SYNTHESIS OF TOPOLOGICALLY-ORDERED POROUS MAGNESIUM

A thesis submitted in partial fulfilment of the requirements for the Degree

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BY

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This thesis is submitted as a partial requirement for the degree of Doctor of Philosophy in Mechanical Engineering. This research was conducted under the supervision of Dr. Tim B.F. Woodfield and Dr. Mark P. Staiger in the Mechanical Engineering Department, University of Canterbury, between June 2008 and November 2011, which included five months extension as a result of seismic events.
Abstract

Magnesium (Mg) and its alloys offer potential as a new class of degradable metallic orthopaedic biomaterials. In comparison with current metallic orthopaedic implant materials, Mg offers advantages such as, high specific strength, closer-to-bone stiffness and biodegradability, thereby eliminating the need for a second surgery to remove hardware.

The use of porous metal foams as biomaterial scaffolds has been widely adopted, however, many of these porous structures are manufactured with pore architectures that are inherently random. This makes structural optimisation for a specific purpose challenging. Scaffolds containing ordered pore architectures can be fabricated to meet design criteria, such as porosity, stiffness, and volume fraction. Currently there are few methods described in the literature to manufacture ordered porous Mg.

The main aim of this thesis was to determine the resolution of a novel indirect solid free-form fabrication (SFF) process for producing topologically-ordered porous Mg (TOPM) structures from pure Mg and commercial Mg alloys. The produced structures were examined for properties such as dimensional accuracy, microstructure, surface properties, mechanical properties and corrosion behaviour. The capability of the process was further examined in manufacturing structures with complex architecture for potential application as degradable metallic orthopaedic devices, namely a spinal fusion device (SFD) and screw. With the produced structures aimed at load-bearing applications in bone, the mechanical properties and behaviour of the TOPM and SFD made from Mg alloys were investigated using finite element analysis (FEA) and compression testing.

The relationship between surface roughness and degradation behaviour in Mg biomaterials has received limited interest and is still a controversial issue. Therefore, it was necessary to accurately determine the effect of surface roughness on corrosion rate of Mg, especially samples manufactured from SFF and casting of molten Mg. Given the well-established need for improved corrosion resistance of Mg, two coating techniques, including biomimetic calcium phosphates and electrochemically-assisted deposition coating, were applied on Mg substrates cast via the SFF process. Corrosion testing was employed to investigate the effectiveness of the coating layers in improving corrosion resistance.

In this thesis, the capability of the SFF manufacturing process and properties of the produced structures were thoroughly investigated. Results and findings contribute to the development of topology optimised, degradable Mg devices for biomedical applications.
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<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer-aided design</td>
</tr>
<tr>
<td>CaP</td>
<td>Calcium phosphate</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>ECAD</td>
<td>Electrochemically-assisted deposition</td>
</tr>
<tr>
<td>Ecorr</td>
<td>Corrosion potential</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>FEA</td>
<td>Finite element analysis</td>
</tr>
<tr>
<td>hr</td>
<td>Hour</td>
</tr>
<tr>
<td>H₂(g)</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>i_{corr}</td>
<td>Corrosion current density</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>NCSM</td>
<td>Non-contact strain measurement</td>
</tr>
<tr>
<td>PDP</td>
<td>Potentiodynamic polarisation</td>
</tr>
<tr>
<td>RP</td>
<td>Rapid Prototyping</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SFD</td>
<td>Spinal fusion device</td>
</tr>
<tr>
<td>SFF</td>
<td>Solid free-form</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>TOPM</td>
<td>Topologically ordered porous magnesium</td>
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</table>
CHAPTER 1

Introduction
1.1 Overview of the problems

Magnesium (Mg) and its alloys offer advantages over current orthopaedic implant materials such as degradable polymers and bioceramics, or non-degradable stainless steel, cobalt-chrome, titanium (Ti) or titanium alloys (Ti6Al4V). These advantages include the increasing body of evidence demonstrating the safe biodegradation of Mg/Mg alloys in vivo, and more favourable mechanical properties (Young’s modulus) closer to that of native bone [1-3] compared with non-degradable Ti or cobalt-chrome. While certain types of bio-ceramics, such as calcium phosphate (CaP) and hydroxyapatite (HA), are also biodegradable and osteoconductive, they can be less suitable for load bearing applications due to brittleness [4]. Natural and synthetic polymers offer the advantage of controlled biodegradation in vivo, however, the drawback is that they exhibit poor mechanical properties, particularly for porous structures applied in load bearing conditions [5]. On the other hand, stainless steel and Ti alloys have good mechanical properties and corrosion resistance, but are limited in terms of degradability. Therefore, these implants remain permanently in the body, or require a second surgery to remove the implant [6]. For these reasons, porous biodegradable Mg-based implants have the potential to be an ideal alternative.

Porous metals have applications across a wide variety of industries, including lightweight composites, electrical screening, filtration systems and medical devices. While many of these porous metal structures (or foams) are commercially available, it is their applications in orthopaedic devices and tissue engineering fields that have more recently attracted significant attention [7, 8]. As biomaterials, porous metals have advantages of being strong enough to provide suitable mechanical properties for the implanted site while remaining lightweight. More importantly, the porous architecture helps facilitate tissue growth and anchoring of the implant to the recipient tissue (e.g. bone), as well as supporting flow of tissue fluid carrying nutrient, which are two of the most important requirements for successful application of porous biomaterial scaffolds in the repair or replacement of damaged or diseased tissues [9].

