium metal is heated to liquid temperature, flows down the cooling slope. The melt is rapidly cooled as it reaches the tip of the launder (nozzle). The slope is maintained at a constant temperature as an adiabatic boundary condition in the tundish. The melt is further dragged onto the surface of the lower roll from the tundish. Solidification starts immediately after the melt leaves the tundish, hence, in the TRC process, the tip sustains the melt at a constant level thereby improving the integrity of the solidified strip, minimizing the turbulence and distributing the melt to the required strip width [28]. Due to contact with water cooled rolls, the melt solidifies into a continuous casting strip [29]. The transformation from liquid to solid includes a semi-solid region. When the solidifying metal reaches adequate strength, determined by its ‘rigidity point’, the material experiences a degree of hot working before leaving the roll bite [30, 31]. Therefore, TRC process combines solidification and hot rolling deformation into a single process. A schematic diagram of the TRC process is shown in Fig. 2.15.

2.5.3 Defects produced during TRC processing

2.5.3.1 Introduction

TRC processing aims at production of near-net shape strip castings with sound surface condition, simultaneously reducing the fabrication costs by eliminating various steps during casting and rolling as well as down stream processing. However, some defects arise during the processing stage as summarized below:
2.5.3.2 Centre Line Segregation

Macro-segregation in conventional casting processes is caused by the movement of liquid or solid phases within the mushy zone, which is due to thermal contraction, solidification shrinkage and density difference within the mushy zone [2]. Jin et al. suggested that centreline segregation in a TRC process could be due to the squeezing effect of the rolls (i.e. roll separating force) on the mushy region forcing the remaining liquid, enriched in alloying elements, to be squeezed out towards the centre-line [33]. Thomas et. al., reported that when the casting process is carried out under hot conditions central segregation forms (e.g. small setback, high speed, large freezing range alloy and high metal feed temperatures) and it can usually be reduced or removed by reverting to colder conditions by increasing the roll separating force [34].

2.5.3.3 Edge Cracking

Rolling of conventional strip casting of materials causes edge cracking. Thickness reduction through length increase at the centre of the strip occurs when it passes through the rolls, while the edges undergo a thickness reduction through lateral spreading. Due to the tension located at the strained edges of the strip, rolling forces edge cracking [37].

2.6 Melt-conditioned twin roll casting (MCTRC) process

2.6.1 Introduction

In order to address the issues in conventional twin roll casting, including coarse, non-uniform microstructure, centre-line segregation, voids, macro-segregation, agglomeration of intermetallics, etc, Fan et. al., at BCAST, Brunel University developed an innovative method to minimize the defects in strip casting.
2.6.2 Principle of the MCTRC process

MC-TRC (melt conditioned twin roll casting), developed by BCAST [40, 41], is a novel casting technique to overcome the disadvantages of the conventional TRC process. Here, grain refinement in magnesium alloy casting strip is achieved by conditioning the liquid metal prior to solidification processing. A schematic representation of the MCTRC process is shown in Fig. 2.16.

This technology produces high quality strip by focusing on the control of solidification by a MCAST (melt conditioning by advanced shear technology) unit, which feeds a twin roll caster. The MCAST unit consists of a twin screw device, in which pair of co-rotating, fully intermeshing and self-wiping screws rotate at high speed inside a heated barrel with precise temperature control. The specially-designed screws provide a high shear rate and a high intensity of turbulence [42]. The conditioned melt is then supplied to a TRC machine for the direct production of high quality thin strip.

2.6.3 Melt-conditioning by advanced shear technology (MCAST) process

Figure 2.17 presents a schematic diagram of the MCAST unit, which consists of a liquid metal feeder, a twin-screw extruder and a central control unit. The most vital feature of the MCAST machine is a twin-screw extruder, which consists of a barrel and a pair of closely intermeshing, self-wiping and co-rotating screws. The screws have a specifically designed profile to achieve a high shear rate and high intensity of turbulence, and to improve the positive displacement pumping action. A high shear rate, high intensity of turbulence and cyclic variation of shear rate are characteristics of the fluid flow in the closely intermeshing, self-wiping and co-rotating twin-screw extruder in the MCAST machine. Consequently, the temperature field and composition field in a MCAST machine are anticipated to be homogeneous and uniform.

The procedure for melt conditioning before the twin roll casting process is given below:
(a) An appropriate amount of melt (~3.5 kg) at a temperature of ~30°C above the liquidus temperature is taken from the melting furnace.

(b) Once in the passageway of the MCAST machine, the fed liquid alloy is quickly cooled to the desired temperature while being mechanically sheared by twin screws in a pre-set shearing time ($shear\ t$), and screw rotation speed ($N$).

(c) The conditioned liquid under a protective gas mixture of nitrogen containing 0.4 vol. % sulphur hexafluoride is injected at a pre-determined discharge time from the outlet valve into a well isolated stainless steel crucible.

(d) The conditioned melt is then transferred under the protective gas and fed into the TRC machine to produce MC-TRC strips.

During MC-TRC strip casting, the melt temperature in the tundish is measured to ensure the true pouring temperature is nearly the same as the shearing temperature in the MCAST machine. The transfer time of the conditioned melt from the MCAST unit into the TRC machine should be as rapid as possible (~5 s), to avoid severe burning and oxidation of the melt, which has a detrimental effect on the final strip quality.

MC-TRC is a cost-effective process that reduces processing steps, resulting in a significant saving in capital investment, operating cost and manpower compared with the conventional hot and cold rolling of the large rolling blocks route. The MCAST unit can be attached readily to different twin roll casters for the production of magnesium sheet for a wide range of alloys. High quality, reduced cost magnesium sheet products could greatly facilitate the penetration of wrought magnesium alloys into transport applications to provide both reduced fuel consumption and CO$_2$ emissions.

2.6.4 Grain refinement through enhanced heterogeneous nucleation

The MCAST process produces a highly refined grain size, with improved chemical and microstructural uniformity [63]. The advantages of the MCAST process are its simplicity and cost effectiveness for feedstock production. However, the accuracy and uniformity of
the temperature control and consistency of the results in large scale production are challenges for industrial applications [61].

The microstructural evolution from a coarse dendritic to a refined equiaxed morphology in the MCAST process, was proposed by growth controlled mechanism, being one of the probable mechanisms under forced convection for grain refinement. According to this theory, the melt flow is essentially laminar at low and intermediate shear rates, and it is unlikely that laminar flow can interact with the secondary dendrite arms to apply a bending force. In addition, all the experimental and theoretical investigations on microstructure evolution under forced convection have been limited to simple shear flow with a low to intermediate shear rate of usually less than 1000 per second.

Hence, Fan et al. proposed a mechanism under high shear rate and high intensity of turbulence, provided by MCAST process [61]. Fan et. al. further elaborated that the intensive melt shearing provided by the MCAST process can effectively disperse the oxide films and oxide skins into individual MgO particles of 100-200 nm in size. These fine MgO particles can act as potent nucleation sites for both Al₈Mn₅ intermetallics and the primary α-Mg phase. This results in significant grain refinement of both the primary α-Mg and Al₈Mn₅ intermetallics, which is termed the enhanced heterogeneous nucleation mechanism [62, 66].

Experimental investigations on the effect of various turbulent flows on the solidification morphology of different alloy systems were carried out by Ji and Fan, which has revealed that forced convection promotes finer particles with a non-columnar dendritic morphology. At the same time, the turbulent flow accelerates crystal growth due to the enhanced mass transport during solidification. Turbulent flow influences the particle size and morphology much more significantly than laminar flow. Therefore, due to adequate temperature control and uniform chemical composition achieved by shearing the liquid melt by the MCAST process, heterogeneous nucleation occurs, which increases the chance of survival of all the nuclei possible, contributing to the microstructural refinement [62].
2.7  Welding

2.7.1 Introduction

With increasing demand of magnesium alloys in the automobile and aerospace sectors, and with welding of magnesium alloys still facing many challenges, the necessity of a reliable joining method remains vital to enhance application. Welding of magnesium alloys has been used only to repair structures because of the occurrence of many defects such as oxide films, cracks and cavities. Magnesium alloys can be joined using a wide range of welding processes, but conventional processes have exhibited some disadvantages such as a large heat affected zone (HAZ), porosity, evaporative loss of the alloying elements and high residual stresses [154]. Friction Stir Welding (FSW) is one of the alternative methods, which could overcome the above limitations. FSW is a solid state joining process, it producing pore-free joints, with the thermal gradients and the microstructural changes are smoother than conventional joining methods.

2.7.2 Friction stir welding (FSW) process

Friction stir welding is a solid-state joining technique [150]. It was initially developed to join aluminium alloys (such as highly alloyed 2xxx and 7xxx series), which could not be welded using conventional processes because of their solidification microstructure and because of the porosity occurring in the fusion zone induced a significant loss in the mechanical properties of the joint. Indeed, FSW can achieve metallic bonding below the material melting point, and substantially avoid metallurgical problems associated with the solidification process such as porosity and cracking. Further advantages of FSW include the absence of sample preparation, shielding gas or consumable filler material.

The basic principle of the FSW process is illustrated in Fig. 2.18. A non-consumable, rotating tool, composed of a pin with a shoulder, is inserted into the abutting edges of the plates to be joined, which are clamped to prevent the joint faces from being forced apart.
Due to the friction between the tool and the sample, the material is heated to temperatures below their melting point. The material around the pin eventually softens, allowing the tool to traverse along the weld line. The combination of tool rotation and its translation transfers the plasticized material from the front to the back of the pin and to be forged by the tool shoulder contact. The FSW process can achieve 0.8 to 65 mm thick welds for several materials including aluminium, copper, magnesium, lead, and zinc alloys [159, 160].

2.7.3 Advantages of FSW process

The FSW process has several advantages over conventional fusion welding processes as indicated below [151-153]:

✓ The process does not require use of consumable filler metal; instead, a tool, usually made of steel, is used for joining aluminium alloys. The tool can weld up to 1000 metres of aluminum before replacement.
✓ Hot cracking and porosity defects, usually experienced in fusion welding processes are not associated with FSW process, due to the fact that the material within the stir zone is not melted, hence, liquid to solid transformation does not occur.
✓ The weld produced by the FSW process has good mechanical properties compared with conventional fusion welded alloys. This is attributed to the reduced amount of heat generated during the joining process compared with fusion welding processes. Furthermore, the structure of the weld produced by the FSW process has fine, equiaxed and recrystallized grains.
✓ The FSW process is environmental friendly, such as it does not produce fumes or spatters and it does not require use of shielding gas.
✓ Generally, the welds produced by the FSW process have a good appearance, and, hence, extra weld (capping) is not necessary. Thus, there is no requirement for grinding or machining after welding to remove the excess weld material, fluxes and sparks.
✓ The process causes less distortion to the component after welding.
✓ The process can operate in all welding positions.
2.7.4 Friction stir weld microstructure

Threadgill et. al. studied the friction stir weld microstructure in different materials, including 2xxx, 5xxx, 6xxx and 7xxx and cast aluminium alloys, titanium alloys, ferritic steels, pure copper, magnesium alloys and pure zinc. FSW processed alloys possess a distinct variation in the alloy microstructure, which is characterized by material flow and accordingly called the weld nugget, thermo-mechanically affected zone (TMAZ), heat affected zone (HAZ) and the parent metal zone as shown in Fig. 2.19. The individual zones are now considered. As in case of FSW of aluminium alloys, microstructural weld zones are formed in FSW of magnesium alloys [199, 201, 202].

A. Weld nugget zone

The weld nugget zone is defined as the region of the thermomechanically affected zone that has experienced mechanical deformation and thermal cycling produced from the friction between the probe and the material. It is a part of the TMAZ and it is located under the probe at the centre of TMAZ. The nugget is characterized by a fine and equiaxed structure resulting from the effect of dynamic recrystallization that takes place in this zone, which is further characterized by formation of circular rings, also known as an “onion ring structure”. Several theories are suggested for the formation of onion rings, namely variation in second phase particle-rich bands, grain size and variations in texture, etc. The hardness in the nugget is usually higher than that of the heat affected zone [155, 156].

The weld nugget zone in FSW of magnesium alloys is with a basin or elliptical shape, characterized by fine recrystallized grains. However, Lee et. al. [200] reported that the weld nugget can be divided into two zones, zone I, located on the upper side of the weld nugget showed partially recrystallized, with deformation layers throughout the grains and zone II, showing full recrystallization with no deformation layers such as twins, etc.

Generally, FSW resulted in generation of fine recrystallized grains in the weld nugget in magnesium alloys [199, 201, 202]. In as-cast magnesium alloys, the coarse α-Mg phase and
β-Mg$_{17}$Al$_{12}$ second phase disappeared after FSW [199-201]. Lee et. al. [201] and Park et. al. [202] reported that the grain size in the weld nugget became larger with increase in the tool rotation rate and lower traversing speed due to increasing heat input which promoted growth in recrystallized grains.

B. Thermomechanically affected zone (TMAZ)

TMAZ is located on the advancing as well as the retreating sides of the weld nugget. The microstructure is significantly deformed and rotated due to tool shearing. On the advancing side, TMAZ is characterized by the presence of material flow on the upper surface of the weld. This arm consists of material that is dragged by the shoulder from the retreating side of the weld around the rear of the tool and deposited on the advancing side [155].

C. Heat affected zone (HAZ)

HAZ is a common weld zone that is present in many welding processes. It is clearly seen in the fusion welds rather than in friction welding due to the high amount of heat implemented in fusion welding compared with that of the FSW process. The HAZ in FSW is not subjected to the mechanical deformation during welding, but it undergoes a thermal cycling. The temperature gradient in HAZ is lower than that in TMAZ and has a reduced effect on the microstructure and the mechanical properties compared with the fusion welding. Usually, in heat treatable aluminium alloys, the HAZ exhibits a reduction in hardness, which is attributed to the coarsening of constituent phases being dominant [157, 158].
2.7.5 Friction stir welding parameters

2.7.5.1 Tool rotation rate (W) and welding speed (V)

Several studies have been undertaken to investigate the effect of welding speed and tool rotation rate on the weldability of magnesium alloys. These two parameters are critical for generating sound welds since they directly influence the heat input and the flow of plastic material. The heat input per unit length can be expressed by:

\[ \text{Heat input} = \frac{Q}{V} \]

Where \( Q \) is the heat generated by friction, and \( V \) is the welding speed. The heat generated by friction increases with the tool rotation rate, but not in a monotonic way since the coefficient of friction at the interface also varies with tool rotation rate. Therefore, increasing tool rotation rate or decreasing welding speed induces a higher temperature, easier flow and enhances weldability. This observation is consistent with all the studies carried out previously [177, 182].

Studies have reported that, for a constant welding speed, a low tool rotation rate leads to formation of inner voids since the frictional heat is not sufficient to promote material flow. These defects disappeared with increasing the tool rotation rate \( W \), but at very high tool rotation rates, inner voids, lack of bonding and surface cracks initiated due to excess expulsion of the material created [161].

Experiments performed at a constant tool rotation rate showed that increasing welding speed resulted in inner voids and lack of bonding caused by insufficient material flow. Yan et al. [162] observed that a low welding speed could provide controlled dynamic recrystallisation leading to a fine grained structure.

Gharacheh et al. [163], using \( W/V \) ratio as processing parameter, observed that increasing the ratio led to an increase in the heat input, an improved material flow and a wider and a deeper weld nugget. The hardness increased with increasing welding speed. Increasing welding speed over a critical value was observed to decrease the ultimate tensile strength.
while the yield strength was kept constant. Gharacheh et. al. also used the W/V ratio to study the influence of processing parameters on the mechanical properties. They observed that increasing the W/V ratio resulted in a decrease in yield strength (YS), ultimate tensile strength (UTS), and elongation. Increasing the tool rotation rate resulted in an increase in the tensile strength [180, 183]. Increasing the welding speed produced an increase in the weld tensile strength until reaching the base metal tensile strength. With further increase in welding speed, the tensile strength dropped, due to grain refinement.

In case of FSW of magnesium alloys, recent studies reported that the quality of the weld is highly sensitive to the tool rotation rate and the traversing speed. Nakata et. al. [199] reported that square butt FSW was conducted successfully using a narrow range of FSW parameters, i.e. high tool rotation rates and low traversing speeds. Higher tool traversing speeds and lower rotation rates than the optimum parameters caused formation of inner voids due to lack of bonding. Successful FSW of magnesium alloys has been reported in literature between 800-1600 rpm tool rotation rates and 50-500 mm/min [197-204].

2.7.5.2 Welding pressure

Zhang et al. [164] studied the influence of welding pressure at the same welding rate (V = 200 mm/min, W = 1000 RPM). The welding pressure was observed to affect the temperature produced by friction. Increasing the welding pressure produced sound welds, while at low pressure, pore formation was observed.

2.7.5.3 Tilt angle

A suitable tilt angle of the tool must be selected to ensure optimum efficiency of the tool. It mainly depends on the shoulder geometry. It is usually set to 3° for a plain shoulder [177, 179], and varied to 1.5° for a concave shoulder and between 0 and 1° for a scroll shoulder [184].
2.7.5.4 Insertion depth

The insertion depth has to be controlled, mainly when using smooth tool shoulders. If it is too deep, a large amount of flash is produced, leading to local thinning of the welded plates because the shoulder penetrates through the material. When the insertion depth is too shallow, there is no contact between the shoulder and the work piece surface, which prevents complete stirring and induces surface groove formation.

2.7.5.5 Preheating or cooling

It can be necessary to preheat materials with higher melting point, prior to FSW, since materials such as steel and titanium or high conductivity such as copper, as the heat produced by the process may not be sufficient. Cooling can be useful to prevent grain growth and precipitate dissolution when welding materials of low melting point such as aluminium and magnesium.

2.7.6 Material flow in FSW process

The material flow during FSW is complex, and depends on the tool geometry, FSW process parameters including tool rotation rate, traverse speed, plunge depth, spindle angle as well as the material to be welded. Figures 2.20 (a) and (b) demonstrates the different zones from the metal sheet namely, extrusion zone, forging zone, deformation zone, from which the material flow patterns are actually produced. The material flow in the FSW process was studied by a number of techniques, including, tracers or markers as well as FSW of dissimilar alloys to follow the material flow patterns. Colligan et. al. [165, 166] suggested that the material movement in FSW is either by simple extrusion or by chaotic mixing. FSW of AA6061 (T6) and AA7075 (T6) plates, embedding small steel spheres at different locations within the weld joint, showed that along with the material stirred by the tool, most of the material moved simply by extrusion around the retreating side.
Li et. al. [186, 187] studied the microstructures of dissimilar FSW of AA2024 and AA6061 aluminium alloys and reported that the material movement within the weld was done to dynamic chaotic mixing. Seidel and Reynolds [185] analyzed the material movement in several friction stir welds using a marker insertion technique and observed no chaotic mixing at the weld surface. Schmidt et. al. [188] observed a portion of the shear layer rotates with the pin during FSW.

### 2.7.7 Flaws in FSW

Wayne et. al. classified the types of flaws arose during FSW into three types: voids, joint line remnants and lack of penetration. Flaws are further classified according to codes into acceptable and non acceptable flaws. Flaws within the weld can be generated if incorrect welding parameters are employed. The use of a damaged probe tip, a short probe, a high or low rotation rate, improper traversing speeds and low pressure may lead to improper forging of the material and lack of bonding [167-170]. A summary of the possible flaws/defects arising due to inadequate control of the FSW parameters has been summarized by W. Arbegast, as shown in Fig. 2.21. The graphical representation of the friction stir welding speed (V) vs the welding rotation rate (W), demonstrates the operational process window for obtaining a successful weld in case of aluminium alloys. A slight change in the welding speed or the rotation rate may produce flaws including, worm-hole defect, lack of penetration, lack of fusion, nugget collapse, scalloping, root flaw defect, etc., usually noticed in the metallographic examination of the FSW microstructures [252].

#### 2.7.7.1 Voids

This type of defect is generated within the weld if a high traversing speed and slow rotation rate [189, 190], inadequate welding pressure [191], as well as non adequate joint gap [191, 192] arise. The use of a small shoulder also leads to lack of material consolidation. Void formation is usually observed on the advancing side of the weld [164]. If the welding pressure is inadequate, the weld receives insufficient forging action from the tool shoulder.
to achieve full consolidation [191]. During FSW at high traversing speeds and slow tool rotation rates, the material receives less work per unit of weld length, i.e. fewer tool rotations per mm. Under such conditions, the plasticized material may not reach a sufficiently high temperature [190].

2.7.7.2 Joint line remnants

The friction stir welds may contain discontinuity regions, which form as a result of improper material deformation due to absence of the pressure required to deform the material. The result of improper dispersion of the oxides that comes from the component surface due to poor surface cleaning, prior to joining, which lead to improper bonding [193]. This discontinuity is usually formed at either the root of the weld and/or at the interface of the material. Joint line remnants also referred as kissing bond, lazy S, zigzag line; can be easily detected during metallographic examination, destructive testing using bend test and/or in severe conditions, can be observed in the weld root by visual examination.

It can also form as a result of oxide accumulation within the weld line interface. Metallographic examination has revealed semi-continuous oxide particles distributed around the original joint-line. The extent of the oxide particles determines the severity of this imperfection and the effectiveness on the structure integrity [191, 194, 195]. Using high traverse speed and a large shoulder diameter, as well as improper tool alignment with the joint line, can lead to formation of such defects. Proper control of the welding parameters and removal of the oxides from the surface by machining, prior to welding can eliminate such flaws.

2.7.7.3 Root flaw/Lack of penetration

The use of a short, bad profiled or a damaged probe, incorrect plunge depth, poor joint alignment or a variation in thickness of the work pieces may lead to formation of joint line features called root flaws also referred as lack of penetration. In butt welds, the most
serious joint line flaws are usually those located at the weld root. The correct depth of penetration of the tool is essential to ensure that mixing occurs over the full plate thickness. Lack of precision in any of the above discussed parameters leads to root flaw formation, indicating lack of bonding [196].

2.7.7.4 Other flaw types

Flash type features are observed on the top surface, usually caused by large plunge depths. However, high flash levels are sometimes introduced to ensure adequate penetration, especially in weld where the fit up is poor. Local melting during FSW has been a topic of continual debate. However, FSW of 7050-T7451, produced at TWI [205], showed region of the TMAZ beneath the tool, providing a clear evidence of liquation. However, according to the number of cases reported of liquation cracking, the rarity of the phenomenon occurring in FSW rather than in case of aluminium arc welds. Johnson et. al. [206] reported liquation occurring in the TMAZ region during FSW of ZK60 magnesium alloy, which could be eliminated by optimizing the FSW parameters. Liquation has also been reported by Sato et. al. [207] during dissimilar FSW of AA1050 to a magnesium alloy, due to melting of Mg$_{17}$Al$_{12}$ intermetallic phase, as the temperature during the FSW process, exceeds the melting point of the second phase in the magnesium alloy.
2.8 Corrosion of magnesium and its alloys

2.8.1 Corrosion (pure magnesium)

As it is observed in metals with negative corrosion potentials, the stability of magnesium depends on the formation of a surface film, able to inhibit the attack of the surface when it is exposed to a corrosive media. In the case of pure magnesium, the surface film formed shows a poor performance; hence it is susceptible to breakdown.

The magnesium corrosion reaction follows the overall equation:

\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \]  \hspace{1cm} (1.1)

This simplified equation can be broken down into the cathodic and anodic partial reactions:

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2\bar{\varepsilon} \text{ (anodic reaction)} \]  \hspace{1cm} (1.2)
\[ 2\text{H}_2\text{O} + 2\bar{\varepsilon} \rightarrow \text{H}_2 + 2\text{OH}^- \text{ (cathodic reaction)} \]  \hspace{1cm} (1.3)

The evolution of hydrogen plays a vital role in the corrosion process of magnesium. Hydrogen molecules can be generated in the reduction reaction and by a chemical reaction between magnesium and water:

\[ 2\text{Mg}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{Mg}^+ + 2\text{OH}^- + 2\text{H}^+ \]  \hspace{1cm} (1.4)

The main corrosion product formed is magnesium hydroxide. However, different atmospheres and solutions will produce other types of corrosion products such as carbonates and hydrated carbonates (in the presence of carbonic acid or CO\(_2\) dissolved in water) or sulphites and sulphates (in the presence of diluted sulphuric acidic or sulphur containing contaminants) [131].

\[ \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \text{ (corrosion product formation)} \]  \hspace{1cm} (1.5)
The main conclusions that can be made from the above equations and the hydrogen evolution are:

1) The corrosion of magnesium does not show an effect due to dissolved oxygen in the corrosive media [67, 122, 131];

2) If the volume of the electrolyte is small, a significant alkalinization of the solution can be attained.

Magnesium has a very active standard potential of -2.37 V (SHE) [67, 131]. However, the standard potential is much nobler in 3% NaCl solutions -1.63 V (SCE), or -1.38 V (SHE) [254], which indicates that the metallic surface is not in direct contact with the solution and is covered by an hydroxide layer. This layer covers the surface, conferring some corrosion protection in alkaline solutions. The thermodynamics of aqueous solution are described by the Pourbaix diagram (Fig. 2.19). The Pourbaix diagram shows that the divalent ion is stable in solutions until a pH value of about 11. After this point, the hydroxide Mg(OH)$_2$ becomes the stable species.

The corrosion in pure magnesium is usually associated with localized corrosion [67]. The surface film on magnesium is metastable and partially protective. For this reason, magnesium shows to have a pitting potential ($E_{pit}$) more negative than the free corrosion potential ($E_{corr}$). The corrosion process starts with the formation of irregular and shallow pits on the surface. The pits display a rather unusual penetration compared with the pits formed in other systems like stainless steels, aluminium, etc. where instead of penetrating vertically in depth, they tend to spread laterally covering the entire surface. Therefore, pitting corrosion is actually rarely observed, having deep pits. This corrosion behaviour is a consequence of the alkalinization of the solution caused by the cathodic reaction. The increase in the pH in the due course of the corrosion process, stabilizes the surface film i.e. magnesium hydroxide Mg(OH)$_2$ and slows down the dissolution process inside the pit. The attack then proceeds at the edges of the pits where the pH is low enough for anodic dissolution to occur. This constitutes a self-limiting characteristic of the corrosion process; which is different from other pitting mechanisms that are self catalytic and generally accelerate the corrosion activity. As the corrosion process spreads laterally, it provokes the
undermining and formation of particles that fall away from the surface. The process of second phase undermining is very common in magnesium alloys.

2.8.2 The negative difference effect (NDE)

In the corrosion of pure magnesium, a rather controversial phenomenon which defies the basic electrochemical theory, named the Negative Difference Effect (NDE) is observed. In most of the metals, when the potential of the surface increases, the rate of anodic dissolution in acidic media increases. This is accompanied by the predictable reduction of the hydrogen evolution rate (HER). In the case of magnesium, however, the HER increases as the potential becomes more positive, which is contradictory with the basic electrochemistry. This process has been verified experimentally in the anodic polarization experiments, where the hydrogen gas evolved, is recovered to estimate corrosion rates, and according to the principle (Eq. 1.1) that the dissolution of one atom of magnesium will release one mol of hydrogen gas [88, 102, 120, 240].

As displayed in Fig. 2.20, when a noble potential (\(E_{appl}\)) is applied, above \(E_{corr}\), the anodic partial reaction should follow the line \(I_a\) and increase until the point \(I_{Mg,e}\). Consequentially, the cathodic partial reaction should decrease along the line \(I_c\), which represents the normal electrochemical behaviour, until the point \(I_{H,e}\). The experimental verification of the increase in HER implies that the cathodic partial reaction must follow a line along \(I_H\) until the point \(I_{H,m}\), corresponding to a cathodic current much higher than the predicted by normal polarization behaviour.

A second experimental evidence of NDE is manifested by another unusual behaviour of magnesium corrosion: the anodic dissolution of magnesium, verified in the experiments on the lost mass during the dissolution process, increases faster than expected, according to the polarization curve \(I_a\) [88, 102, 120, 240]. The weight loss was observed to exceed the predicted values by Faraday’s Law and should follow the curve \(I_{Mg}\) until the point \(I_{Mg,m}\) that corresponds to a higher anodic current than expected.
Although, when the experimental verification of NDE is fairly simple, the explanation of the mechanisms by which it occurs is much more difficult. There are many efforts made to explain the negative difference effect, however, this phenomenon, there are four possible mechanisms have been proposed till date [102], but there is no unanimous agreement on the correct one because of the controversial experimental evidences [88, 102, 120].

**Mechanism I:** According to this approach, the explanation of the NDE is described in terms of the breakdown of the partially protective oxide/hydroxide film that covers the magnesium surface. The higher the potential, the more it deteriorates the film. This mechanism is not satisfactory in explaining the corrosion of magnesium in acidic and neutral media, where the film is not very stable.

**Mechanism II:** The second explanation attributes the NDE to the undermining and falling away of second phase particles during corrosion. As these phases are cathodic, relative to the magnesium matrix, they will accelerate anodic dissolution around them. When enough mass has been lost around them, the particles will fall away, justifying the added weight loss.

**Mechanism III:** The third mechanism explains the abnormal HER by the formation of the unstable monovalent magnesium ion (Eq. 1.3) in an intermediate step. The monovalent ion reacts with hydrogen ions to form H₂ according to the equation:

\[
2\text{Mg}^+ + 2\text{H}^+ \rightarrow 2\text{Mg}^{2+} + \text{H}_2 \quad (1.6)
\]

(Eq. 1.6) provides a chemical reaction to be added to electrochemical hydrogen evolution.

**Mechanism IV:** The fourth mechanism justifies the NDE through the formation of magnesium hydride by electrochemical reduction (Eq. 1.7), predicted by the thermodynamical data. The hydride, which is not stable, reacts with water to form hydrogen.
These mechanisms proposed for the negative difference effect, also apply to magnesium alloys, which show identical behaviour. The negative difference effect is closely related with corrosion resistance: a strong negative difference effect is usually observed in alloys with low corrosion resistance [67].

2.8.3 Kinetics of surface film formation

Generally, the corrosion of magnesium also depends on the characteristics of the surface film. However, limited information is available on the nature of surface film on magnesium in different solutions. Lunder et. al. [103], has reported that, in dry environments, pure magnesium is protected by a stable air-formed oxide whereas, in wet environments, the air-formed oxide film is replaced by a less stable, hydrated oxide, resulting from the electrochemical metal oxidation. More recently, researchers reported about the analysis performed after the initial growth of the surface film on magnesium in aqueous solution across a wide range of pH [104]. Variously, the surface film is considered to be crystalline [82, 98] or hydrated or an amorphous magnesium hydroxide film, different from the bulk magnesium hydroxide film [84-86].

The XPS data has revealed the formation of an external magnesium hydroxide layer of thickness dependent on the immersion time, with an internal ultra-thin MgO layer, probably of constant thickness, after long immersion times in neutral aqueous solutions. It was suggested that the outer hydroxide layer formed at room temperature was porous. Analysis of films formed on magnesium alloys containing Al, Mn or Zn, exposed to atmosphere, showed enrichment of the alloying elements [81]. In particular, Lunder et. al., [110], reported that when the aluminium content reaches 8wt.%, the corrosion resistance of the magnesium alloys could be greatly improved. It is likely that the beneficial effect of aluminium is related to the tendency of aluminium to form a stable surface film [81].
2.8.4 Impurity elements

The influence of impurities resulting in the corrosion of magnesium also needs to be considered. In terms of their influence on the corrosion behaviour of magnesium, different elements have different effects: some improve the resistance while the others are extremely detrimental.

In general, there are four elements that must be controlled: Fe, Ni, Cu and Co. They have been found to posses a very deleterious effect on the corrosion of magnesium when present at contents superior to 0.2% wt [67]. This is known as the Tolerance Limit, as shown in Figs. 2.29 and 2.30. The critical contaminant limit or the ratio for the iron/manganese content in AS, AM or AZ series commercial magnesium alloys, usually does not exceed 0.032. The mechanism has been associated with the segregation of these elements and due to their low solubility in the magnesium matrix; these impurities behave as active sites for localized corrosion. The two main explanations for the accelerated corrosion rates of magnesium in the presence of the elements, both related with microgalvanic effects:

1) As the magnesium matrix corrodes, the impurity elements also dissolve into the solution. The elements will later reprecipitate as metallic Fe, Ni, Cu and Co, at the surface, accelerating corrosion.

2) The impurities at concentrations beyond their solubility limits precipitate as second phases that serve as cathodic sites.

2.8.5 Corrosion of magnesium alloys

The most important factors, rather crucial in understanding of the corrosion behaviour of magnesium alloys are the surface film resistance and the hydrogen evolution. The increase in the corrosion resistance due to alloying elements has been associated with a greater stability of the natural protective film formed on the surface. It has been reported that aluminium, zirconium and rare earth elements are added to magnesium alloys and are found to be associated with the improvement in the corrosion resistance.
It has been mentioned earlier that magnesium has a pitting potential \((E_{\text{pit}})\) more negative than its free corrosion potential \((E_{\text{corr}})\). This corrosion behaviour has been verified in case of many magnesium alloys, however, there are evidences reported in literature, where the pitting behaviour varies with the corrosion testing parameters \([88, 102, 115, 120, 122, 125, 240]\). The AZ series magnesium alloys tend to follow the corrosion behaviour of pure magnesium, presenting \(E_{\text{pit}}\) lower than \(E_{\text{corr}}\).

While explaining the corrosion behaviour of magnesium alloys, the individual contribution of the second phases in the alloy, with dissimilar behaviours, in the magnesium matrix, have to be considered, as reported by Song et. al. [67]. There is no specific model to explain the different \(E_{\text{pit}}\) in magnesium alloys and the possible relation with a more stable surface layer due to alloying elements, however, the most widely accepted trend from the referred literature is that the magnesium alloys containing Zr always present a \(E_{\text{pit}}\) above \(E_{\text{corr}}\). The hydrogen evolution rate is closely related with galvanic effects on the surface, and more specifically, with the electrochemical behaviour of the \(\alpha\)-Mg matrix in relation with second phase particles.

In the alloys based in the Mg-Al system (AM, AS and AE alloy series) it can be hard to distinguish from the effect of the Al in solid solution (\(\alpha\)-Mg phase) and the influence of the \(\beta\)-phase (intermetallic phase \(\text{Mg}_{17}\text{Al}_{12}\)). The increase in Al content leads to a significant decrease in corrosion rate [67]. However, for aluminium contents above 2 %wt, formation of \(\beta\)-phase at the grain boundaries, is observed. The \(\beta\)-phase is more stable than the \(\alpha\)-Mg matrix because it is nobler, having a higher corrosion potential, and passive over a wider pH range, contrary to magnesium, which shows a pitting potential above the free corrosion potential [67]. Although the \(\beta\)-phase itself is very stable, it is very detrimental for the overall corrosion resistance, since it creates a strong microgalvanic effect. The \(\beta\)-phase exhibiting a more positive surface potential, behaves as an active cathode, accelerating the hydrogen evolution rate and the corrosion of the \(\alpha\)-Mg phase.

As reported by Song et. al., it can be concluded that the second phases in magnesium are usually nobler than the \(\alpha\)-Mg matrix, hence the possibility of their microgalvanic effect.
surely cannot be ruled out. For this reason, no matter how complicated the corrosion process of a specific alloy might be, the α-Mg matrix will always corrode preferably over other microconstituents, in a multiphase alloy. The second phases will be undermined by the corrosion of the matrix, due to their localized nobility and eventually be released from the surface.

2.8.6 Types of corrosion

2.8.6.1 Galvanic corrosion

The alloying in magnesium generates second phases in the microstructure, which results in high susceptibility to galvanic corrosion in magnesium alloys. As magnesium itself, is a very active metal, and its alloys, in particular, have the most negative $E_{corr}$ of all the structural materials. For this reason, when in contact with another metal or alloy, magnesium will corrode preferentially, called macrogalvanic corrosion. Song et. al., have very clearly illustrated the macro-galvanic corrosion occurring in magnesium alloys, resulting in the consumption of the magnesium matrix, when in contact with a lesser active metal [67], as shown in Fig. 2.21 (A). Micro-galvanic corrosion in magnesium alloys occurs due to lower corrosion potential of the anodic magnesium matrix than the second phases. The higher activity of magnesium matrix resulting in localized attack, when in contact with the intermetallic microconstituents, which act as cathodes. These cathodes may be external, namely impurities in the alloy or internal, second phases or particles like, $\text{Al}_8\text{Mn}_5$, $\text{Mg}_2\text{Si}$, $\text{Mg}_2\text{Pb}$, etc. Fig. 2.25 (B) illustrates an example of the galvanic corrosion in magnesium alloys [67]. Metals with low hydrogen overvoltage, such as Ni, Fe, and Cu, constitute efficient cathodes, and cause severe galvanic corrosion. High purity does not provide magnesium alloys with a defence against galvanic corrosion, when coupled with a different metal. Therefore, the galvanic corrosion rate increases by the following factors: high conductivity of the medium, large potential difference between anode and cathode, low polarisability of the anode and cathode, large area ratio of cathode to anode, and small distance from the anode to the cathode [67].
Microgalvanic corrosion occurring in magnesium alloys due to the internal elements from the microstructure mainly constitutes second phase particles, i.e. $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase, considerably influencing the corrosion resistance of the magnesium alloys. The die-cast AZ91 magnesium alloy microstructure displays a high degree of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase along the grain boundaries. $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase is cathodic compared with the $\alpha$-$\text{Mg}$ matrix and exhibits a noble behaviour over a wide range of pH. The localized nobility of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase leads to galvanic corrosion in most magnesium alloys.