To date, the manufacturing of porous cellular metals has primarily focused on the fabrication of random architectures (e.g. cellular foams) from different materials, such as Ti, Ti alloys, tantalum and aluminium (Al). For example, a three dimensional (3D) fibre deposition and powder sintering method was used to produce porous Ti-6Al-4V structures with interconnected pores and porosity of up to 90% [10]. Laser-engineered net shaping (LENS™)
techniques have been used by Krishna et al. to make porous Ti–6Al–4V scaffolds for load-bearing implants [11], whereas, in a different study, a multi-stage rapid prototyping technique together with a powder sintering process produced porous Ti scaffolds aimed for orthopaedic applications [12]. However, while these random porous architectures may meet mechanical requirements, they are generally not suitable for the purposes of optimising scaffold properties such as porosity, stiffness and permeability [13], and do not allow precise control over pore architecture. These random porous structures typically have homogenous mechanical and biological properties at the macro level, but not at the micro level. This results in undesirable behaviour in the material, such as reduced effective stress and strut bending and twisting [14]. Manufacturing routes which permit the design and fabrication of topologically-ordered porous structures allow accurate control over pore structure, which inherently provides desired characteristics in certain regions, while other regions can be tailored for other functional requirements.

While reasonable attention has been paid to manufacturing materials such as Ti, Al, ceramics and polymers in ordered porous form [12, 15-19], most porous Mg scaffolds reported in the literature have relied on existing foam fabrication methods resulting in random porous architectures. For example, Gu and colleagues manufactured lotus-type porous pure Mg using metal/gas eutectic unidirectional solidification method (GASAR process) [20]. Ho et al. adopted a lost foam casting method to produce a micro-truss sandwich core foam from Mg alloy AZ91 [21], whereas Wen et al. made porous pure Mg scaffolds using a powder metallurgical process [22]. Recently, Tan et al. used a mechanical perforation technique to produce porous Mg structures with controllable pore size, pore arrangement and hence, porosity [23], however, the manufacturing method was limited by pore shape and regional optimisation.

Solid free-form fabrication (SFF) methods, which adopt a layer-by-layer fabrication process from computer aided design (CAD) models, have been shown as an ideal solution for manufacturing complex 3D porous structures by accurate control of pore topology. Different techniques are available, such as fibre deposition, laser sintering and 3D printing [7]. However, due to the difficulties in powder processing or sintering of Mg, very few studies have focussed on developing reliable, safe and relatively low cost methods for manufacturing topologically-ordered porous Mg (TOPM) scaffolds. In this thesis, the solid free form fabrication (SFF) manufacturing process for manufacturing TOPM scaffolds will be
investigated. This process was developed with the aims of precise control of pore size and shape of the porous structure to meet specific biological requirements.

It is well established in biomaterials literature for bone interfacing implants that surface macro- and micro-topography plays a critical role in directing *de novo* bone formation, osteoconduction and osseointegration in a range of biomaterials including titanium (Ti) alloys, ceramics and coatings [24-29]. For example, micro-topographies generated on Ti substrates in the range of areal surface roughness of $S_a > 1-2 \mu m$ have been suggested to be the predominant factor for platelet activation during early *de novo* bone formation resulting in enhanced osteoconduction and bone contact [28, 30, 31]. As a result, one could hypothesise that the natural progression for the development of degradable bone-interfacing Mg devices, is to adopt identical topographies to those described for Ti above. However, for degradable metals, the presence of rough surfaces to enhance the biological response, such as tissue formation and implant fixation, may need to be carefully considered if there is any associated increase in corrosion rate, particularly in relation to the timing of the desired tissue remodelling and repair processes. Previous studies on stainless steel found that increasing surface roughness resulted in increasing corrosion rate and pitting potential [32-34].

However, the relationship between surface roughness and degradation behaviour of Mg is less thoroughly understood. Previous results have been contradictory, with most studies not targeted at biomaterials applications of Mg, and the commonly adopted methods for testing *in vitro* biocorrosion behaviour of Mg not used [35-37]. Furthermore, the roughness values examined in these studies was relatively narrow, ranging from approximately 80 to 430 nm, as compared to studies comparing bone formation and osteoconduction on Ti substrates which typically range from less than 0.5 µm to 10 µm and above [28]. This thesis will aim to accurately determine the role of surface roughness on the corrosion rate of pure Mg biomaterial as manufactured using the developed SFF method, as well as investigate suitable methods to improve the corrosion behaviour of the material.

The major problem faced by Mg as a biomaterial is its fast degradation rate in the physiological system due to pH levels and the high chloride environment [38-41]. A significant amount of interest and effort has been paid to investigate mechanisms for improved corrosion resistance of Mg, primarily via alloying Mg with other elements or applying coating layers on the Mg surface. Therefore, the developed SFF manufacturing route needs to be capable of manufacturing accurate structures in a range of Mg alloys.
Chapter 1 – Introduction

Regarding the applying coating, techniques such as alkaline treatment, heat treatment, microarc oxidation, electrodeposition and ion implantation have been investigated to increase corrosion resistance of Mg [42]. In this study, biomimetic CaP and electrochemically-assisted deposition (ECAD) coating will be applied on the samples with rough surface, thereby seeking to improve corrosion protection. In vitro corrosion testing will be performed to evaluate the effectiveness of each coating technique.

As biomaterials, TOPM has the potential to be used for a wide range of applications, from bone grafting to orthopaedic medical devices [9, 43]. In this thesis, the capabilities of the SFF manufacturing route will be tested with the aim to produce a prototype biodegradable cervical spinal fusion device (SFD) and screw. This work was considered a proof-of-concept and a pilot study, from which the experience and conclusions would contribute to future work in using the manufacturing process for making orthopaedic devices from Mg and its alloys.

References


Chapter 1 – Introduction


1.2 **Aims and Thesis Outline**

1.2.1 **Aims**

The main aims of this thesis were to determine the capability and resolution of a solid free-form fabrication (SFF) method developed for manufacturing topologically-ordered porous magnesium (TOPM) structures, and to evaluate properties of the produced TOPM scaffold in relation to its potential application as biomaterial. Via a range of well-established techniques, the structural, mechanical and corrosion properties of the TOPM structures will be characterised. The specific aims are as follow:

**I. Synthesis of TOPM structures**

*Aim*: To manufacture scaffolds with defined architectural properties from both Mg and Mg alloys using an indirect SFF method.

The capability of a multi-step SFF method for manufacturing TOPM structures with different level of structural complexity from pure Mg is examined. The resolution limits of each step of the manufacturing process will be systematically characterised to compare the final dimensions and architecture of as-produced Mg structures with those parameters from the original CAD design. This work also focuses on testing the capability of the manufacturing technique to cast scaffolds from Mg alloy (AZ91D). The structural properties of the AZ91D TOPM scaffolds will be compared with that of pure Mg TOPM samples for any improvement introduced in response to change of casting material.

**II. Effect of surface roughness on the corrosion behaviour of pure Mg**

*Aim*: To determine the role of surface roughness on the corrosion rate of pure Mg biomaterial, and therefore understand the corrosion properties of pure Mg TOPM scaffolds

Samples for the corrosion tests are produced from the SFF technique to generate similar surface properties as of the TOPM scaffolds. The results will help evaluate the corrosion behaviour of the pure Mg TOPM structures. The corrosion properties are evaluated via a range of well-defined corrosion testing techniques, including hydrogen evolution, mass loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP).
III. Improving corrosion resistance via coating techniques

*Aim*: To evaluate the performance of two coating techniques in improving the corrosion resistance of cast Mg samples with rough surface finish

Two coating techniques, including biomimetic calcium phosphate (CaP) and electrochemically-assisted deposition coating (ECAD), will be applied on Mg sample cast via the SFF method. The effectiveness of each coating method is evaluated via examining the corrosion behaviour of coated samples.

IV. Mechanical properties of TOPM scaffolds

*Aim*: To evaluate the mechanical properties of as-produced AZ91D TOPM scaffolds and determine the relationship between actual and predicted mechanical properties of the porous scaffold

The predicted mechanical properties of the AZ91D TOPM structures as determined by finite element analysis (FEA) will be compared to that of the actual compression testing as performed on the produced structures. The outcome will help validate the TOPM scaffolds in terms of having predictable mechanical properties.

V. Cervical spinal fusion device

*Aim*: To test the capability of the SFF fabrication route in applied to the manufacture of porous biomedical devices

In an attempt to combine the findings collected from aims I to IV, a prototype biodegradable cervical spinal fusion device (SFD) and screw are selected for manufacturing. Based on the understanding about the porous architecture of the TOPM scaffold, the SFDs are designed with two different internal porous architectures. Mechanical properties of the SFD will be examined using FEA and compression testing, and evaluated for the suitability for use in the intended application.
1.2.2 Thesis outline

The chapters of this thesis are summarised as follows:

**Chapter 2** provides an overview of Mg, its properties and applications, especially as a biomaterial. Corrosion testing methods and corrosion protection for Mg are also discussed, as well as presenting the current state-of-the-art techniques for manufacturing of ordered porous structure. This will be followed by an overview discussing the potential and challenges involved in adopting Mg in orthopaedic applications, specifically as a spinal fusion device.

**Chapter 3** describes the SFF method developed in detail and the six main steps involved. Properties of the produced TOPM structures are examined via dimensional accuracy, surface area, volume and porosity changes, surface properties and microstructure. Structures with complicated architecture will be manufactured via this method.

**Chapter 4** presents a systematic investigation of the *in vitro* corrosion rate of samples manufactured using the SFF technique in relation to substrate surface roughness.

**Chapter 5** investigates the role of coating systems on improving the corrosion resistance of cast Mg samples and the influence of surface roughness based on topographies studied in Chapter 4. Biomimetic CaP and ECAD coating techniques are investigated.

**Chapter 6** demonstrates the capabilities of manufacturing TOPM scaffolds from Mg alloys (AZ91D) and characterisation of the as-manufactured structures.

**Chapter 7** investigates the mechanical properties of the various TOPM structures manufactured from AZ91D by means of FEA and compression testing to validate the capabilities of the TOPM method to allow direct control over desired mechanical properties for orthopaedic applications.

**Chapter 8** describes a proof-of-concept study for applying the SFF method and TOPM in manufacturing bone-interfacing orthopaedic devices with controlled architecture and properties specifically for spinal fusion and screw fixation applications.