Song and co-workers revealed that the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase has two major influences namely, as a corrosion barrier and as a galvanic cathode. The behaviour of the $\beta$ phase depends on the volume fraction of the $\beta$-phase ($f$) in the alloy microstructure. Usually the $\beta$-phase, acting as a galvanic cathode accelerates the corrosion process when the volume fraction of the $\beta$-phase ($f$) is less and in cases of higher volume fraction of the $\beta$-phase ($f$), a corrosion barrier effect is observed retarding the corrosion process [67].

Fig. 2.26 illustrates the corrosion morphology of the transverse section of the magnesium alloy surface, revealing the preferential dissolution of the $\alpha$-$\text{Mg}$ phase, where the $\beta$-phase acts as a corrosion barrier, restricting the corrosion front. In addition, Song, et. al., measured the polarization curves for the $\alpha$-$\text{Mg}$ and the $\beta$-phase, where the $\alpha$-$\text{Mg}$ phase displayed a pitting potential about 15 mV more negative than its free corrosion potential, while the $\beta$-phase exhibited a much higher cathodic activity revealing its anodic dissolution rate (below its pitting potential) much lower than the $\alpha$-$\text{Mg}$ phase.

Along with the $\beta$-phase, other intermetallic phases including iron-rich and manganese rich phases in magnesium alloys are found to be highly detrimental cathodes, forming microgalvanic couples, leading to corrosion in magnesium alloys. The $\alpha$-$\text{Mg}$ matrix which is comparatively anodic to the second phases gets preferentially corroded. The $\alpha$-$\text{Mg}$ matrix (primary $\alpha$) and the $\alpha$-eutectic (eutectic richer in Al), differ in the aluminium contents, exhibit different electrochemical behaviour and thereby form galvanic cells with the $\beta$-phase [87, 88]. Therefore, there are two kinds of corrosion morphologies: (1) the dissolution of the primary $\alpha$-$\text{Mg}$ phase and (2) the undermining of the $\beta$-phase due to the
dissolution of the $\alpha$-eutectic phase. This phenomenon is illustrated in Fig. 2.27, which shows the galvanic corrosion occurring due to the galvanic coupling between the primary $\alpha$ and the eutectic $\alpha$, resulting in dissolution of the $\alpha$-Mg phase and subsequent removal of the $\beta$-phase.

### 2.8.6.2 Localized corrosion

Magnesium is a naturally passive metal that undergoes pitting corrosion at its corrosion potential, $E_{corr}$, when exposed to chloride ions in a non-oxidizing medium [81, 89]. In neutral or alkaline solutions, magnesium alloys suffer from aggressive attack of the chloride ions on the alloy surface, resulting in pitting. It is generally observed that pits initiate at flaws adjacent to second phase particles, for example, the Al-Mn intermetallic particles, as a result of breakdown of passivity [81]. High impurity levels promote general pitting attack. Formation of an electrolytic cell occurs, where the second phases including the $\beta$-Mg$_{17}$Al$_{12}$ phase, intermetallics, including Al-Mn, Mg$_2$Si, etc., impurities such as Fe, Si, etc., act as cathodic sites, present in the magnesium matrix, resulting in localized corrosion. This is generally found in Mg-Al alloys. Figure 2.28 shows a schematic diagram of pitting corrosion occurring in the as-extruded AM60 magnesium alloy [252]. Initially, the alloy surface is covered with a protective oxide film, which on immersion in sodium chloride solution, is aggressively attacked by the chloride ions. The breakdown potential of the protective film reaches the free-corrosion potential approximately (-1.53 V for AM60) then forcing the magnesium matrix around the Al-Mn intermetallic particle to dissolve, forming a corrosion pit. The corrosion product namely, Mg(OH)$_2$ is precipitated along with hydrogen evolution. Eventually, the pH reaches a value of about 10.5 owing to the magnesium dissolution, where Mg(OH)$_2$ formed is stable, as evident from the E-pH diagram shown in Figs. 2.22, 2.23 (a) and (b) [78]. As explained earlier, pitting in magnesium alloys follows an irregular mode of development, where instead of growing vertically in depth; it spreads laterally, covering the alloy surface.

Filiform or cosmetic corrosion is caused by formation of galvanic cells across the metal surface. The head of the track is anodic while the tail is cathodic. Filiform-like corrosion is
usually not observed on bare magnesium, but it occurs under protective coatings and anodized layers [71]. However, evidence of filiform corrosion occurring on uncoated AZ91 magnesium alloy was reported by Lunder et. al [73]. According to their observations, the initiation of corrosion showed a characteristic of pitting as well as filiform corrosion. Dexter et. al., has reported in the metals handbook [1984] that filiform corrosion in magnesium alloys was influenced by the oxygen concentration between the head and the tail, proposing a model, which is contradictory with the theory that magnesium corrosion is relatively insensitive to oxygen concentration differences.

Crevice corrosion does not occur with magnesium alloys as it is relatively insensitive to oxygen concentrations differences [92]. However, filiform corrosion is one of the special types of crevice corrosion. There is an argument that as filiform corrosion can occur in case of magnesium then crevice corrosion can also proceed. This type of corrosion initiates in narrow gaps, hence the name “crevice” corrosion. This corrosion occurs due to retention of moisture in the crevices and it promotes the metal surface to corrode. It was suggested by Ghali et. al., that crevice corrosion could be initiated due to hydrolysis reactions in magnesium and magnesium alloys, where it is believed that oxygen does not play a key role in the corrosion mechanism [91].

2.8.6.3 Intergranular corrosion

In some cases, magnesium alloys is observed, which occurs at the grain boundaries due to the precipitation of second phases. The grain boundaries are the most preferred sites where the precipitation and segregation takes place. It is considered that alloys with intermetallic phases are highly susceptible to intergranular corrosion. According to Maker, et. al., in the case of magnesium, intergranular corrosion is normally not encountered, as the second phases on the grain boundaries are cathodic compared with the magnesium matrix and tend to remain passive. Corrosion tends to initiate in the areas adjacent to the grain boundaries until, eventually, till the magnesium grain is completely corroded [92].
2.8.6.4 Stress corrosion cracking (SCC)

Stress corrosion cracking in magnesium is mainly transgranular; however, sometimes intergranular stress corrosion cracking occurs due to Mg$_{17}$Al$_{12}$ precipitation along the grain boundaries in Mg-Al-Zn alloys. It may occur in moist air, high purity water, NaCl+K$_2$CrO$_4$ solution, NaBr, Na$_2$SO$_4$, NaC1, NaNO$_3$, Na$_2$CO$_3$, H$_2$SO$_4$, KF, KCl, NaI, MgCO$_3$, NaOH, HNO$_3$, and hydrogen chloride solutions [107]. Alloys additions namely, aluminium and zinc can promote stress corrosion cracking [95]. Zirconium-containing alloys are free from SCC, except at stresses approaching the yield stress.

SCC in magnesium alloys is attributed to one of the two groups of mechanisms, namely continuous crack propagation by anodic dissolution at the crack tip or discontinuous crack propagation by a series of fractures at the crack tip [94]. Therefore, two models are proposed for SCC, namely the dissolution model and the brittle fracture model. The former includes a preferential attack model, film rupture model, tunneling theory, etc; the later involves cleavage process and hydrogen embrittlement (HE) theory [78]. Magnesium alloys appear to be highly resistant to stress corrosion cracking in alkaline media above pH 10.2. However, in neutral solutions containing chlorides, etc, there is a possibility of SCC to occur [255].

2.8.6.5 Corrosion fatigue

Speidel et. al. studied the corrosion fatigue of magnesium alloys and suggested that it is due to cracks that propagate in a mixed transgranular or intergranular mode; further the corrosion fatigue crack growth rate was accelerated in similar environments to those that accelerate SCC growth [95]. There is relatively little research on the corrosion fatigue of magnesium alloys, and the available data is rather inconclusive, as most of the fatigue data are concerned with the fatigue life. Magnesium alloys possess an endurance limit in air. The fatigue strength improves as the grain size decreases [96]. However, the reverse was found to be the case for the fatigue crack propagation resistance. Experimental results showed a significant reduction in the fatigue strength in chloride containing solutions.
According to Stepan et al., the corrosion fatigue resistance of AZ91-T6 was significantly reduced in 3.5% NaCl relative to that in air [97]. Therefore, the corrosive media can markedly reduce the fatigue life of extruded magnesium alloys compared with the die-cast magnesium alloys [96].

2.8.7 Factors influencing the corrosion behaviour

2.8.7.1 Influence of principal alloying elements

Commercial magnesium alloys mainly constitute two systems, namely, Mg–Al and Mg–Zr. However, magnesium alloys with rare earth alloying are also used for high-end and specific applications. Mg-Zr alloys generally exhibit a good corrosion resistance in salt solutions and are relatively insensitive to iron and nickel. In fact, these impurities are maintained to very low level by precipitation with zirconium before casting [81]. The solubility of zirconium in magnesium is low; therefore, it acts as a remarkable grain refiner for magnesium alloys [107].

Aluminium is partly present in solid solution, and partly precipitated as a continuous β phase (Mg17Al12) along grain boundaries as well as in the eutectic phase, of a lamellar structure [81]. Generally, alloying magnesium with aluminium, improves the corrosion resistance [67]. It is reported that corrosion rate decreases rapidly with the increase of aluminium content up to 4%, but further addition to 9% results only in a modest improvement in corrosion resistance [81]. The advantage of aluminium is generally attributed to β phase precipitation, which depending on its distribution can increase the corrosion resistance by acting as a corrosion barrier [67, 88, 108]. The aluminium enrichment in anodic films, with increase of aluminium content from the substrate, was suggested to be the reason of the higher passive film stability for Mg-Al alloys [109].

However, it was also found that aluminium can have a negative influence on corrosion, reduces the iron tolerance limit almost linearly with increase of aluminium content [81]. The aluminium content in α phase is also crucial to the overall corrosion performance of
dual phase alloys [81, 110]. Due to the effect of segregation during the solidification process, the aluminium concentration can vary from a few percent in the grain interior to 10% in the vicinity of β phase; thus, Lunder et. al. [110] proposed that aluminium accelerates anodic dissolution below 8%, whereas it decreases corrosion above 10%. Mathieu et. al. [111], suggested that the semi-solid process (SSP), leading to aluminium enrichment in the α-phase, is a way of reducing corrosion in AZ91 alloys. In fact, the galvanic corrosion rate between the two main constituents (α and β) decreased with increase of aluminium content, in neutral pH conditions.

The presence of zinc in magnesium alloys can increase the tolerance limits by dissolution and effectively reduce the effect of impurity [81]. Lunder et al. [110] found that generally zinc appeared to render the α and β phase more noble. However, the sensitivity of AZ alloys to filiform corrosion increased as the zinc content increased in the range of 0-3% [81].

Generally, an improvement in microstructure and mechanical properties of magnesium alloys can be achieved by the addition of minor alloying elements, such as rare earth elements [112-114]. In particular, rare earth elements can improve strength at elevated temperature as well as creep resistance [114]. In addition to favourable high temperature properties, certain Mg-RE alloys present good corrosion resistance [100]. Zucchi et al., [115] analyzed the corrosion behaviour of a WE43 magnesium alloy (3.92% Y, 2.09% Nd and 0.48% Zr) in sulphate and chloride solutions. They observed an improvement of the protective performances of the corrosion product film provided by RE elements. Moreover, the formation of less cathodic intermetallic compounds can justify the higher corrosion resistance exhibited by the Mg-RE alloys [100].

2.8.7.2 Influence of impurity elements

The corrosion behaviour of magnesium alloys depends on their metallurgy and on environmental factors. Concerning the metallurgical aspects, the impurity elements are very crucial from the generation of the microconstituents in the resultant microstructure,
rendered after alloying. Hanawalt et. al., studied the impact of the 14 elements on the salt water corrosion rate, illustrated in Fig. 2.29. They summarized that iron, nickel, copper and cobalt had a profound accelerating influence on the salt water corrosion rate at concentrations of less than 0.2%. Silver, calcium and zinc exhibited more modest influence at concentrations of 0.5 to 5% while aluminium, tin, cadmium, manganese, silicon and sodium had very little influence at concentrations up to 5%.

In particular, the literature reports that Fe, Cu, and Ni are extremely deleterious because they have low solid solubility limits and provide effective cathodic sites [81]. The corrosion rate was measured at the concentrations less than 0.2%. This effect is attributed to the low solid solubilities and the abilities to act as active cathodic sites [98]. At the same concentration, the detrimental effect decreases in the following order: Ni > Fe > Cu [81]. However, iron is generally of most concern since it is introduced to the melt from steel pots and casting moulds and it is present as an impurity in the alloying elements [101]. Figure 2.29 displays the tolerance limit of iron in pure magnesium in 3% NaCl solution.

When the impurity exceeds the tolerance limit, the corrosion rate is greatly accelerated. Song et. al., defined the tolerance limit for the alloying elements as illustrated in Fig. 2.28, from the experimental data revealing the corrosion rates accelerating by a factor of 10 to 100, when the concentrations of these critical contaminants, namely, Fe, Ni and Cu were increased. The tolerance limits are influenced by the method of manufacture and the solidification rate, and also by the presence of third elements such as manganese in Mg-Al alloys [81, 101].

Manganese, added in small amounts, improves the corrosion resistance of Mg-Al alloys [68, 101]. In this case, the iron tolerance limit is equal to 0.032 of the manganese concentration (by weight) [81]. As reported in literature [67], manganese reduces the corrosion rate of magnesium alloys firstly because it combines with the iron in the molten magnesium alloy during melting and forms an intermetallic compound which settles to the bottom of the melt, thus lowering the iron content in the alloy; secondly, manganese encapsulates iron particles that remain in the metal during solidification, thereby rendering
them less active as cathodic sites (magnesium-manganese galvanic coupling is less effective than magnesium-iron coupling) [81].

Nickel is more harmful than iron, both in pure magnesium and in magnesium alloys, because of it has a lower tolerance limit. As nickel has a low solid solubility, it must be present as a separate phase, thus becoming more detrimental. The nickel tolerance limit is independent from other alloying element additions, but it is affected by the casting method. The addition of copper to Mg-Al-Zn alloys has a detrimental effect on corrosion resistance, probably due to its incorporation in the eutectic phase.

2.8.7.3 Influence of second phases

In general, the corrosion performance of magnesium alloys is mostly dependent on chemical composition and the distribution of its constituent phases. Mg-Al-Zn alloys mainly display two phases, the α-phase, a substitutional solid solution of aluminium in magnesium, and the β-phase, an intermetallic compound (Mg$_{17}$Al$_{12}$), present as precipitates along the grain boundaries. It has been demonstrated [108, 110, 111] that the study of the corrosion behaviour of α and β phases is the foundation for understanding the corrosion processes of Mg-Al-Zn alloys and the effects on corrosion of others factors such as alloying elements and impurities. It is reported in the literature [81, 108] that the β-phase in AZ91 alloy acts as inert corrosion barrier so that its presence improves the corrosion resistance; however, there is also another view that the β-Mg$_{17}$Al$_{12}$ precipitates, being cathodic with respect to α-Mg matrix, are detrimental for corrosion resistance. The role of β-phase actually depends on its volume fraction $f = V_β/V_α$ in the microstructure. It can act as a corrosion barrier or being cathodic with respect to the α-Mg matrix cause galvanic corrosion [88, 99]. If $f$ is lower, the β-phase behaves as a cathode and accelerates galvanic corrosion in the α-Mg matrix and when $f$ is higher, the β-phase acts as a corrosion barrier, inhibiting general corrosion [88].

Song et al. [88, 108], from the polarization behaviour of the α and β phases in 1N NaCl solution, it was found that the β-phase had higher cathodic reaction activity than the α-Mg
phase, but the anodic dissolution rate was much lower, below its pitting potential; than that of the \( \alpha \)-Mg phase. At their corrosion potentials, the corrosion current density of the \( \beta \)-phase was much lower than the \( \alpha \)-Mg phase. These findings led researchers to the conclusion that the \( \beta \)-phase was very stable in NaCl solutions and was inert to corrosion. However, \( \beta \) phase is also an effective cathode for \( \alpha \)-Mg matrix, thus they suggested that the \( \beta \)-phase served mainly as a galvanic cathode and accelerated the corrosion process in the \( \alpha \)-Mg matrix, if its volume fraction was small. On the contrary, if the volume fraction of the \( \beta \)-phase was high, it may act as a corrosion barrier, to inhibit the overall corrosion of the alloy because, in this case, corrosion only occurs on a limited surface area of the \( \alpha \)-Mg phase.

### 2.8.7.4 Influence of microstructure

Microstructural parameters such as grain size and phase distribution also have influence on the corrosion behaviour [81]. The microstructure varies with the method of processing or the subsequent heat treatments; however, the same production techniques conducted by different researchers may reveal different microstructures and present apparent contradictory electrochemical behaviour [70]. Even for the same specimen, the microstructures can vary depending on the examined sections. For example, Song et al. [88] in a study on the effect of the microstructure on the corrosion behaviour of a die-cast AZ91D alloy, showed that the skin of the die-cast alloy showed better corrosion resistance than the interior. This was attributed to a combination of a higher volume fraction of the \( \beta \) phase, and a more continuous \( \beta \) phase distribution around finer \( \alpha \) grains, and to a lower porosity in the skin layer than in the interior of the die casting. The authors concluded that the casting method strongly influences the corrosion performance through microstructure control, with higher solidification rates being of potential benefit. In fact, [81] rapid solidification, generally improves the corrosion resistance since it leads to significant grain refinement, a more homogenized microstructure than in ingot metallurgy and increases the limit of solid solubility, allowing detrimental elements to exist in less harmful locations or phases, as suggested by Makar and Kruger [92].
Other researchers [99] have examined the different corrosion behaviour of a die-cast and ingot AZ91D alloy. The die-cast alloy showed higher corrosion resistance and improved passivity than the AZ91D ingot due to the fine grain structure and an increased volume fraction of the $\beta$-phase. Coring of aluminium also showed a more significant influence on corrosion behaviour in the ingot material. In fact, the lower aluminium content of the eutectic $\alpha$ phase in the ingot compared to the die-cast alloy makes it susceptible to corrosion, when tested for longer exposure times, thus led to undermining of the $\beta$-phase.

Semi-solid processing (thixomolding) is an innovative production technology, where magnesium alloys, maintained in a thixotropic semisolid state by a vigorous stirring, are injected under pressure into a mould [116, 125]. In a comparative study of the corrosion behaviour of an AZ91D alloy produced by semi-solid processing (SSP) and the same alloy produced by high pressure die-casting (HPDC) [120], it was observed that the corrosion resistance of semi-solid AZ91D alloy was higher than the same alloy produced by HPDC. In this case, the improved corrosion resistance of the SSP AZ91D can not be due to the $\beta$-phase acting as a barrier since this phase is present as large discontinuous grains. The improved performance was attributed mainly to the particular composition of the $\alpha$-phase, resulting from the treatment of the semi-solid alloy, prior to injection in the mould. It is reported that [125] stirring breaks the dendritic structure, leading to rounded-shape pre-existing $\alpha$-Mg grains with an aluminium content (about 3.7 wt.%) higher than that of the $\alpha$ solid solution (1.8 wt.% Al) of the die-cast alloy.

Micro-porosities in magnesium alloys can also have a detrimental effect on corrosion resistance [81]. Castings usually have some porosity. The amount and form of porosity strongly depend on the alloy composition, the casting method employed, the design of the casting and the thermal and feeding parameters [88]. High porosity means that the exposed surface is more active. Usually micropores originate from shrinkage defects, which result in forming active points for corrosion to occur. Moreover, the formation of corrosion products inside a micropore can lead to the development of an auto-catalytic corrosion cell within the pores and thus to a serious localized corrosion breakdown [88].
Heat treatment can change the microstructure of magnesium alloys [78]. For example, it was observed [117] that moderate temperature ageing of a die cast AZ91D, in the early stages, led to a rapid precipitation of the β-phase in the aluminium-rich areas of the α-Mg matrix. The β-phase precipitation occurred mainly on grain boundaries, forming an almost continuous network along the grain boundaries. This β-phase distribution has a beneficial effect on corrosion resistance, acting as a barrier to corrosion propagation in the α-Mg matrix. However, in the later aging stages, the precipitation of rod shaped β phase further away from the grain boundaries, determined an aluminium content decreasing in the centre of the α-Mg grains; this effect made the α matrix more active, causing an increase of the alloy corrosion rate.

With increasing applications of magnesium alloys in the aerospace, aircraft and automotive fields, post processing techniques such as laser welding will become important for these alloys. Evidently, welding process parameters may influence their corrosion resistance [118]. Generally, the high welding speed and fast cooling rate of the welds, as in the case for high power laser welding, may improve the corrosion resistance of the weld zone connected with the same material because of the resultant fine grain size and generation of solid solutions of increased aluminium content [68, 118]. The corrosion behaviour of the magnesium weld zone and the effects of the welding process parameters on corrosion, stress corrosion cracking and corrosion fatigue, however, are not well known and further research is necessary [78].

2.8.7.5 Influence of environment

The corrosion resistance of materials always refers to some specific environments. Magnesium alloys are rarely stable in aqueous media compared with other materials, like steels and aluminium alloys. However, limited literature is available and has been reported on the influence of environment on the corrosion behaviour of magnesium alloys. Usually, the corrosion resistance in aqueous solution is influenced not only by solute concentration and pH, but also by the volume, movement and temperature of the liquid [105]. In general, magnesium alloys are stable in basic solutions, but in neutral and acidic media they
dissolve at high rates, as indicated in the Pourbaix diagram in Fig. 2.23 [81]. In neutral and basic solutions, the corrosion resistance is relatively high because of the formation of a partially protective Mg(OH)$_2$ layer on the alloy surface [81, 119]. Song et. al. compared the electrochemical behaviour of magnesium in Na$_2$SO$_4$ and NaCl, and suggested that the presence of chloride ions could make the surface film more active or increase the film-free area, and thereby accelerate the electrochemical reaction rate from magnesium to magnesium univalent ions (the intermediate species Mg$^+$) [120]. Thus, the corrosion rate usually increases with increasing of the chloride concentration. Sulphate ions are believed to have much less influence than the chloride ions [120]. Ambat et. al. [43], showed that the corrosion rate for ingot and die-cast AZ91D was very high in highly acidic solutions (pH 1-2) compared with neutral and highly alkaline solutions (pH 4.5-12.0), and the rate increased with chloride ion concentration at all pH levels. They suggested that the increase in corrosion rate with increasing chloride ion concentration at pH 7.25 and 12.0 may be attributed to the participation of chloride ions in the dissolution reaction.

Dissolved oxygen does not appear to influence the corrosion of magnesium and magnesium alloys in chloride solutions [81] or in sodium sulphate solution [122], whereas the corrosion rate of magnesium is dependent on HCO$_3^-$ concentration, naturally present in aerated solutions. In sodium sulphate solutions, it was observed that the presence of HCO$_3^-$ ions destabilized the MgO/Mg(OH)$_2$ layer initially formed on the magnesium surface by formation of soluble salts. Evidently, in sodium chloride solutions, the aggressiveness of chlorides masks the role of HCO$_3^-$ [122].

Neutral or alkaline fluorides from insoluble MgF$_2$ and are not appreciable corrosive. Magnesium fluoride is very insoluble in hydrofluoric acid and, as a consequence, magnesium does not dissolve in this acid. However, in dilute aqueous hydrofluoric acid, magnesium is not stable and results in pitting. Magnesium is readily soluble in dilute sulphuric acid and no protective film is formed in this environment, with the attack being rapid [81].
A clean unprotected magnesium alloy surface exposed to indoor or outdoor atmospheres free from salt spray develops a gray film that protects the metal from corrosion [81]. Corrosion of magnesium alloys increases with increase of relative humidity (RH). At low humidity levels, the rate of the corrosion attack is negligible. At 30% humidity, only minor corrosion may occur. At 80% humidity, the surface may exhibit considerable corrosion. In marine atmospheres heavily loaded with salt spray, magnesium alloys require protection for prolonged survival [123].

The presence of NaCl and/or CO₂ in the atmosphere affects the mechanism of corrosion of magnesium alloys in humid environments [126]. It was reported [124] that the sodium chloride-induced atmospheric corrosion of magnesium alloys is inhibited by ambient concentrations of CO₂. The inhibitive effect of CO₂ was partly attributed to the formation of a slightly protective carbonate-containing film.

The rate of corrosion is low in dry air, dry gases and many organic solvents. Further, the rate of corrosion is low in aqueous solutions where a stable corrosion product film is formed, [115] e.g.

1. pH > 10.5 producing a film of Mg(OH)₂ or stagnant pure water.
2. Fluoride-containing solutions forming an insoluble MgF₂ film.
3. In concentrated sulphuric acid forming MgSO₄ film.
4. Oxidising conditions free from film-breakdown agents including chlorides.
5. Boiling solution of chromic acid forming a stable oxide/hydroxide film.

A high rate of corrosion is observed under conditions leading to the surface film-breakdown e.g. chloride solutions, etc.
Fig. 2.1 Microstructure of magnesium [current research].

Fig. 2.2 Principal planes (I, II) and directions (III) in the magnesium hcp unit cell. [Polmear 2006]

Fig. 2.3 A single hcp lattice with (A) Miller indices notation for the coordinate system, and examples of (B) basal slip, (C) prismatic slip, and (D) pyramidal slip [5]
Fig. 2.4 Section of binary phase diagram for Mg-Al binary alloy [7].

Fig. 2.5 The Mg-rich portion of Mg–Al phase diagram with marked chemistries and preheating temperatures of alloys investigated.
**Fig. 2.6** Effect of Al and Zn contents (wt.%) on die castability of Mg–Al–Zn alloys [19].

**Fig. 2.7** The effect of aluminium content, zinc content and cooling rate on eutectic morphology in permanent mould cast hypoeutectic Mg-Al alloys [7].

**Fig. 2.8** Grain size vs. manganese addition for high purity Mg–3%Al, Mg–6%Al & Mg–9%Al alloys [12].
Fig. 2.9 Microstructures of Mg–Al alloys as-cast and after solution heat-treatment [11].
Fig. 2.10 Metallographic photos of Mg–Zn alloys as-cast and after heat-treatment [11].
Fig. 2.11 Micrographs of magnesium-aluminum alloys with increasing aluminum content. The transition from a globular dendritic structure to a fully developed dendritic structure with increasing aluminium content is readily noticeable [7].

Fig. 2.12 Possible morphologies of Mg-Al Eutectic [17].
Fig. 2.13 Schematic diagram for solidification process in terms of microstructure of AZ91 magnesium alloy [Fan et. al. 2009, Ohno et. al. 2006, Dahle et. al. 2001].

Fig. 2.14 Schematic diagram for the conventional eutectic (I) and the non-conventional eutectic (II) formation in the AZ91 magnesium alloy.
Fig. 2.15 Schematic diagram of the TRC machine used for strip casting of Mg alloys.
Fig. 2.16 A schematic diagram of the ‘Melt Conditioned Twin-roll casting’ (MC-TRC) as a novel process used for production of high quality Mg alloys strips, [BCAST, Brunel University].

Fig. 2.17 Schematic diagram of the ‘MCAST’ machine used in MC-TRC process [BCAST, Brunel University]
Fig. 2.18 Schematic diagram of FSW process

Fig. 2.19 Schematic cross-section of a typical FSW weld showing four distinct zones: (A) base metal, (B) heat-affected, (C) thermomechanically affected and (D) stirred (nugget) zone.
Fig. 2.20 (a) Metal flow patterns and (b) metallurgical processing zones developed during friction stir welding (after Arbegast [210]).
Fig. 2.21 Characteristic defect types observed at variable FSW parameters in friction stir welds [252].
Fig. 2.22 Potential-pH diagram for the Mg-H$_2$O system at 25°C [88].
Fig. 2.23 (a) Potential-pH diagram for the Mg-Al alloy system at 25°C
(b) pH range showing corrosion and passivation zones for Mg-Al alloys[253].
Fig. 2.24 The negative difference effect (NDE [67].
Fig. 2.25 a) External galvanic corrosion. b) Internal galvanic corrosion [67].
Fig. 2.26 Schematic presentation of the overall corrosion where the $\beta$-phase acts as a corrosion barrier; (A) Initial surface, (B) Final surface [67].
Fig. 2.27 Schematic diagram presenting the undermining of the $\beta$-phase, eventually after the preferential corrosion occurring in the primary $\alpha$ and eutectic $\alpha$–phase [67].
Fig. 2.28 Corrosion rate for binary alloys exposed for 16 weeks to alternate immersion in 3% NaCl (30 s in solution; 2 min in air) [92].

Fig. 2.29 Generalized curve showing the influence of element X on the corrosion rate of magnesium: X = Fe, Ni, Cu [67].
CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 General Introduction

Mg-Al alloys mainly constituting AZ31, AZ61 and AZ91 magnesium alloys produced by twin roll casting (TRC) and melt conditioned twin roll casting (MCTRC) were supplied by BCAST, Brunel University. The optimum casting parameters for both the cast processes, carried out at BCAST are as follows:

<table>
<thead>
<tr>
<th>Casting Process</th>
<th>Roll speed (mm/s)</th>
<th>Roll gap (mm)</th>
<th>Roll setback (mm)</th>
<th>Pouring temp. (°C)</th>
<th>Shearing temp. (°C)</th>
<th>Shearing speed (rpm)</th>
<th>Shearing time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRC</td>
<td>22.5</td>
<td>3</td>
<td>38-43</td>
<td>615</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCTRC</td>
<td>22.5</td>
<td>3</td>
<td>43</td>
<td>-</td>
<td>615</td>
<td>600</td>
<td>60</td>
</tr>
</tbody>
</table>

Adequate down stream processing was carried out on AZ31 magnesium alloy specimens, i.e. homogenization at 370°C up to 6 hrs, followed by hot rolling at 400°C, at a fixed rolling speed of 190 mm/s and finally annealed at 345°C for 2 hrs [127].
Friction stir welding of AZ91 and AM60 magnesium alloys was carried out at The Welding Institute (TWI), UK. Friction stir butt welding was performed at a constant tool rotation speed of 300 rpm and variable traversing speeds of 200, 250 and 300 mm/min for AM60 magnesium alloys and 250, 300 and 350 mm/min for AZ91 magnesium alloys.

### 3.2 Specimen preparation

All specimens were cut to dimensions of 10x10 mm from the magnesium alloy strip. The specimens were taken from the near surface along the rolling direction (RD) as shown in Fig. 3.1 (A) and from the cross-section along the transverse direction (TD) as shown in Fig. 3.1 (B), for surface and transverse section microstructure characterization respectively. For texture characterization, the specimens were cut from the middle of the strip along the rolling direction and examination was undertaken on the longitudinal plane or ND-RD plane as shown in Fig. 3.1 (C).

After sectioning, the specimens were mounted in a cold cure epoxy resin, Araldite, and prepared for metallographic examinations by successive mechanical grinding on silicon carbide abrasive papers, from 240 to 4000 grades. Final polishing was achieved using 3 µm and 1 µm diamond pastes, followed by one-quarter micron polishing, using non-aqueous lubricant, PM Mecaprex, to avoid oxidation of the specimen surface. The specimens were then subjected to ultrasonic cleaning in ethanol, immersed in a water bath for 30 minutes.

In order to reveal the microstructures and intermetallics on the surface and the transverse sections, the tested specimens were subjected to chemical micro-etching, according to the E-407 (99) ASTM standards, using the following etchants:

- 2% Nital solution – to reveal the general features in the microstructure and
- Acetic-picral solution {5 ml acetic acid +10 ml water + 6 g picric acid +100 ml ethanol (95%)} to reveal the second phases and the intermetallics in the microstructure.

For texture measurements, the specimen surfaces were electropolished in a solution of 15% nitric acid in ethanol at -30°C, 12V for 15 seconds.
3.3 Optical microscopy

Microstructure characterization was carried out using the following microscopes:

- Zeiss light microscope: for plane polarized light microscopy (*Software Axio Vision*)
- Leica DC Viewer microscope: for normal light microscopy (*Software Image J*)

Both microscopes were connected to a personal computer for image analysis. The grain size measurement values reported in this study are recorded from at least 5 different locations along the strip cast magnesium alloys. Initial imaging was performed at low magnification (5x) that was increased gradually to high magnification (100x). The optical micrographs were further scaled with the Image J software. Optical micrographs for complete transverse sections in the case of friction stir welded specimens were integrated into a single shot image and saved as tiff images.

3.4 Scanning Electron Microscopy with EDX microanalysis (SEM)

3.4.1 Introduction

SEM enables material scientists to probe into the microstructure, including second phases, surface morphology and micro-constituent analysis at selected locations and features. A scanning electron microscope (SEM) uses beam of electrons generated either from a tungsten (W) filament, lanthanum hexaboride (LaB₆) or a Schottky emitter, which makes it possible to achieve a much higher magnification than the optical microscope. For high magnification SEM study, a field emission electron gun is preferred.

The fundamental principle in SEM is based on a narrow beam of electrons, generated from a cathode, which is accelerated and further passed through a series of condenser lenses before being focused on the specimen surface. The condenser lenses produce a beam of electrons with a diameter of approximately 3 to 10 nm on the specimen surface. On striking the specimen surface, the interaction between the electrons and the specimen generates a number of particles and types of electromagnetic (EM) radiation. These are emitted from
the surface of the specimen and include backscattered electrons, Auger electrons, secondary electrons, X-rays and fluorescent light. These electrons are collected in a specific quantum by a plate and are transmitted to the amplifier. The amplifier transfers the output to a cathode ray tube (CRT). The intensity of the spot produced by the CRT is directly proportional to the amount of current reaching the plate. A schematic representation of a typical SEM is shown in Fig. 1.34. The backscattered and secondary electrons are used to create the SEM micrographic image. Further, the primary electrons may eject an electron from one of the inner shells of an atom in the specimen. An electron from one of the higher shells of the atom will subsequently fill the vacancy that is thus caused, emitting energy in the process. The atom can emit this energy in one of two ways, either by emitting an X-ray photon, or by emitting an “Auger” electron. The X-ray emitted has an energy that is unique for the type of atom from which it was emitted. A small portion of the X-ray signal generated from the sample can be made to impinge onto an analyzing crystal, which determines the energy of the X-ray, and thus the identity of the atom from which it was emitted.

The scanning electron microscopes, equipped with energy dispersive X-ray (EDX) analysis to carry out elemental probing were operated at an accelerating voltage of 20 kV.

- Philips XL30-FEGSEM, with Quantax software for EDX micro-analysis.
- ZEISS EVO-50 SEM, with INCA software for EDX micro-analysis.

### 3.4.2 High resolution scanning electron microscopy

High resolution scanning electron microscopic imaging enables revelation of the surface information at low voltage as illustrated in Fig. 3. 4. Low voltage scanning reduces the penetration impact of the electron beam into the sample surface, thereby revealing the near surface details and reducing the signal from the matrix.

Microscopic analysis was performed using ULTRA55 HRSEM equipped with 4 detectors including:
1. In Lens SE (SE1) detector revealing only voltage contrast details.
2. Lower SE (SE2) detector revealing topographic contrast details.
3. In Lens BSE (ESB) detector revealing phase contrast details and
4. Lower BSE (ASB) detector revealing crystallographic contrast details.

HRSEM analysis proved to be beneficial in aggregating the microstructure details covering large specimen surfaces as well as micro details including precipitation, intermetallics, their morphology and composition to precise and acceptable standards.

### 3.4.3 Electron backscattered diffraction (EBSD)

The specimens prepared were analyzed with a CamScan Maxim SEM operating at 20 kV and equipped with an Oxford Instruments HKL EBSD system. EBSD data, considered for texture determination, were generated, using Oxford Instruments Channel 5 software.

As severe deformation can cause orientation uncertainty and orientation noise, possibly leading to blurring of the grain boundaries, misorientations below 1° were not considered. Boundaries with misorientations (2-15°) were defined as low angle grain boundaries (LAGB), and those of misorientation >15° as high angle grain boundaries (HAGB). EBSD maps presented in the thesis represent the grains, coloured according to the standard colour code and presented as the inverse pole figure in the rolling direction (RD).

### 3.5 Transmission electron microscopy (TEM)

#### 3.5.1 Introduction

TEM operates slightly different to the SEM. Here, the electron beam is transmitted through the specimen surface while in case of SEM it is incident and then scattered or reflected in backward direction and secondary electrons are collected. For the electron beam to be
transmitted through the specimen, relatively high beam energies are used, in the range 40-200 keV [14], while for SEM the beam energies range from 1-50 keV.

The operation phenomenon is as follows:
Initially the electron beam passes through a set of condenser lenses which lead the beam through the condenser aperture onto the specimen from which it is transmitted. The transmitted beam moves through the objective lens and the selected area aperture as shown in the Fig. 1.37, to a series of intermediate lenses. Subsequently, it passes through the projector lens, which magnifies the image and projects the image on the main screen. The images or photographs can be taken automatically, due to the mechanism which moves the fluorescent screen out of the way to expose a negative.