**Chapter 9** presents the overall conclusions of the research and discusses areas for future work.
CHAPTER 2

Literature review
2.1 Chapter preface

This chapter provides an overview of magnesium (Mg), and an introduction to its history, properties and applications. The suitability of Mg for use as biomaterial will be discussed in terms of the role of Mg in the human body, previous studies implanting Mg in vivo, and issues facing researchers in the use of Mg as a biomaterial. This is followed by the review of the manufacturing techniques of porous metallic structures. Finally, state of art and challenges in developing spinal fusion device will be presented.

2.2 Introduction to magnesium

2.2.1 A brief history of Magnesium

Mg is the 7th most abundant element in the Earth’s crust by mass [1]. It was first discovered by a Scottish chemist, Joseph Black, in 1755. However, the element was not successfully isolated until 1808 by Sir Humphrey Davy by means of electrolysis. In this method, wet Mg sulphate was decomposed using a voltaic cell and a mercury cathode [2-3]. In the natural environment, Mg does not exist in metallic form, but in ionic form, since it is highly reactive ($E^0 = -2.375$ V) [4]. Mg can be extracted from natural raw materials, such as magnesite, dolomite, bischofite, carnallite, serpentine, and sea water.

Over the years, different Mg production technologies have been developed and used widely around the world. Among these, electrochemical and thermal reduction methods are the two basic techniques. As the name suggests, in the electrochemical method, the extraction is performed using electric current applied to the electrolyte cells, while thermal reduction methods use high temperature as a means of reduction [5-7]. The latter method consumes relatively more energy than the former one, however, produces higher purity metal extraction [8].

Since its discovery, Mg and its alloys have been studied and developed for use in various sectors from household appliances, automobiles, and aircraft to military. At the beginning, Mg usage was limited and mainly studied for curiosity. This was due to three main factors, including difficulty in its isolation, rapid corrosion and poor mechanical properties [2]. However, with the technological development and the growing interest in light weight metals,
Mg studies started to attract more attention and achieved significant results. Typically, it was used in the car industry as car frame or engine block due to its high specific strength. For example, being approximately 4.5× lighter than stainless steel, the yield strength of Mg is only 2.7× lower than that of stainless steel. Furthermore, the elongation properties of Mg are similar to that of titanium (Ti) alloy while its density is roughly 3× lower than that of Ti [9-12].

During World War I and II, Mg was one of the main construction metals for German aircraft [2]. Figure 2.1 illustrates other examples of Mg alloy products, such as a lawn-mower housing and rocket.

![Figure 2.1: Mg (A) lawn-mower housing and (B) Titan I rocket [2]](image)

2.2.2 **Magnesium properties**

Mg is a chemical element in the alkaline earth metal group with atomic number 12 and common oxidation number +2. Physical properties of Mg are as shown in Table 2.1 with data collected from [2, 9, 11, 13-14]. Mg burns at approximately 3100 °C and produces intense, bright and white light. Since Mg is highly flammable, safety precautions when working with Mg need to be taken seriously.
Table 2.1: Physical properties of Mg

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>650 ± 2°C</td>
<td>Thermal Conductivity at 25 °C</td>
<td>155 W/(kg K)</td>
</tr>
<tr>
<td>Latent Heat of Fusion</td>
<td>0.37 MJ/kg</td>
<td>Linear Coefficient of Thermal Expansion at 20 °C</td>
<td>25.2 x 10^-6 K^-1</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>1107 ± 10°C</td>
<td>Electrical Resistivity at 20 °C</td>
<td>4.45 µΩ cm</td>
</tr>
<tr>
<td>Latent Heat of Evaporation</td>
<td>5.25 MJ/kg</td>
<td>Volume Change During Solidification</td>
<td>4.2 %</td>
</tr>
<tr>
<td>Heat of Combustion</td>
<td>25.1 MJ/kg</td>
<td>Density at 20 °C</td>
<td>1.738 g/cm³</td>
</tr>
<tr>
<td>Specific Heat</td>
<td></td>
<td>Density at 600 °C</td>
<td>1.622 g/cm³</td>
</tr>
<tr>
<td>At 20 °C</td>
<td>1030 J/(kg K)</td>
<td>Density at 650 °C (solid)</td>
<td>1.65 g/cm³</td>
</tr>
<tr>
<td>At 600 °C</td>
<td>1178 J/(kg K)</td>
<td>Density at 650 °C (liquid)</td>
<td>1.58 g/cm³</td>
</tr>
</tbody>
</table>

Table 2.2 shows the mechanical properties of Mg in comparison with Ti alloy and stainless steel, which are among the most popular metals. Generally, Mg is weaker than Ti and stainless steel with Young’s modulus approximately 3× and 5× lower than that of Ti and stainless steel, respectively.

Table 2.2: Mechanical properties of Mg, Ti alloy and stainless steel [9-12]

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>TiAl6V4</th>
<th>Stainless Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>90-220</td>
<td>830-1025</td>
<td>480-620</td>
</tr>
<tr>
<td>Compressive Yield Strength (MPa)</td>
<td>21-115</td>
<td>760-880</td>
<td>170-310</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>2-15</td>
<td>12</td>
<td>30-40</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>41-45</td>
<td>114</td>
<td>193</td>
</tr>
<tr>
<td>Specific strength (kN×m/kg)</td>
<td>158</td>
<td>288</td>
<td>254</td>
</tr>
</tbody>
</table>
2.2.3  

*Mg corrosion*

Mg and its alloys are known to degrade in aqueous environments via an electrochemical reaction which releases hydrogen gas (\(H_2(g)\)). The overall corrosion reaction of Mg is as shown in equation 2.1.

\[
\text{Mg}(s) + 2\text{H}_2\text{O}(aq) \rightarrow \text{Mg(OH)}_2(s) + \text{H}_2(g) \tag{2.1}
\]

Equations 2.2-2.4 show the partial reactions that compose the overall reaction.

\[
\begin{align*}
\text{Mg}(s) & \rightarrow \text{Mg}^{2+}(aq) + 2 \text{ e}^- \text{ (anodic reaction)} \tag{2.2} \\
2\text{H}_2\text{O} + 2 \text{ e}^- & \rightarrow \text{H}_2(g) + 2 \text{ OH}^- \text{ (cathodic reaction)} \tag{2.3} \\
\text{Mg}^{2+}(aq) + 2 \text{ OH}^- \text{ (aq)} & \rightarrow \text{Mg(OH)}_2(s) \text{ (product formation)} \tag{2.4}
\end{align*}
\]

In moist environments, Mg forms a thin layer on the surface that consists mainly of Mg(OH)\(_2\). Formation of the layer is as explained in equation 2.1. This layer is described to be discontinuous and offers limited corrosion protection [14-17]. Corrosion of Mg and its alloys is dependent on the composition of the alloy and the aqueous environment. For example, in a solution with chloride concentration of 30 mmol/L or above, Mg(OH)\(_2\) converts quickly into highly soluble MgCl\(_2\). Because of this active and rapid dissolution, the corrosion rate is increased [15]. Furthermore, the pH value of the electrolyte solution can significantly affect the corrosion behaviour of Mg [18]. At a pH above 12, a stable and self-healing protective layer (Mg(OH)\(_2\)) is formed on Mg substrates [19]. As shown in the Pourbaix diagram (Figure 2.2), at a pH of 10-11, the layer stays between stable and unstable states [19].
Furthermore, alloying elements have a significant role in controlling the corrosion rate and behaviour of Mg. Figure 2.3 shows the changes in corrosion rate of binary Mg alloys according to added constituent in 3% NaCl solution [21].

![Figure 2.2: The Pourbaix diagram for pure Mg in water at 25 °C [20-21]](image)

**Figure 2.2: The Pourbaix diagram for pure Mg in water at 25 °C [20-21]**

In most cases, corrosion of Mg initiates from a localised but shallow corrosion, then spreads and covers the entire surface [16, 23]. Tunold et al. found that corrosion of commercially...
pure Mg was normally transgranular, while it was more uniform for Mg alloys [24]. This is one of the main reasons that pure Mg is not commonly used in everyday applications, but alloyed with other elements. Mg alloys can be tailored to meet certain requirements, such as increased corrosion resistance, in conjunction with increased mechanical properties and reduced grain size [25-27]. Mg can form solid solutions with many elements, although the most common commercial alloys are based on additions of aluminium (Al), calcium (Ca), lithium (Li), manganese (Mn), silicon (Si), silver (Ag), zinc (Zn), copper (Cu), tin (Sn) and iron (Fe) [2, 13]. Rare earth elements (REs), such as yttrium (Y) and thulium (Tm), are also popular alloying elements [2, 9, 13]. Adding the alloying elements has been known to contribute to the generation of specific properties for the alloy and also increase the ease of manufacturing. For example, Al is the most common alloying element and has been known to improve strength and ductility [2]. Meanwhile, Zr is an excellent grain refining agent and can be used with other elements, such as Zn, Al, Tm and other REs [2-3, 28-29] to also enhance mechanical properties. Moreover, the corrosion behaviour of Mg alloys can vary greatly depending on the alloying element. For example, pitting corrosion was more likely to occur in Mg-Al alloys due to corrosion attack along the Mg$_{17}$Al$_{12}$ network [30]. Furthermore, while Ca is a popular alloying element, it was found to increase the corrosion rate of Mg significantly when alloyed above the solid solubility limit of 1.34 wt.% [31-32].

2.3 **Magnesium as biomaterial**

2.3.1 *Biomaterials - definition*

Even though the term “biomaterial” has only been more recently coined [33], humans have been using biomaterials for medical purposes for centuries. For example, gold was used by the Romans, Chinese and Aztec in dentistry more than 2000 years ago. History also reported common use of glass eyes and wooden teeth [33-34]. With the development of science and technology in the early 20th century, synthetic plastics started to be used as biomaterials. For instance, poly (methyl methacrylates) (PMMA) was introduced in dentistry in 1937. Just after World War II, parachute cloth (Vinyon N) was used as a vascular prosthesis [33, 35]. In the early 1960s, PMMA, ultrahigh-molecular-weight polyethylene and stainless steel were developed by Charnley for total hip replacement applications [33, 36-37]. Even though the research and development of materials for medical applications were reported during this
period, the term “biomaterial” was still not officially defined until a decade later, and was marked by the formation of the Society for Biomaterials in 1975 [33]. Since then, research in biomaterials has been well-developed and classified into different but interconnected fields, such as drug delivery, biosensors, and medical devices.