TEM investigation was carried out using Jeol FX 200 electron microscope operating at 120 kV fitted with EDX for the compositional microanalysis. The micrographs were taken on a film from which the negatives were developed and scanned to obtain the images.

**3.5.2 High resolution TEM**

In order to obtain substantial information regarding the phases and intermetallics present in the microstructure, high resolution TEM investigation was carried out using F30 G² 300 kV Tecnai FEGTEM which combines imaging, diffraction, at high spatial resolution and detection efficiency. The high brightness and high coherency gun allows large electron probe currents to be focussed onto nanometre sized areas of the specimen. High resolution bright and dark field imaging equipped with EDX micro-diffraction facility and high angle annular dark field (HAADF) imaging with magnifications up to >1 million times enables revelation of the lattice parameters of nano sized precipitates and micro-diffraction with digital micrographs assisting in determining the precise microstructural analysis.
3.6 Precision Ion beam Polishing (PIPS)

Specimen preparation for TEM poses serious challenges such as magnesium alloys tend to oxidize readily on fresh exposure to the atmosphere. Conventional routes to making TEM specimens, namely, ultramicrotomed slices, twin-jet electropolished discs, focussed ion beam milled sections, etc., fail to produce a successful specimen. Problems including induction of mechanical stresses, oxidation, artefacts like destruction of morphology due to high current densities in FIB, scratches produced during sectioning, etc., to name a few, make it a challenging task.

PIPS™ is a user-friendly, precision ion polisher designed to produce high quality TEM specimens with minimal effort. Precision ion polishing is achieved with two miniature Penning ion guns (PIG’s) aimed at glancing angles of incidence to the specimen in an argon atmosphere. The specimen is in the form of a 3 mm disc, mounted on a GATAN specimen holder, where the specimen is clamped, so as to firmly locate the specimen during rotation. The specimen disc is initially mechanically grinded to less than 100 µm thickness. The specimen is mounted in the PIPS chamber, which is air locked and the specimen is thinned in a vacuum atmosphere to avoid contamination.

The sputtering time and quality also depend on the alloy to be polished. The sputtering is preferably undertaken at low angles to avoid radiation damage and beam heating while producing specimens of exceptionally large, clean, electron transparent areas. Ideally, the thinned area should be less than 10 nm thick to reveal features in the microstructure, especially for the high resolution imaging. A schematic representation of a specimen is as shown in Fig. 3.6.

Specimen preparation times can be reduced by dimpling, a procedure done prior to mounting the specimen for sputtering in the PIPS chamber. In dimpling, the 3 mm disc is finely polished to produce a crater at the centre of the disc, so as to reduce the thickness at the centre and to reduce the time required for sputtering. Specimen preparation times for dimpled specimens can vary from 0.5 to 2 hours depending on the initial specimen
Experimental Procedure

thickness. Specimens are mounted on the GATAN single side specimen post in order to minimize specimen contamination by secondary sputtering. The specimen post also provides an excellent heat sink which stops specimens from becoming overheated by the ion beam. The PIPS is equipped with a low powered optical microscope situated directly above the specimen. The microscope can be used to inspect the specimen in its working position or in the airlock at any time during the thinning process. Transmission and reflection illuminators are provided to facilitate specimen viewing.

Ion gun alignment is particularly critical when thinning specimens at very low angles. In the PIPSTM, the ion guns are mounted in universal joints and can be tilted very precisely using micrometre drives. The beam is centered on the specimen with the aid of a fluorescent viewing screen, which makes the path of the ion beam clearly visible. The screen is placed in the specimen plane by loading it through the WhisperlokTM similar to the normal TEM specimen. The ion guns are then tilted until the beams intersect precisely at the center of the screen. The screen may also be used to set the optimum gas flow needed to obtain the minimum beam diameter.

The parameters for precision ion polishing are as follows:

- **Milling angle**: +10° to -10° (adjustable)
- **Ion beam energy**: 100 eV to 6 keV
- **Ion current density**: 10 mA/cm²
- **Rotation**: 1 to 6 rpm
- **Gas**: Argon at 25 psi

### 3.7 Scanning Kelvin probe force microscopy (SKPFM)

The scanning Kelvin probe force microscopy (SKPFM) technique, along with topographic atomic force microscopy (AFM), has been used to understand the microstructure as well as the corrosion behaviour of magnesium alloys. SKPFM, being a non-destructive technique is used to measure the relative surface potential, also referred to as the Volta potential, which is linearly proportional to the open circuit potential (OCP), measured under a thin
Experime

tal Procedure

electrolyte [72, 73]. Both the techniques provide unique information on the local nobility of different intermetallic particles and phases on a submicron scale. The scanning Kelvin probe (SKP) technique measures the surface distribution of the Volta potential in a non-destructive manner. The scanning Kelvin probe has been used in corrosion studies since 1980s, when Stratmann et. al., demonstrated that the corrosion potential depends on the Volta potential under a thin electrolyte layer in a linear manner [18-20].

The scanning Kelvin probe force microscopy (SKPFM) is a development of the AFM. SKPFM has been used since the late 1980s, mainly by physicists to investigate the behaviour of thin films [26, 27]. Frankel et. al., were the first to use SKPFM in the corrosion field to study intermetallic particles in aluminium alloys [21, 28]. The resolution of the SKPFM technique is much higher than that of the SKP technique, better than 0.1 μm [21]. The high resolution is a consequence of the small separation of the scanning tip and the specimen, approximately 100 nm. The scanning Kelvin probe, in contrast, has a tip-sample separation of 50 μm and a resolution of approximately 100 μm.

The detection principle of SKPFM is slightly different from that of the SKP. The small separation of the tip and the specimen in SKPFM leads to its increased resolution. This resolution means that the Volta potential signal is collected from a far smaller area than that of the SKP technique, and the value of the Volta potential determined will contain contributions from fewer different species. The Volta potential does not depend on the distance between the tip and the sample [23], but this distance does affect the experimental results at the very high levels of resolution of SKPFM. This is because van der Waal’s forces become significant at distances closer than 100 nm, in addition to the electrostatic forces (Fig. 4). Van der Waals forces lead to a rapid increase in surface potential at distances closer than approximately 100 nm. The feedback signal between the tip and the control circuits becomes out of phase with the scanning control when scanning rough surfaces and the tip comes too close to the sample. This gives peaks in both the topographic signal and the Volta potential signal. An electrically conductive cantilever is given an electrostatic bias relative to the specimen in SKPFM. This bias results in an electrostatic
force between the cantilever and the surface of the specimen. The voltage between the tip and the specimen as a function of time (V(t)) is given by:

\[ V(t) = V_{dc} - V_s + V_{ac} \sin(\omega t) \]  

(6)

where \( V_{dc} \) is the DC offset potential, \( V_s \) is the surface potential (the Volta potential) of the sample, and \( V_{ac} \) is the amplitude of the applied AC voltage with frequency \( \omega \).

The electrostatic force between the tip and the sample can then be expressed as:

\[ F = q*E = q*V/d = C*V^2/d \]  

(7)

where \( q \) is the charge, \( E \) the electric field, \( d \) the tip to sample distance, and \( C \) is capacitance.

Combining Equations (6) and (7) gives:

\[ F(t) = (C/d)*V^2(t) \]  

(8)

\[ (C/d)* [(V_{dc} - V_s)^2 + \frac{1}{2}V_{ac}^2] \]  

(9a)

\[ + 2*(C/d)*(V_{dc} - V_s)*V_{ac}\sin(\omega t) \]  

(9b)

\[ - \frac{1}{2}(C/d)*V_{ac}^2\cos(2\omega t) \]  

(9c)

The total deflection signal, representing the force between the tip and the sample consists of three independent parts, namely, a DC part, an AC part with a frequency of \( \omega \), and an AC part with a frequency of \( 2\omega \). \( V_{dc} \) and \( V_{ac} \) in Eq. 9b are known, but it is not possible to separate the contributions from the capacitance and the surface potential.

However, the \( 2\omega \) signal can be obtained from Eq. 9c and, thus, the contribution from the \( V_s \) signal (surface potential) can be obtained. The surface charge causes the deflection of the cantilever. This deflection is then recorded in the normal AFM mode.

Prior to the SKPFM measurements, the alloy specimens were polished to a 0.1 \( \mu \)m diamond finish and cleaned in an ultrasonic bath using ethanol. The surface potential measurements were conducted using a Nanoscope Dimension\textsuperscript{TM} 3100 microscope (Digital Instruments), working in tapping and surface potential modes, using a silicon tip with a platinum coating of 20 nm thickness as the reference electrode. The instrument measures the surface topography and the relative Volta potential distribution simultaneously.
3.8 Corrosion performance assessment

Immersion testing experiments were performed by exposing the specimens to 3.5% NaCl solution for 24 hr to determine the corrosion fronts and the specimens were exposed to 0.005M NaCl solution for 4 hr to determine the initiation of corrosion process. As 3.5% NaCl solution is highly aggressive and readily attacks the specimen surface, it becomes rather difficult to examine the initiation process in corrosion; therefore use of 0.005M solution as a corrosive media is preferred. The experiments were carried out at room temperature and in an aerated atmosphere. Corrosion products were mechanically removed by means of sample immersion in acetone and ultrasonic cleaning for a few minutes to achieve constant weight. The samples were further embedded into an epoxy resin and transversally sectioned. The exposed surface and the transverse sections were then subjected to microscopic analysis.

3.9 Electrochemical measurements

Electrochemical measurements were performed using an ACM instruments Gill AC computer-controlled potentiostat and a conventional three-electrode cell, employing a platinum counter electrode and a saturated calomel reference electrode (SCE). The working electrode was the test material and the solution was naturally aerated 3.5% NaCl solution at room temperature (22°C). Variations of the open circuit potential (OCP) were recorded with immersion time and linear polarization curves were obtained for selected times, at a scan rate of 0.3 mV/s from -150 mV to +250 mV with respect to the OCP. Measurements were performed twice to ensure the reproducibility of the results.

Specimens were mechanically grinded to 4000 grit size and ultrasonically cleaned in ethanol for 30 minutes in a water bath. The specimens were coated with lacquer 45 to cover the unwanted areas before revealing the desired area of 1 cm² for electrochemical measurements.
Experimential Procedure

Fig. 3.1 Schematic representation of sectioning the specimens for microstructure and texture characterization; A - Surface examination, B - Transverse section, C – Texture study (EBSD)

Fig. 3.2 Schematic representation of a typical SEM (11)
Fig. 3.3 Signal detection in SEM.

Fig. 3.4 Schematic representation of electron beam interactions in HRSEM.
Fig.3.5 Schematic representation of a typical TEM (15)
Fig. 3.6 Schematic illustration of the PIPS™ work chamber, showing the Penning ion gun, the specimen exchange mechanism, the Faraday cup, the airlock and the specimen post.

Fig. 3.7 (A) The cantilever in the AFM
(B) Atomic forces between the scanning tip of the AFM and the specimen surface.
CHAPTER 4

MICROSTRUCTURES OF AZ SERIES Mg-Al ALLOYS

4.1 Introduction

According to the Mg-Al equilibrium phase diagram, shown in Fig. 2.4 in the Literature Review, the maximum solid solubility of aluminium at the eutectic temperature (437°C) is about 13 wt% Al. A eutectic between α-Mg and the intermetallic β-Mg_{17}Al_{12} is present at about 33 wt% Al [7]. The microstructure of magnesium alloys displays formation of a non-equilibrium, metastable, eutectic, during the solidification in the as-cast microstructure in Mg-Al alloys with aluminium contents as low as 2 wt%. However, the volume fraction of eutectic decreases as the aluminium content is decreased, and the eutectic morphology gradually transforms to a divorced eutectic [38, 39]. Heat treatment can therefore result in a complete dissolution of the β-Mg_{17}Al_{12} intermetallic phase.

As a consequence of the previous factors, the as-cast microstructure produced from conventional casting methods reveals a coarse eutectic microstructure with a random distribution of the Al-Mn intermetallics, the β-Mg_{17}Al_{12} phase on the grain boundaries and localized micro-porosity, as shown in Fig.1.4. Further developments in the casting methods, including die-casting, twin roll casting, semi-solid metal processing, etc., have reported considerable improvement in the refinement of the microstructures of magnesium alloys. The melt-conditioned twin roll casting (MCTRC) process developed at BCAST, Brunel University, involves melt-conditioning by advanced shear technology (MCAST)
prior to twin roll casting. Fan and co-workers at BCAST have reported considerable improvement in the refinement of the microstructures of magnesium alloys, by employing the MCTRC process. The solidification of the magnesium alloys results in a uniform compositional distribution owing to the intensive shearing, giving rise to a highly refined as-cast microstructure. This chapter focuses on the microstructure of Mg-Al alloys produced by conventional twin roll cast (TRC) and melt conditioned twin roll cast (MCTRC) technologies. Metallographic investigations were performed with the main objective of understanding the influence of the MCAST process on the microstructure of the MCTRC magnesium alloys. The MCAST process also reveals that the defects produced due to the TRC process, including hot tearing, segregation, etc. can be successfully eliminated.

4.2 Microstructure investigation of TRC and MCTRC magnesium alloys

Magnesium alloys investigated in the current research include AZ31, AZ61 and AZ91 alloys, where the individual alloy compositions differ in their aluminium contents which range from 3% to 9%, produced by TRC and MCTRC processes at BCAST, Brunel University. The nominal compositions of the alloys, according to Magnesium Elektron are as displayed in Table 4.1.

4.2.1 Microstructure characterization of AZ31 magnesium alloys

Plane polarized light optical microscopy was employed to reveal the microstructure across the transverse sections of AZ31 magnesium alloys. Figure 4.1 (A) shows a representative region from the transverse section of the MCTRC processed alloy, constituting a homogeneous grain structure, with a uniform grain size, averaging 72 µm. However, the TRC processed alloy displayed a microstructure, as shown in Fig. 4.1 (B) that could be separated into three distinctive zones, namely a chill zone, with fine grain structures (I & V) near to the surfaces and the columnar zone revealing a coarse columnar grains with an
average grain size of 520 µm (II & IV). Centre-line segregation, indicated by the arrow and localized hot tears in the chill zones, indicated by arrows near to the surfaces, are some of the commonly observed defects in the TRC alloy, as shown in Fig. 4.1 (B). Shear bands and twinning, encircled within the coarse columnar α-Mg grains, occurring due to extensive rolling stresses exerted on the sheets during casting, were some of the commonly observed mechanical deformation features in the microstructure.

The effect of intensive shearing in the MCAST process prior to solidification is clearly evident, resulting in uniform microstructures, across the transverse section of MCTRC magnesium alloys. The AZ31 TRC magnesium alloy displayed grain sizes from 350 µm in the chill zone (near the surface region), 910 µm in the columnar regions and 500 µm in the equiaxed regions, while the AZ31 MCTRC magnesium alloys displayed a uniform grain size of 70-90 µm, across the sheet thickness.

The specimen preparation for scanning electron microscopy included mechanical grinding to a grit size of 4000 µm followed by diamond polishing to ¼ µm. The specimen surface was subjected to ultrasonic cleaning in ethanol for 30 minutes and finally electropolished to reveal the eutectic microstructure. High magnification microscopic examination of the AZ31 magnesium alloys was performed using an ULTRA55 scanning electron microscope, operated at low voltage ~1.5 kV, to reveal the compositional contrast of the microconstituents.

The surface microstructure of the AZ31 TRC magnesium alloy was characterized by a coarse bimodal α-Mg grains, α-eutectic and fully divorced β-Mg_{17}(Al,Zn)_{12} phase, as shown in the scanning electron micrograph in Fig. 4.2 (A). Evidence of localized segregation of the β-phase, shown by the arrow, was observed on the grain boundary regions of the alloy surface. The in-lens secondary electron image in Fig. 4.2 (B) reveals microporosity in the eutectic regions, shown by the arrows. Continuous β-precipitation in the α-Mg grains, along with solute segregation, is evident in the scanning electron micrograph of Fig. 4.2 (C). Large volumes of randomly distributed, submicron size Al_{8}Mn_{5} intermetallics particles, with high contrast in the segregated regions, are also evident in the
image. High resolution scanning electron microscopy was employed to determine the eutectic structure, revealing the morphology of the β-precipitates to be plate-like as shown in Fig. 4.2 (D). The EDX analysis showed zinc enrichment (~2.7%) in the α-eutectic, compared with the α-Mg grains (0.67%).

Figure 4.3 (A) shows the surface microstructure of the AZ31 MCTRC alloy, which comprised equiaxed α-Mg grains with the grain boundaries decorated by the β-Mg$_{17}$(Al,Zn)$_{12}$ phase. The α-Mg grains showed uniform grain sizes and reduced microporosity compared with that of the AZ31 TRC magnesium alloy. The AZ31 MCTRC magnesium alloy exhibited a uniform network of the α-eutectic, evident in the in lens secondary electron micrograph of Fig. 4.3 (B), owing to the intensive stirring in the MCAST process, facilitating uniform compositional distribution. β-precipitation is observed at localized sites in the α-eutectic regions, adjacent to the β-phase, indicated by the arrow in Fig. 4.3 (C). The high resolution backscattered image in Fig. 4.3 (D) displays the eutectic microstructure revealing the lozenge-shaped β-precipitates, indicated by arrows.

Transmission electron microscopy was performed on the AZ31 TRC specimens to probe the eutectic structure, Al$_8$Mn$_5$ intermetallic morphology and spatial distribution within the magnesium matrix. Figure 4.4 (A) displays a bright field transmission electron micrograph revealing the fully divorced morphology of the β-phase located on the grain boundary. The rosette/flower shaped morphology of the Al$_8$Mn$_5$ intermetallic in the α-Mg grain is evident in Fig. 4.4 (B). The bright field transmission electron micrograph in the Fig. 4.4 (C) shows the Al$_8$Mn$_5$ intermetallic located on the β-Mg$_{17}$Al$_{12}$ phase. The Al$_8$Mn$_5$ intermetallics located on the grain boundary, indicated by the arrow, are shown in the HAADF transmission electron micrograph of Fig. 4.4 (D). These Al$_8$Mn$_5$ intermetallic particles have an average size of 200-400 nm and are randomly distributed across the surface microstructure, as evident from the bright field transmission electron micrographs shown in Fig. 4.4.
TEM-EDX examination conducted on the β-phase in the AZ31 TRC magnesium alloy revealed the presence of impurities including approximately 1.21% Si, and 1.1% Fe. High resolution transmission electron microscopy was performed to reveal the orientation relationship between the interfaces of the microconstituent phases in the microstructure. Figure 4.5 presents the lattice images and the fast Fourier transform (FFT) patterns, recorded by tilting the specimen disc, so as to align one of the phases to the zone axis, e.g. aligning the incident beam parallel to [100] orientation. The α-Mg/β interface and the corresponding FFT patterns are shown in Fig. 4.5 (A), while the Al-Mn/α-Mg interface and the corresponding FFT patterns are displayed in Fig. 4.5 (B). The measured d-spacings of the crystal planes Mg (0002) and Mg (11-20) were 0.259 nm and 0.162 nm, respectively. These values are comparable with the corresponding d-spacing of 0.260 nm and 0.160 nm calculated according to the reported lattice parameters, a = 0.320 nm and c = 0.521 nm, for the HCP structured pure Mg at 25°C [36]. FFT patterns taken from the area including both the Al₈Mn₅ particle and the α-Mg grain are displayed in Fig. 4.5 (B) where, in addition to the diffraction spots from the α-Mg matrix at [100] direction, the extra spots arise from the intermetallic particle. When the α-Mg matrix is in the [100] zone axis orientation, the Al₈Mn₅ intermetallic does not coincide with any low index orientation. This indicates that there is no well-defined orientation relationship (OR) between these two crystals along the [100] zone axis.

Bright field transmission electron micrographs from the AZ31 MCTRC magnesium alloy, revealing continuous β-precipitation, are displayed in Fig. 4.6 (A). These randomly distributed β-precipitates display a lozenge-shaped morphology. The TEM-EDX results show that the eutectic region is associated with a relatively high zinc content compared with the α-Mg matrix, as presented in Table 4.2. Dahle et. al. [32], reported that these precipitation reactions occur mostly in the α-Mg matrix near the β-phase, since these regions have higher aluminium contents (~10-13 wt% Al) than the centres of the dendrites, where the aluminium contents may be as low as 2 wt% Al. Figure 4.6 (B) displays the HAADF transmission electron micrograph of the rosette/flower shaped Al₈Mn₅ intermetallic, similar to that found in the TRC processed magnesium alloy.
4.2.2 Microstructure characterization of AZ61 magnesium alloys

The transverse sections of AZ61 TRC alloy (Fig. 4.7 (B) and the AZ61 MCTRC alloy (Fig. 4.7 (A), were examined by optical microscopy. The transverse section of the AZ61 MCTRC magnesium alloy displayed a uniform dendritic microstructure, while the AZ61 TRC magnesium alloy showed distinctive zones, namely a chill zone, closer to the rolls, revealing a finer grain structure due to the under-cooled liquid closer to the water cooled rolls, shown in (I & III), and a central zone (II) displaying a coarser grain structure. Hence a non-uniform microstructure with a large volume fraction of the primary solidified grains observed in the central zone along with the chill zone with the finer grain structure [247]. Localized segregation of the β-phase in the interdendritic regions along with the centre-line segregation at the centre, indicated by arrows, were also evident in the AZ61 TRC magnesium alloy. The AZ61 MCTRC magnesium alloy showed a highly refined and uniform microstructure, with a finer grain size and reduced defects compared with the TRC processed alloy.

The surface microstructures of the AZ61 TRC magnesium alloy and the MCTRC processed alloys were examined by scanning electron microscopy together with EDX analysis, to reveal the phase compositions and intermetallics. Figure 4.8 (A) shows the surface microstructure of the AZ61 TRC magnesium alloy that is characterized by a bimodal microstructure with coarse primary solidified grains, the fine secondary solidified grains, surrounding α-eutectic and the β-phase. The random and non-uniform distribution of the β-phase in the microstructure (shown by arrows) is clearly evident from the in-lens secondary electron image in Fig. 4.8 (B). The eutectic region, shown in the backscattered scanning electron image in Fig. 4.8 (C), reveals aluminium and zinc segregation in the β-phase, indicated by the arrow. The high resolution back scattered scanning electron micrograph in Fig. 4.8 (D) displays the partially divorced eutectic morphology, with α-islands in the β-phase.

Figure 4.9 (A) presents the surface microstructure of AZ61 MCTRC magnesium alloy, showing a highly refined microstructure with a network structure of the β-phase. The
volume fraction of the β-phase is uniformly distributed compared with the AZ61 TRC magnesium alloy, which can be attributed to the intensive shearing of the liquid melt prior to the casting stage. The in-lens secondary electron image provides a closer scrutiny of the eutectic structure, revealing precipitation of the β-phase on the interdendritic boundaries, as evident from Fig. 4.9 (B). The α-eutectic regions show rosette-shaped Al₈Mn₅ intermetallics located on the β-phase, as indicated by the arrows in Fig. 4.9 (C). Increased volumes of Al₈Mn₅ intermetallic particles, usually associated with the β-phase, suggests a possibility of Al₈Mn₅ intermetallics acting as potent sites for the nucleation of β-phase during the solidification process. The high resolution backscattered image in Fig. 4.9 (D) reveals the compositional contrast between the eutectic, darker compared with the α-Mg matrix. The scanning electron micrographs clearly indicate the effect of intensive shearing prior to solidification as there is no evidence of primary solidified grains, segregation defects, micro-porosity, etc. Secondly, the eutectic structure is rather uniformly distributed in the AZ61 MCTRC magnesium alloy compared with the TRC processed alloy.

The bright field transmission electron micrograph of Fig. 4.10 (A) reveals the discontinuous β-precipitation in the α-Mg grains close to the β-phase in the AZ61 TRC magnesium alloy. The region (shown by arrows) displays needle-shaped discontinuous β-precipitation with sizes averaging from 50 nm to 300 nm. Along with the needle-like morphology of the β-precipitates, sub-micron size globular β-precipitates, (point 1 and point 2) have been identified. The darker region at point 3 in the bright field transmission electron micrograph reveals the β-phase on the interdendritic boundaries. The HAADF transmission electron micrograph in Fig. 4.10 (B) shows a representative α-eutectic region, displaying α-Mg grain (point 1), β-precipitate (point 2), β-phase (point 3) and Al₈Mn₅ intermetallic (point 4). The HAADF transmission electron micrograph shows the phase contrast revealing the difference in the composition of the corresponding phases in the microstructure. The TEM-EDX analysis reveals that the aluminium contents increase from the core of the α-Mg grains to the β-phase on the grain boundaries, as shown in Table 4.3. This depletion of the aluminium contents across the grain interiors has been reported by Dahle et. al. [7], and as the compositional distribution in TRC magnesium alloys is non-uniform, it can be expected in AZ61 TRC magnesium alloys.
The characteristic features in the microstructure of the AZ61 MCTRC magnesium alloy shown in the bright field transmission electron micrograph in Fig. 4.11 (A), reveal the β-phase (1), rosette-shaped Al₈Mn₅ intermetallic (2) and the α-Mg matrix (3) along with the corresponding SAED patterns. The HAADF transmission electron micrograph shown in Fig. 4.11 (B) reveals the lozenge-shaped precipitates in the α-Mg matrix close to the β-phase. The TEM-EDX analysis reveals that the β-precipitates (pts. 1 and 2) show reduced aluminium contents compared with the β-phase (pt. 3), given in Table 4.4.

### 4.2.3 Microstructure characterization of AZ91 magnesium alloys

The AZ91 magnesium alloys were examined by plane polarized optical light microscopy to reveal the grain structure and grain size variations across the transverse section. Figure 4.12 (A) displays the AZ91 MCTRC magnesium alloy with a uniform grain size averaging 69 μm, distributed across the sheet thickness. The AZ91 TRC magnesium alloy reveals a random distribution of grains with variable grain sizes averaging 302 μm and centre-line segregation defect in the central equiaxed zone as shown in Fig. 4.12 (B) with arrows.

The chill zone microstructure near the rolls (I & III) shows finer grain sizes compared with that of the equiaxed zone. The grains showed a reduction in size from 420 μm in the AZ91 TRC magnesium alloy to 69 μm in the AZ91 MCTRC magnesium alloy. The significant reduction in the grain sizes in the MCTRC AZ91 magnesium alloy clearly reveals the influence of intensive shearing in the MCAST process, which reduces the size of the MgO particles, acting as potent sites for nucleation. The intensive shearing also assists in the uniform distribution of the MgO particles across the liquid melt and enhances the chances of maximum survival of these nucleation sites to promote heterogeneous nucleation and render a uniform, refined grain size across the sheet thickness [126].

Scanning electron microscopy shows a random, dendritic microstructure with evidence of segregation of β-phase on the interdendritic boundaries in AZ91 TRC magnesium alloy, indicated by the arrows, in the backscattered scanning electron micrographs of Fig. 4.13 (A). The in-lens secondary electron image reveals the random distribution of the β-phase.
forming a network structure, as shown in Fig. 4.13 (B). The β-phase exhibits a partially divorced morphology as shown in Fig. 4.13 (C), along with a high population of sub-micron size rosette/flower shaped Al₈Mn₅ intermetallics, usually located on the β-phase. The high resolution backscattered image in Fig. 4.13 (D), displays the needle-like β-precipitation (~500 nm) in length.

The surface microstructure of the AZ91 MCTRC magnesium alloy is characterized by a highly refined grain structure, with a uniform grain size, as shown in Fig. 4.14 (A). The in-lens secondary electron image reveals a uniformly distributed network of the β-phase on the interdendritic boundaries, as displayed in Fig. 4.14 (B). The β-phase displays a partially divorced morphology, i.e. islands of α-Mg evident within the β-phase, along with the rosette shaped Al₈Mn₅ intermetallics on the β-phase, indicated by arrows in Fig. 4.14 (C). The high resolution backscattered image in the Fig. 4.14 (D) reveals a heavy deposition of the β-precipitates in the eutectic regions compared to the AZ91 TRC magnesium alloy. The β-precipitation is continuous and in the form of plate-like structures rather than conventional lamellar (α+β) eutectic reported for the magnesium alloys. The morphology of the precipitation largely depends on the cooling rates associated with solidification, where lamellar precipitation occurs at slower cooling rates while, in the case of TRC and MCTRC processes, where the cooling rates are relatively high, sub-micron sized, plate-like discontinuous β-precipitation is exhibited.

The bright field transmission electron micrograph of Fig. 4.15 (A) displays the typical morphology of β-phase in the AZ91 TRC magnesium alloy. Discontinuous β-precipitation in the form of lozenge-shaped, plate-like structures, randomly distributed in the eutectic, is shown in the bright field transmission electron micrograph in Fig. 4.15 (B). The HAADF transmission electron micrograph in Fig. 4.15 (C) shows the partially divorced morphology of the β-phase with islands of the α-Mg phase in the β-phase, shown by arrows. The rosette/flower shaped morphology of the Al₈Mn₅ intermetallics, with average size of 100-500 nm, is evident in the HAADF transmission electron micrograph shown in Fig. 4.15 (D). The location of the Al₈Mn₅ intermetallics indicates that they nucleate and grow three
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donimensionally as they are partially buried into the matrix/eutectic structure, as revealed in Fig. 4.15 (C).

Similar $\text{Al}_8\text{Mn}_5$ intermetallics, having a flower-shaped morphology and located on the $\beta$-phase, have been reported by Wei et. al. [35]. The TEM-EDX analysis presented in Table 4.6, from the Al-Mn intermetallic shown in Fig. 4.15 (D) confirms to be $\text{Al}_8\text{Mn}_5$. Considering the average compositional distribution of oxygen and magnesium, on the arms of the rosette Al-Mn intermetallic, being fairly proportionate (1:1), indicates a possibility of the presence of an MgO particle, presumably the site for nucleation of $\text{Al}_8\text{Mn}_5$ intermetallics. However, it can not be confirmed solely on the basis of TEM-EDX results, and further investigation needs to be undertaken to validate the observations. The increased magnesium content in point 5 possibly shows a contribution from the $\alpha$-Mg matrix.

High resolution transmission electron microscopy was conducted on the interfaces between the constituent phases to reveal the lattice images and corresponding FFT patterns. The microstructure of the AZ91 magnesium alloy displayed a bimodal distribution of $\alpha$-Mg (hcp structure, space group $\text{P}6_3\text{mmc}$, $a = 0.32094$ and $c = 0.52105$ nm) grains together with $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase (cubic crystal structure, Space group $\text{I}^-\text{4}3\text{m}$, $a = 1.056$ nm). The bright field transmission electron micrograph shown in Fig. 4.16 presents the micro-constituent features in the AZ91 TRC magnesium alloy, showing the distribution and morphology of the $\text{Al}_8\text{Mn}_5$ intermetallics (1), $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase (2) and the $\alpha$-Mg matrix. The sizes of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ intermetallics are mostly about several micrometres while the $\text{Al}_8\text{Mn}_5$ intermetallics are of dimensions of $\sim50$-$500$ nm. Figure 4.16 (A) shows a high resolution image of the interface between the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase and the $\alpha$-Mg matrix. FFT patterns indicate that the incident beam is parallel to [111]$_\beta$. The interplanar spacings of (1-10) and (10-1) planes in the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase are calculated to be 0.7467 nm. Figure 4.16 (A) clearly reveals the typical trigonal crystal structure of $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase along [111] zone axes. The interplanar spacings of (1-10) and (10-1) planes of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase are measured to be $\sim0.75$ nm, which is consistent with the calculated result.
FFT patterns in Fig. 4.16 (B) indicate that the Mn-rich phase has a hexagonal crystal structure with lattice parameters of $a = 1.27$ nm and $c = 1.59$ nm, which are consistent with the crystal structure and lattice parameters of the $\text{Al}_8\text{Mn}_5$ phase (hexagonal crystal structure, $a = 1.273$ nm and $c = 1.588$ nm). Figure 4.16 (B) shows a high resolution image of the $\text{Al}_8\text{Mn}_5$ phase and the matrix. The incident beam is parallel to [-1101]$\text{Al}_8\text{Mn}_5$. The interplanar spacings of (1-101) and (01-1-1) planes in the $\text{Al}_8\text{Mn}_5$ phase in Fig. 4.16 (B) are about 0.9 nm, which is very close to the calculated 0.9056 nm.

From the high resolution transmission electron microscopy results, it is evident that the interfaces between the $\text{Al}_8\text{Mn}_5$ intermetallic and the dominant $\alpha$-$\text{Mg}$ and $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phases do not reveal a well defined orientation relationship, because when the $\beta$-phase was adjusted on the [1-210] zone axis, the $\text{Al}_8\text{Mn}_5$ phase was found to be off any low index zone axis orientation.

The AZ91 MCTRC magnesium alloy was examined by transmission electron microscopy to determine the microfeatures in the microstructure resulting from the intensive shearing prior to solidification. Precision ion beam polished 3 mm discs were probed to reveal the morphology of micro-constituent phases and precipitates in the magnesium matrix. Figure 4.17 (A) shows the ultra-fine sized $\beta$-phase morphology (area 1) with an average size of ~500 nm. The TEM-EDX analysis revealed a Mg/Al ratio of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase of 57.54/35.25, showing it to be slightly higher than 17/12. The excess Mg content in the spectrum may possibly arise from the $\alpha$-$\text{Mg}$ matrix, as the beam penetration in case of the HRTEM is slightly deeper.

Needle-shaped $\beta$-precipitates in the eutectic are evident in the HAADF transmission electron micrograph (point 1) in Fig. 4.17 (A); the $\beta$-precipitates are approximately 25 - 250 nm in length and show reduced aluminium contents compared with the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase. Evidence of twinning is also evident in Fig. 4.17 (B). Tension twinning with a misorientation angle of 86° in the $\alpha$-$\text{Mg}$ matrix has been reported during rolling of magnesium alloys, by Barnett et. al. [144]; these deformation features are formed as a consequence of rolling stresses and are not unusual in the AZ91 magnesium alloy.
microstructure. The bright field transmission electron micrograph of the Al\textsubscript{8}Mn\textsubscript{5} intermetallic in Fig. 4.17 (C) reveals a rosette/flower morphology as observed in TRC processed alloy. It should be emphasised that the bright field transmission electron micrographs carry inverse contrast to HAADF imaging in the TEM and BSE imaging in the SEM. In the case of TEM, the ‘dark’ areas are intermetallic phase, with the ‘light’ phase being the α-Mg matrix. TEM-EDX analysis shows the compositional variations in the eutectic, as shown in Fig. 4.18. EDS line scan analysis revealed a sharp increase in the aluminium and zinc contents in the β-precipitates and the β-Mg\textsubscript{17}Al\textsubscript{12} phase, as evident from the HAADF transmission electron micrograph shown in the Fig. 4.18. The high contrast particle reveals the Al-Mn intermetallic phase showing an increase in the aluminium and manganese contents.

4.3 Defects produced during twin roll casting

The formation of defects in Mg-Al alloys largely depends on the solidification sequence. At the same time, the casting technologies may also influence the formation of defects such as the intrinsic micro-porosities reported in the die-cast AZ91 magnesium alloys, mechanical deformation in the high pressure cast AM60 magnesium alloys, etc. These defects may occur locally or may also be continuous or segregate to form bands in the case of long thin sections. Metallographic examination performed on the TRC magnesium alloys under investigation revealed some commonly occurring defects due to the twin roll casting process, namely centre-line segregation, localized plastic deformation/shear bands and hot cracking/tearing.

4.3.1 Centre-line segregation

Centre-line segregation, as observed in Fig. 4.1 (B), 4.7 (B) and 4.12 (B), suggests a common phenomenon occurring at the centre-line, during the solidification stage in the TRC processed alloys. The segregation behaviour is associated with solute enrichment at the centre-line, due to the rejection of the solute from the solid to the surrounding liquid.
This solute is forced in front of the columnar grain growth occurring in the TRC alloys, reaching the centre-line, evident in the AZ91 TRC magnesium alloy in Fig. 4.19 (B). This movement of the solute results in equiaxed grain nucleation in the highly enriched solute because of higher constitutional supercooling, as shown in Fig. 4.19 (A).

Such a phenomenon does not occur in the case of the MCTRC alloys as the MCAST process involves intensive shearing of the liquid melt prior to solidification. The MCAST process ensures a uniform distribution of the potent sites for nucleation which results in equiaxed grain growth. Therefore, the segregation tendency of the rejected solute from the solid to the surrounding liquid is retarded as the movement of the rejected solute becomes difficult due to the lack of columnar channels which are otherwise available in case of TRC magnesium alloys.

4.3.2 Localized plastic deformation/shear bands

Focusing on maximum deformation during the hot rolling process, the TRC process aims at producing uniform and refined microstructure with reduced surface defects. As the TRC process involves excessive stresses, that are required to weld the pre-solidified structures between the rolls, the solute-rich liquid is forced to be squeezed out from the growing columnar dendritic structures. This results in severe segregation problems and other casting defects like bleeding, etc., probably, due to the heavy deformation during the TRC process. A representative region from the transverse section of AZ91 TRC magnesium alloy, as shown in Fig. 4.20, reveals shear bands formed in the columnar zone as a consequence of the twin roll casting process. In the course of the solidification process, at a critical value, the columnar grains impinge on one another, referred to as dendrite coherency solid fraction [43]. According to Dahle et. al. [32], under a compressive load, the yield strength of the equiaxed dendritic mushy zone is much lower than the columnar dendritic mushy zone area. This results in a lower local applied forces on the intergranular liquid and more ready deformation of the equiaxed grains by grain rearrangement through sliding and rolling compared with columnar grains which are deformed plastically since the
rearrangement of columnar grains is constrained due to their morphology and the uneven enriched solute in intergranular spaces [34].

4.3.3 Hot cracking/tear

Figure 4.21 displays a representative region from the AZ61 TRC magnesium alloy showing macrosegregation of β-phase on the surface microstructure. Higher contrast regions constitute localized segregation of Al and Zn, as evident from the SEM-EDX results, leading to hot cracking. When the grains begin to impinge, touching one another while still surrounded by a continuous liquid film, hot tears or hot cracks in the intergranular macrosegregation can be formed, i.e. at the dendrite coherency point [44]. During the TRC process, very complex fields of stresses are applied to the solidifying metal in between the two rolls such as compression, tension and shear forces which can promote the formation of hot tears at grain boundaries.

4.4 Microstructure of downstream processed AZ31 magnesium alloys

The downstream processing, comprising of homogenization followed by hot rolling and finally annealing, as a part of the post treatment procedure on the AZ31 TRC and MCTRC magnesium alloys. The homogenization was conducted on the as-cast AZ31 magnesium alloy specimens at 370°C for up to 6 h, followed by hot rolling at 400°C at a fixed rolling speed of 190 mm/s and finally annealing at 345°C for 2 h. This experimental procedure was conducted at BCAST, Brunel University [127]. The response to the homogenization treatment was studied in order to evaluate the microstructure evolution in the TRC and MCTRC AZ31 magnesium alloy strips.

The surface microstructure was characterized by optical microscopy after chemical etching with 2% nital solution. The optical micrograph in Fig. 4.22 (A) displays a representative region from the surface of AZ31 TRC magnesium alloy, revealing a bimodal microstructure with newly recrystallized grains with an average size of 12.4 to 14.3 μm,
along with a high volume fraction of twins and randomly distributed Al-Mn intermetallics (dark in contrast). The AZ31 MCTRC magnesium alloy surface revealed a highly refined microstructure with a uniform grain size averaging 8.4 to 10 µm as shown in the Fig. 4.22 (B). The improvement in the refinement in the grain structure can be attributed to the initial grain size in the AZ31 TRC magnesium alloy (~616 µm), resulting in slower rate of recrystallization and random grain size distribution. Experimental results reported by Bayandorian et. al. show that the rate of recrystallization in case of AZ31 MCTRC magnesium alloy is faster (~6 times) than the AZ31 TRC magnesium alloy, producing a homogeneous and finer microstructure with a narrow distribution of grain sizes.

The as-cast microstructure of the AZ31 magnesium alloys shows a large volumes of β-phase on the grain boundaries (Figs. 4.2 and 4.3), which are absent in the microstructure of the downstream processed AZ31 magnesium alloys. The reduction in grain size and the dissolution of the β-phase in the α-Mg grains, suggests further improvement in the corrosion resistance as well as reducing the susceptibility to galvanic corrosion as the β-phase also acts as a cathodic site for galvanic corrosion to occur in the magnesium alloys, as reported earlier by Song et. al., [87, 88]. The high magnification scanning electron micrograph of the AZ31 TRC magnesium alloy reveals that the rosette-shaped Al-Mn intermetallics still persists on the surface microstructure with evidence of microporosity, indicated by arrows, as shown in Fig. 4.23 (A). However, the AZ31 MCTRC magnesium alloy surface shows newly formed sub-micron size Al-Mn intermetallics, across the microstructure, as shown in Fig. 4.23 (B). The near surface microstructure in the AZ31 TRC magnesium alloy shows a cracking defect from the hot rolling process, (Fig. 4.24 (A)). According to Barnett et. al., the occurrence of significant twinning during downstream processing can cause premature fracture forming cracks [149].

Transmission electron microscopy shows evidence of twinning, indicated by the arrow, in the AZ31 TRC magnesium alloy (Figs. 4.25 (A) and 4.26 (A)). During high temperature deformation of magnesium alloys, due to lack of sufficient number of slip systems, the activation of non-basal slip systems or twinning occurs [149]. Barnett et. al., also reported that the twinning becomes more widespread as the grain size increases. Rosette-shaped Al-
Mn precipitates are observed on the grain boundaries, confirmed by TEM-EDX analysis. The HAADF transmission electron micrograph of Fig. 4.25 (B) reveals the continuous precipitation behaviour on the surface of AZ31 TRC magnesium alloys revealing no precipitate free zone (PFZ). However, Si impurity was detected on the grain boundary as shown in the image. The effect of downstream processing on the precipitates was clearly evident from the HAADF image that showed nano-sized Al-Mn precipitates distributed across the grain structure. However, the grain boundary microstructure in the AZ31 MCTRC magnesium alloy shows no precipitation on the grain boundary and an ultra fine precipitation, mostly Al-Mn type precipitates, shown in Fig. 4.26 (B).

Evidence of block-shaped nickel impurity (0.62 at.%), precipitated in the magnesium matrix is given in the HAADF transmission electron micrograph of Fig. 4.27 (A). Such nickel precipitates in the magnesium matrix have been reported earlier to be rather detrimental, since they have been proven to be efficient cathodic sites, resulting in galvanic corrosion [82]. An increased population of twins was evident in the magnesium matrix from the transmission electron micrograph of Fig. 4.27 (A). The high density of twins in the AZ31 TRC magnesium alloys can be attributed to the fact that the alloy specimen has a larger grain size compared with the AZ31 MCTRC magnesium alloy. This is due to the Hall-Pitch relationship, i.e. \( T_{\text{twinning}} \propto d^{-1/2} \), which relates the twinning stresses \( T_{\text{twinning}} \) to the grain size \( d \) [45]. From the data available on the grain sizes, the AZ31 TRC magnesium alloy exhibits a larger grain size compared with that of the AZ31 MCTRC magnesium alloy. Hence, it is clear that the onset of the twinning mode will be postponed in the AZ31 MCTRC magnesium alloy. The bright field transmission electron micrograph of Fig. 4.27 (B) shows a significant amount of deformation features, resembling twins in the magnesium matrix. However, from the morphology of the deformation features and the SAED patterns recorded for \( \alpha \)-Mg matrix (point 1) and band (point 2), it is confirmed that they can not be twins and, hence, are shear bands. These shear bands can occur due to inadequate temperature control during the down stream processing of the magnesium alloys. The TEM-EDX analysis from point 3 reveals \( \beta \)-phase, evident from [110] plane in the SAED pattern.
The AZ31 MCTRC magnesium alloy on down stream processing shows rod-like Al-Mn nanoprecipitates that are randomly distributed in the $\alpha$-Mg matrix (Fig. 4.28 (A)); these are confirmed by TEM-EDX analysis, shown in Table 4.7. The average size of the newly synthesized rod-like Al-Mn precipitates measures $\sim$100-150 nm in length, evident from the bright field transmission electron micrograph of Fig. 4.28 (B).

Electron backscattered diffraction was employed to understand the texture evolution after down stream processing of the AZ31 TRC magnesium alloy and AZ31 MCTRC magnesium alloy. The inverse pole figure image, shown in Fig. 4.29 (A) and the all Euler colouring image, shown in Fig. 4.29 (B), display the orientation contrast of the recrystallized grains in the AZ31 TRC magnesium alloy exhibiting a bimodal microstructure with a grain size, averaging from 5-20 $\mu$m. The significant decrease in the grain size from the as-cast condition can be attributed to active deformation modes namely, twinning contributing to the static recrystallization mechanism and the high density of shear bands resulting in sites for recrystallization to occur.

It can be seen that the AZ31 TRC magnesium alloy exhibits twinning (red in colour) as shown in Fig. 4.29 (C). The band contrast image reveals a relatively reduced population of low angle grain boundaries (2-15°) in white than the high angle grain boundaries (>15°) in black. A typical twin present in the Kikuchi band contrast image was analyzed, revealing 86° $\{10\overline{1}2\}$ tension twin boundaries in Fig. 4.29 (E). The 3D mis-orientation angle distribution shown in Fig. 4.29 (D) clearly indicates that the tension twin density is relatively high i.e. 86°, confirming it as the dominant deformation mode in the AZ31 TRC magnesium alloy. The density of newly recrystallized grains is highlighted from the mis-orientation profile at $\sim$30°, shown by the arrow. Pole figures recorded along the rolling direction, shown in Fig. 4.29, indicate a strong basal texture, as reported in AZ31 magnesium alloys.

The AZ31 MCTRC magnesium alloy revealed a fully recrystallized microstructure with an average grain size of 3.5-14.3 $\mu$m, as shown in Fig. 4.30. It is clear from the EBSD maps that there is no evidence of twinning observed from the alloy surface, displayed in Figs.
4.30 (A), 4.30 (B) and 4.30 (C) as well as from the 3D mis-orientation angle distribution data. The high population density of newly recrystallized grains is confirmed from the 3D mis-orientation angle distribution, shown at ~30°, indicated by arrow in Fig. 4.30 (D). The newly formed recrystallized grains, specifically those finer in size, indicated by red arrows in Fig. 4.30 (C), are noticed at the grain boundary areas indicating strain-induced grain boundary migration (SIBM), as a possible mode of deformation. SIBM has been reported in the case of magnesium alloys [46], where grain boundary bulging acts as a precursor for the formation of recrystallized grains [51, 52, 53, 148]. Pole figures recorded along the rolling direction, as shown in Fig. 4.30, indicate a strong basal texture similar to TRC specimen.

4.5 Discussion

The metallographic investigation reveals subtle differences in the microstructures of the magnesium alloys produced by twin roll casting and melt-conditioned twin roll casting processes. This can be attributed to the fundamental difference in the solidification behaviour and the nucleation mechanism associated with the casting processes. The microstructure modification in MCTRC magnesium alloys can be attributed to the technological innovation, i.e. melt-conditioning by advanced shear technology, MCAST process, conducted prior to the solidification stage.

4.5.1 Solidification behaviour of MCTRC magnesium alloys

Conventional TRC process integrates casting and rolling into a single process. In conventional twin roll casting, solidification occurs by heterogeneous nucleation of the chilled liquid at the mould walls (water-cooled rolls) after the initial pouring of the liquid melt. This mechanism, known as Big Bang by Chalmers, reveals that the nuclei formed on the chilled zone are transferred by convection caused by rotating the rolls to the overheated liquid zone and finally dissolve [55]. Hence, the columnar growth of dendrites as observed in the TRC alloys is a typical feature of the resultant microstructure. However, the solidification in MCTRC alloys is a two-step process. In the primary stage, the liquid melt
is intensely sheared at a high rate in the MCAST unit. This conditioned melt is further fed into the water cooled rolls of the TRC machine, associated with a relatively high cooling rate, where complete solidification occurs, i.e. the second stage. The final solidification occurs via heterogeneous nucleation, resulting in highly refined microstructure.

The refinement in the resultant microstructure is due to the increased number of potent sites for heterogeneous nucleation to occur with finer sizes of MgO particles (100-200 nm) and then uniform dispersion of potent sites occurring through intensive shearing of the liquid melt. Enhanced and effective nucleation offered by MCAST process significantly improves the heterogeneous nucleation of the primary phase, thus resulting in finer and uniform equiaxed $\alpha$-Mg dendrites [126].

As discussed earlier, the liquid melt in the TRC process contains oxide films or particles (1-2 $\mu$m) that act as potent sites of nucleation. The resultant microstructure is coarse and non-uniform, possibly because of the reduced number of potent sites of nucleation and the lack of homogeneity in their distribution throughout the liquid melt. On the microscopic levels, results obtained from Fan and co-workers, showed that non-sheared liquid melts of magnesium alloys usually contained clusters of oxide particles and oxide films that are non-uniformly dispersed, resulting in different morphologies of MgO particles, often considered as potent sites for nucleation of Al-Mn intermetallics and $\alpha$-Mg primary phase [62].

From the nucleation mechanism associated with the solidification, the low survival rate of the nuclei results in a coarse and non-uniform microstructure in TRC magnesium alloys. However, enhanced nucleation rate and higher survival rates of the nuclei are necessary to improve grain refinement. Uniform temperature control, uniform distribution of chemical composition and rapid extraction of latent heat are essential parameters to increase the survival rate of the nuclei [42].

According to the free growth model proposed by Greer and co-workers, larger oxide particles require reduced under-cooling to behave as active, potent sites for effective
heterogeneous nucleation and vice versa. And as the grain growth starts from the larger particles acting as nucleation sites, the relatively smaller potent sites are deprived from contributing to the effective grain refinement, as they are probably re-melted. Hence, it can be concluded that size distribution of nucleant particles is crucial. The MCAST process involves intensive shearing of liquid melts at near liquidus temperatures, producing a uniform dispersion of MgO particles of 100-200 nm, promoting effective nucleation [62, 128].

4.5.2 Influence of casting processes on as-cast microstructure

Metallographic examinations have shown significant improvement in the refinement of the microstructure of MCTRC magnesium alloys compared to TRC alloys in terms of grain size, reduction in porosities, uniform distribution of intermetallics, reduction in micro-segregations of β-phase as well as intermetallics, reduced impurity levels, etc.

4.5.2.1 Grain size

The grain sizes in TRC magnesium alloys are considerably larger compared with the MCTRC magnesium alloys, which can be explained by the nucleation mechanisms. The intensive shearing at 600 rpm for 60 s, in the MCAST process, facilitates uniform dispersion of the micro-nuclei within the liquid melt. The primary solidification stage is also accompanied by formation of Al-Mn intermetallics. The survival rate of maximum potent sites for nucleation is a crucial factor, promoting refined grain growth on feeding the conditioned melt into the caster [126]. The influence of MCAST process is reflected on the microstructure in Figs. 4.1 (A), 4.7 (A) and Fig. 4.12 (A) of the transverse sections of AZ31, AZ61 and AZ91 MCTRC alloys respectively, showing uniform grain growth with considerable refinement in grain sizes across the transverse sections and no centre-line segregation.

Concerning the TRC process, the non-sheared liquid melt is directly fed into the twin roll caster. As a result, the sites for nucleation are larger in size compared with the MCTRC
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alloys, fewer in number, non-uniformly distributed and have a low survival rate, thereby limiting the rate of nucleation and contributing to the random microstructure with large columnar grains in TRC alloys. Figures 4.1 (B), 4.7 (B) and 4.12 (B) of the transverse sections of AZ31, AZ61 and AZ91 TRC alloys, showing the respective transverse sections, reveal the chill zone microstructure to be relatively fine and equiaxed, due to the initial thin-solidified shell being formed on the roll surface where the temperature gradient is very high. As the solidification proceeds, the heat extraction rate and temperature gradient of the melt decrease further, causing the formation of elongated columnar dendrites, towards the centre of the alloy strips.

The AZ31 TRC magnesium alloy exhibited an average grain size of 350 µm in the chill zone and 520 µm in the columnar zone compared with the AZ31 MCTRC alloys showing an average of 70-90 µm. In the case of the AZ61 TRC magnesium alloy, primary solidified grain growth was witnessed with the grain size averaging 120 µm in the chill zone to 300 µm in the equiaxed zone compared with 100-120 µm exhibited by the AZ61 MCTRC magnesium alloys. The AZ91 TRC magnesium alloys displayed an average grain size of ~280-320 µm, compared with the AZ91 MCTRC alloy that showed an average grain size of 60-90 µm. It can therefore be concluded from the microscopic examinations performed that the MCTRC magnesium alloys revealed uniform grain sizes and highly refined microstructure across the section thickness.

4.5.2.2 Eutectic morphology, composition and precipitation

The resultant microstructures of the as-cast TRC and MCTRC magnesium alloys were characterized by α-Mg dendrites, α-eutectic and the β-Mg17Al12 phase, that was located on the interdendritic boundaries. The EDX results showed that there was a depletion in the distribution of the aluminium content across the dendrites, being least at the centre of α-Mg dendrites (~2 wt.%) and gradually increasing towards the interdendritic boundaries (~12 wt.%), also referred as Al-coring effect. From the metallographic investigations, it is clear that the TRC magnesium alloys displayed a coarser microstructure compared to the MCTRC magnesium alloys, evident from Figs. 4.1, 4.7 and 4.12. Therefore, the coarser
grains will show larger depletion in aluminium contents, compared with the smaller grains, suggest superior corrosion resistance exhibited by the smaller grains in magnesium alloys [5]. Hence due to the refinement in the MCTRC magnesium alloys resulting in smaller grain sizes and lesser depletion in aluminium content, suggests an improved corrosion behaviour compared with the TRC magnesium alloys.

According to the literature, considered by Polmear et. al., eutectic solidification controls the size, shape and distribution of $\beta$-Mg$_{17}$Al$_{12}$ phase in the resultant microstructure. The eutectic morphologies are directly influenced by the composition and the associated cooling rates. Usually magnesium alloys with aluminium contents approaching the eutectic composition i.e. ~33% display regular lamellar eutectic microstructures while those with lesser aluminium contents, i.e. ~10%, exhibit fully or partially divorced eutectic morphologies, elaborately discussed in the literature review. The effect of aluminium and zinc content, as well as the cooling rates [7] show a transition from lamellar to fully divorced and vice versa as shown in Fig. 2.7.

As the zinc content in all three alloys, i.e. AZ31, AZ61 and AZ91 magnesium alloys is 1%, and the process parameters for the TRC and MCTRC processes were optimized and fixed, the effect of increasing aluminium content and the cast processes involved, on the eutectic solidification and their morphologies can be discussed. As the aluminium contents are below 10%, eutectic morphologies observed have been either partially divorced or fully divorced.

The AZ31 magnesium alloys (Figs. 4.4 (A) and 4.6 (A) displayed a fully divorced eutectic morphology with the $\beta$-phase surrounded by of eutectic $\alpha$-Mg. A partially divorced eutectic morphology, with the islands of eutectic $\alpha$-Mg within the $\beta$-phase, was observed in the AZ61 magnesium alloys (Figs. 4.8 (D) and 4.9 (B). The AZ91 magnesium alloys also showed partially divorced eutectic morphology as shown in Figs. 4.13 (C) and 4.14 (C). Dahle et. al. [7], has reported earlier that the eutectic morphologies show a transition from the fully divorced type to partially divorced eutectic morphology as the aluminium content gradually increases as shown in Fig. 2.7. However, it is evident that the TRC and MCTRC
processes do not show any significant difference in the eutectic morphologies during solidification of the magnesium alloys. Since both casting processes are carried out at relatively high cooling rates, therefore, the eutectic solidification can possibly attain the same eutectic morphology. However, characteristics including accurate temperature control and fast heat removal associated with the MCTRC process can definitely enhance the eutectic solidification process compared with that of TRC process, impacting on the microstructural characteristics.

The final step in the eutectic solidification process of cast Mg-Al alloys occurs through precipitation in supersaturated areas of the $\alpha$-Mg dendrites. Precipitation can be of two types namely continuous or discontinuous. Conventionally, precipitation in the form of $\alpha$ and $\beta$ plates in a lamellar morphology has been reported [7], as discussed in the literature survey. The TRC and MCTRC magnesium alloys showed a significant difference in the precipitate morphologies, compared with the conventional castings, reported earlier. This phenomenon can be attributed to the casting processes, as in the case of both TRC and MCTRC methods, rapid solidification occurs compared with the conventional casting processes, undergoing slow solidification, producing coarse microstructures with lamellar precipitate morphologies in the $\alpha$-eutectic, as reported earlier [5].

Continuous precipitation is clearly evident in AZ31 MCTRC magnesium alloy from the bright field transmission electron micrographs in Fig. 4.6 (A), which appears in the form of lozenge-shaped plate-like structures randomly oriented in the $\alpha$-Mg matrix adjacent to the $\beta$-phase. Similar plate-like structures in the AZ61 MCTRC magnesium alloy were observed in Fig. 4.11 (B) and the AZ91 magnesium alloy shown in Fig. 4.14 (D) revealing the $\beta$-precipitates.

Precipitation in case of the TRC magnesium alloys showed a wide variety of precipitates, ranging from fine bead-like structures in the case of AZ31 TRC magnesium alloys shown in Fig. 4.2 (B) to needle-shaped structures with varied lengths, plate-like, globular as observed in Fig. 4.10 (A) and the AZ91 magnesium alloys in Fig. 4.15 (B) that show lozenge-shaped plate-like structures with random orientations. Therefore, it can be concluded by controlling the casting parameters, the precipitate morphologies can be
manipulated and controlled while inadequate controls during the casting process could alter
the morphologies and sizes of the β-precipitates as observed from the TRC magnesium
alloys.

4.5.2.3 Micro-constituents and intermetallic morphology

According to the earlier literature reports, manganese has been incorporated with a view to
improve grain refinement. To improve the corrosion properties, the manganese-rich phases,
tend to form intermetallics in combination with aluminium, e.g. Al₈(Mn,Fe)₅ particles,
incorporating iron from the liquid melt [132, 135]. At the same time, these manganese-rich
intermetallics, such as Al₈Mn₅ display considerably high cathodic current density; hence,
excess manganese concentrations can be detrimental to the corrosion resistance of the
magnesium alloys [64, 65, 67]. During solidification of Mg-Al magnesium alloys,
manganese is partly distributed in the magnesium matrix and partly present in the form of
Al₈Mn₅ intermetallic particles, distributed in the microstructure [133-135]. Trembley et. al.,
have reported that the population density of the rosette/flower morphology Mn-rich
intermetallics at the surface is considerably high. The relatively low cooling rates
prevailing within the plaster moulds during solidification and the reduced thermal gradients
at the mould/metal interface allow the nucleation and growth of Al-Mn particles onto the
surface. Al-Mn intermetallic particles have been reported to be of various morphologies,
namely angular blocky, needle-shaped, flower-like, etc. varying in size, distributed in the
matrix and sometimes in the eutectic [136-140].

The magnesium alloys, ranging from 3% to 9% Al under investigation, mainly revealed Al-
Mn intermetallic particles, apart from impurities like Si, Fe, etc., observed in scarce
amounts. Microscopic investigations revealed typical morphologies of the Al-Mn
intermetallics namely, rosette/flower shaped usually located on the β-phase, observed in the
AZ61 (Figs. 4.10 and 4.11) and the AZ91 magnesium alloys (Figs. 4.15 and 4.17).
However, these intermetallics were dispersed randomly in the magnesium matrix as well as
on the interdendritic spaces in the AZ31 magnesium alloys (Figs. 4.4 and 4.6). As it has
been noticed that the TRC magnesium alloys show localized segregation, the clustering
effect of Al-Mn particles on the $\beta$-phase in the segregated areas was observed. The MCTRC magnesium alloys reveal a uniform distribution of Al-Mn particles in the microstructure. This can be explained as a consequence of the MCAST process retarding the segregation behaviour in the microstructure. As the Al-Mn intermetallics can act as cathodes, relative to the magnesium matrix, the uniform distribution of these microconstituents in the MCTRC magnesium alloys, suggests further improvement in the corrosion resistance of these alloys.

As both the TRC and MCTRC processes are rapid solidification processes, the intermetallic particle size is expected to be relatively small compared with the conventional casting processes, which ranges from 100–500 nm. The EDX results showed an increased amount of Mg in $\text{Al}_8\text{Mn}_5$ intermetallics in the AZ31 magnesium alloys, which is possibly from the underlying magnesium matrix as the microscopic examinations were conducted on 300 kV HRTEM; however, the EDX analysis is semi-quantitative.

From the solidification studies conducted at BCAST, it is believed that $\text{Al}_8\text{Mn}_5$ particles are nucleated on the MgO particles, potent sites for nucleation of $\alpha$-Mg dendrites in magnesium alloys. Al-Mn particle from AZ91 magnesium alloy specimen, as shown in Fig. 4.27, was investigated on each arm of the rosette-shaped intermetallic but insufficient evidence of presence of oxygen was found to confirm the fact. However, it is difficult to quantify features on a scale of nanometres and rely only on the quantification data alone [127].

### 4.5.3 Influence of downstream processing on AZ31 magnesium alloys

The downstream processing of AZ31 magnesium alloys in both the TRC and MCTRC processes resulted in the reduction in grain size and the reduction in the $\beta$-phase. According to the Literature Review, in the magnesium alloys, the reasons for the possible mechanisms for static recrystallization include SIBM, i.e. strain induced boundary mitigation, occurring at the grain boundaries [46], twins, as they provide nucleating sites at higher temperatures for recrystallization in deformed magnesium alloys [146, 147] and PSN, i.e. particle
simulated nucleation, due to second phase particles [148], resulting in newly formed recrystallized grains. During the hot rolling process, dynamic recrystallization could possibly occur via grain boundary sliding, i.e. GBS [46] or activation of non-basal slip, i.e. twinning [149]. Effective recrystallization would be dependent on the type of casting methodology, further resulting in improvement of mechanical and corrosion properties of the magnesium alloys. Hence, it is important to investigate the mode of deformation in the TRC and MCTRC magnesium alloys.

4.5.3.1 Microstructure

The TRC magnesium alloys exhibit a comparatively large grain size across the sheet thickness compared with the MCTRC alloys, revealing a relatively small and uniform grain size. The EBSD maps show evidence of twinning (Fig. 4.29) and the 3D misorientation profile indicates a peak at 86°, suggesting tension type twins; suggesting that the recrystallization in AZ31 TRC magnesium alloy should occur via twinning. Twinning in magnesium alloys occurs due to lack of non-basal slip systems, which increases with the increase in grain size. The AZ31 TRC magnesium alloy also reveals a high density of dislocations along with shear bands as noticed in the Fig. 4.27 (B). According to Barnett et. al., these shear bands occur from double twinning during the course of hot rolling and such banded material is more favourably aligned to shear [144]. EBSD maps also show a chain/necklace formation of newly recrystallized grains, again exhibiting a banding effect.

From the EBSD maps shown in Fig. 4.30, it is clear that there is no evidence of twinning of shear bands in AZ31 MCTRC alloy specimen. The 3D misorientation profile shows a high density of newly formed recrystallized grains at 30°, with no evidence of twinning at 86°. Therefore, a recrystallization mechanism different from the AZ31 TRC magnesium alloys must be dominant, possibly strain-induced grain boundary migration (SIBM), also reported in the case of magnesium alloys [46], where grain boundary bulging acts as a precursor for the formation of recrystallized grains [51, 52, 53]. This type of newly recrystallized grains at the grain boundaries evident from Fig. 4.30 (A), supported by Humphreys et. al., suggests that if DRX results in highly refined grains, i.e. ≤10 µm, then deformation may
occur via SIBM. The possibility of deformation through the SIBM route is relatively high due to the uniform and refined grain size, produced in MCTRC as-cast magnesium alloys compared with the random and large grain structure in TRC magnesium alloys. Experimental evidences provided by Bayandorian et. al., from BCAST, supports the possibility of SIBM mechanism in MCTRC magnesium alloys.

4.5.3.2 Texture

Pole figures recorded along the rolling direction, shown in Figs. 4.29 and 4.30, indicate a strong basal texture in the case of AZ31 TRC and MCTRC magnesium alloys, respectively. Transmission electron microscopy reveals a high volume fraction of twins and shear bands in the AZ31 TRC magnesium alloy, as shown in Fig. 4.27. At the same time, evidence of twinning in the case of AZ31 MCTRC magnesium alloys has also been represented in Fig. 4.26 (A). According to Barnett et. al., these shear bands would possibly result in softening of the texture. The texture analysis shown in Fig. 4.29 reveals that the AZ31 TRC magnesium alloy gives an intensity of 12.0 compared with 14.7 for MCTRC alloys, resulting in texture softening [144]. However, macrotexture results do not show a significant difference in the textures of AZ31 magnesium alloys, exhibiting a strong basal fibre texture.

4.6 Summary

- The as-cast microstructure of the magnesium alloys under study was composed of α-Mg matrix, the α-eutectic and the β-phase. Rosette/flower-shaped Al-Mn intermetallics (~100-500 nm), located on the β-phase, Fe/Si impurities in the α-Mg matrix and the plate-like lozenge-shaped β-precipitates were some of the microconstituents found in the microstructure of Mg-Al alloys under study.
- The as-cast TRC magnesium alloys, i.e. the non-sheared magnesium alloys, showed a coarse and random microstructure with non-uniform compositional distribution of Al-Mn intermetallics and microsegregation of the β-phase. The strip castings revealed defects, including centre-line segregation, hot cracking and localized
plastic deformation; these deteriorate the alloy properties and result in a relatively poor performance.

- The influence of melt conditioning through advanced shear technology (MCAST process), employed in the MCTRC process showed marginal improvement in grain refinement with finer grain sizes and reduced levels of segregation. The transformation from coarse columnar grains to refined equiaxed grain structure was clearly evident from the metallographic investigation. Uniform eutectic distribution, improving chemical homogeneity, forming a network of β-phase, would result in better corrosion properties of the MCTRC magnesium alloys.

- Intensive shearing ensures uniform distribution of the Al-Mn intermetallics across the sheet thickness, thereby improving the surface resistance to corrosion susceptibility. Reduced impurity levels and minimal microporosity could possibly result in improved microstructural characteristics and, in turn, better mechanical and corrosion properties of the MCTRC magnesium alloys.

- The downstream processed AZ31 magnesium alloys showed considerable refinement in the grain sizes and reduction in the β-phase in the microstructure. However, sub-micron sized β-precipitation and Al-Mn intermetallics were evident, across the AZ31 TRC alloy microstructure. The grain sizes in the AZ31 MCTRC magnesium alloy was finer compared to the TRC magnesium alloy, owing to the coarse as-cast TRC alloy microstructure and suggesting higher post treatment times for recrystallization.

- Deformation features in the form of shear bands were noticed in the AZ31 MCTRC magnesium alloys and tension twinning was evident in AZ31 TRC magnesium alloys, suggesting incomplete recrystallization, due to inadequate temperature monitoring or improper processing, during the post treatment of the strip castings.
### Table 4.1 Nominal composition (wt.%) of AZ series alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Chemical composition of the elements (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>AZ31</td>
<td>2.5-3.5</td>
</tr>
<tr>
<td>AZ61</td>
<td>5.8-6.8</td>
</tr>
<tr>
<td>AZ91</td>
<td>9.0</td>
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### Table 4.2 TEM-EDX results for AZ31 MCTRC magnesium alloy

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<tr>
<th>Phases</th>
<th>Atomic weight %</th>
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</thead>
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<tr>
<td></td>
<td>Mg</td>
</tr>
<tr>
<td>β - phase</td>
<td>59.85</td>
</tr>
<tr>
<td>β - precipitates</td>
<td>83.66</td>
</tr>
</tbody>
</table>

### Table 4.3 TEM-EDX results for AZ61 TRC magnesium alloy

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<th>Point</th>
<th>Atomic weight %</th>
</tr>
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<tr>
<td></td>
<td>Mg</td>
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<tr>
<td>Point 1</td>
<td>96.81</td>
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<tr>
<td>Point 2</td>
<td>86.32</td>
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<td>Point 3</td>
<td>70.26</td>
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<tr>
<td>Point 4</td>
<td>52.18</td>
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</tbody>
</table>
**Table. 4.4**  TEM-EDX results for AZ61 MCTRC magnesium alloy

<table>
<thead>
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</thead>
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<td>Mg</td>
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<tr>
<td>Point 1</td>
<td>91.91</td>
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<tr>
<td>Point 2</td>
<td>93.97</td>
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<tr>
<td>Point 3</td>
<td>70.04</td>
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**Table. 4.5**  Microstructure properties of TRC and MCTRC magnesium alloys

<table>
<thead>
<tr>
<th></th>
<th>TRC</th>
<th>MCTRC</th>
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<tr>
<td>Distribution</td>
<td>Random</td>
<td>Uniform</td>
</tr>
<tr>
<td>Size of β-phase</td>
<td>Coarse (~1-2µm)</td>
<td>Fine (Sub-micron)</td>
</tr>
<tr>
<td>β-precipitation volume</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Segregation</td>
<td>Yes</td>
<td>No</td>
</tr>
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</table>
Table. 4.6 TEM-EDX analysis of $\text{Al}_8\text{Mn}_5$ intermetallic in AZ91 TRC magnesium alloy

<table>
<thead>
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<th>Atomic %</th>
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<tbody>
<tr>
<td></td>
<td>O  Mg  Al Mn</td>
</tr>
<tr>
<td>Point 1</td>
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<tr>
<td>Point 2</td>
<td>2.87 3.77 55.51 35.60</td>
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<tr>
<td>Point 3</td>
<td>2.35 2.46 59.43 34.63</td>
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<td>Point 4</td>
<td>3.10 2.45 56.50 35.66</td>
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<tr>
<td>Point 5</td>
<td>2.65 14.49 50.87 29.47</td>
</tr>
<tr>
<td>Point 6</td>
<td>2.31 2.59 56.35 36.00</td>
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</table>

Table. 4.7 TEM-EDX results for Al-Mn intermetallics in AZ31 MCTRC magnesium alloy after downstream processing

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<th></th>
<th>Atomic %</th>
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<tbody>
<tr>
<td></td>
<td>Mg  Al  Zn Mn</td>
</tr>
<tr>
<td>Point 1</td>
<td>0.75 53.55 0.82 44.88</td>
</tr>
<tr>
<td>Point 2</td>
<td>0.82 53.42 0.89 44.87</td>
</tr>
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</table>
Fig. 4.1 Plane polarized light optical micrographs of transverse sections of AZ31 magnesium alloy; (image taken at Brunel University)

(A) MCTRC processed alloy
(B) TRC processed alloy showing
(I & V) chill zone microstructure, evidence of hot tearing shown by arrows
(II & IV) Columnar zone microstructure with coarse columnar grains
(III) Equiaxed zone
Evidence of centre-line segregation, indicated by arrow
Fig. 4.2 Scanning electron micrographs of AZ31 TRC magnesium alloy
(A) Back scattered image showing general surface microstructure
(B) In lens secondary electron image revealing localized porosities in the eutectic
(C) $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase along with the $(\alpha+\beta)$ eutectic
(D) High resolution back scattered image showing discontinuous $\beta$-precipitation
Fig. 4.3 Scanning electron micrographs of AZ31 MCTRC magnesium alloy
(A) Back scattered image showing general surface microstructure
(B) In lens secondary electron image revealing eutectic structure
(C) $\beta$-Mg$_{17}$Al$_{12}$ phase along with $(\alpha+\beta)$ precipitation in the eutectic, indicated by arrow
(D) High resolution back scattered image showing discontinuous $\beta$-precipitation
Fig. 4.4 Transmission electron micrographs revealing features in the microstructure of AZ31 TRC magnesium alloy

A – $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase along the grain boundary,
B – Rosette morphology of $\text{Al}_8\text{Mn}_5$ intermetallic particle in the $\alpha$-$\text{Mg}$ matrix,
C – $\text{Al}_8\text{Mn}_5$ intermetallic particle on the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase
D – $\text{Al}_8\text{Mn}_5$ intermetallic particle on the grain boundary
Fig. 4.5 Lattice images revealing the interfaces in AZ31 TRC magnesium alloy
(A) Interface between $\alpha$-Mg matrix and $\beta$-Mg$_{17}$Al$_{12}$ phase and the corresponding FFT
micro diffraction patterns
(B) Interface between $\alpha$-Mg matrix and Al$_5$Mn$_5$ intermetallic and the corresponding FFT
micro diffraction patterns.
Fig. 4.6 Bright field TEM micrographs of AZ31 MCTRC magnesium alloy revealing
(A) $\beta$-precipitation near the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase
(B) Rosette shaped Al-Mn intermetallic particle in the magnesium matrix
Fig. 4.7 Optical micrographs of transverse sections of AZ61 magnesium alloy
(A) MCTRC processed alloy
(B) TRC processed alloy showing
(I & III) chill zone microstructure
(III) Central zone microstructure
Localized micro segregations, indicated by arrows
Fig. 4.8 Scanning electron micrographs of AZ61 TRC magnesium alloy
(A) General surface microstructure showing primary solidified grains and localized porosities
(B) In lens secondary electron image revealing distribution of the eutectic
(C) Segregation of Al & Zn in the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ in the (α+β) eutectic
(D) Back scattered image showing partially divorced eutectic with α-islands
Fig. 4.9 Scanning electron micrographs of AZ61 MCTRC magnesium alloy
(A) General surface microstructure revealing highly refined dendritic microstructure
(B) In lens secondary electron image revealing eutectic structure
(C) Rosette shaped Al$_8$Mn$_5$ intermetallic particles in the (α+β) eutectic
(D) Back scattered image showing (α+β) eutectic with β-Mg$_{17}$Al$_{12}$ phase
Fig. 4.10 Transmission electron micrographs of AZ61 TRC magnesium alloy
(A) Eutectic microstructure revealing $\beta$-precipitation in the $(\alpha+\beta)$ eutectic, with needle shaped and globular morphologies along with $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase
(B) HAADF transmission electron micrograph showing the $\alpha$-$\text{Mg}$ matrix (1), $\beta$-precipitation (2), $\beta$-phase (3) and $\text{Al}_8\text{Mn}_5$ intermetallic (4)
Fig. 4.11 Transmission electron micrograph from AZ61 MCTRC magnesium alloy
(A) Bright field image revealing (1) Al$_8$Mn$_5$ intermetallic, (2) β-Mg$_{17}$Al$_{12}$ phase and (3) α-Mg matrix and their corresponding SAED patterns
(B) HAADF micrograph showing the β-precipitation in the α-Mg matrix and the β-phase
Fig. 4.12 Plane polarized light optical micrographs revealing the transverse sections of AZ91 magnesium alloy; (image taken at Brunel University)