There are many different definitions for “biomaterials”, none of which are universally accepted. The definition suggested by Williams defined biomaterials as “a nonviable material used in a medical device, intended to interact with biological systems” [38]. However, this definition fails to cover the application of natural biomaterials in tissue engineering. A more commonly accepted definition by the Clemson University Advisory Board for Biomaterials defined it as “a systematically and pharmacologically inert substance designed for implantation within, or incorporation with, living systems” [34]. Yet this description does not include certain biomaterials that are not inert. Given that the short and concise definitions could not cover the whole range of biomaterials, the most relevant definition is relatively longer; it is “materials of synthetic as well as natural origin in contact with tissue, blood, and biological fluids, and intended for use for prosthetic, diagnostic, therapeutic, and storage applications without adversely affecting the living organism and its components” [39].

2.3.2 Biomaterials – standards and requirements

Depending on the desired application, biomaterials need to satisfy certain requirements, including toxicity, biocompatibility, mechanical properties and performance, ethics and regulations. With regards to toxicology, a biomaterial should not be toxic unless it is specifically designed for a certain purpose, such as in cancer treatment. This is because toxic materials kill cells via inhibiting key metabolic pathways [33]. Furthermore, biocompatibility is another primary concern in considering the suitability of biomaterials, and can be defined as the acute and chronic inflammatory responses and the fibrous capsule formation that is observed over various time points following the implantation of the material in vivo [40-41]. Appropriate selection of biocompatible materials can be based on the level that the body can tolerate that material [42].

Each biomaterial or device is subjected to mechanical and performance requirements, which are set by the location and function of the affected site in vivo [33]. For example, a knee or hip replacement must be strong and rigid to support physiological loads in the body as well as
provide long term articulation for joint motion [43-44]. Meanwhile, intravascular stents need to be flexible enough to be delivered to the site and have low elastic radial recoil in order to achieve the final diameter as originally designed [45-46]. With regard to ethical issues, several questions should be addressed when working with biomaterials, such as animal and human testing, the life of the device, and the balance between cost of the device with the financial goal of the company [33, 47]. Similarly, research and development of biomaterials must follow regulatory systems such as those imposed by the Food and Drug Administration (FDA) and International Standards Organization (ISO), that were set up to ensure safe medical devices for the patients [33-34, 48].

2.3.3  **Magnesium and the human body**

Mg is the 4th most abundant cation in the body [49], with approximately 760 mg at birth, which increases up to 25 g in the adult [50-52]. The recommended intake of Mg is 400 mg per day [53]. Approximately 50-60% of physiological Mg is located in bone tissue [54], where it is one of the important ions of the biological appetites that make up the bulk of bone mineral. In recent studies, Mg has been shown to increase the rate of bone formation when ingested orally or incorporated into ceramic coatings [55-58]. The remainder of Mg is normally found in muscles and soft tissues [59-60]. Additionally, Mg is essential to human metabolism, whereby it acts as a co-factor in many enzymatic reactions involved in energy metabolism, and is a regulator for more than 350 proteins. Mg also plays a role in stabilising the structures and synthesis of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) [61-63].

In regulating blood sugar and heart rhythm, the level of Mg in the normal blood serum ranges from 0.73-1.06 mmol/L [64]. Exceeding this level can lead to muscular paralysis, hypotension and respiratory distress [63], or more seriously, cardiac arrest at Mg levels of 6-7 mmol/L [65]. With such important roles in the human body, Mg deficiency can also lead to serious problems, especially cardiac arrhythmia and pulmonary oedema [66-67]. More commonly, a decline in Mg level is marked with symptoms such as nausea, muscular weakness, staggering and weight loss [59, 66]. The majority of Mg in the body is absorbed via daily food intake [68]. Meanwhile, control over excess Mg in the body is regulated via storage in bone and muscle and excretion via the kidneys [69-70].
In addition to being an essential element for the human body which can be safely removed from the body via the kidney, Mg is considered to be biocompatible and non-toxic [54, 63, 71]. With these advantages, Mg has the potential to be an ideal biomaterial, especially for orthopaedic implants [72-73].

2.3.4 History of magnesium as a biomaterial

There have been an increasing number of studies investigating the potential of Mg for biomedical purposes in recent years, with proposed applications ranging from cardiovascular stents, to screws, plates, fixation devices and bone-interfacing implants [62, 72, 74-80]. Recently, biodegradable cardiovascular Mg stents have been successfully investigated in animals [81-83] and in clinical trials in humans [81, 84-85]. Furthermore, Mg chips were studied in applications for vertebral fusion in sheep [86]. In other studies, porous scaffolds made from Mg alloys were investigated as load bearing biomaterials for tissue engineering [87-89].

The first application of Mg as a medical device dates back to 1878 when the physician Huse successfully used Mg wires as ligatures to stop bleeding vessels. In the report, he suggested that the corrosion of Mg was slower in vivo and dependent on the size of the wire [90]. However, the most influential initial research on Mg was performed by the Austrian physician Erwin Payr. In his studies, Mg was used in various applications and his reports inspired many other scientists [91]. In particular, Payr made an important proposal on the corrosion mechanism of Mg. He proposed that tissue oxygen, water content, carbon dioxide, the dissolved salts in blood, and chemical processes in cells were responsible for in vivo corrosion of Mg [91-92]. Later, work performed by Albin Lambotte and Jean Verbrugge, included using an Mg plate and steel nails to secure a leg fracture in both animal experiments and clinical studies [93-96].