(A) MCTRC processed alloy

(B) TRC processed alloy showing

(I & III) chill zone microstructure

(II) Columnar zone microstructure where centre-line segregation evident, indicated by arrow in AZ91 TRC magnesium alloy
Fig. 4.13 Scanning electron micrographs of AZ91 TRC magnesium alloy
(A) General surface microstructure revealing localized micro segregation
(B) In lens secondary electron image revealing eutectic structure
(C) Partially divorced eutectic structure with rosette shaped Al₈Mn₅ intermetallics
(D) High resolution back scattered image showing discontinuous β-precipitation and rosette morphology of Al-Mn intermetallics located on the β-phase
Fig. 4.14 Scanning electron micrographs of AZ91 MCTRC magnesium alloy
(A) Surface revealing highly refined microstructure
(B) In lens secondary electron image revealing eutectic structure
(C) $\beta$-Mg$_{17}$Al$_{12}$ phase along with Al$_3$Mn$_5$ intermetallics
(D) High resolution back scattered image showing discontinuous $\beta$-precipitation
Fig. 4.15 Transmission electron micrographs of AZ91 TRC magnesium alloy
(A) $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase
(B) $\beta$-precipitation
(C) and (D) Rosette shaped $\text{Al}_8\text{Mn}_5$ intermetallics on the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase
Fig. 4.16 Bright field transmission electron micrograph of AZ91 TRC magnesium alloy
(1) Rosette shaped Al₈Mn₅ intermetallics
(2) β-Mg₁₇Al₁₂ phase
Lattice images of the interfaces between the micro-constituent phases and their corresponding FFT patterns
(A) α-Mg matrix and β-phase
(B) α-Mg matrix, β-phase and Al₈Mn₅ intermetallic
Fig. 4.17 Bright field transmission electron micrographs of AZ91 MCTRC magnesium alloy

(A) $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase (area 1) and needle-shaped $\beta$-precipitate (point 1)

(B) Tension twinning in $\alpha$-Mg matrix

(C) Rosette shaped $\text{Al}_8\text{Mn}_5$ intermetallic on the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase
Fig. 4.18 HAADF transmission electron micrograph of AZ91 MCTR C magnesium alloy and corresponding EDS line scan analysis (A-B) revealing the compositional variations in the eutectic region.
Fig. 4.19 Optical micrograph revealing centre-line segregation in AZ91 TRC magnesium alloy
(A) Equiaxed grain growth
(B) Solute enriched liquid
(C) Columnar dendritic grains revealing the rejected solute
Microstructures of AZ Series Magnesium Alloys

Fig. 4.20 Localized deformation in AZ91 TRC magnesium alloy, indicating shear bands

Fig. 4.21 Scanning electron micrograph hot cracking in AZ61 TRC magnesium alloy
High contrast areas indicating Al & Zn segregation, shown by arrows
Fig. 4.22 Optical micrographs showing surface microstructure after down stream processing (A) AZ31 TRC specimen (B) AZ31 MCTRC specimen

Fig. 4.23 High magnification scanning electron micrographs showing evidence of Al₃Mn₅ precipitates on the surface, voids shown by arrows (A) AZ31 TRC specimen (B) AZ31 MCTRC specimen

Fig. 4.24 SEM micrographs revealing cracking defect in AZ31 TRC alloy
Fig. 4.25 HAADF transmission electron micrographs of AZ31 TRC magnesium alloy (A) Evidence of twinning in the α-Mg matrix (B) Si impurity on the grain boundary

Fig. 4.26 HAADF transmission electron micrographs of AZ31 MCTRC magnesium alloy (A) Twinning (B) No evidence of precipitation across the grain boundaries
Fig. 4.27 Transmission electron micrographs from AZ31TRC magnesium alloy
(A) HAADF image revealing tension twins along with Al-Mn precipitate containing nickel
(B) Bright field image revealing shear bands and β-precipitate in the magnesium matrix
SAED patterns from (1) Mg matrix, (2) shear bands and (3) β-precipitation.
Fig. 4.28 Transmission electron micrographs of Al-Mn intermetallics in AZ31 MCTR C magnesium alloy
(A) HAADF image revealing newly formed rod shaped Al-Mn precipitates
(B) Bright field image of the rod shaped Al-Mn precipitate
Fig. 4.29 Microstructure and texture of hot rolled AZ31 TRC Mg alloy, annealed at 400°C, revealing (A) IPF image, (B) All Euler imaging with grain boundaries, (C) Band contrast imaging with high angle grain boundaries (>15°)-black, low angle grain boundaries (2-15°)-white, twins-red, (D) Corresponding 3D mis-orientation distribution showing high density of LAGB’s at 30° and {10-12} tension twinning at 86°, both shown by arrows, (E) Line profile analysis of 86° twinning shown in C, Corresponding {0002}, {10-10}, {11-20} pole figures showing basal fiber texture along the rolling direction RD.
Fig. 4.30 Microstructure and texture of hot rolled AZ31 MCTR C Mg alloy, annealed at 400°C, revealing (A) IPF image, (B) All Euler imaging with grain boundaries, (C) Band contrast imaging with high angle grain boundaries (>15°)-black, low angle grain boundaries (2-15°)- white (D) Corresponding 3D mis-orientation distribution showing LAGB’s at 30°, Corresponding {0002}, {10-10}, {11-20} pole figures showing discontinuous basal fiber texture along the rolling direction RD.
CHAPTER 5

CORROSION BEHAVIOUR OF AZ SERIES Mg-Al ALLOYS

5.1 Introduction

The corrosion resistance of magnesium alloys has been reported to be influenced by the alloy microstructure, microconstituents, including Fe, Ni, Cu, Si and Co as well as the environment [3]. The microstructure of Mg-Al magnesium alloys comprises the α-Mg phase, a substitutional solid solution of aluminium in magnesium, and the β-phase that is present as an intermetallic compound (Mg₁₇Al₁₂) in the α-eutectic [4]. However, the distribution and the volume fraction of the constituent phases depends on the particular casting technology and, subsequently, on the solidification behaviour of the magnesium alloys [1]. Therefore, the role of microstructure in the corrosion process has attracted significant attention in terms of evaluation of the microstructural impact on the corrosion properties of magnesium alloys, which further leads to alloy development through different casting technologies aimed at microstructure improvement. The aim of the selected process is to improve the microstructure and, in turn, the corrosion properties of magnesium alloys. Melt-conditioned twin roll casting (MCTRC) is directed at producing alloys with highly refined microstructures and consequent improvement in the corrosion behaviour.
Song et al. [229] investigated the influence of the \( \beta\)-Mg_{17}Al_{12} \) phase on the corrosion behaviour of die-cast AZ91 magnesium alloys in 1 M NaCl solution and suggested that the \( \beta\)-Mg_{17}Al_{12} \) phase works both as a corrosion barrier and as a site for the cathodic reaction. If the fraction \( f \) of the \( \beta\)-Mg_{17}Al_{12} \) phase is low, it serves mainly as a galvanic cathode and accelerates the overall corrosion of the \( \alpha\)-Mg matrix. However, if the fraction \( f \) is high, then the \( \beta\)-Mg_{17}Al_{12} \) phase acts as a barrier for the anodic reaction, retarding the overall corrosion attack. If the \( \alpha\)-grains are fine and the \( \beta\)-Mg_{17}Al_{12} \) phase fraction is nearly continuous, then it can be expected that \( f \) increases during corrosion and, finally, becomes sufficiently high to make the \( \beta\)-Mg_{17}Al_{12} \) phase act as a corrosion barrier.

Lunder et al. [103] reported that immersion of the AZ91 magnesium alloy in sodium chloride solution resulted in pitting at localized sites, initiating due to Al-Mn-Fe intermetallics. The corrosion behaviour of the \( \beta\)-Mg_{17}Al_{12} \) phase in AZ91 magnesium alloy [110] showed that the cathodic behaviour of \( \beta\)-Mg_{17}Al_{12} \) phase was relatively weaker than the cathodic nature of Al-Mn intermetallics. It has been reported that electrochemical investigations performed in solution at pH 10.5 showed that the pH has a strong influence on the activity of the Mg–Al phases [110,111]. Magnesium is passive in alkaline solutions, but exhibits an increasing corrosion rate at lower pH, while aluminium is passive in neutral solutions but active in alkaline solutions [110, 111]. The \( \beta\)-Mg_{17}Al_{12} \) phase is passive over a wide pH range of 4–14 [110]. Therefore, the corrosion behaviour of the Mg-Al magnesium alloys largely depends on the distribution of the intermetallics across the microstructure.

Taking into account the distribution of the microconstituent phases, their morphologies and their corrosion behaviour in aqueous solutions, the main objective in the current research is to investigate the effect of the microstructural modification, due to melt-conditioning, using advanced shear technology (MCAST), on the MCTRC magnesium alloys in comparison with the TRC magnesium alloys. The magnesium alloys investigated were as-cast AZ31, AZ61 and AZ91 as well as AZ31 magnesium alloys after down stream processing.
Scanning Kelvin probe force microscopy (SKPFM) successfully contributed to enhancing the understanding of the possible corrosion behaviour of microconstituent phases, providing supplementary information to the results obtained by classical electrochemical methods. Investigations were progressed by microscopic characterization of the magnesium alloys using electron microscopy and SKPFM, with corrosion testing subsequently utilised to confirm the microgalvanic interactions suggested by SKPFM. Corrosion testing including immersion tests and the electrochemical measurements, including open circuit potential (OCP) and polarisation measurements in 3.5% NaCl solution, were conducted to reveal the influence of MCAST process on the corrosion behaviour of the magnesium alloys.

5.2 Scanning Kelvin force probe microscopy (SKPFM)

The SKPFM technique has been extensively employed for the investigation of aluminium alloys [217-225]. Previously, it has been reported in the literature that SKPFM has been used to study magnesium and magnesium alloys [214-216]. Blucher et. al. [214] utilized SKPFM to determine the role of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase on the corrosion behaviour of cast AZ91 magnesium alloy, showing that the corrosion attack of the magnesium matrix was influenced by the surface potential of the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase. Andreatta et. al. [213] characterized the surface, revealing the potential differences for different intermetallic phases present in the microstructure of AZ80 magnesium alloy, showing that the intermetallic phases exhibited positive surface potentials relative to the magnesium matrix and, in turn, higher cathodic activity compared with the magnesium matrix.

In the current research, surface analysis, revealing the topographic and surface potential maps of the magnesium alloys, was recorded using the SKPFM technique with a Nanoscope Dimension™ 3100 microscope (Digital Instruments), working in the tapping and surface potential modes. The SKPFM characterization was carried out in air at room temperature. The scan height in the lift mode was 100 nm. The topography and the potential were sampled with a pixel density of 256×256, with a scan frequency of 0.1 Hz. For all measurements, commercially available n$^+$-silicon tips coated with PtIr$_5$ were used.
The specimens were immediately mounted on the scanning Kelvin probe to avoid any contamination. Further, the fresh alloy surface is prone to oxidation as magnesium alloys are highly active and tend to form an oxide film on the alloy surface. The surface potential measurements were performed on at least 10 different regions on the surface to ensure reproducibility of the results obtained. The selection of the surface area for SKPFM measurements was performed by observing the specimen surface under the optical microscope associated with the scanning Kelvin probe. The microscopic observation enabled the identification of the features in the microstructure, marked previously during metallographic examination in the scanning electron microscope. After recording the surface potential maps, the WSXm software was used to analyze the maps and to reproduce the individual surface potential readings. The average values of the surface potentials calculated from the individual line profiles, for each microconstituent phase, are considered for each alloy surface.

### 5.2.1 AZ31 magnesium alloys

The surface potential maps are obtained from the alloy surfaces, representing the features across the microstructure as shown in the surface analysis. A representative region from the alloy surface of the AZ31 MCTRC magnesium alloy is displayed in the 2D surface potential map (Fig. 5.1 (1)) and 3D surface potential map (Fig. 5.1 (2)), where the higher contrast regions correspond to cathodic sites with relatively positive surface potentials and the darker regions represent the anodic areas with relatively lower surface potentials. The corresponding line profiles recorded from the alloy surface show the relative surface potential differences compared with the adjacent magnesium matrix and are labelled to reveal the typical micro-constituent composition.

Al-Mn intermetallics exhibited an average positive surface potential difference of +95 mV, with the β-phase averaging +75 mV, relative to the adjacent magnesium matrix. Both the Al-Mn intermetallics and the β-phase appear to be cathodic with respect to the magnesium matrix. The regions in the magnesium matrix close to the β-phase show fine peaks, indicating β-precipitation, which reflects a surface potential difference averaging +65 mV.
(line profiles C-D and I-J). From the SEM-EDX results, it is evident that the β-phase shows a higher aluminium content compared with the individual β-precipitates, thereby reflecting the relative surface potential difference between the two intermetallics. The SKPFM results suggest that the individual β-precipitates in the magnesium matrix would behave as sites for microgalvanic corrosion, thereby initiating the corrosion of the magnesium matrix preferentially. From the SKPFM results, it is clear that the nobility of the microconstituents in the microstructure decreases from Al-Mn intermetallics followed by the β-phase and finally the β-precipitates compared with the adjacent magnesium matrix. The relative surface potential values of the microconstituents are presented in Table 5.1 for the AZ31 MCTRC magnesium alloy and, therefore, show the local nobility of the different phases in the microstructure.

The 2D surface potential map (Fig. 5.2. (1)) and 3D surface potential map (Fig. 5.2. (2)) recorded from a representative region on the surface of the AZ31 TRC magnesium alloy reveal the microconstituents with positive surface potentials in high contrast and the magnesium matrix in the darker regions. The random distribution of the β-phase, segregated on the interdendritic boundaries, shows a high positive surface potential difference. The positive surface potential exhibited by the Al-Mn intermetallics, averaging +120 mV, is evident from the high contrast areas; the β-phase averages about +100 mV relative to the adjacent magnesium matrix. However, the α-eutectic showed higher surface potential +75 mV, suggesting aluminium segregation. The line profiles revealed consistency in the surface potential measurements, as presented in Table 5.2.

In comparison with the AZ31 MCTRC alloy, the AZ31 TRC alloy showed significantly higher potential differences across the microstructure due to the non-uniform distribution of the aluminium content in the α-Mg matrix. Due to coarser grain sizes in the AZ31 TRC alloy compared with the AZ31 MCTRC alloy, the depletion in the aluminium contents in the α-Mg grains is higher, which is reflected from the higher surface potential differences. The difference in the surface potentials up to 80 mV within a single phase (α-Mg phase) in AZ91 magnesium alloy was reported by Jonsson et. al., emphasizing on the non-uniform compositional distribution within the phase [243]. Secondly, the β-phase in the AZ31 TRC
magnesium alloy exhibited a higher surface potential compared with the MCTRC processed alloy, suggesting a higher corrosion rate, due to the surface potential difference created between the microconstituents and the adjacent $\alpha$-Mg matrix. In the AZ31 TRC alloy, the positive surface potentials exhibited by the microconstituent phases suggest that the nobility of these phases would be thermodynamically important in deciding the cathodic and anodic behaviours of these phases in the corrosive environments.

### 5.2.2 AZ61 magnesium alloys

Figure 5.3 shows the surface potential maps (2D and 3D) recorded from the alloy surface of the AZ61 MCTRC magnesium alloy, revealing the relative surface potential values of the microconstituent phases in the microstructure. Al-Mn intermetallics exhibited a positive surface potential value of (~190 mV) relative to the adjacent magnesium matrix. The $\beta$-phase exhibited a surface potential difference of +110 mV relative to the adjacent magnesium matrix. It is evident from the surface potential maps that the size and the volume of the $\beta$-phase, distributed in the microstructure is comparatively larger in the AZ61 magnesium alloys than the AZ31 magnesium alloys, due to the increase in the aluminium contents from 3% to 6%Al. The $\alpha$-eutectic phase exhibited a relative surface potential difference of +75 mV compared with the adjacent magnesium matrix. The surface potential measurements represented in Table 5.3 showed consistency across the alloy surface. It is noted that minor variations in the relative surface potential values may be due to the variation in the compositions of the intermetallics [243].

The surface potential maps obtained for the AZ61 TRC magnesium alloy are displayed in Fig. 5.4. Al-Mn intermetallics, with an average size of 500 nm, exhibited a relative surface potential difference of about +165 mV and the Al-Mn intermetallics, of reduced in size ~300 nm, showed a surface potential difference of +140 mV relative to the adjacent magnesium matrix. The $\beta$-phase revealed a surface potential difference of about +125 mV, while the needle shaped $\beta$-precipitates revealed a surface potential difference of +85 mV relative to the magnesium matrix. The average surface potential values represented in Table 5.4 exhibited by the respective microconstituents show consistency across the alloy surface.
From the SKPFM results presented in Tables 5.3 and 5.4, it is clear that the Al-Mn intermetallics in the MCTRC alloy exhibit higher surface potential values ($\Delta V \pm 40 \text{ mV}$) and the $\beta$-phase shows higher surface potential values ($\Delta V \pm 15 \text{ mV}$), relative to the magnesium matrix, in the TRC alloy. The surface potential maps from the TRC alloy reveal broader peaks indicating that the size of the $\beta$-phase is much larger as well as the distribution of the $\beta$-phase is non-uniform in the TRC alloy. The $\alpha$-eutectic phase showed a positive surface potential difference of $+95 \text{ mV}$ relative to the magnesium matrix, probably due to segregation of Al and Zn, mentioned in the microscopic observations in Fig. 4.36.

### 5.2.3 AZ91 magnesium alloys

The AZ91 MCTRC magnesium alloy was characterized by SKPFM, and the surface potential maps are shown in Fig. 5.5. The SKPFM analysis reveals that the Al-Mn intermetallics, usually located on the $\beta$-phase, exhibit a Volta potential difference of $+120 \text{ mV}$, relative to the adjacent magnesium matrix. The $\beta$-phase, relatively thicker than evident from the AZ31 and AZ61 magnesium alloys, revealed a Volta potential difference of about $+95 \text{ mV}$, while the $\beta$-precipitates exhibited a surface potential difference of about $+80 \text{ mV}$ relative to the magnesium matrix. The population density and the size of the $\beta$-precipitates were larger than those evident in AZ31 magnesium alloys. The results show consistency with the microscopic observations performed earlier, and the average surface potential values are displayed in Table 5.5. The surface potential maps indicate a uniform distribution of the $\beta$-phase, suggesting the corrosion barrier effect due to the $\beta$-phase, preferentially consuming the adjacent magnesium matrix.

The surface potential maps from the AZ91 TRC magnesium alloy, shown in Fig. 5.6, reveal that Al-Mn intermetallics exhibited a relative Volta potential difference of about $+150 \text{ mV}$ while the $\beta$-phase displayed a Volta potential difference of about $+100 \text{ mV}$ relative to the adjacent magnesium matrix. The $\alpha$-eutectic exhibited a surface potential difference of $+95 \text{ mV}$ relative to the magnesium matrix, attributed to aluminium.
enrichment. The average surface potential values of the microconstituents are presented in Table 5.6.

5.3 Corrosion of as-cast TRC and MCTRC magnesium alloys

Standards ASTM tests relevant to assess the corrosion performance, were employed; the tests includes (1) G 1-90 - Standard practice for preparing, cleaning, and evaluating corrosion test specimens and (2) G 31-72 - Standard practice for laboratory immersion corrosion testing of metals. The corrosion studies were conducted in 3.5% NaCl solution as well as a lower concentration of 0.005M NaCl solution. Microscopic examination of the corrosion tested specimens was conducted to reveal the corrosion morphologies, corrosion product analysis and the extent of deterioration of the alloy surface. As 3.5% NaCl solution is highly aggressive, the alloy surface is severely attacked within minutes. It becomes increasingly difficult to rectify the initiation sites of the corrosion process due to the heavy deposition of the corrosion product on the alloy surface. Hence, corrosion testing was also conducted in 0.005 M NaCl solution, a relatively low concentration, to reveal the reasons that are responsible for the initiation of the corrosion process.

5.3.1 AZ31 magnesium alloys

Figure 5.7 (A) displays backscattered scanning electron micrographs showing the effect of immersion in 3.5% NaCl solution on the surface microstructure of the as-cast AZ31 MCTRC magnesium alloy, with selected regions preferentially attacked. The high magnification backscattered image shows a representative region on the surface, indicating a filiform-like corrosion morphology, where the α-Mg matrix is preferentially consumed, leaving the β-phase in the interdendritic spaces intact (Fig. 5.7 (B)). The propagation path of the corrosion indicates a progressive attack on the α-Mg matrix, as evident from the micrograph. The β-phase exhibits a barrier effect, limiting the corrosion front within the magnesium matrix, indicated by arrow, evident in Fig. 5.7 (C). The corrosion front is retarded at the grain boundary, showing the α-Mg matrix is preferentially corroded. The backscattered image of Fig. 5.7 (D) presents a corrosion site within the α-eutectic after 4 h
immersion in 0.005M NaCl solution. This indicates localized galvanic corrosion due to Al-Mn intermetallics in the $\alpha$-eutectic, shown by the arrow, and further propagating in the $\alpha$-Mg matrix. From the SKPFM results, it was evident that Al-Mn intermetallics, exhibiting a positive surface potential relative to the magnesium matrix, can act as an individual cathodic site, finally forming a micro-galvanic couple. Evidence of intergranular corrosion is displayed in the backscattered image in Fig. 5.7 (E), showing the corrosion at the grain boundary region, possibly initiating from the galvanic coupling between the $\beta$-phase and the underlying magnesium matrix.

Localized corrosion associated with the iron impurity in the magnesium matrix is displayed in the back scattered image in the Fig. 5.8 (A), showing formation of a spherical corrosion morphology. The galvanic corrosion occurring due to the iron impurity is clearly evident in the image. The spherical corrosion morphology suggests formation of a hydrogen gas bubble at the corrosion site, as hydrogen evolution is usually associated with dissolution of magnesium ions. The hydrogen gas bubble separates the neighbouring alloy surface from the corrosion site, with the Fe-impurity. Hence, the alloy surface inside the bubble is inhibited from corrosion. The preferential dissolution of the $\alpha$-Mg matrix is facilitated due to the pH gradient formed at the interface of the hydrogen gas bubble and the alloy surface, thereby developing a spherical corrosion morphology, with the corrosion product deposited on the interface. The EDS line profile in the SEM-EDX analysis reveals the formation of the corrosion product on the boundary of the spherical corrosion morphology. In situ SVET scans reported by William et. al., showed formation of minute spherical corrosion morphologies, which gradually expand with time and eventually consume the whole metal surface, owing to the intensified anodic activity, i.e. dissolution of magnesium on the alloy surface. [246].

Evidence of localized microgalvanic corrosion within the $\alpha$-Mg matrix, due to an Al-Mn intermetallic particle, is shown in the backscattered image in Fig. 5.8 (B); the presence of the intermetallic particle confirmed from the corresponding EDX results. After 24 h exposure in 3.5% NaCl solution, the corrosion has penetrated to an average corrosion depth of 90 $\mu$m. It is evident from the micrograph that the corrosion front follows a continuous
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path with dissolution of the underlying magnesium matrix shown in Fig. 5.8 (D), revealing that the α-Mg matrix is preferentially attacked and the corrosion front is restricted by the β-phase.

SEM-EDX mapping of the corrosion tested AZ31 MCTRC magnesium alloy is displayed in Fig. 5.8 (E), which shows the localized corrosion due to an Al-Mn intermetallic at the centre of the spherical corrosion morphology, following similar corrosion mechanism as shown in Fig. 5.8 (A). The EDX results reveal individual maps for Mg, Al, Mn, O and Zn, showing the partially protected region surrounding the Al-Mn intermetallic, due to the hydrogen gas bubble formation. The spherical corrosion morphology suggests that the region inside the hydrogen gas bubble is protected from the outer electrolyte hence the region shows inhibition and the corrosion progresses from the periphery of the hydrogen gas bubble, as evident from the EDX mapping results displaying oxide formation in the outer area and the inner area free from any corrosion product.

Backscattered scanning electron micrographs of the corrosion tested AZ31 TRC magnesium alloy displayed in Fig. 5.9, show general corrosion where the magnesium matrix in the individual grains is preferentially attacked and the β-phase remaining intact. The corrosion morphology reveals preferential corrosion occurring in coarser grains, evident from the image. The difference in the corrosion behaviour is observed due to the non-uniform compositional distribution in the magnesium matrix, in the TRC alloys. Also it has been reported that the smaller grains show superior corrosion resistance than the coarser grains in magnesium alloys due to the non-uniform distribution in the coarser grains. Similar corrosion behaviour, due to the difference in the grain sizes, in the AZ91D magnesium alloy, has been reported by Jonsson et. al., showing preferential corrosion in the coarser grains [75]. Coarser grains showing higher depletion of aluminium contents, hence corroding faster than the smaller grains with lesser depletion, corroding later.

Figure 5.9 (B) shows the similar spherical corrosion morphology, observed earlier, in the AZ31 TRC magnesium alloy, due to formation of a hydrogen gas bubble on the alloy surface. The magnesium dissolution is accompanied by hydrogen evolution in the corrosion
process of magnesium from the α-Mg matrix [102, 248]. The hydrogen gas evolution initially forms a gas bubbles on the surface and when the gas bubble persists, it forms two separate regions, namely the region inside the gas bubble inhibited from corrosion and the outer region preferentially corroded, as evident from the image. Such hydrogen gas bubble formation, have been usually observed on the alloy surface, partially protecting the alloy surface till the gas bubble exists. The transverse sections displayed in Figs. 5.9 (C) and (D) represent overall corrosion, when exposed to 0.005M NaCl solution for 4 h, revealing the corrosion front, progressing without any barrier effect due to the β-phase. The penetration of the corrosion front is evident from the transverse section in Fig. 5.9 (E), when the specimens were exposed to 3.5% NaCl solution for 24 h, indicating severe corrosion, due to the higher concentration of the NaCl solution used for immersion tests. The transverse section highlights preferential dissolution of the α-Mg matrix, with the β-phase remaining intact, evident from Fig. 5.9 (F).

5.3.2 AZ61 magnesium alloys

The corrosion tested AZ61 MCTRC magnesium alloy specimens, displayed in the backscattered images in Fig. 5.10, present channel-like spherical corrosion morphologies, preferentially attacking the magnesium matrix. The high magnification image of the spherical corrosion morphology on the surface presented in Fig. 5.10 (A) clearly reveals the corrosion front progressing in a continuous manner, irrespective of the individual grain structure in the form of spherical channel-like structures. The α-Mg matrix is preferentially consumed within the spherical channels, shown by arrows, leaving the β-phase intact, in Fig. 5.10 (B). The corrosion morphology shown in Fig. 5.10 (C) reveals localized corrosion occurring in the magnesium matrix and is confined within the grain, while the corrosion front is prohibited from further propagation by the β-phase. This corrosion morphology indicates that the β-phase acts as barrier and the network of β-phase tends to restrict further progress of corrosion.

Localized galvanic corrosion exhibited due to Al-Mn intermetallic particle, producing a galvanic couple, is shown in Fig. 5.10 (D). The propagation of corrosion resulting in
trenching of the Al-Mn intermetallic is evident in Fig. 5.10 (E) and the EDX analysis is presented in Fig. 5.10 (F). The transverse sections, shown in Figs. 5.10 (G) and (H), reveal the preferential dissolution of the α-Mg matrix and the corrosion front being restricted to 30 µm, by the β-phase, showing a barrier effect. The scanning electron image also indicates that the β-phase tends to remain unaffected, and restricts the corrosion front from progressing further.

From the microstructural investigations performed in Chapter 4, the AZ61 TRC magnesium alloy shows a bimodal microstructure with large primary solidified α-Mg grains and segregation of β-phase. As a result, the corrosion process is highly affected by the random grain size distribution and the distribution of the β-phase in the microstructure. Figure 5.11 (A) displays a representative region revealing the corrosion morphology on the surface, where the corrosion front is restricted by the β-phase, acting as a barrier. The corrosion morphology also indicates that the corrosion progresses by consuming the α-Mg matrix in the individual grains. Evidence of localized corrosion due to the Al-Mn intermetallic, leading to galvanic corrosion, is shown in Fig. 5.11 (B).

A typical example of localized corrosion, occurring at the sub-micron sized β-precipitates located in the primary solidified α-Mg grains in the AZ61 TRC magnesium alloy, is shown in Fig. 5.11 (C), with the corresponding EDX analysis in Fig. 5.11 (F). The β-precipitates initiate the localized corrosion by forming a galvanic couple with the underlying magnesium matrix, shown in Fig. 5.11 (E). Evidence of intergranular corrosion, occurring at the grain boundaries is displayed in Fig. 5.11 (D). The transverse section of the AZ61 TRC magnesium alloy, shown in Figs. 5.11 (G) and (H) indicates overall corrosion, where the corrosion front indicates that the α-Mg matrix is preferentially attacked and the β-phase shows a barrier effect.

5.3.3 AZ91 magnesium alloys

The scanning electron micrographs shown in Fig. 5.12 reveal the corrosion morphologies in the corrosion tested AZ91 MCTRC magnesium alloy. The spherical corrosion morphology as observed in AZ31 and AZ61 magnesium alloys is observed in the AZ91
MCTRC alloy, initiating the corrosion front from the channel-like feature, shown in Fig. 5.12 (A). The corrosion front initiates from the spherical corrosion morphology, in the form of individual filaments, further progressing into the α-Mg matrix. The backscattered image in Fig. 5.12 (B) shows typical filiform-like corrosion morphology, initiating at the α-Mg/α-eutectic interface, following the filiform-like track and further progressing into the α-Mg grains.

The possible reasons for such corrosion morphologies developing on the alloy surface are:

- Al-Mn intermetallics located on the β-phase, forms a galvanic couple with the α-Mg matrix, due to the relative surface potential difference between the Al-Mn intermetallics and the α-Mg matrix, as evident from the SKPFM results.
- The β-precipitates in the α-Mg matrix located close to the α-eutectic, initiate the corrosion front in the form of individual corrosion sites, further resulting in a continuous filiform-like corrosion morphology.

Localized corrosion due to silicon impurity is displayed in Fig. 5.12 (C) and the corresponding EDX analysis in Fig. 5.12 (D). The transverse section in Fig. 5.12 (E) shows overall corrosion leading to the deterioration of the surface with the corrosion depth of 150 µm is shown in Fig. 5.12 (F). The corrosion front shows preferential attack on the magnesium matrix, evident from Fig. 5.12 (G), also revealing the barrier effect of the β-phase.

The corrosion tested specimens of AZ91 TRC magnesium alloy in the backscattered images show localized corrosion, propagating into the α-Mg matrix, as displayed in Figs. 5.13 (A) and (B). Localized galvanic corrosion was associated with the presence of Si-impurity in the magnesium matrix, confirmed by the EDX analysis, shown in Figs. 5.13 (C) and (D). The transverse section reveals the preferential dissolution of the α-Mg matrix with the β-phase acting as a barrier, which is clearly evident from Figs. 5.13 (E) and (F).
5.4 Electrochemical measurements of as-cast TRC and MCTRC magnesium alloys

ASTM G 59-97 standard test procedures relevant to assess the polarization behaviour of TRC and MCTRC magnesium alloys were employed. The electrochemical measurements were conducted in 3.5% NaCl solution in naturally aerated media, initially recording the open circuit potential (OCP) for 1 h, followed by polarization within the potential range of -150 mV to +250 mV, employing a three-electrode set up and a scan rate of 0.3 mV/sec. After the measurements, surface examination was conducted using optical microscopy and SEM. Figure 5.14 displays the potentiodynamic polarization curves obtained from TRC and MCTRC magnesium alloys namely AZ31, AZ61 and AZ91, under similar experimental conditions. The magnesium alloy specimens presented a similar pattern of cathodic polarization behavior, with linear rise in the cathodic current densities, as evident from the polarization curves. On the other hand, the anodic polarization curves do not show apparent passivation and the anodic current densities increase with the applied potentials. Besides the formation of the corrosion product i.e. Mg(OH)$_2$, the chemical dissolution of Mg(OH)$_2$ may have simultaneously taken place when chloride ions were absorbed in the surface film. The $E_{corr}$ and $I_{corr}$ values were determined by the Tafel extrapolation method from the potentiodynamic polarization curves as shown in Fig. 5.14 are presented in Table 5.7. In general, the $E_{pit}$ values were almost identical to the $E_{corr}$ values demonstrated by the AZ series magnesium alloys indicating that the alloy surface is immediately attacked by the chloride ions resulting in pitting. However, eventually, with to magnesium dissolution and, rise in pH values, as expected in the polarization behaviour of magnesium alloys, a stable layer of corrosion product must be formed on the alloy surface, as revealed by the passivation regions of the polarization curves and as expected in the $E$-$pH$ diagram of the Mg-H$_2$O system.

The $E_{ocp}$ values recorded during the polarization measurements, displayed in Fig. 5.15, showed a sharp rise initially and then a very slow increase, which are attributed to the stable growth of a protective surface film. It has been reported that the formation of the metal–hydroxyl–chloride complex compounds, which results in an easier anodic
dissolution of magnesium accompanied by the dissolution of the Mg(OH)_2 films in highly concentrated NaCl solutions [244, 245].

The free corrosion current densities $I_{corr}$, recorded from the polarization curves, indicated that the $I_{corr}$ values can be ranked as TRC alloys > MCTRC alloys. It is well known that the free corrosion current density is correlated with the corrosion resistance of metals. The lower the free corrosion current density, the higher the corrosion resistance and vice versa. The current densities of the cathodic branch and, therefore, the growth of corrosion products on the alloy surface, after microscopic examinations were quite high, suggesting overall corrosion on the surface.

5.5 Corrosion of downstream processed AZ31 magnesium alloys

The metallographic investigations performed in Chapter 4 showed that down stream processing has a profound effect on the microstructure evolution of AZ31 magnesium alloys. The TRC alloy exhibited a complete transformation from a columnar grain structure to a bimodal, equiaxed grain structure with reduced grain size, while the MCTRC alloy revealed a highly refined grain structure with uniform grain size. The influence of downstream processing showed dissolution of the β-phase to a great extent, evident from the metallographic examination, which would further translate into improvement of the corrosion properties of these alloys.

The corrosion tested specimens of the AZ31 TRC magnesium alloy, examined after exposure in 3.5% NaCl solution for 24 h, showed a spherical corrosion morphology with an average diameter of 500 µm, as shown in Fig. 5.16 (A). Localized corrosion sites, showing susceptibility of corrosion due to Al-Mn intermetallics resulting in micro-galvanic corrosion are indicated by the arrow. The high magnification backscattered image reveals the corrosion morphology, showing an outer, concentric channel-like formation, followed by the corrosion front propagating inside the spherical structure in Fig. 5.16 (B). The surface deterioration is evident from the channel-like structures and is not confined within individual or specific grains. The filiform-like corrosion morphology shown in Fig. 5.16
(C) reveals general corrosion across the alloy surface. Figure 5.16 (D) presents the backscattered image, revealing the corrosion front leading to preferential dissolution of the magnesium matrix, with an average corrosion penetration depth of ~100 µm. The spherical corrosion morphologies in the AZ31 MCTRC magnesium alloy, shown in Fig. 5.17 (A), present a similar corrosion mechanism to the TRC alloy. The corrosion front was observed to follow similar filiform-like corrosion across the alloy surface. The transverse section revealed overall corrosion, with the corrosion depth of ~50-70 µm. The corrosion depth indicates an improved corrosion resistance to that of the TRC alloy.

5.6 Electrochemical measurements of downstream processed AZ31 magnesium alloys

The polarization curves recorded from the downstream processed AZ31 magnesium alloys displayed in Fig. 5.18 (A), showed a shift in the anodic corrosion densities, compared with the as-cast AZ31 magnesium alloys, shown in Fig. 5.18 (B). The $E_{corr}$ and $I_{corr}$ values determined from the electrochemical measurements are presented in Table 5.8. The downstream processed AZ31 magnesium alloys revealed a shift in the corrosion potential $E_{corr}$ towards more noble values, and the improved corrosion current densities $I_{corr}$ were approximately one order of magnitude lower than the $I_{corr}$ values recorded for the as-cast AZ31 magnesium alloys. This shift in the corrosion densities indicates improved passivation of the alloy surfaces due to the grain refinement in the downstream processed AZ31 magnesium alloys. The improvement in the corrosion resistance can also be attributed to the reduced amount of the β-phase in the downstream processed AZ31 magnesium alloys, further reducing the susceptibility to galvanic corrosion. However, no significant improvement in the cathodic corrosion densities was observed, indicating susceptibility to galvanic corrosion due to presence of Al-Mn intermetallics, leading to the deterioration of the alloy surface, reflected from the immersion tested specimens.
5.7 Discussion

From the microscopic examination results, it is clear that the magnesium alloys were characterized by three main constituents in the microstructure, namely, the \( \alpha \)-Mg phase, the \( \alpha \)-eutectic phase and the \( \beta \)-phase. The distribution of the aluminium content within the three constituents increases from \( \alpha \)-Mg phase (2%) > \( \alpha \)-eutectic phase > \( \beta \)-phase (24%), as evident from the SEM-EDX results, mentioned in Chapter 4. The distribution of the alloying elements in the microstructure also depends on the casting process and the solidification associated as the resultant grain size distribution affects the corrosion behaviour of the alloy microstructure [67]. From the microstructure investigations performed in Chapter 4, it is clear that the TRC alloys show a coarser microstructure and random distribution of grain sizes across the sheet thickness. However, by applying the MCAST process, due to the intensive shearing of the liquid melt, the resultant microstructure shows a high degree of grain refinement and uniform grain size distribution across the sheet thickness. At the same time, due to the finer grain sizes in the MCTRC alloys, the uniform distribution of the alloying elements is attained, evident from the SKPFM results, suggesting an improvement in their corrosion behaviour.

The grain size, the depletion in distribution of aluminium content within the \( \alpha \)-Mg phase, the size and spatial distribution of the \( \beta \)-phase, makes the alloy surface electrochemically heterogeneous. The coarser \( \alpha \)-Mg grains in the TRC magnesium alloys show a larger depletion in the distribution of the aluminium contents from the centre of the grains to the grain boundaries, due to the random grain size distribution while the MCTRC magnesium alloys, with refined grain sizes, show reduced effect due to the distribution of aluminium content. As the aluminium content increases from the centre of the grains to the grain boundaries, the \( \alpha \)-Mg phase becomes anodic and the rate of corrosion increases, due to micro-galvanic effects [110]. However, as reported by Song et. al., the corrosion resistance in magnesium alloys increases with the increased amount of the \( \beta \)-phase, as the \( \beta \)-phase behaves as a corrosion barrier, instead of showing the microgalvanic effect occurring between the \( \alpha \)-Mg phase and the \( \beta \)-phases [81, 108, 232]. Abady et. al., reported that magnesium alloys ranging from Mg-5%Al to Mg-15%Al, showed relatively lower
corrosion rates in the range of neutral and high pH solutions. This can be explained by the formation of a barrier layer of Mg(OH)$_2$, which is insoluble in basic solutions [56]. In the acidic pH solutions, the barrier layer is completely soluble, showing relatively higher corrosion rates, while in neutral pH solutions, the barrier Mg(OH)$_2$ layer is partially soluble and, hence, a decrease in the corrosion rate was recorded.

The effect of aluminium on the corrosion behaviour of magnesium can be clearly understood by comparing the potential–pH diagram of Mg and Mg–Al presented in Chapter 2 (Figs. 2.19 (A) and (B)) [212]. According to the potential-pH diagrams, magnesium corrodes in aqueous solutions, forming a film of Mg(OH)$_2$ on the surface. However, this Mg(OH)$_2$ film is soluble in acidic media (low pH solutions) leading to higher corrosion rates. In basic solutions, the Mg(OH)$_2$ film formed on the metal surface, is insoluble and passive, which inhibits the corrosion process, resulting in reduced corrosion rates.

The corrosion behaviour of the material also depends on the behaviour of the microconstituents to the corrosive media, giving rise to different corrosion mechanisms. The resultant corrosion behaviour of the magnesium alloys can also be attributed to the processing routes, namely TRC and MCTRC, in the current research. The metallographic examination and the corrosion studies show a considerable influence of the casting processes on the microstructural heterogeneity, especially the size and the spatial distribution, volume fraction and the nature of the β-phase on the corrosion behaviour of the magnesium alloys. A detailed discussion of the results now follows.

### 5.7.1 Influence of microstructure on the corrosion behaviour

Rapid solidification processes can refine the microstructure to improve the corrosion properties of materials. The relationship between corrosion behaviour and microstructure of Mg-Zn-Y alloys produced by rapid solidification method at various cooling rates was reported by Izumi et. al. [233]. It shows that variation in the cooling rate has a strong influence on the corrosion behaviour of Mg-Zn-Y alloys. An increase in the cooling rate,
resulting in the grain refinement and formation of a supersaturated single $\alpha$-Mg phase solid solution in the magnesium alloys, delays the occurrence of filiform-like corrosion. Moreover, by rapid solidification, the mechanism of corrosion can be changed essentially from pitting corrosion of Mg-Al magnesium alloys to overall corrosion [234].

The corrosion studies conducted on slowly solidified die-cast AZ91D in 1N NaCl at pH 11, by Song et. al., show that the skin of the die cast AZ91D magnesium alloy exhibits better corrosion resistance than the interior, due to larger volume of the $\beta$-phase on the surface [88]. This is attributed to a combination of the following: a higher volume fraction of the $\beta$-phase, continuous distribution of the $\beta$-phase distribution and lower porosity in the skin layer than in the interior of the die cast AZ91D magnesium alloy.

As evident from the microstructure investigations in Chapter 4, the influence of the MCAST process on the resultant microstructure of the MCTRC magnesium alloys showed a high degree of grain refinement and uniform distribution of grain sizes across the microstructure. However, the conventional twin roll casting produces a random microstructure, characterized by a fine grain structure in the chill zones, followed by coarse columnar grain structure toward the centre of the sheet thickness and an equiaxed grain structure at the centre along with macro centre-line segregation. Pertaining to the microstructure investigation results, it is important to understand the influence of these microstructures on the corrosion behaviour of magnesium alloys. The influence of the casting processes on the constituent phases has been addressed in Chapter 4 and the key points related to the corrosion behaviour are now considered below.

The grain size refinement from 520 $\mu$m in the TRC alloy to 72 $\mu$m in the MCTRC alloy of the AZ31 magnesium alloys, and a grain size reduction from 302 $\mu$m in the TRC alloy specimens to 69 $\mu$m in the MCTRC alloy, in the AZ91 magnesium alloys were observed. The influence of the intensive shearing of the liquid melt in the MCAST process, prior to solidification in the MCTRC magnesium alloys accounts for the grain size refinement. As it is evident that the reduction in grain size has a direct influence on the corrosion behaviour of magnesium alloys, the MCTRC magnesium alloys are expected to show an
improved corrosion resistance. The TRC magnesium alloys showed a bimodal microstructure, with random distribution of grain sizes, evident from Figs. 4.1, 4.7 and 4.12. The coarser grains in the TRC magnesium alloys showed higher susceptibility to corrosion, hence corroded faster, while the smaller grains exhibited higher corrosion resistance.

Graph 1 (Pg. 234) presents the average thickness loss of the specimen surface of the TRC and MCTRC processed magnesium alloys revealing the fact that the TRC alloys showed a greater thickness loss as compared with the MCTRC alloys. At the same time, as the aluminium content in the magnesium alloys increases from 3% to 9%, the corrosion resistance significantly improved indicating that the gradual increase in the aluminium content further increased the corrosion resistance of the magnesium alloys. To conclude, the MCTRC magnesium alloys with higher aluminium contents showed improvement in the corrosion resistance compared with the TRC magnesium alloys with lower aluminium content.

The SKPFM results also revealed that the surface potential values across the coarser grains in the TRC magnesium alloys showed a higher Volta potential difference; indicating the heterogeneous distribution of aluminium content which, in turn, resulted in the lower corrosion resistance of the coarser grains. This effect was clearly noticed in the microscopic examinations of the immersion tested specimens of the TRC magnesium alloys, showing preferential corrosion in coarser grains, where the $\alpha$-Mg matrix was completely consumed. However, the $\beta$-phase remained unaffected, showing a barrier effect on the corrosion process. The MCTRC alloys revealed an overall corrosion tendency, where the magnesium matrix in the $\alpha$-Mg grains was preferentially consumed, leaving the $\beta$-phase intact.

Segregation of aluminium and zinc, observed in the TRC magnesium alloys, due to non-uniform distribution of the alloying elements, resulted in the increased surface potential differences between the secondary phases and the magnesium matrix, thereby producing active sites for galvanic corrosion. Segregation of the Al-Mn intermetallics located on the
β-phase, in TRC magnesium alloy specimens, resulted in the formation of localized sites for galvanic corrosion. The SKPFM results reveal that the Al-Mn intermetallics are comparatively nobler than the adjacent magnesium matrix, suggesting increased susceptibility to galvanic corrosion. Hence, the Al-Mn intermetallics show an increased detrimental effect on the alloy surface, when exposed to the corrosive media. The AZ61 TRC magnesium alloy typically revealed large primary solidified α-Mg grains with sub-micron sized β-precipitates, revealing localized corrosion, occurring at the α-Mg/β interface, as evident from Fig. 5.11 (C), leading to the deterioration of the alloy surface.

As the breakdown of the passive film of the alloy surface leads to the initiation of corrosion in magnesium alloys, in the TRC magnesium alloys, possibly, the preferential breakdown of the passive film, due to the segregated Al-Mn intermetallics, may initiate the corrosion process at localized sites, which further results in the aggressive corrosion occurring in the coarser α-Mg grains. However, in the MCTRC magnesium alloys, due to the refined grain size, uniform compositional distribution and reduced microsegregation, the α-Mg grains possibly show enhanced passivity by the surface film, resulting in the higher corrosion resistance, as evident from the corrosion testing experiments. However, the breakdown of the passive film occurs due to Al-Mn intermetallics or Fe, Si impurities at localized sites, leading the corrosion process across the alloy surface.

The effect of the MCAST process on the MCTRC magnesium alloys is the formation of a highly refined network of the β-phase, which acts as a barrier to restrict further corrosion, as observed from the transverse sections of MCTRC magnesium alloys. As reported by Song et. al., the uniform distribution of the β-phase, results in the improved corrosion resistance of the skin of die-cast AZ91 magnesium alloy [67]. The MCAST process ensures the uniform distribution of the β-phase in the form of a network structure, resulting in the β-phase exhibiting a corrosion barrier effect. Jonsson et. al. and Andreatta et. al., reported that the β-phase and the Al₈Mn₅ phase both operate as local cathodes when coupled to the α-Mg phase under atmospheric weather conditions [213, 243]. As the surface coverage of the β-phase (40%) is much higher than that of the Al–Mn phases (1%), the β-phase
consequently showed corrosion barrier effect at the grain boundaries rather than initiating the corrosion process [54].

The as-cast magnesium alloys showed a filiform-like corrosion morphology observed in the form of spherical, channel-like or individual filaments, initiating at the interface of the magnesium matrix and the secondary phases present in the microstructure, due to their surface potential difference. Fundamentally, hydrogen evolution, occurring in the cathodic reaction, followed by the anodic polarization, results in the initiation of the filiform corrosion. Therefore, the filiform-like corrosion, which initiates at the $\alpha$-Mg/$\beta$, the $\alpha$-Mg/$\alpha$-eutectic or the $\alpha$-Mg/Al-Mn interfaces, further proceeds to the interior of the $\alpha$-Mg grains. The $\beta$-phase remains unaffected as observed from the corrosion experiments.

5.7.2 Influence of microconstituents on the corrosion behaviour

It has been reported that aluminium in single-phase Mg–Al alloys has a beneficial effect on the corrosion behaviour in chloride media [64, 72, 239]. However, the influence of aluminium in two-phase Mg–Al alloys is still not well understood since it depends on many factors, including the morphology and distribution of the $\beta$-phase, the grain size, the $\alpha$-eutectic, intermetallic phases and impurities like iron, silicon, etc. [238]. As a result, galvanic interactions between magnesium and other metals are a serious concern. Thus, the corrosion resistance of the Mg–Al alloys depends on the alloying elements resulting in active cathodes, including, iron, silicon, etc., where the iron-rich and Al-Mn phases form some of the most detrimental potential cathodes [78].

The corrosion studies in the current research have shown that the $\beta$-phase and the Al-Mn intermetallic particles have been crucial in determining the corrosion behaviour of the AZ series magnesium alloys. According to the SKPFM analysis, the Al-Mn intermetallics exhibit a positive surface potential relative to the magnesium matrix and result in the formation of galvanic sites for the initiation of the corrosion process, evident in Figs. 5.8 (B), 5.8 (E). The TEM studies have revealed that Al-Mn intermetallics are randomly distributed in the AZ31 magnesium alloys, and, since they are potential cathodic sites,
resulted in microgalvanic corrosion, evident from Figs. 5.7 (C), 5.8 (C) and 5.8 (E). However, in the AZ61 and AZ91 magnesium alloys, as they are usually located on the β-phase; the reduced galvanic effect on the corrosion behaviour was observed, when exposed to corrosive media. As the TRC magnesium alloys show random compositional distribution, segregation of the Al-Mn intermetallics has been noticed resulting in aggressive corrosion in the segregated areas while in the MCTRC magnesium alloys due to uniform compositional distribution, the increased corrosion resistance of the alloy surface was observed. The microscopic examinations conducted after the immersion testing revealed that the trace amounts of impurities including iron and silicon showed evidence of galvanic corrosion occurring at localized sites (Fig. 5.8 (A)), resulting in the breakdown of the partially protective film on the alloy surface.

Previous investigations reported that distribution of the β-phase determines the corrosion resistance of the Mg–Al alloys [54, 69, 78, 81, 110, 235, 240]. Song et. al., [67] have reported two different corrosion behaviours associated with the β-phase, where lower volume fractions of the β-phase exhibiting a galvanic effect, resulting in accelerating the corrosion process in the α-Mg phase, a corrosion behaviour of the β-phase as a galvanic cathode. In case of large volume fractions of the β-phase, a corrosion barrier effect is observed, where the overall corrosion diminishes [108, 236]. The corrosion studies in the current research showed that the volume fraction of the β-phase gradually increases from AZ31 to AZ91 magnesium alloys, evident from the microstructure characterization results. The corrosion behaviour of the β-phase essentially showed a galvanic effect in AZ31 magnesium alloys (Figs. 5.8(D) and 5.9 (D)) while a corrosion barrier effect was observed in the AZ61 magnesium alloy, evident from Figs. 5.10 (G) and 5.11 (G). Similar corrosion barrier effect was observed in the AZ91 magnesium alloys (Figs. 5.12 (G), 5.13 (E)), restricting the corrosion front. The random distribution of the β-phase in the TRC magnesium alloys resulted in segregation defects leading to reduced corrosion resistance compared with the MCTRC magnesium alloys, due to reduced segregation owing to the uniform distribution of β-phase.
From the SKPFM results, the anodic and cathodic behaviour of microconstituents, namely, the Al-Mn intermetallics and the impurities including iron, silicon, etc., in the magnesium matrix was distinguished on immersion in corrosive media. These microconstituents formed galvanic couples at the Al-Mn/α-Mg and the impurity/α-Mg interfaces, resulting in micro-galvanic corrosion, evident from Figs 5.8 (A), 5.10 (D) and 5.13 (C). The galvanic corrosion process, initiated at localized sites, eventually progressed, consuming the α-Mg matrix in the grains, evident from the immersion tests. Accordingly, the schematic representation of the corrosion mechanism associated with the microconstituents has been displayed in Fig. 5.21, presenting the initiation and propagation of the corrosion process.

5.8 Corrosion mechanism

When pure magnesium is exposed to the atmosphere or aqueous solutions, a grey oxide (mainly magnesium hydroxide, brucite) forms on the surface, which is stable for a wide range of pH values [241]. Nevertheless, in presence of chloride anions, this surface film breaks down and magnesium appears unprotected. This eventually creates surface areas protected with the passive film and film-free areas, also reported by Song et. al. [67].

It is generally reported that the corrosion of magnesium occurs by anodic and cathodic reactions in aqueous environments, as explained: Firstly, the magnesium on the surface dissolves, producing Mg\(^{2+}\) (aq) cations (Eq. (1)), possibly through intermediate steps involving monovalent magnesium ion [72, 242]. Secondly, magnesium dissolution is accompanied by hydrogen evolution (Eq. (2)), since magnesium in neutral and low pH aqueous solutions is well below the region of water stability.

\[
\begin{align*}
\text{Mg (s)} & \rightarrow \text{Mg}^{2+} \text{ (aq) + 2} \bar{\epsilon} \text{ (anodic reaction)} \\
2\text{H}_2\text{O} + 2\bar{\epsilon} & \rightarrow \text{H}_2 + 2\text{OH}^{-} \text{ (aq) (cathodic reaction)} \\
\text{Mg}^{2+} \text{ (aq) + 2OH}^{-} \text{ (aq)} & \rightarrow \text{Mg(OH)}_2 \text{ (s) (product formation)}
\end{align*}
\]

Finally, the pH increases, due to the formation of OH\(^{-}\), which favours the formation of Mg(OH)\(_2\)(s), according to Pourbaix diagram [212].
The corrosion and the electrochemical behaviour of AZ series magnesium alloys is significantly influenced by the microstructure, as well as factors including pH and chloride ion concentration; it is understood to be also governed by the characteristics of its surface film [67, 76, 81, 102, 108, 120]. The surface film on magnesium alloys in aqueous solutions is thought to be mainly Mg(OH)$_2$ [67, 76, 87]. The corrosion mechanism of magnesium alloys in aqueous environments generally proceeds by the electrochemical reaction with water to produce hydrogen gas and magnesium hydroxide. Magnesium dissolution takes place immediately after immersion in the solution \( \text{Eq. (1)} \). Hydrogen evolution is associated with magnesium dissolution \( \text{Eq. (2)} \). The pH increases due to production of OH$^-$ ions, which favours the formation of magnesium hydroxide film by the precipitation reaction \( \text{Eq. (3)} \).

The influence of pH during the corrosion process needs to be taken into account, as shown in the magnesium E-pH diagram (Pourbaix diagram) [212]. It can be predicted from the thermodynamics and the E-pH diagram that there is no film on a magnesium surface in a solution with a pH lower than 10.5 because Mg(OH)$_2$ is not stable under such conditions, as the pH value required for the formation of Mg(OH)$_2$ is ~10.5. However, even though the surface film is not thermodynamically stable at low pH values, the dissolution kinetics may be slow and a surface film may be formed, provided the dissolution kinetics is slower than the formation kinetics.

It has been reported that the alloying effect of aluminium, results in the formation of Al$_2$O$_3$·3H$_2$O film, on the alloy surface at pH$\geq$4, leading to the inhibition of the corrosion process and stabilizing the Mg(OH)$_2$ layer. At pH range 8–12, the formation of the magnesium aluminate layer, blocks the active sites present in the Mg(OH)$_2$ protective layer. It should be noted that the formation of second phases, due to the alloying of aluminium in the microstructure, leads to the stabilization of the protective layer on the alloy surface and increases the corrosion resistance in magnesium alloys [58, 111, 117].
Further, a pH value of 8.7 was theoretically calculated and experimentally measured in the electrolyte layer near a corroding magnesium electrode, even though the bulk solution had a pH value as low as 5.6, i.e. there is significant alkalization near the magnesium surface in an acidic medium and this alkalization is associated with the formation of surface film, consistent with \{Eq. (2)\} [71]. Such corrosion behaviour is possibly governed by a partially protective surface film in magnesium alloys [67, 76, 81, 102, 108, 120], with the corrosion reactions occurring predominantly at the breaks or imperfections of the partially protective film.

As the magnesium alloy specimens were immersed in the 3.5% NaCl solution, magnesium dissolution initiated along with the hydrogen evolution, evident from visual observation. Increased hydrogen evolution was noticed at localized sites, namely, the impurities (Fe, Si) and the Al-Mn intermetallics, which are cathodic, evident from the SKPFM results, initiating galvanic coupling. The galvanic corrosion at localized sites, suggest that the breakdown of the protective surface film must occur and further magnesium dissolution takes place. As the formation and stability of the corrosion product also determines the extent of corrosion, evidences of a continuous and compact corrosion product layer, preventing fresh alloy surface being exposed and retarding the corrosion process, has been reported. Apart from the microstructure, the composition of the corrosion layer itself, may also improve the corrosion resistance of the magnesium alloys. For instance, Nordlien et. al. [237] reported that the alumina components form a continuous skeletal structure in the oxide layer on the surface of the magnesium alloy, with passivating properties much better than Mg(OH)$_2$ and MgO layers.

The OH$^-$ ions generated from the cathodic reaction increase the local pH, favouring the formation of Mg(OH)$_2$, in areas adjacent to the micro-constituents. In the case of MCTRC magnesium alloys, as the β-phase forms a network structure, it is evident from the corrosion tested specimens that the β-phase restricts the corrosion front, thus retarding the corrosion process, evident from the microscopic investigations.
The surface potential determines the localized nobility of the microconstituents and the susceptibility to galvanic corrosion depends on the relative surface potential difference between the microconstituents and the α-Mg matrix. Higher the relative surface potential difference of the microconstituent, higher is the susceptibility to galvanic corrosion. The microconstituents present in the microstructure of the magnesium alloys studied revealed that the localized nobility relative to the α-Mg matrix, decreased from \( \text{Al}_8\text{Mn}_5 \) > \( \beta \)-phase > \( \beta \)-precipitates > α-eutectic

Metallographic examinations of the immersion tested alloy specimens revealed the morphology of the corrosion products, as shown in the schematic in Fig. 5.19. As the magnesium alloys only differed in their aluminium contents namely, AZ31, AZ61 and AZ91, the XRD analysis shown in Fig. 5.20, mainly revealed two corrosion products, namely:

1. \( \text{Mg}_6\text{Al}_2(\text{OH})_{18}.4.5\text{H}_2\text{O} \) (magnesium aluminium hydroxide hydrate)
2. \( \text{Mg(OH)}_2 \) (brucite, syn)

For the TRC magnesium alloy specimens that attained steady state corrosion conditions, the cathodic reaction, also assumed to be hydrogen evolution, occurs on the corroding surface, possibly on the surface of corrosion products, i.e. \( \text{Mg(OH)}_2 \). Hydrogen evolution is much faster on the surface after steady state corrosion has been attained. This means that, if a corroding area (coarser grains) is adjacent to a non-corroded area (smaller grains), a galvanic cell formation occurs, causing the galvanic acceleration of the corrosion rate of the non-corroded area, finally consuming the α-Mg matrix. The corrosion across the surface of the TRC magnesium alloys in the current study was similar to that observed in case of the MEZ alloy, by Song et. al. [69].

Figure 5.21 (I) shows the corrosion morphology across the alloy surface, indicating localized galvanic corrosion, occurring due to the Al-Mn intermetallics, Fe/Si impurities and the \( \beta \)-precipitates in the magnesium matrix. These localized corrosion sites are responsible for the initial breakdown of the passive film, protecting the alloy surface, finally consuming the α-Mg matrix. The spherical corrosion morphology, at the localized
corrosion sites, shown in Fig. 5.21 (II), surrounding the Al-Mn intermetallics, Fe/Si impurities or on the alloy surface in general, can be explained according to the following mechanism. Initially, as the alloy specimens are immersed in the 3.5% NaCl solution, magnesium dissolution starts accompanied by hydrogen evolution. The hydrogen evolution occurs in the form of bubbles and in some cases the hydrogen gas bubble persists on the alloy surface. The hydrogen gas bubble formation on the alloy surface separates the inner region of the bubble from the outer region, thereby inhibiting the corrosion process inside the gas bubble. The corrosion product formation on the periphery of the gas bubble indicates that the corrosion initiates and progresses from the periphery of the gas bubble, evident from Figs. 5.8 (A), 5.8 (E), 5.9 (B) and 5.12 (A). The EDX mapping results revealed similar corrosion morphology, showing corrosion product formation on the periphery of the spherical corrosion morphology indicating the inner alloy surface to be protected by the thin oxide film. The schematic of the corrosion morphology, shown in Fig. 5.21 (II) reveals the surface view with the corrosion product outside the spherical morphology while the inner alloy surface protected by the oxide film.
5.9 Summary

- Due to the non-uniform distribution of random grain sizes and the microsegregations of aluminium and zinc, leading to the depletion in the aluminium contents, resulted in the deterioration of the alloy surfaces in the TRC magnesium alloys. However, the MCTRC magnesium alloys, characterized by highly refined grain structure with uniform grain size and uniform distribution of the β-phase, resulted in improvement of the corrosion resistance.

- The transverse section microstructure revealed that the corrosion front was restricted by the β-phase showing preferential dissolution of the magnesium matrix. Deterioration of the alloy surface was mainly due to galvanic corrosion at localized sites at the Al-Mn/α-Mg and impurities/α-Mg interfaces.

- Downstream processing showed a significant influence on the grain size refinement and reduction in the second phases, in turn, improving the corrosion resistance of the magnesium alloys.

- The SKPFM analysis reveals that the microconstituent distribution and the cathodic activity of the Al-Mn intermetallic particles and impurities including Fe and Si, determine the corrosion tendency of the respective magnesium alloys. Volta potential differences show a profound effect on the susceptibility to microgalvanic corrosion in the order of $\text{Al}_8\text{Mn}_5 > \beta$-phase > β-precipitates > α-eutectic, relative to the adjacent magnesium matrix.

- Localized corrosion initiating from microgalvanic coupling has been observed due to the Al-Mn intermetallics and impurities including iron and silicon. Filiform-like corrosion showing spherical, channel-like and individual filaments were some of the main corrosion morphologies observed in the magnesium alloys, resulting from galvanic corrosion mechanisms.

- The polarization curves revealed no passivation effect, suggesting that the alloy surface must be continuously attacked, suggesting localized corrosion occurring due to Al-Mn intermetallics and Fe/Si impurities, in the as-cast magnesium alloys. However, slight improvement in the anodic polarization behaviour of downstream processed AZ31 magnesium alloys has been observed attributed to the grain refinement.
Table 5.1 Surface potentials of micro-constituents in AZ31 MCTRC magnesium alloy

<table>
<thead>
<tr>
<th>Line Profile</th>
<th>Peak 1 ΔV (mV)</th>
<th>Peak 2 ΔV (mV)</th>
<th>Micro-constituent</th>
<th>ΔV (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B</td>
<td>95 ± 5</td>
<td>75 ± 5</td>
<td>Al-Mn phase</td>
<td>95 ± 10</td>
</tr>
<tr>
<td>C-D</td>
<td>65 ± 5</td>
<td>75 ± 5</td>
<td>β-phase</td>
<td>75 ± 5</td>
</tr>
<tr>
<td>E-F</td>
<td>90 ± 5</td>
<td>55 ± 5</td>
<td>β-precipitates</td>
<td>60 ± 10</td>
</tr>
<tr>
<td>G-H</td>
<td>85 ± 5</td>
<td>75 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-J</td>
<td>55 ± 5</td>
<td>75 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-L</td>
<td>80 ± 5</td>
<td>95 ± 5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2 Surface potentials of micro-constituents in AZ31 TRC magnesium alloy

<table>
<thead>
<tr>
<th>Line Profile</th>
<th>Peak 1 ΔV (mV)</th>
<th>Peak 2 ΔV (mV)</th>
<th>Peak 3 ΔV (mV)</th>
<th>Micro-constituent</th>
<th>ΔV (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B</td>
<td>95 +/- .5</td>
<td>55 ± 5</td>
<td></td>
<td>Al-Mn phase</td>
<td>120 ± 5</td>
</tr>
<tr>
<td>C-D</td>
<td>65 +/- .5</td>
<td>45 ± 5</td>
<td>75 ± 5</td>
<td>β-phase</td>
<td>100 ± 5</td>
</tr>
<tr>
<td>E-F</td>
<td>60 +/- .5</td>
<td>100 ± 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-H</td>
<td>100 +/- .5</td>
<td>120 ± 5</td>
<td></td>
<td>α-eutectic (&gt;Al)</td>
<td>75 ± 5</td>
</tr>
<tr>
<td>I-J</td>
<td>80 +/- .5</td>
<td>75 ± 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-L</td>
<td>100 +/- .5</td>
<td>115 ± 5</td>
<td>70 ± 5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3 Surface potentials of micro-constituents in AZ61 MCTRC magnesium alloy

<table>
<thead>
<tr>
<th>Line Profile</th>
<th>Peak 1 ΔV (mV)</th>
<th>Peak 2 ΔV (mV)</th>
<th>Peak 3 ΔV (mV)</th>
<th>Micro-constituent</th>
<th>ΔV (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B</td>
<td>90 ± 5</td>
<td>100 ± 5</td>
<td></td>
<td>Al-Mn (~500 µm)</td>
<td>210 ± 5</td>
</tr>
<tr>
<td>C-D</td>
<td>120 ± 5</td>
<td>110 ± 5</td>
<td></td>
<td>Al-Mn (~100 µm)</td>
<td>170 ± 5</td>
</tr>
<tr>
<td>E-F</td>
<td>55 ± 5</td>
<td>65 ± 5</td>
<td>45 ± 5</td>
<td>β-phase</td>
<td>110 ± 10</td>
</tr>
<tr>
<td>G-H</td>
<td>100 ± 5</td>
<td>45 ± 5</td>
<td></td>
<td>α-eutectic (&gt;Al)</td>
<td>75 ± 10</td>
</tr>
<tr>
<td>I-J</td>
<td>210 ± 5</td>
<td>170 ± 5</td>
<td>80 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-L</td>
<td>100 ± 5</td>
<td>70 ± 5</td>
<td>75 ± 5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4 Surface potentials of micro-constituents in AZ61 TRC magnesium alloy

<table>
<thead>
<tr>
<th>Line Profile</th>
<th>Peak 1 ΔV (mV)</th>
<th>Peak 2 ΔV (mV)</th>
<th>Micro-constituent</th>
<th>ΔV (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B</td>
<td>165 ± 10</td>
<td></td>
<td>Al-Mn (~500 µm)</td>
<td>165 ± 10</td>
</tr>
<tr>
<td>C-D</td>
<td>95 ± 5</td>
<td>85 ± 5</td>
<td>Al-Mn (~100 µm)</td>
<td>140 ± 5</td>
</tr>
<tr>
<td>E-F</td>
<td>75 ± 5</td>
<td>80 ± 5</td>
<td>β-phase</td>
<td>125 ± 10</td>
</tr>
<tr>
<td>G-H</td>
<td>110 ± 5</td>
<td>125 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-J</td>
<td>120 ± 5</td>
<td></td>
<td>B-precipitates</td>
<td>85 ± 10</td>
</tr>
<tr>
<td>K-L</td>
<td>140 ± 10</td>
<td>160 ± 5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.5 Surface potentials of micro-constituents in AZ91 MCTRC magnesium alloy

<table>
<thead>
<tr>
<th>Line Profile</th>
<th>Peak 1 $\Delta V$ (mV)</th>
<th>Peak 2 $\Delta V$ (mV)</th>
<th>Micro-constituent</th>
<th>$\Delta V$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B</td>
<td>110 ± 5</td>
<td>85 ± 5</td>
<td>Al-Mn phase</td>
<td>120 ± 10</td>
</tr>
<tr>
<td>C-D</td>
<td>65 ± 5</td>
<td></td>
<td>$\beta$-phase</td>
<td>95 ± 10</td>
</tr>
<tr>
<td>E-F</td>
<td>100 ± 5</td>
<td>120 ± 5</td>
<td>$\beta$-precipitates</td>
<td>80 ± 5</td>
</tr>
<tr>
<td>G-H</td>
<td>85 ± 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-J</td>
<td>80 ± 5</td>
<td>110 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-L</td>
<td>120 ± 5</td>
<td>110 ± 5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.6 Surface potentials of micro-constituents in AZ91 TRC magnesium alloy

<table>
<thead>
<tr>
<th>Line Profile</th>
<th>Peak 1 $\Delta V$ (mV)</th>
<th>Peak 2 $\Delta V$ (mV)</th>
<th>Micro-constituent</th>
<th>$\Delta V$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-B</td>
<td>110 ± 10</td>
<td></td>
<td>Al-Mn phase</td>
<td>150 ± 10</td>
</tr>
<tr>
<td>C-D</td>
<td>110 ± 10</td>
<td>80 ± 5</td>
<td>$\beta$-phase</td>
<td>110 ± 10</td>
</tr>
<tr>
<td>E-F</td>
<td>110 ± 10</td>
<td></td>
<td>$\alpha$-eutectic (&gt;Al)</td>
<td>95 ± 10</td>
</tr>
<tr>
<td>G-H</td>
<td>80 ± 5</td>
<td>110 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-J</td>
<td>110 ± 10</td>
<td>150 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-L</td>
<td>95 ± 10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.7 Electrochemical response of as-cast TRC and MCTRC magnesium alloys in 3.5% NaCl solution

<table>
<thead>
<tr>
<th>Material</th>
<th>$I_{corr}$ (A/cm$^2$)</th>
<th>$E_{corr}$ (V$_{SCE}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31 TRC</td>
<td>2.6 x 10^{-5}</td>
<td>-1.545</td>
</tr>
<tr>
<td>AZ31 MCTRC</td>
<td>9.8 x 10^{-4}</td>
<td>-1.560</td>
</tr>
<tr>
<td>AZ61 TRC</td>
<td>8.3 x 10^{-4}</td>
<td>-1.551</td>
</tr>
<tr>
<td>AZ61 MCTRC</td>
<td>9.4 x 10^{-4}</td>
<td>-1.548</td>
</tr>
<tr>
<td>AZ91 TRC</td>
<td>7.9 x 10^{-4}</td>
<td>-1.550</td>
</tr>
<tr>
<td>AZ91 MCTRC</td>
<td>2.2 x 10^{-5}</td>
<td>-1.530</td>
</tr>
</tbody>
</table>

Table 5.8 Electrochemical response of down stream processed TRC and MCTRC AZ31 magnesium alloys in 3.5% NaCl solution

<table>
<thead>
<tr>
<th>Material</th>
<th>$I_{corr}$ (A/cm$^2$)</th>
<th>$E_{corr}$ (V$_{SCE}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31 TRC</td>
<td>6.7 x 10^{-5}</td>
<td>-1.515</td>
</tr>
<tr>
<td>AZ31 MCTRC</td>
<td>7.5 x 10^{-5}</td>
<td>-1.510</td>
</tr>
</tbody>
</table>

Table 5.9 Average surface potentials of the magnesium alloy surfaces

<table>
<thead>
<tr>
<th>Material</th>
<th>Average surface potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31 TRC</td>
<td>217</td>
</tr>
<tr>
<td>AZ31 MCTRC</td>
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<tr>
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Fig. 5.2 SKPFM study of AZ31 TRC magnesium alloy
(1) 2D-Surface potential map (2) 3D-Surface potential map
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(1) 2D-Surface potential map (2) 3D-Surface potential map
Fig. 5.4 SKPFM study of AZ61 TRC magnesium alloy
(1) 2D-Surface potential map (2) 3D-Surface potential map
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<th>Chemical Formula</th>
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</thead>
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<td>* Magnesium Zinc</td>
<td>α-Mg phase</td>
</tr>
<tr>
<td>*</td>
<td>* Magnesium Aluminum</td>
<td>β-Mg₆₇Al₁₂</td>
</tr>
<tr>
<td>*</td>
<td>* Brucite, syn</td>
<td>Mg(OH)₂</td>
</tr>
<tr>
<td>*</td>
<td>* Magnesium Aluminum Hydroxide Hydrate</td>
<td>Mg₆Al₂(OH)₁₈•4.5H₂O</td>
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CHAPTER 6

FRICION STIR WELDING OF MAGNESIUM ALLOYS

6.1 Introduction

Friction stir welding has been considered to be one of the most significant and effective developments in metal joining. The process was developed at The Welding Institute, UK, in 1991. It is also said to be “green” technology, due to its energy efficiency, environment friendliness and versatility [150, 211]. Friction stir welded alloys have been successfully used in the industrial sectors, for automobile, transport and power-train applications. Major efforts in the research and development associated with the FSW technique have been focused on aluminium alloys and accordingly commercial applications of FSW aluminium alloys have eventually increased. However, in the case of magnesium alloys, very limited work has been conducted [35, 47, 48, 49, 50, 57, 59, and 60]. Hence, comprehensive investigation with respect to the FSW of magnesium alloys is essential in order to understand the influence of FSW on the microstructure and the mechanical and corrosion properties of the system. It is usually difficult to weld cast magnesium alloys due to porosity formation in the weld [131]. Furthermore, the relatively large coefficient of expansion of magnesium alloys causes a high degree of deformation in the weld. Therefore, a solid-state welding technique should be an optimum choice for joining cast magnesium alloy sheets.
As the quality of the friction stir welds of magnesium alloys is highly sensitive to tool rotation rate and traverse speed, the investigation of the mechanical and corrosion properties of the weld zone microstructures of FSW magnesium alloys has attracted significant interest. The research work undertaken here is desired at developing a thorough understanding of the microstructure evolution in the weld zones of the FSW magnesium alloys, using different traversing speeds with a constant tool rotation rate. Further, the influence of the weld zone microstructure on the corrosion behaviour is examined using advanced microscopic techniques and conventional corrosion testing methods.

Friction stir welded die-cast AM60 and AZ91 magnesium alloys, using a narrow range of FSW parameters, were investigated for their weld zone microstructures and the corrosion behaviour. The FSW procedure was conducted at TWI, UK, at a tool rotation rate \( W \) of 300 rpm with traverse speeds \( V \) ranging from 200-350 mm/min. For the FSW of AM60 magnesium alloys having speeds of 200, 250 and 300 mm/min was employed. Therefore, the \( W/V \) ratios were 1.5, 1.2 and 1.0 respectively. For the AZ91 magnesium alloys, the traverse speeds were 250, 300 and 350 mm/min, giving \( W/V \) ratios of 1.2, 1.0 and 0.85 respectively. The process window of the welding parameters has been established on earlier FSW experiments conducted on die-cast magnesium alloys at TWI. The weld zone microstructures were examined using advanced microscopic techniques, including optical light microscopy, plane polarized light optical microscopy, scanning electron microscopy (SEM) and electron back scattered diffraction (EBSD) techniques.