However, research and interest in using Mg for biomedical applications were slow after this period due to consistent problems in controlling Mg corrosion rate [97]. The concept of alloying Mg with other elements to improve its properties emerged around this time. In 1924, Seelig found that Mg wires available in the market were too brittle and he suggested that it should be alloyed with other metals to increase ductility [98]. In 1948, Troitskii and Tsitrin reported the successful treatment for 34 pseudarthrosis cases, in which a plate and screw
made of Mg-Cd alloy were used [73]. In 1969, a patent for alloying Mg with Cd to improve corrosion properties was submitted by Stroganov, where he reported that a pin made of RE Mg alloy with diameter of 8 mm lasted for 11 months in the in vivo environment [99].

In recent years, there have been an increasing number of studies seeking to improve the corrosion resistance of Mg for biomedical purposes via alloying. For example, Witte et al. explored four alloys with different alloying elements, two of which contained Al and Zn, while the others had RE elements [100]. It was found that the alloying element affected the in vivo corrosion behaviour and corrosion rate of the Mg alloy following the implantation in guinea pig femur [100]. Consequently, Mg research changed to focus more on the effect of certain types of alloying element and adopting the use of simulated body fluid for in vitro testing. For instance, Kirkland et al. and Kim et al. investigated the influence of Ca addition on Mg corrosion in vitro by varying the percentage of Ca added into the alloy [31, 101]. Similarly, Huan et al. compared the degradation behaviour and cytocompatibility of different Mg-Zn-Zr alloys [102].

Meanwhile, many other studies have explored the effect of heat treatment on the corrosion properties [103-105]. Song et al. reported a strong correlation between corrosion rate and ageing time for AZ91D. When aged at 160 °C, corrosion rate of AZ91D decreased as ageing time increased in the initial stages. However, after ageing times of 45 hr and above, the corrosion rate increased with increasing ageing time. This dependence was suggested to relate to the changes in microstructure and local composition during the ageing process [103]. In a more recent study, Zhou et al. found that treating AZ91D at 200 °C for 8 hr, 16 hr and 24 hr reduced the corrosion rate from 30% up to 60% compared with as-cast samples [105].

A number of studies have investigated the performance of various Mg alloys in vivo in animal models. For instance, in an experiment performed by Witte et al., an Al-Zn alloy was implanted in femoral defects in rabbits, and after 3 months in vivo, the implant had largely degraded with most of the Mg disappeared and replaced by new bone [87, 100, 106]. In other studies, Mg was investigated as a degradable coronary stent, and was reported to be successful with minimal impact to the surrounding tissues [81, 107-108].
2.3.5 Advantages of Mg as biomaterials

2.3.5.1 Density and specific strength

Mg is an exceptionally light weight metal with density of approximately 1.74 g/cm$^3$, compared with 2.7 g/cm$^3$ for Al, 4.4 g/cm$^3$ for Ti or 7.9 g/cm$^3$ for stainless steel [72, 109-110]. Moreover, the density of Mg is similar to that of natural bone, which ranges from 1.8-2.1g/cm$^3$ [111]. Therefore, medical devices made from Mg will not introduce significant weight increase as compared to other metallic biomaterials [111-112]. For instance, the common medical-grade Ti alloy implant can be more than 50% denser due to its higher density compared with that of Mg [113].

Furthermore, special treatment to Mg alloy, such as rapidly solidified, can increase specific strength of Mg$_{85}$Zn$_{12}$Ce$_3$ from 130 kN×m/kg up to 360 kN×m/kg [114], which is higher than that of commonly used Ti alloy Ti6Al4V. Therefore, orthopaedic devices made of Mg can be lightweight, while providing required mechanical function for the affected site.

2.3.5.2 Stress shielding

As biomaterials, Mg and its alloys offer advantages over current orthopaedic implant materials such as degradable polymers and bioceramics, or non-degradable stainless steel, cobalt-chrome, Ti or Ti alloys [62, 72]. The advantages include the more favourable mechanical properties, which are closer to that of native bone [72, 100, 115] compared with non-degradable biometals, degradable ceramic hydroxyapatite (HA) and polymers such as polycaprolactone (PCL) and poly(ether-ether-ketone) (PEEK) (Table 2.3). While certain types of bio-ceramics, such as calcium phosphate (CaP) and HA, are also biodegradable and osteoconductive, they can be less suitable for load bearing applications due to brittleness [116]. Natural and synthetic polymers such as PCL offer the advantage of controlled biodegradation in vivo, however, the drawback is that they exhibit poor mechanical properties, particularly for porous structures applied in load bearing conditions [117].

Moreover, stress shielding is one of the biggest concerns for load-bearing biomaterials, which occurs when the stiffness of the orthopaedic device is different from that of the surrounding or integrating bone, and leads to an uneven stress distribution between bone and implant. If the stiffness of the implant is higher than that of bone, the stress concentration in the
surrounding bone will be lower than usual and can cause bone resorption and loosening of the implant. In the opposite case, if the implant is not sufficiently stiff, micro-motion can cause fibrous encapsulation and loosening at the implant-bone interface, or potential implant failure due to higher stress concentrations [118-120]. Stress shielding can affect bone remodelling and normal healing processes since under-loaded bone will adapt to the low stress environment and become more porous and weak [121]. Stress shielding-related problems were observed in orthopaedic devices based on non-degradable biometals, such as stainless steel and Ti [121-122]. For these reasons, Mg, with its favourable mechanical properties (Young’s modulus) close to that of native bone, has the potential to minimise the risk of stress shielding [72-73, 87-88].