6.2 Microstructure of FSW AM60 magnesium alloy

6.2.1 Parent alloy microstructure: Die-cast AM60 magnesium alloy

The microstructure of die-cast AM60 magnesium alloy, taken from the parent plate of the weld, is displayed in Fig. 6.1 (A), revealing equiaxed \( \alpha \)-Mg grains, surrounded by the \( (\alpha+\beta) \) eutectic. The increased magnification scanning electron micrograph in Fig. 6.1 (B) displays the fully divorced \( \beta \)-phase, decorating the grain boundaries, along with the randomly dispersed Al-Mn intermetallic particles with high contrast, in the microstructure, indicated
by arrows. The EDX analysis of the microconstituents in the die-cast AM60 parent alloy microstructure, presented in Table 6.1 show that the aluminium content increases from 3% to 26% from the centre of the grains (α-Mg phase) to the grain boundary (β-phase). The Al-Mn intermetallics represent the Al₈Mn₅ phase.

From the FSW experiments conducted at TWI, Threadgill et. al., [178, 181] have shown that FSW reveals three characteristic weld zones, as displayed in the schematic in Fig. 2.20 in the Literature Review, associated with differing material flow and temperature changes. The friction stir/weld nugget zone is associated with a high material flow and is also associated with the highest temperature experienced by the material. TMAZ, the thermomechanically affected zone, positioned next to the friction stir zone, experiences a reduced material flow and medium temperature. HAZ, the heat affected zone, besides the TMAZ, is associated with no material flow, but a medium temperature influence. Considering the results reported earlier on the FSW of magnesium alloys at TWI, the microstructures obtained from the FSW with traverse speeds ranging from 200-300 mm/min, operating at a tool rotation rate of 300 rpm, are discussed as follows:

### 6.2.2 Specimen A: FSW parameter \((W/V)\) ratio 1.5

Figure 6.2 displays the transverse section of the FSW AM60 magnesium alloy that employed a tool rotation rate of 300 rpm and traverse speed of 200 mm/min, i.e. \((W/V)\) ratio 1.5. A basin shaped friction stir/weld nugget zone, measuring 4.45 mm is revealed, where the region on the advancing side (A) shows a dynamically recrystallized grain structure with the material flow patterns, while the region on the retreating side (B) displays heavy deformation, with a partially recrystallized grain structure. The regions are separated shown by a dotted line. A porosity at the weld root is evident that is possibly developed due to lack of fusion. Such a defect is usually observed in the FSW of magnesium alloys using lower welding speeds. It is generally observed that at lower welding speeds, the intense stirring causes an increase in the trapped oxide particles, which can be responsible for the weld defects. According to Nakata et. al., at lower rotation rates, the frictional heat generated is not sufficient to promote the material flow, forming inner
voids along the weld that are also referred as “the tunnelling phenomenon” [174]. The TMAZ (C) was characterized by heavily deformed microstructure on both the advancing and retreating sides while the HAZ (D) exhibited similar grain structure to that of the parent alloy.

The friction stir/weld nugget zone reveals a dynamically recrystallized (DRX) grain structure, with an average grain size ranging from 2-10 µm, across the transverse section of the alloy sheet, as shown in Fig. 6.3. The advancing side and the top of the transverse section of the weld exhibited larger grain sizes compared with those on the retreating side and the bottom of the transverse section owing to heavy deformation and the influence of the high pressure exerted by the tool shoulder. The high magnification scanning electron micrograph displays the DRX grains in the friction stir/weld nugget zone, where the grain boundaries are decorated with fine β-precipitates, formed after the FSW process, evident from Fig. 6.4 (A). The morphology of the β-phase observed in the parent alloy microstructure is completely absent in the friction stir zone and the EDX analysis shows ~10% Al, which is much lower than the conventional β-phase. The high magnification image of the porosity in the friction stir zone, shown in Fig. 6.4 (B), indicates that it is localized rather than a continuous tunnel formation, as reported in the literature [174].

The scanning electron micrographs of Figs. 6.4 (C) and (D) display the TMAZ, revealing a highly deformed microstructure on the advancing and retreating sides. The friction stir welding process affects to show a great influence on the β-phase morphology, evident from the dendritic growth of the β-phase and solute segregation on the grain boundaries of the elongated grains. This suggests that the β-phase possibly undergoes eutectic melting, followed by dendritic growth in the partially melted regions. Such a phenomenon is promoted by the low eutectic melting temperature (430°C) as compared with that of pure magnesium (615°C), which has also been reported in the friction stir processing of AZ91 magnesium alloy by Robson et. al. [48]. It is important to note that the TMAZ and the friction stir/weld nugget experience the highest temperature influences compared with the HAZ, which are sufficient to induce partial melting of the β-phase. The EDX analysis also
reveals an increase in aluminium content, comparatively higher than the conventional β-phase in the parent alloy, which is presented in Table 6.3.

The microstructure beneath the shoulder on the advancing side revealed evidence of liquation occurring, as shown in Fig. 6.4 (E); thus indicated a localized increase in the temperature, resulting in the partial melting of the β-phase (430°C). Evidence of such localized melting has also been reported by Goodfellow and Leonard in the case of FSW of AA7075 [80]. Localized segregation of the β-phase in TMAZ regions at the weld root, below the friction stir/weld nugget zone, is shown the backscattered scanning electron micrograph of Fig. 6.4 (F).

6.2.3 Specimen B: FSW parameter (W/V) ratio 1.2

The transverse section of FSW AM60 magnesium alloy, using a tool rotation rate of 300 rpm and a traverse speed of 250 mm/min, i.e. (W/V) ratio of 1.2, is shown in Fig. 6.5. The friction stir zone microstructure reveals an elliptical shape of the weld zone, a transition from the basin shape observed in specimen A and shown in Fig. 6.2. The friction stir zone measured 3.75 mm, showing a reduction in size compared with that of specimen A. The advancing side of the friction stir zone (A) clearly reveals a fully recrystallized grain structure and the widening of the weld zone with material flow patterns resulting in a banded microstructure, as observed in specimen A. The retreating side of the friction stir zone (B) displays a heavily deformed microstructure. The two distinct regions are shown by dotted line of the transverse section. No evidence of porosity formation at the weld root is evident, indicating a sound weld formation.

The influence of FSW on the grain size in the friction stir/weld nugget zone is presented in Fig. 6.6, revealing larger grain sizes on the advancing side as compared with the retreating side, and a decrease in the grain size from the top toward the bottom of the transverse section. The grain size varies from 4-10 µm on the advancing side to 2-6 µm on the retreating side and is approximately similar from the top to the bottom of the transverse section. The α-Mg grains revealed a large volume of β-precipitation, on the grain
boundaries, indicated by arrows. However, the morphology of the β-phase is completely different from the β-phase, observed in the parent alloy, suggesting evidence of partial melting and re-solidification occurring, during the friction stir welding process.

The heavily deformed grain structure in the TMAZ is evident from the scanning electron micrographs shown in Fig. 6.7, which reveals the influence of localized temperature variation leading to liquation below the shoulder region (Fig. 6.7 (A), solute segregation on the retreating side (Fig. 6.7 (B) and elongated grain structure in the middle regions of the friction stir zone (Fig. 6.7 (C). A high degree of plastic deformation, leading to random scattering of the β-precipitates was observed in the friction stir zone, presented in Fig. 6.8 (A). Solute segregation was observed in TMAZ regions, below the friction stir zone, at the weld root, which is evident in Figs. 6.8 (B) and (C).

6.2.4 Specimen C: FSW parameter (W/V) ratio 1.0

The transverse section of the FSW AM60 magnesium alloy generated using a tool rotation rate of 300 rpm and a traverse speed of 300 mm/min, i.e. (W/V) ratio of 1.0, is shown in Fig. 6.9. The micrograph reveals the weld zones that are characterized by a friction stir/weld nugget zone, measuring 3.5 mm, which is much smaller than that evident in specimens A and B. The friction stir zone shows a centralized porosity defect, with material flow patterns resulting in a banded microstructure. The plastically deformed region on the retreating side is significantly large compared with specimens A and B, resulting in a reduction in size of the DRX grained friction stir/weld nugget zone. The grain size measurements shown in Fig. 6.10 reveal an average size of 2-10 µm, which is similar to the other specimens. However, the material flow patterns showed a clear distinction in the friction stir zone, with grains free from β-precipitates (region I) and zones with heavy deposition of the randomly scattered β-precipitates (region II), as shown in the scanning electron micrograph of Fig. 6.11 (A). Also, evidence of randomly distributed Al-Mn intermetallics within the DRX grains was revealed, indicated by arrows, in Fig. 6.11 (B). A hexagonally shaped Fe impurity, confirmed by EDX analysis, in the friction stir zone is present in the friction stir zone (red star), in Fig. 6.11 (B). Such Fe impurities occur in the
friction stir zone due to the melting of the β-phase which is known to dissolve iron from the rotating tool used for stirring. Evidence for these Fe impurities has been cited by other authors [230] in the FSW of magnesium alloys. Evidence of partial melting and re-solidification of the β-phase in the melted areas of the TMAZ is observed, on the advancing side (Fig. 6.11 (A) and retreating side (Fig. 6.11 (B), showing heavy deformed grain structure and re-solidified β-phase, confirmed by EDX results.

The FSW parameters employed for specimen C were observed to produce flaws in the welded section, leading to liquation below the shoulder on the advancing side as indicated by arrow in Fig. 6.12 (A), random scattering of the β-precipitates, along the material flow patterns shown in Fig. 6.12 (B) and linear cracking followed by solute segregation below the shoulder region, as indicated by arrows in Fig. 6.12 (C). An unwelded root flaw defect, usually observed in FSW magnesium alloys due to lack of penetration at the weld line, was clearly observed in specimen C, as indicated by the arrows in the optical micrograph in Fig. 6.12 (D).

6.2.5 Grain size variations in different weld zones

Plane polarized light optical microscopy reveals the grain size variations in the heat affected zones (HAZ) in specimens A, B and C, as shown in Fig. 6.13. Specimen A reveals a random distribution of enlarged grains, ranging from 200-700 µm along with smaller grains ranging from 50-150 µm. In the case of specimen B, randomly distributed enlarged grains with sizes ranging from 125-300 µm are present along with smaller grains ranging from 50-100 µm. Specimen C showed an increase in the grain size, ranging from 100-400 µm across the transverse section. Therefore, the effect of frictional heat on the increase in the grain sizes is clearly evident from the micrographs, indicating a trend from randomly distributed enlarged grains in specimen A to periodic arrangement of enlarged grains in the heat affected zones in specimen C.

EBSD maps reveal the grain structure in the parent alloy microstructure of AM60 magnesium alloy, with an average grain size of 20-70 µm. Figure 6.14 shows the inverse
pole figure configuration (IPF) image indicating majority of the grains with high angle grain boundaries (HAGB) in black (>15°) and some low angle grain boundaries (LAGB) in white (2°-15°). The misorientations below 2° were ignored during the EBSD mapping. The corresponding band contrast image shows the twinned boundaries in red. Figure 6.15 displays the grain structure in the friction stir zone in the EBSD maps from the top, middle and bottom of the transverse section of the friction stir zones of specimens A, B and C, revealing the effect of the traverse speed on the grain sizes. The majority of the dynamically recrystallized grains showed high angle grain boundaries and the percentage of low angle grain boundaries decreased from the top to bottom along with the grain size. The average grain sizes from the respective regions along the transverse sections from specimens A, B and C are listed in Table 6.4, showing a decrease in the grain sizes from the advancing side to the retreating side and from the top to bottom owing to the high amount of plastic deformation occurring on the top regions of the transverse section and the advancing sides as well. Inverse pole figure EBSD maps also show a very high density of LAGB’s on the top of the transverse sections, indicating extensive recovery occurring before recrystallization, as there is a significant plastic flow in the material below the shoulder compared with the bottom of the transverse section.

6.3 Microstructure of FSW AZ91 magnesium alloy

6.3.1 Parent alloy microstructure: Die-cast AZ91 magnesium alloy

Die-cast AZ91 magnesium alloy displays a bimodal microstructure, comprising equiaxed α-Mg grains with a dense α-eutectic network, as shown in Fig. 6.16 (A). The high magnification backscattered scanning electron micrograph shown in Fig. 6.16 (B) reveals the morphology of the eutectic microstructure, with a partially divorced β-Mg₁₇Al₁₂ phase on the grain boundaries along with the lamellar (α+β)-precipitation. The EDX analysis confirms the increase in aluminium composition from the centre of the grains (~3%) to the grain boundaries where the β-Mg₁₇Al₁₂ phase shows the highest aluminium content (~22%); the EDX data are presented in Table 6.5. The die-cast AZ91 magnesium alloy shows some commonly observed defects that have been reported in the literature, namely
localized intrinsic porosity, shown in the scanning electron micrograph in Fig. 6.16 (C) and interdendritic shrinkage porosity, shown in Fig. 6.16 (D), across the surface microstructure.

6.3.2 Specimen D: FSW parameter (W/V) ratio 1.2

Figure 6.17 reveals the transverse section of the friction stir welded AZ91 magnesium alloy, using a tool rotation rate of 300 rpm and a traverse speed of 250 mm/min, i.e. a (W/V) ratio of 1.2. The characteristic weld zones across the transverse section define a basin shaped friction stir/weld nugget zone, measuring 4.5 mm, with material flow patterns evident from the optical micrograph of the transverse section. The curved line indicates the separation between the heavily deformed grain structure in the top of the friction stir zone on the retreating side and the dynamically recrystallized zone on the advancing side of the friction stir zone of the transverse section. Localized porosity and linear cracks are evident in the friction stir zone, as shown by arrows, in Fig. 6.17.

The TMAZ displays heavily deformed microstructures on both the advancing side (Fig. 6.18 (A) and the retreating side (Fig. 6.18 (B) revealing elongated grains decorated with plastically deformed β-phase on the grain boundaries. EDX analysis shows aluminium enrichment in the β-phase (~28%) compared with that observed in the parent alloy microstructure (~22%), suggesting solute segregation on the grain boundaries in the TMAZ, compositional analysis presented in Table 6.6. Increased quantities of zinc was evident from the EDX data revealing ~1% zinc on the grain boundaries compared with ~0.67% zinc distributed in the α-Mg grains in the parent alloy microstructure.

However, the friction stir zone microstructure in Fig. 6.18 (C) shows dynamically recrystallized grains with fine grain sizes averaging 2-10 µm. The grain boundaries showed traces of fine β-precipitates with average aluminium contents of 10%. The solid solution in the friction stir zone showed a higher content of aluminium than that observed in the α-Mg grains in the parent alloy microstructure (~9%), evident from the EDX analysis presented in Table 6.7. The friction stir zone reveals evidence of a banded microstructure, shown in Fig. 6.18 (D), similar to the onion ring structures in the weld nugget of FSW aluminium.
alloys reported in the literature. However, the banded microstructure in FSW AZ91 magnesium alloy (specimen D) is not exactly spherical and continuous as observed in the weld nugget of FSW aluminium alloys. The EDX results revealed no major observable difference in the β-precipitates and that of the banded microstructures, except minor aluminium and zinc enrichment. The high magnification scanning electron micrographs from representative regions in the friction stir zone are shown in Fig. 6.19, displaying the material flow patterns and the banded microstructures, composed of very fine β-precipitates. The banded microstructures show bands of the β-phase with different thickness, randomly separated and these bands follow the material flow patterns, as evident from the micrographs. Localized porosity formed due to lack of fusion in the friction stir zone, is evident from Fig. 6.19 (B) and the banded microstructures are revealed to emerge from close proximity to the porosity. The material flow patterns suggest having a significant influence on the extrusion of the material during the FSW process, leading to the porosity formation due to lack of fusion, in the friction stir zone.

6.3.3 Specimen E: FSW parameter (W/V) ratio 1.0

With a reduced (W/V) ratio of 1.0, with FSW parameters of a tool rotation rate of 300 rpm and traverse speed of 200 mm/min, the transverse section of the FSW AZ91 magnesium alloy revealed a comparatively small basin-shaped friction stir/weld nugget zone, measuring 4.35 mm, as shown in Fig. 6.20. The plastically deformed region on the retreating side, indicated by the curved line reveals that the material extruded was much less than that in the specimen D and the friction stir zone showed a larger region of DRX grains on the advancing side. The friction stir zone was free from large central porosity; however, linear cracking below the shoulder was evident, indicated by an arrow, together with the micro-porosity, shown by arrows, in the transverse section.

The TMAZ displayed heavy deformation in the magnesium matrix on both the advancing side (Fig. 6.21 (A) and retreating side (Fig. 6.21 (B), with the β-phase on the grain boundaries. The scanning electron micrographs revealed a highly recrystallized grain structure in the friction stir zone shown in Fig. 6.21 (C), with randomly distributed Al-Mn
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intermetallics in the microstructure. The localized temperature differences resulting in solute segregation below the shoulder on the advancing side are evident from Fig. 6.21 (D), which show (α+β)-eutectic forming a lamellar morphology.

6.3.4 Specimen F: FSW parameter (W/V) ratio 0.85

The transformation from a basin-shaped friction stir/weld nugget zone to an elliptical friction stir zone is clearly evident from the transverse section of the FSW AZ91 magnesium alloy, shown in Fig. 6.22, where a tool rotation rate of 300 rpm and traverse speed of 350 mm/min, i.e. (W/V) ratio of 0.85, was used. The size of the friction stir zone showed a further reduction, measuring 4.10 mm, and reduced deformed microstructure, compared with specimens D and E. The curved line indicates the two distinct regions namely fully recrystallized zone (A) and the deformed zone (B) with elongated grain structure. No linear cracking or any porosity was observed across the transverse section, indicating a sound welding condition to produce successful friction stir welds. The material flow patterns indicated uniform mixing of the extruded material in the weld nugget zone.

The scanning electron micrographs from the TMAZ regions on the advancing side (Fig. 6.23 (A) and the retreating side (Fig. 6.23 (B) resembled to specimen E, with no porosity or linear cracking defects. The transition zone shown in Fig. 6.23 (C) showed no evidence of random scattering of the β-precipitates in the friction stir zone. However, the grain boundaries did show evidence of the fine β-precipitates, as observed in specimens D and E in Fig. 6.23 (D).

The surface microstructure of the weld zones in specimens D, E and F are shown in Fig. 6.24, revealing the spherical material flow patterns from the advancing side to the retreating side. Specimen D shows flash formation, shown by arrows, formed due to the random distribution of the extruded material and partially melted β-phase. Specimen E showed evidence of a banded microstructure composed of β-precipitates in the friction stir zone. Specimen F shows a very smooth material flow with minimized defects, indicating sound weld formation.
6.3.5 Grain size variations in different weld zones

The heat affected zone microstructure in the FSW AZ91 magnesium alloy specimens is shown in the plane polarized optical micrographs in Fig. 6.25, which displayed a microstructure similar to the parent alloy with some enlarged grains, measuring ~250 µm and interdendritic porosity evident in the images.

The EBSD maps shown in Fig. 6.26 represent the parent alloy microstructure of the AZ91 magnesium alloy, with equiaxed grains showing high angle grain boundaries (black) and low angle grain boundaries (white) and the fluorescent regions on the grain boundaries constituting the β-phase. The friction stir zone revealed a highly refined DRX grain structure with the banded microstructure, evident from the fluorescent patterns, indicating β-precipitation as observed in specimen D. The DRX grains mainly exhibited high angle grain boundaries (black), with a grain size of 2-10 µm. The EBSD maps revealed the average grain sizes across the transverse sections from the top, middle and bottom of the friction stir zones of the specimens D, E and F, shown in Fig. 6.27, and indicated that there was no significant variation, ranging from 2-10 µm, with the DRX grains with high angle grain boundaries (black). However, the regions in the middle section of specimen D indicate a high volume of randomly distributed β-precipitates, as mentioned earlier.

6.4 Corrosion studies of FSW AM60 magnesium alloy

6.4.1 Electrochemical measurements of FSW AM60 magnesium alloys

The polarization curves obtained from the parent metal zone and the weld zones of the friction stir welded AM60 alloy, are shown in Fig. 6.28. The free corrosion potentials \((E_{corr})\) and the current densities \((I_{corr})\) of the respective weld zones and the parent metal zone, determined from the slopes by Tafel extrapolation method, are presented in Table 6.9. It is clear from the polarization curves that there is no linear region for accurate comparison of the corrosion rates hence the corrosion current densities were roughly
estimated from the approximate linear fits to the curves starting from 25 mV on either side of the corrosion potential and extending over about an order of magnitude range of current density.

The polarization curve of the parent metal zone reveals no evidence of pitting occurring on immersion in 3.5% NaCl solution; however it is evident from the \( E_{corr} \) and \( E_{pit} \) values of the weld zones which are almost the same, that instant pitting occurs when the weld zones are in contact with the corrosive media. The cathodic polarization curves show the effect of hydrogen evolution during the polarization process on the alloy surfaces. The cathodic corrosion densities represented by the friction stir/weld nugget zones indicate better protection of the alloy surface compared with the parent metal zone, suggesting breakdown of the passive film on the alloy surface of the parent metal zone due to localized corrosion occurring due to cathodic phases, present in the microstructure including Al-Mn intermetallics and the \( \beta \)-phase.

Therefore, the polarization behaviour exhibited by the parent metal zone revealed higher corrosion rates compared with the individual weld zones in the FSW AM60 alloy specimens, especially the friction stir/weld nugget zones, evident from Fig. 6.28. The HAZ and TMAZ showed evidence of pitting at frequent intervals indicating localized corrosion occurring due to the cathodic phases present in the microstructure. However, a significant shift in the magnitude of the cathodic corrosion densities of the weld zones was recorded.

It is apparent from the polarization curves that the corrosion resistance of the friction stir zones in the welding conditions used in the current research is attributed to the refined grain size of the DRX grains in the friction stir zone compared with the coarser grain size in the parent metal zone. Secondly the dissolution of the \( \beta \)-phase in the friction stir/weld nugget zone, evident from the EDX results accounts for higher corrosion resistance of the magnesium matrix in the weld zone. The corrosion current \( (I_{corr}) \) values given in Table 6.9 illustrate that the corrosion rate of the parent metal zone is higher than that of the weld zones. It has previously been demonstrated that the corrosion resistance of magnesium alloys can be improved through grain refinement [3, 81].
6.4.2 SKPFM investigation of FSW AM60 magnesium alloys

SKPFM studies performed on the characteristic weld zones of the FSW AM60 alloy, provide a highlight of the surface potential variations across the weld zone microstructure and assist in predicting the corresponding corrosion behaviours of the weld zones. The surface potential values of the micro-constituents in the parent metal zone, as shown in the surface potential map displayed in Fig. 6.29, reveals the Volta potential difference of Al-Mn intermetallics (175-200 mV) and the β-Mg_{17}Al_{12} phase (120-150 mV) relative to the magnesium matrix. Owing to be comparatively noble potential than the magnesium matrix, the difference in the relative surface potential values compared to the magnesium matrix indicate the susceptibility to galvanic corrosion in the parent metal zone as mentioned earlier in the Literature Survey.

However, the friction stir zone displays a recrystallized microstructure, with finer grain sizes, as evident from the surface potential map displayed in Fig. 6.30. The magnesium matrix in the friction stir zone, now richer in aluminium, owing to the dissolution of the β-Mg_{17}Al_{12} phase, accounts for the surface potential values of 25-55 mV. The EDX data reveals that the DRX α-Mg grains from the friction stir zone show an aluminium content of ~5% which is comparatively higher than the aluminium content exhibited by the α-Mg grains which is ~3%, in the parent metal zone, as presented in Tables 6.1 and 6.2. The increase in the aluminium content in the magnesium matrix and the reduced grain size, consequently reflect in the rise in the surface potential values, suggesting an improvement in the corrosion resistance, to be exhibited by the friction stir zone. The improved surface potential values of the magnesium matrix displayed in the friction stir zone further reduce the surface potential difference between the micro-constituent phases (Al-Mn) in the microstructure resulting in the improvement in the corrosion behaviour of the friction stir zone. The heat affected zone shows a higher surface potential difference from the values exhibited by the micro-constituents, relative to the magnesium matrix, resembling the corrosion behaviour to that of the parent alloy microstructure, displayed in Fig. 6.31.
6.4.3 Corrosion testing of FSW AM60 magnesium alloys

Representative regions from the different weld zones of the immersion tested specimens of FSW AM60 in 3.5% NaCl solution for 24 h are displayed in Figs. 6.32 and 6.33. The corrosion behaviour of the AM60 magnesium alloy (parent alloy microstructure), showed lower corrosion resistance, evident from the electrochemical measurements as well as the SKPFM studies conducted. The corrosion testing results revealed general corrosion occurring in the magnesium matrix, with cracking at the grain boundaries of the coarser grains, indicated by arrows. These coarser grains showed preferential corrosion, probably because of higher depletion in the aluminium contents within the coarser grains compared with the smaller grains and the intergranular cracking, evident from the grain interiors could also be due to shrinkage defects. However, similar intergranular cracking has been reported in the corrosion studies conducted on FSW AM50 magnesium alloys [249]. The β-phase on the grain boundaries remained intact, restricting the corrosion front, suggesting a barrier effect. Such corrosion behaviour of the magnesium alloys and the β-phase has been reported by Song et. al. [67], where the β-phase preferentially acts as a barrier.

The weld zone presented in Fig. 6.33 (A) shows the friction stir zone on the right and the TMAZ on the left side of the backscattered scanning electron image. There is no visible evidence of corrosion in the friction stir zone, attributed to the finer grain sizes of the DRX grains; however, the region close to the friction stir zone revealed corrosion fissure formation due to localized surface irregularities, indicated by arrows. The corrosion studies conducted on FSW AM50 magnesium alloys, have reported similar elongated corrosion morphologies occurring at surface irregularities in the transition zone, close to the friction stir zone, by Zeng et. al. [249]. Figure 6.33 (B) shows the TMAZ after immersion testing, indicating general corrosion.

The optical microscopy results showed grain enlargement in the heat affected zone and as expected, the coarser grains showed preferential corrosion on immersion testing, evident from Figs. 6.33 (C) and (D), where the coarser grains were covered with the corrosion products. The smaller grains have superior corrosion resistance compared with the coarser
grains, as explained by Song et. al. [108]. However, the electrochemical response of the HAZ revealed lower free corrosion potentials compared with the friction stir zone and accordingly, the immersion testing results are in agreement with the polarization results.

6.5 Corrosion studies of FSW AZ91 magnesium alloy

6.5.1 Electrochemical measurements of the FSW AZ91 alloys

The electrochemical responses from the parent metal zone and the weld zones in the FSW conditions employed in the current research are shown in Fig. 6.34. The free corrosion potentials \( (E_{corr}) \) and the corrosion current \( (I_{corr}) \) values of the welded zones and the parent metal zone are calculated from the sloped by Tafel extrapolation method, as explained earlier, are presented in Table 6.11.

The polarization curves obtained from the FSW AZ91 magnesium alloy specimens (D, E and F) in Fig. 6.34 reveal that the weld zones exhibited more positive free corrosion potential values \( (E_{corr}) \) than the parent metal zone. The \( E_{corr} \) and the \( E_{pit} \) values were almost the same, indicating that the pitting initiated instantly when the weld zones were in contact with the corrosive media. However, the \( I_{corr} \) values represented by the parent metal zone revealed lower cathodic current densities, suggesting the corrosion barrier effect of the \( \beta \)-phase, in the parent metal zone of the die-cast AZ91 magnesium alloy, as stated by Song et. al. [108].

It is apparent that there is no significant difference observed in the corrosion resistance of the parent alloy and the weld zones in the AZ91 magnesium alloy. However, the recrystallized grain structure has an influence on the corrosion behaviour of the friction stir zones in the welded specimens. The finer grain sizes and the dissolution of the \( \beta \)-phase in the friction stir zone accounts for the corrosion resistance in the weld zone while the higher fraction of the \( \beta \)-phase in the parent alloy provides a corrosion barrier effect ensuring the corrosion resistance of the alloy. Therefore, no major difference in the corrosion resistances
of the weld zones and the parent alloy microstructure is observed suggesting a uniform
electrochemical response to the corrosive media, across the welded structure.

### 6.5.2 SKPFM investigation of FSW AZ91 magnesium alloys

The parent metal zone in the AZ91 magnesium alloy comprises the equiaxed α-Mg grains,
β-Mg$_{17}$Al$_{12}$ phase and the Al-Mn intermetallics dispersed in the microstructure, as shown
in the surface potential map displayed in Fig. 6.35. The average surface potential values of
the micro-constituents presented in Table 6.12, are >150 mV of the Al-Mn intermetallics
and 80-100 mV for the β-Mg$_{17}$Al$_{12}$ phase, relative to the adjacent magnesium matrix. Both
the micro-constituents, cathodic to the magnesium matrix, indicate a noble behaviour and
suggest the preferential degradation of the adjacent magnesium matrix.

The relative surface potential values of the friction stir zone of 70-90 mV, which displays a
highly recrystallized microstructure with fine grain sizes, as shown in the surface potential
map in Fig. 6.36, indicate enrichment in aluminium owing to the dissolution of the β-
Mg$_{17}$Al$_{12}$ phase. Hence, the relative surface potential values of the magnesium matrix in the
friction stir zone account for the improvement in the corrosion behaviour of the weld zone.
The difference in the surface potential values of the micro-constituent phases (β-
precipitates) and the magnesium matrix is negligible, suggesting an improved corrosion
resistance of the friction stir zone. The Al-Mn phase display a surface potential of 160-180
mV relative to the adjacent magnesium matrix.

The heat affected zone shows the surface potential values of the micro-constituents, which
are relatively higher than the magnesium matrix, and resemble the behaviour patterns to the
parent alloy microstructure as displayed in Fig. 6.37.
6.5.3 Corrosion testing of FSW AZ91 magnesium alloys

The backscattered scanning electron micrograph in Fig. 6.38 (A) displays the transition zone of the FSW AZ91 magnesium alloy (specimen D) after immersion in 3.5% NaCl solution for 24 h. The degradation of the weld zone initiates with fissure formation developing a continuous linear, filiform-like corrosion morphology. The flash formation on the transition zone, evident in the optical micrograph from the surface of the specimen D, shown in Fig. 6.24, possibly leads to the deterioration of the weld joint. The representative region from the friction stir zone of FSW AZ91 magnesium alloy, shown in Fig. 6.38 (B), displays a localized filiform-like corrosion morphology that consumes the magnesium matrix. The parent alloy, displaying a bimodal microstructure, shows general corrosion initiating in coarser grains as indicated by arrows in Fig. 6.38 (C) as the smaller grains exhibit higher corrosion resistance, stated by Song et. al. [108]. The heat affected zone shows intergranular corrosion cracking and transgranular corrosion cracking, shown by arrows, in Fig. 6.39. Evidence of intergranular and transgranular corrosion cracking in AZ91 magnesium alloy has been reported by Chen et. al., claiming hydrogen diffusion towards the interior of the matrix, which enriches and forms hydrides at the grain boundaries [250,251]. The corrosion morphology in the parent alloy is, therefore, highly influenced by the distribution of the β-phase, where the linear corrosion morphology is observed to follow the β-phase along the grain boundaries, evident from the immersion testing results.

6.6 Discussion

Threadgill et. al. [16], reported the FSW of commercial die-cast magnesium alloys, including AZ91, AM50, and AM60 and wrought AZ31 magnesium alloys, producing sound welds, using a tool rotation rate of 355 rpm and traverse speeds ranging from 160-224 mm/min. Lee et. al., [201] and Park et. al., [202] reported that successful friction stir welds of the AZ91 magnesium alloys can be produced by employing higher tool rotation rates (800-1600 rpm), using a wide range of traverse speeds. Nakata et. al., [199] reported
sound welding of the AZ91 magnesium alloys, using higher tool rotation rates (1250-1750 rpm) and lower traverse speed of 50 mm/min.

The current research, investigating the FSW microstructures, using a narrow range of FSW parameters, with lower tool rotation rates and traverse speeds compared with those reported by fellow researchers, shows resemblance in the microstructure evolution. The minimum tool rotation rate required to produce successful weld joints is ~200 rpm. Although, the process window of the FSW parameters used in this research was relatively narrow, the microstructure investigation revealed successful FSW specimens. The weld joints displayed a recrystallized equiaxed grain structure with the β-phase dissolved into the α-grains. The friction stir/weld nugget zone was slightly larger than that is normally observed in FSW of aluminium alloys. The width of the nugget zone depends on the combination of the tool design, welding parameters and the alloy composition. The friction stir zones in both the AM60 and AZ91 FSW magnesium alloys showed gradual decrease in the size, as the \((W/V)\) ratio decreased, evident from Figs. 6.2, 6.5 and 6.9 (for AM60 alloys) and 6.17, 6.20 and 6.22 (for AZ91 alloys). A similar observation has been reported by Gharacheh et. al. [163], where increasing the \((W/V)\) ratio showed an increase in the size of the weld nugget (width and depth). This is due to the high heat input and stirring increment in the weld metal owing to the increased \((W/V)\) ratio. Therefore, a large amount of frictional heat is produced and because of easy material flow a larger weld nugget is formed.

The transformation in the shape of the friction stir/weld nugget zone from basin-shaped (Fig. 6.2 (AM60), 6.17 (AZ91)) to an elliptical shape (Fig. 6.9 (AM60), 6.22 (AZ91)) was observed as the \((W/V)\) ratio decreased in both the FSW magnesium alloys. Recently, Ma et. al. [228], reported an investigation on the effect of FSP parameter on the microstructure and properties of cast A356, showing that a lower tool rotation rate of 300–500 rpm and tool traverse speed of 51 mm/min i.e. \((W/V)\) ratio 5.88 resulted in generation of a basin-shaped nugget zone, whereas an elliptical nugget zone was observed by FSP at higher tool rotation of >700 rpm and traverse speed 203 mm/min, i.e. \((W/V)\) ratio 4.43. This indicates that as the \((W/V)\) ratio decreases, owing to the increased traverse speed, the regions below the shoulder undergo heavy deformation that results in broadening of the friction stir/weld
nugget zone on the top of the transverse section and with transformation in shape from basin to elliptical occurring by simply changing the processing parameters.

Norman et. al. [210] and Karlsen et. al. [226] reported that the centre of the weld, commonly referred as the weld nugget zone, consists of very fine grains with a grain size of 1-10 µm. The equiaxed grains in the friction stir zone are formed by dynamic recrystallization [203]. The grain size in the friction stir/weld nugget zone decreases with increasing welding speed due to lower heat input. Commin et. al. [121], reported that the grain size in the weld nugget depends on the FSW process parameters, revealing relatively small grain size at low rotation rates \((W)\) and traverse speeds \((V)\). This is mainly due to the relationship between FSW parameters and the temperature reached during welding. As is well known, the heat input and the processing temperature decrease with increasing welding speed. Thus, less time is available at higher welding speed for grain growth. The decrease in grain size with increasing welding speed can also be attributed to greater straining of the metal which, in turn, activates more strain free nucleation sites [130]. The greater the nucleation rate, the more competitive the grain growth and hence the finer the final grain size [130]. Indeed, in the current research, the FSW parameters with comparatively lower tool rotation rates and traverse speeds, the relative increase in the traverse speed \((V)\) from 200-350 mm/min, showed a gradual decrease in grain size, due to the lower frictional heat during the FSW process, evident from Figs. 6.15 and 6.27.

Generally, FSW resulted in generation of fine recrystallized grains in the stirred zone in magnesium alloys [199, 201, 202]. For as-cast magnesium alloys, the coarse \(\alpha\)-Mg phase and \(\beta\)-Mg\(_{17}\)Al\(_{12}\) intermetallic phase disappeared after FSW [199-201]. The friction stir/weld nugget zone, characterized by finely recrystallized grains, can be divided into two subzones, namely, stir zone I (SZ I) on the retreating side and stir zone II (SZ II) on the advancing side in both FSW AM60 and AZ91 magnesium alloys. The SZ I, located at the centre and upper side of the stirred zone, was characterized by partial dynamic recrystallization, and deformation layers were observed throughout the grains. In the SZ II, full dynamic recrystallization and grain growth had occurred, and no deformation structures such as twins and deformation layer were observed [200]. The majority of the
grain boundaries of the DRX grains in the friction stir zone were high angle grain boundaries, evident from Figs. 6.15 and 6.27 and are believed to form through dynamic recrystallization during the stirring process.

The FSW parameters employed in the current research have shown that at a tool rotation rate of 300 rpm, using traverse speeds in the range of 200-350 mm/min, sound welds can be produced. However, within this process window, with the tool rotation rates being low, the higher heat input results in partial melting of the intermetallic compounds including $\beta$-Mg$_{17}$Al$_{12}$ at the grain boundaries. There are two consequences observed as a result of localized increase in the temperatures, in the weld specimens:

1. Liquation, due to partial melting of the $\beta$-Mg$_{17}$Al$_{12}$ phase, occurring below the shoulder on the advancing side of the friction stir zone, evident from Figs. 6.4 (E), 6.7 (A) and 6.12 (A) (AM60).
2. Partial melting and re-solidification of the $\beta$-Mg$_{17}$Al$_{12}$ phase, in the transition regions, evident from Figs. 6.4 (C) and (D) (AM60), 6.11 (C) and (D) (AZ91).

It has been reported earlier that the FSW of magnesium alloys usually did not result in generation of a liquid phase [197-204]. However, peak temperatures of 460°C were reported by Nagasawa et. al., [141] in the friction stir zone of the FSW AZ31 magnesium alloy. Lee et. al. [201] and Park et. al. [202] also reported peak temperatures of 370-500°C in the FSW of AZ91 magnesium alloy. As a consequence of the low eutectic melting point of the $\beta$-Mg$_{17}$Al$_{12}$ phase (430°C) compared with that of pure magnesium, an increase in temperature above the eutectic melting point would result in the generation of a liquid phase.

The partial melting of the $\beta$-Mg$_{17}$Al$_{12}$ regions, followed by dendritic growth into the partially melted regions in the FSP of AZ91 alloy, has been reported by Robson et. al., [227]. The microstructural features, indicating partial melting and re-solidification of the $\beta$-Mg$_{17}$Al$_{12}$ phase, mainly in the TMAZ and the friction stir zone of the FSW AM60 alloy and the FSW AZ91 alloy and the peak temperatures reported in the stir zones, suggest a strong possibility of the occurrence of the previously stated phenomenon. The massive growth in
the morphology of the $\beta$-Mg$_{17}$Al$_{12}$ phase, evident from Figs. 6.4 (C), (D), 6.7 (B), 6.11 (C) and (D) (AM60 alloys) and Figs. 6.18 (A) and (B), 6.21 (A) and (B), 6.23 (A) and (B) (AZ91 alloys), in complete contrast with the parent alloy microstructure, evident from Fig. 6.1 (AM60 alloy) and Fig. 6.16 (AZ91 alloy), indicates solute segregation as a consequence of the localized partial melting. The high volume of the $\beta$-Mg$_{17}$Al$_{12}$ phase present in the as-cast AZ91 magnesium alloy, when subjected to the FSW conditions producing high frictional heat, results in localized temperature increase, for example below the shoulder regions and generates liquation of the $\beta$-Mg$_{17}$Al$_{12}$ phase. Kohn et. al. [83] also reported the occurrence of melting in the FSW of AZ91 magnesium alloy, resulting in a complex microstructure. According to Kohn, a melted and re-solidified region with a central heavily stirred zone and a melted layer on the top of the weld plates were observed.

Lee et. al., [201] and Park et. al., [202] also stated that higher tool rotation rates caused the formation of an inner cavity, surface cracks and the lack of bonding in AZ91 magnesium alloys. Nakata et. al., [199] reported that higher traverse speeds or lower rotation rates than the optimum parameters caused the formation of inner voids or a lack of bonding in the weld, which is due to the inherent poor formability of the cast AZ91 magnesium alloy with a significant intermetallic compounds, $\beta$-Mg$_{17}$Al$_{12}$, present at grain boundaries. Compared with the tool rotation rates and traverse speeds employed in the FSW of magnesium alloys [199, 201, 202], lower rotation rates and traverse speeds used in the current research have also shown defects, including central porosity formation in the lower section of the friction stir zones in the weld specimens of FSW AM60 magnesium alloys, evident from Figs. 6.2 and 6.9. It has been reported that the formation of porosity is mainly due to two mechanisms, namely (i) volume deficiency and (ii) inadequate material flow and mixing [59]. Excessive metal loss may cause subsurface pores, which usually occur at the upper half of the stir zone on the advancing side. The porosities observed in this work mainly appeared near the bottom surfaces of the specimens. It is probably formed mainly due to inadequate material flow and mixing. Inadequate stirring and mixing can be caused by too fast a joining speed, or inadequate combination of welding speed and pin tool rotational rate [79, 93, and 106]. When the traverse speed and the tool rotational rate are not effective
sufficiently to stir the plasticized material in front of the probe and to completely fill the rear of the trailing edge, pores can be formed.

Linear cracking, evident below the shoulder in Figs. 6.20, 6.17, is observed in the FSW AZ91 magnesium alloy. However, at low welding speed, linear crack-like defects are most probably formed due to the lack of bonding caused by inadequate material flow and mixing [57]. Also, due to poor formability, these types of defects are more likely to be formed in the friction stir welding of magnesium alloys. At 300 mm/min, the AM60 friction stir/weld nugget zone showed an elliptical friction stir/weld nugget zone, beginning to leave a potentially unwelded root at the bottom of the weld, evident from Fig. 6.12 (D). As it is well known that the correct depth of penetration of the tool pin is essential to ensure that mixing occurs over the full plate thickness, in cases where a shortened pin is used and the tool plunge depth is incorrectly set, or there is poor alignment of the tool relative to the joint line, a root flaw can be produced, also indicating a complete lack of bonding.

The corrosion behaviour of magnesium alloys depends on the distribution of the micro-constituents and the β-phase in the microstructure. Die-cast AM60 and AZ91 magnesium alloys possess a bimodal microstructure with the β-phase located on the grain boundaries. As evident from the SKPFM analysis, the relative surface potential of the β-phase is comparatively higher than that of the magnesium matrix, it can act as a cathode, relative to the adjacent magnesium matrix. However, according to Song et. al., the volume of the β-phase determines the corrosion behaviour of the magnesium alloy, whether the β-phase acts as a site for galvanic corrosion or as a corrosion barrier. In case of AZ91 magnesium alloys, since the volume of the β-phase is comparatively high, it has been reported that the β-phase acts as barrier, improving the corrosion resistance of the alloy surface. However, general corrosion is dominant, occurring due to Al-Mn intermetallics of high surface potential relative to the magnesium matrix, which acts as sites for galvanic coupling and initiating the corrosion process in the magnesium matrix [132]. Figures 6.32 and 6.39 reveal intergranular cracks along the β-phase in the grain boundary regions of the parent alloy and heat affected zones of the AM60 and AZ91 alloys respectively. Similar corrosion morphologies have been reported in case of AZ91 magnesium alloys [231, 246].
Friction stir welding of the magnesium alloys generates a friction stir zone and the high heat input results in the dissolution of the $\beta$-Mg$_{17}$Al$_{12}$ phase. The FSW process also develops a finely recrystallized microstructure with a grain size averaging 2-10 µm in both the FSW AM60 and FSW AZ91 magnesium alloys, which results in the improved corrosion resistance of the weld zone, evident from the SKPFM results. The FSW AM60 magnesium alloy showed traces of Fe-impurities in the friction stir zone. These Fe-impurities are incorporated from the wear of the tool used for the FSW process. The high heat input due to lower traverse speeds leads to peak temperatures above the eutectic melting point of the $\beta$-Mg$_{17}$Al$_{12}$ phase (430°C), causing dissolution of the $\beta$-Mg$_{17}$Al$_{12}$ phase. As the $\beta$-Mg$_{17}$Al$_{12}$ phase is aggressive to steel, iron gets easily dissolved, hence the inclusion of Fe impurity to the friction stir zone. However, it has been reported by Skar et. al. [230] that trace amounts of iron shows no obvious effect on the corrosion rate of the magnesium alloy.

Otherwise, the FSW AM60 magnesium alloy showed superior corrosion resistance in the friction stir zone, evident from the immersion testing results. However, the FSW AZ91 magnesium alloy showed failure in the transition zone, owing to flash formation and the banded microstructure irregularities that were observed in the metallographic examination. The TMAZ in both the AM60 and AZ91 magnesium alloys suffered localized corrosion, developing fissures/filiform-like corrosion morphologies. The heat affected zones in both the AM60 and AZ91 magnesium alloys, showed similar corrosion resistance as that of the parent alloys.
6.7 Summary

1. The tool rotation rate of 300 rpm and traverse speeds of 200-350 mm/min showed promising prospects, for optimum welding conditions for the FSW of AM60 and AZ91 magnesium alloys.

2. The weld microstructure displayed a prominent friction stir zone, differentiated into two main regions, partially recrystallized zone on the retreating side below the shoulder regions with a highly deformed microstructure and DRX zone on the advancing side with refined grain structure having an average grain size ranging from 2-10 µm. The shape of the friction stir zone transformed from basin shape to elliptical as the traverse speeds increased owing to increased deformation. The size of the friction stir zone gradually decreased with the increase in the traverse speed on both the FSW alloys due to the increase in the rate of deformation, leading to widening of the friction stir zone.

3. The TMAZ showed heavily deformed microstructure in both alloys with elongated grain structure with the grain boundaries decorated with highly deformed β-phase. The localized increase in temperatures, due to the lower tool rotation rates and traverse speeds, to values above the eutectic melting point (430°C), resulted in partial melting and re-solidification of the β-phase in the TMAZ. The morphology of the β-phase clearly revealed solute segregation, completely different from the β-phase observed in the parent alloy microstructure.

4. Apart from the increase in the grain sizes, no significant modification was observed in the HAZ microstructure.

5. Evidence of liquation was noticed on the advancing side of the transverse section in the FSW AM60 magnesium alloy, as a consequence of localized increase in temperature, below the shoulder, leading to the partial melting of the β-phase.

6. Welding flaws including localized central porosity due to lack of fusion and unwelded root flaw due to lack of penetration were observed in the FSW AM60 magnesium alloy while microporosities and linear cracking in the friction stir zone were observed in the FSW AZ91 magnesium alloy.
7. The electrochemical response of the weld zones in the FSW AM60 alloy showed an improved corrosion resistance compared with the parent metal zone. The SKPFM results revealed that the magnesium matrix in the friction stir zone showed lower surface potential values compared with the parent alloy microstructure, due to the dissolution of the $\beta$-phase. The relative increase in the aluminium content in the magnesium matrix accounts for the higher nobility of the primary $\alpha$-Mg phase in the friction stir zone. The immersion testing results were in agreement with the polarization data and the SKPFM analysis, showing an improvement in the corrosion resistance of the friction stir zone, in the FSW AM60 magnesium alloy.

8. The FSW AZ91 magnesium alloy showed no significant variation in the weld zones and the parent alloy zone from the electrochemical measurements. However, the SKPFM results revealed a lower relative surface potential value in the magnesium matrix in the friction stir zone, due to the dissolution of the $\beta$-phase. The immersion testing results revealed susceptibility to corrosion in the transition zone due to the flash formation and banded microstructure, resulting in microstructure irregularities leading to the failure of the weld zone.

9. Corrosion morphologies include fissure formation, leading to filiform-like corrosion in the TMAZ of the FSW AM60 magnesium alloy. Coarser grains in the parent alloy microstructure showed preferential corrosion in the AM60 magnesium alloy. Evidence of intergranular and transgranular cracking in the HAZ and the parent alloy microstructure were apparent in the FSW AZ91 magnesium alloy.
Table 6.1  EDX analysis of the parent alloy microstructure (AM60 magnesium alloy)

<table>
<thead>
<tr>
<th>Features</th>
<th>Mg</th>
<th>Al</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (α-Mg phase)</td>
<td>96.53</td>
<td>3.38</td>
<td>0.09</td>
</tr>
<tr>
<td>2 (β-Mg_{17}Al_{12} phase)</td>
<td>78.23</td>
<td>21.55</td>
<td>0.22</td>
</tr>
<tr>
<td>3 (Al_{8}Mn_{5} intermetallic)</td>
<td>0.0</td>
<td>58.91</td>
<td>41.09</td>
</tr>
</tbody>
</table>

Table 6.2  EDX analysis of the friction stir zone in the FSW AM60 magnesium alloy

<table>
<thead>
<tr>
<th>Features</th>
<th>Mg</th>
<th>Al</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (α-Mg phase)</td>
<td>94.63</td>
<td>4.82</td>
<td>0.25</td>
</tr>
<tr>
<td>2 (β-Mg_{17}Al_{12} phase)</td>
<td>90.65</td>
<td>9.18</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 6.3  EDX analysis of the TMAZ in the FSW AM60 magnesium alloy

<table>
<thead>
<tr>
<th>Features</th>
<th>Mg</th>
<th>Al</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (α-Mg phase)</td>
<td>97.68</td>
<td>2.08</td>
<td>0.24</td>
</tr>
<tr>
<td>2 (β-Mg_{17}Al_{12} phase)</td>
<td>71.87</td>
<td>27.91</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 6.4  Grain and nugget sizes in the friction stir zone of FSW AM60 magnesium alloy

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Grain size (µm)</th>
<th>Nugget size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top</td>
<td>Centre</td>
</tr>
<tr>
<td>A</td>
<td>4 - 10</td>
<td>2 - 8</td>
</tr>
<tr>
<td>B</td>
<td>3 - 10</td>
<td>2 - 6</td>
</tr>
<tr>
<td>C</td>
<td>2 - 10</td>
<td>2 - 6</td>
</tr>
</tbody>
</table>
**Table 6.5** EDX analysis of the parent alloy microstructure (AZ91 magnesium alloy)

<table>
<thead>
<tr>
<th>Features</th>
<th>Mg</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (α-Mg phase)</td>
<td>97.10</td>
<td>2.46</td>
<td>0.35</td>
<td>0.09</td>
</tr>
<tr>
<td>2 (β-Mg₁₇Al₁₂ phase)</td>
<td>77.51</td>
<td>21.79</td>
<td>0.67</td>
<td>0.03</td>
</tr>
<tr>
<td>3 (Al-Mn intermetallic)</td>
<td>0.0</td>
<td>68.74</td>
<td>0.0</td>
<td>31.26</td>
</tr>
</tbody>
</table>

**Table 6.6** EDX analysis of the TMAZ in the FSW AZ91 magnesium alloy

<table>
<thead>
<tr>
<th>Features</th>
<th>Mg</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (α-Mg phase)</td>
<td>96.65</td>
<td>3.11</td>
<td>0.17</td>
<td>0.0</td>
</tr>
<tr>
<td>2 (β-Mg₁₇Al₁₂ phase)</td>
<td>71.47</td>
<td>27.38</td>
<td>1.07</td>
<td>0.08</td>
</tr>
<tr>
<td>3 (Al-Mn intermetallic)</td>
<td>0.0</td>
<td>61.40</td>
<td>0.0</td>
<td>38.60</td>
</tr>
</tbody>
</table>

**Table 6.7** EDX analysis of the friction stir zone in the FSW AZ91 magnesium alloy

<table>
<thead>
<tr>
<th>Features</th>
<th>Mg</th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (α-Mg phase)</td>
<td>90.31</td>
<td>9.35</td>
<td>0.27</td>
<td>0.07</td>
</tr>
<tr>
<td>2 (β-Mg₁₇Al₁₂ phase)</td>
<td>89.91</td>
<td>9.81</td>
<td>0.27</td>
<td>0.01</td>
</tr>
<tr>
<td>3 (β-precipitates)</td>
<td>89.11</td>
<td>10.16</td>
<td>0.58</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**Table 6.8** Grain and nugget sizes in the friction stir zone of FSW AZ91 magnesium alloy

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Grain size (µm)</th>
<th>Nugget size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top</td>
<td>Centre</td>
</tr>
<tr>
<td>A</td>
<td>4 - 10</td>
<td>2 - 8</td>
</tr>
<tr>
<td>B</td>
<td>3 - 10</td>
<td>2 - 6</td>
</tr>
<tr>
<td>C</td>
<td>2 - 10</td>
<td>2 - 6</td>
</tr>
</tbody>
</table>
Table 6.9 Electrochemical response of the weld zones from FSW AM60 magnesium alloy

<table>
<thead>
<tr>
<th>Material</th>
<th>Specimen A</th>
<th>Specimen B</th>
<th>Specimen C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_{corr}$ (A/cm$^2$)</td>
<td>$E_{corr}$ (V$_{SCE}$)</td>
<td>$I_{corr}$ (A/cm$^2$)</td>
</tr>
<tr>
<td>Parent metal zone</td>
<td>5.2 x 10^{-4}</td>
<td>-1.500</td>
<td>5.2 x 10^{-4}</td>
</tr>
<tr>
<td>TMAZ</td>
<td>9.8 x 10^{-4}</td>
<td>-1.460</td>
<td>6.3 x 10^{-6}</td>
</tr>
<tr>
<td>HAZ</td>
<td>7.3 x 10^{-4}</td>
<td>-1.527</td>
<td>8.7 x 10^{-6}</td>
</tr>
<tr>
<td>FSZ</td>
<td>9.4 x 10^{-4}</td>
<td>-1.458</td>
<td>7.3 x 10^{-6}</td>
</tr>
</tbody>
</table>

Table 6.10 Surface potentials of the micro-constituents in the weld zones of FSW AM60 magnesium alloy

<table>
<thead>
<tr>
<th>Weld zone</th>
<th>Micro-constituent</th>
<th>Surface potential $\Delta V$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent metal zone</td>
<td>Al-Mn phase</td>
<td>175-200</td>
</tr>
<tr>
<td></td>
<td>$\beta$-phase</td>
<td>120-150</td>
</tr>
<tr>
<td>Friction stir zone</td>
<td>Magnesium matrix (&gt;Al)</td>
<td>25-55</td>
</tr>
<tr>
<td></td>
<td>Al-Mn phase</td>
<td>&gt;140</td>
</tr>
<tr>
<td>Heat affected zone (HAZ)</td>
<td>Al-Mn phase</td>
<td>&gt;150</td>
</tr>
<tr>
<td></td>
<td>$\beta$-phase</td>
<td>~100</td>
</tr>
</tbody>
</table>
Table 6.11 Electrochemical response of the weld zones from FSW AZ91 magnesium alloy

<table>
<thead>
<tr>
<th>Material</th>
<th>Specimen D</th>
<th>Specimen E</th>
<th>Specimen F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_{corr}$ (A/cm$^2$)</td>
<td>$E_{corr}$ (V$_{SCE}$)</td>
<td>$I_{corr}$ (A/cm$^2$)</td>
</tr>
<tr>
<td>Parent metal zone</td>
<td>1.2 x 10^{-2}</td>
<td>-1.518</td>
<td>1.2 x 10^{-2}</td>
</tr>
<tr>
<td>TMAZ</td>
<td>9.8 x 10^{-1}</td>
<td>-1.530</td>
<td>7.8 x 10^{-1}</td>
</tr>
<tr>
<td>HAZ</td>
<td>9.8 x 10^{-1}</td>
<td>-1.530</td>
<td>2.3 x 10^{-2}</td>
</tr>
<tr>
<td>FSZ</td>
<td>6.4 x 10^{-2}</td>
<td>-1.470</td>
<td>7.3 x 10^{-1}</td>
</tr>
</tbody>
</table>

Table 6.12 Surface potentials of the micro-constituents in the weld zones of FSW AZ91 magnesium alloy

<table>
<thead>
<tr>
<th>Weld zone</th>
<th>Micro-constituent</th>
<th>Surface potential $\Delta$V (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent metal</td>
<td>Al-Mn phase</td>
<td>&gt;150</td>
</tr>
<tr>
<td></td>
<td>$\beta$-phase</td>
<td>80-100</td>
</tr>
<tr>
<td>Friction stir zone</td>
<td>Magnesium matrix (&gt;Al)</td>
<td>70-90</td>
</tr>
<tr>
<td></td>
<td>$\beta$-precipitates</td>
<td>~ 100</td>
</tr>
<tr>
<td></td>
<td>Al-Mn phase</td>
<td>160-180</td>
</tr>
<tr>
<td>Heat affected zone (HAZ)</td>
<td>Al-Mn phase</td>
<td>175-200</td>
</tr>
<tr>
<td></td>
<td>$\beta$-phase</td>
<td>80-100</td>
</tr>
</tbody>
</table>
Fig. 6.1 SEM micrographs showing (A) the parent alloy microstructure of AM60 magnesium alloy (B) high magnification SEM micrograph revealing grain boundary features, α-eutectic and β-phase.
Fig. 6.2 Optical micrograph of the transverse section of friction stir welded AM60 Mg alloy, showing (A) DRX zone, (B) deformed zone, (C) TMAZ and (D) HAZ in the FSW microstructure.

Fig. 6.3 Optical micrographs showing grain size variations in the friction stir zone in Specimen A.
Fig. 6.4 SEM micrographs showing (A) DRX grains in the friction stir/weld zone, (B) Porosity in the centre of the friction stir/weld nugget zone, (C) Advancing side and (D) retreating side, partial melting and re-solidification of β-phase. (E) Evidence of liquation, (F) Segregation of β-phase in the transition zone, below the weld nugget, in Specimen A
Specimen (B) FSW at 300 rpm and 250 mm/min

Fig. 6.5 Optical micrograph of the transverse section of friction stir welded AM60 Mg alloy, showing (A) DRX zone, (B) deformed zone, (C) TMAZ and (D) HAZ in the FSW microstructure.

Fig. 6.6 SEM micrographs showing grain size variations in the friction stir zone in Specimen B.
Fig. 6.7 SEM micrographs revealing (A) liquation below the shoulder, (B) re-solidification of β-phase, (C) deformation in the transition zone, in specimen B.

Fig. 6.8 SEM micrographs revealing segregation of re-melted β-phases in the friction stir zone (A), segregation of β-phases in the transition zone (B) and localized segregation in the transition zone below the friction stir zone (C) in specimen B.
Fig. 6.10 Optical micrographs showing grain size variations in the friction stir zone in Specimen C.
Fig. 6.11 SEM micrographs of specimen (C) revealing microstructures (A) friction stir/weld nugget zone, (B) High magnification image revealing grain structure in friction stir/weld nugget zone, with Al-Mn inclusions in variable sizes and hexagonal shaped Fe impurity (star), (C) TMAZ on the advancing side, (D) TMAZ on the retreating side.
Fig. 6.12 SEM micrographs revealing (A) Liquation below the shoulder on the advancing side, (B) Segregation in the friction stir zone, (C) Segregation of β-phase and linear cracking below the shoulder and (D) Unwelded root flaw below the friction stir zone on the weld line, in Specimen C.

Fig. 6.13 Plane polarized light optical micrographs of the HAZ revealing the influence of heat on the grain size showing greater grain sizes compared with the parent alloy microstructure.
Fig. 6.14 Microstructure of AM60 magnesium alloy, parent alloy, revealing (A) IPF image, (B) Band contrast imaging with high angle grain boundaries (>15°)-black, low angle grain boundaries (2-15°)-white, twins-red

Fig. 6.15 EBSD maps from the friction stir zones of specimens A, B and C revealing the grain size variations in the top, middle and bottom of the transverse section.
Fig. 6.16 SEM micrographs showing (A) the parent alloy microstructure of AZ91 magnesium alloy (B) High magnification micrograph revealing α-Mg phase, lamellar precipitation and partially divorced β-phase, (C) Intrinsic porosities, (D) Interdendritic shrinkage porosity.
Fig. 6.17 Optical micrograph of the transverse section of friction stir welded AZ91 Mg alloy, showing
(A) DRX zone, (B) deformed zone, (C) TMAZ and (D) HAZ in specimen D.

Fig. 6.18 SEM micrographs revealing microstructure in TMAZ, (A) advancing side, (B) retreating side,
(C) High magnification image revealing dynamically recrystallized grain structure in friction stir/weld
nugget, (D) High magnification image of the banded microstructure in the friction stir zone.
Fig. 6.19 SEM micrographs revealing microstructure in friction stir zone (A) Segregation of β-phase scattered along the material flow, (B) Localized porosity with material flow pattern (C) and (D) Banded microstructure in the friction stir/weld nugget zone,
Fig. 6.20 Optical micrograph of the transverse section of friction stir welded AZ91 magnesium alloy, showing (A) DRX zone, (B) deformed zone, (C) TMAZ and (D) HAZ in specimen E.

Fig. 6.21 SEM micrographs revealing microstructure in TMAZ, (A) advancing side, (B) retreating side, (C) Grain structure in the friction stir/weld nugget zone, (D) segregation below the shoulder, in specimen E.
Fig. 6.22 Optical micrograph of the transverse section of friction stir welded AZ91 Mg alloy, showing (A) DRX zone, (B) deformed zone, (C) TMAZ and (D) HAZ in specimen F.

Fig. 6.23 SEM micrographs revealing microstructure in TMAZ, (A) advancing side, (B) retreating side, (C) transition zone, (D) grain structure in the weld nugget, in specimen F.
Fig. 6.24 Optical micrographs revealing surface microstructures along the weld line in specimen D, specimen E and specimen F, showing growth in grain size compared to the parent alloy microstructure.

Fig. 6.25 Plane polarized light optical micrographs revealing heat affected zone microstructures in specimen D, specimen E and specimen F, showing growth in grain size compared to the parent alloy microstructure.
Fig. 6.26 Microstructure of AZ91 magnesium alloy. (A) IPF image of parent alloy microstructure, (B) IPF image of weld nugget microstructure with banded microstructure, high angle grain boundaries (>15°)-black, low angle grain boundaries (2-15°)-white.

Fig. 6.27 EBSD maps from the friction stir zones of specimens D, E and F revealing the grain size variations in the top, middle and bottom of the transverse section.
Fig. 6.28 Potentiodynamic polarization curves showing the corrosion behaviour in the respective weld zones in AM60 FSW magnesium alloys.
Fig. 6.29 SKPFM study of the parent alloy in AM60 magnesium alloy
Surface potential map and line profile analysis, across the surface microstructure.

Fig. 6.30 SKPFM study of the friction stir zone in AM60 magnesium alloy
Surface potential map and line profile analysis, across the surface microstructure.

Fig. 6.31 SKPFM study of the heat affected zone in AM60 magnesium alloy
Surface potential map and line profile analysis, across the surface microstructure.
Fig. 6.32 SEM study of surface of FSW AM60 magnesium alloy, parent alloy surface, after immersion in 3.5% NaCl solution.

Fig. 6.33 SEM study of surface of FSW AM60 magnesium alloy after immersion in 3.5% NaCl solution:
(A) Transition zone, (B) TMAZ, (C) & (D) HAZ.
Fig. 6.34 Potentiodynamic polarization curves showing the corrosion behaviour in the respective weld zones in AZ91 FSW magnesium alloys.
Fig. 6.35 SKPFM study of AZ91 magnesium alloy: Parent alloy surface
Surface potential map and line profile analysis, across the surface microstructure.

Fig. 6.36 SKPFM study of AZ91 magnesium alloy: Friction stir zone
Surface potential map and line profile analysis, across the surface microstructure.

Fig. 6.37 SKPFM study of AZ91 magnesium alloy: Heat affected zone
Surface potential map and line profile analysis, across the surface microstructure.
Fig. 6.38 Backscattered SEM images of FSW AZ91 magnesium alloy after immersion in 3.5% NaCl solution revealing (A) Transition zone—specimen D, (B) high magnification image (friction stir zone), (C) Parent alloy.

Fig. 6.39 Backscattered SEM images of the HAZ in FSW AZ91 magnesium alloy after immersion in 3.5% NaCl solution revealing intergranular cracking and transgranular cracking corrosion.
CHAPTER 7

GENERAL CONCLUSIONS AND FUTURE WORK

7.1 General summary and conclusions

7.1.1 Microstructures of AZ series magnesium alloys

From the previous research reported in the Literature Review, it is clear that microstructure plays a vital role in the improvement of the mechanical and corrosion properties of magnesium alloys. The detailed studies of the microstructures of the TRC and MCTRC magnesium alloys conducted in the current research have shown that the MCAST process utilized to generate the MCTRC magnesium alloys proves to be an efficient way to enhance grain refinement in the AZ series magnesium alloys. The following conclusions are made from the metallographic examination of the AZ series TRC and MCTRC magnesium alloys.

- The as-cast microstructure of the magnesium alloys under study was composed of the \( \alpha \)-Mg matrix, the \( \alpha \)-eutectic and the \( \beta \)-phase. Rosette/flower-shaped Al-Mn intermetallics (\(~100-500\) nm), located on the \( \beta \)-phase, Fe/Si impurities in the \( \alpha \)-Mg matrix and the plate-like lozenge-shaped \( \beta \)-precipitates were some of the microconstituents present in the microstructure of Mg-Al alloys under study.
The conventional twin roll cast magnesium alloys displayed a coarse and random grain size distribution across the sheet thickness, with a non-uniform distribution of Al-Mn intermetallics and microsegregation of the β-phase. The strip castings revealed defects, including centre-line segregation, hot cracking and localized plastic deformation; these deteriorate the alloy properties and result in a relatively poor performance.

The influence of the MCAST process, employed in the development of the MCTRC magnesium alloys, gave rise to an improvement in grain refinement with a uniform distribution of fine grains across the sheet thickness and reduced levels of segregation. The transformation from coarse columnar grains in the TRC alloys to a refined equiaxed grain structure in the MCTRC alloys along with uniform distribution of the β-phase was clearly evident from the metallographic investigation.

The intensive shearing of the liquid melt in the MCAST process results in a uniform distribution of the β-phase and the Al-Mn intermetallics across the sheet thickness, with minimal microporosity, giving rise to improved microstructural characteristics and, in turn, improved corrosion properties of the MCTRC magnesium alloys.

The thermomechanically processed AZ31 magnesium alloys revealed considerable refinement in the grain sizes and reduction in the β-phase in the microstructure. The possible mechanisms for dynamic recrystallization occurring during the downstream processing, reveals evidence of twinning, in the grain refinement of the AZ31 TRC magnesium alloys. Due to lack of slip systems in magnesium alloys, twinning plays a dominant role in the recrystallization of magnesium alloys with larger grain sizes, typically shown by TRC Mg-Al alloys.

In the case of AZ31 MCTRC magnesium alloys, no evidence of twinning is observed, suggesting a possibility of strain-induced grain boundary migration (SIBM) as a preferential mode of recrystallization, resulting in ultra-fine grain sizes (≤10 µm), evident from the EBSD results.
7.1.2 Corrosion behaviour of AZ series magnesium alloys

As the corrosion behaviour exhibited by the magnesium alloys is ultimately a consequence of the grain size in the microstructure, grain refinement can show significant transformation in the resultant corrosion behaviour. The key observations due to the influence of the MCAST process on the microstructure and corrosion behaviour of the AZ series magnesium alloys are as follows:

- The coarse and random distribution of grain sizes and the segregation of the β-phase resulted in the deterioration of the alloy surfaces in the TRC magnesium alloys, evident from the immersion testing results. However, owing to the grain refinement in the MCTRC magnesium alloys, along with the uniform distribution of the β-phase, an improved corrosion resistance was evident, with the β-phase acting as a corrosion barrier, evident from the microscopy results.

- The deterioration of the alloy surface was mainly due to galvanic corrosion at localized sites at the Al-Mn/α-Mg and the impurities/α-Mg interfaces, the transverse sections of the corrosion tested specimens revealing the corrosion front restricted by the β-phase, with preferential dissolution of the α-Mg matrix.

- The SKPFM analysis reveals the nobility of the Al-Mn intermetallic particles and the β-phase in the Mg-Al alloys, suggesting the influence of the microconstituent distribution and, in turn, predicting their cathodic activity. Volta potential differences have shown to have a profound effect on the susceptibility to microgalvanic corrosion in the order of Al₈Mn₅ > β-phase > β-precipitates > α-eutectic relative to the adjacent magnesium matrix.

- Localized corrosion initiating from microgalvanic coupling has been observed due to the Al-Mn intermetallics in the AZ61 and AZ91 magnesium alloys. However, the fine particle size of the β-phase results in the microgalvanic corrosion, in the AZ31 magnesium alloys. Filiform-like corrosion morphologies showing spherical, channel-like and individual filaments were some of the corrosion morphologies observed in the magnesium alloys.
The polarization curves revealed no passivation in the as-cast magnesium alloys, indicating that the alloy surface must be continuously attacked, suggesting localized corrosion occurring due to Al-Mn intermetallics and Fe/Si impurities. However, the polarization curves obtained from the downstream processed AZ31 magnesium alloys revealed a significant shift in the anodic corrosion current densities, possibly suggesting increased corrosion resistance provided by the corrosion products. This improvement in the anodic polarization behaviour of downstream processed AZ31 magnesium alloys can be attributed to the grain refinement and the increased protection offered by the corrosion products on the alloy surface, restricting the passage for the corrosive media.

7.1.3 Friction stir welding of magnesium alloys

The influence of the tool rotation rate and the traversing speed on the microstructure of the friction stir welded magnesium alloys investigated in the current research revealed significant microstructure modification in the friction stir/weld nugget zones of the AM60 and AZ91 FSW magnesium alloys. The tool rotation rate of 300 rpm and traverse speeds of 200-350 mm/min showed promising prospects for optimizing the welding conditions for the FSW of AM60 and AZ91 magnesium alloys. The key observations made on the microstructure and the corrosion behaviour of the FSW magnesium alloys are as follows:

The weld microstructure displayed a prominent friction stir zone, separated into two distinct regions, namely, a partially recrystallized zone on the retreating side below the shoulder, revealing a highly deformed microstructure, and the DRX zone on the advancing side, which displayed an ultrafine grain structure with an average grain size ranging from 2-10 µm. The shape of the friction stir zone transformed from basin shape to elliptical, due to the increased deformation at increased traversing speeds. The size of the friction stir zone gradually decreased with the increase in the traverse speed in both the FSW alloys due to the increase in the rate of deformation, leading to widening of the friction stir zone.
The TMAZ showed heavily deformed microstructures in both alloys, with elongated grain structures and the grain boundaries decorated with highly deformed β-phase. The localized increase in temperatures to values above the eutectic melting point (430°C), due to the lower tool rotation rates and traverse speeds, resulted in partial melting and re-solidification of the β-phase in the TMAZ that was evident from the microstructure investigation. The morphology of the β-phase clearly revealed solute segregation, in contrast to the β-phase observed in the parent alloy microstructure. Apart from the increase in the grain sizes, no significant modification was observed in the HAZ microstructure. Evidence of liquation was revealed on the advancing side of the transverse section in the FSW AM60 magnesium alloy, as a consequence of localized increase in temperature below the shoulder, leading to partial melting of the β-phase.

Welding flaws, including localized central porosity due to lack of fusion and unwelded root flaw due to lack of penetration, were observed in the FSW AM60 magnesium alloy while microporosity and linear cracking in the friction stir zone were evident in the FSW AZ91 magnesium alloy.

The electrochemical response of the weld zones in the FSW AM60 alloy showed an improved corrosion resistance compared with the parent alloy microstructure, as the parent alloy microstructure exhibited coarser grain size, higher depletion in aluminium contents across the grains and the β-phase on the grain boundaries. The SKPFM results revealed that the magnesium matrix in the friction stir zone showed higher surface potential values compared with the parent alloy microstructure, due to the dissolution of the β-phase. The immersion testing results were in agreement with the polarization data and the SKPFM analysis, showing an improvement in the corrosion resistance of the friction stir zone, in the FSW AM60 magnesium alloy.

The FSW AZ91 magnesium alloy showed no significant variation in the weld zones and the parent alloy zone from the electrochemical measurements. However, the SKPFM results revealed a higher relative surface potential value in the friction stir zone, due to the dissolution of the β-phase. The immersion testing results revealed higher susceptibility to corrosion in the transition zone due to the flash formation.
and banded microstructure, resulting in microstructure irregularities leading to the failure of the weld zone.

✓ Corrosion morphologies, including fissure formation leading to filiform-like corrosion were evident in the TMAZ of the FSW AM60 magnesium alloy. The coarse grain size resulted in the preferential corrosion occurring in the parent alloy microstructure in the AM60 magnesium alloy. Evidence of intergranular and transgranular cracking in the HAZ and the parent alloy microstructure were apparent in the FSW AZ91 magnesium alloy.

7.2 Suggestions for future work

Lower concentration of NaCl solution: Since the 3.5% NaCl solution is highly aggressive, the magnesium alloy surface is severely attacked and it is difficult to investigate the initiation sites of corrosion. Therefore, using reduced concentrations of NaCl solutions, e.g. 0.005M NaCl solution, would assist in the investigation of the initiation sites of the corrosion process. Further, the polarization curves conducted in lower concentrations of NaCl solution would provide substantial evidence of any pitting occurring on the alloy surface, as the alloy surface would experience a reduced attack of the chloride ions. The polarization curves obtained in 3.5% NaCl solutions did show evidence of localized pitting in some cases. However, since the alloy surface was aggressively attacked, the effect was not pronounced, which could be obtained from lower concentrations of NaCl solutions.

Using 3D tomography in corrosion studies: 3D tomographic studies of corrosion tested magnesium alloys would assist in determining the corrosion front, and the detailed relationship with the microstructure, which is rather difficult to investigate, using 2D microscopic techniques.

EBSD studies of corrosion tested magnesium alloys: Texture studies of corrosion tested downstream processed magnesium alloys have not been largely reported as yet. Since the deformation behaviour of the microstructure of the alloys depends on the processing parameters and, subsequently, reflects the microstructure evolution, the corrosion
properties would also show the respective impact. The co-relation between the microstructure evolution and the resultant texture, as a consequence of deformation, on the corrosion behaviour of the downstream processed magnesium alloys, would be worth investigating.

Using 3D tomography for defect analysis of FSW magnesium alloys: Friction stir welding is a highly efficient joining method and the success of the technology can be enhanced by minimizing the flaws/defects arising due to the FSW process parameters. Microstructure analysis of friction stir welded magnesium alloys using 3D tomography would assist in determining the actual size and depth of the flaws/defects, which is rather difficult to undertake using scanning electron microscopy and optical microscopy. Corrosion tested specimens of the FSW magnesium alloys subjected to 3D tomography would provide an insight of the actual corrosion penetration and the path of the corrosion front.
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