Table 2.3: Summary of the mechanical properties of popular biometals (Ti and stainless steel), degradable polymers (PCL and PEEK), and degradable ceramics HA in comparison with natural bone and Mg [33, 72-73, 111, 123-133]

<table>
<thead>
<tr>
<th></th>
<th>Elastic modulus (GPa)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cortical bone</td>
<td>3-27</td>
<td>80-190</td>
</tr>
<tr>
<td>Trabecular bone</td>
<td>0.3-3</td>
<td>0.1-100</td>
</tr>
<tr>
<td>Mg</td>
<td>41-45</td>
<td>65-100</td>
</tr>
<tr>
<td>Ti alloy</td>
<td>110-120</td>
<td>758-1117</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>189-210</td>
<td>170-310</td>
</tr>
<tr>
<td>PCL</td>
<td>0.3-0.32</td>
<td>38.7</td>
</tr>
<tr>
<td>PEEK</td>
<td>3-4</td>
<td>93</td>
</tr>
<tr>
<td>HA</td>
<td>114–130</td>
<td>21.3-271.2</td>
</tr>
</tbody>
</table>

2.3.5.3 Degradability

In comparison with Mg, stainless steel and Ti alloys are limited in terms of degradability. Implants made from these materials remain permanently in the body, or require a costly and/or painful secondary surgery for removal [134]. Being biodegradable, devices made from
Mg have the potential to perform a temporary function in vivo and be completely replaced by new tissue growth overtime, thus reduce the risk of stress shielding or the need for secondary surgery. Moreover, with non-degradable load bearing implants, there is a risk of wear debris, particles or metal ions being released from the device and resulting in further problems, such as osteolysis and hypersensitivity reactions [135-139]. Such problems may be avoided with the use of Mg since it is tolerated by the body and the excess can be removed via urinary system [54, 61, 63, 140]. For these reasons, porous biodegradable Mg-based implants have the potential to be an ideal alternative.

A summary of the suitability of Mg as biomaterial is as shown in Table 2.4.

*Table 2.4: Requirement of biomaterial and the corresponding properties of Mg*

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Mg properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-toxicity and biocompatibility</td>
<td>4(^{th}) most abundant cation in the body</td>
</tr>
<tr>
<td></td>
<td>Can be found in bone tissue, muscles and soft tissues</td>
</tr>
<tr>
<td></td>
<td>Essential to human metabolism</td>
</tr>
<tr>
<td></td>
<td>A regulator for more than 350 proteins</td>
</tr>
<tr>
<td></td>
<td>Stabilising the structures and synthesis (DNA) and (RNA)</td>
</tr>
<tr>
<td></td>
<td>Regulating blood sugar and heart rhythm</td>
</tr>
<tr>
<td></td>
<td>Excess Mg can be regulated via storage in bone</td>
</tr>
<tr>
<td></td>
<td>Can be safely removed from the body via the kidney</td>
</tr>
<tr>
<td>Young’s modulus close to that of bone to avoid stress shielding</td>
<td>Closer to that of native bone than other biometals and bioceramics</td>
</tr>
<tr>
<td></td>
<td>Reduced or negligible stress-shielding</td>
</tr>
<tr>
<td>Low density</td>
<td>Light weight with density of 1.74 g/cm(^3)</td>
</tr>
<tr>
<td>Strength higher than that of bone to safeguard the surrounding bone in vivo</td>
<td>Stronger than biodegradable polymers and bioceramics</td>
</tr>
<tr>
<td>Biodegradability</td>
<td>Safely degrade in the body when corrosion rate is properly tailored</td>
</tr>
</tbody>
</table>
2.3.6 **Problems facing Mg biomaterials**

Despite the advantages mentioned above, the use of Mg for biomedical applications is still clinically limited due to a number of problems as described below.

2.3.6.1 *Low elastic modulus*

Even though the mechanical properties of Mg are close to that of human bone and help eliminate problem associated with stress shielding, they can potentially limit Mg from being used for applications that require high fatigue or compressive strength. More importantly, being degradable, Mg implants will lose strength as they corrode throughout the bioresorption and bone or tissue remodelling process. Without a clear understanding about the characteristic of this process under specific *in vivo* applications, there is the risk that Mg implants may not be able to support the load bearing environment for which they were originally designed, and subsequently fail.

2.3.6.2 *Rapid degradation and hydrogen evolution*

The major problem faced by Mg as a biomaterial is its rapid degradation rate in the physiological environment due to the pH levels (7.4-7.6) and the high chloride conditions present *in vivo* [74, 141-143]. This leads to the risk that the implant may degrade too rapidly before the new host tissue can infiltrate and mature in order to support physiological loads in the affected site.

The rapid degradation of Mg can also cause an adverse biological response as Mg and other element ions are released too quickly into the body. Even though alloying elements are selected with non-toxicity as a primary requirement, materials such as Zn, Ca and Mn can be toxic if released at a rate that the body cannot cope with. For example, Zn excess is known to adversely affect human’s health by causing a variety of gastrointestinal, respiratory, cardiovascular and neurological related problems [32, 60].

Furthermore, an increase in degradation rate will result in a corresponding increased rate and volume of $H_{2(g)}$ released. In normal circumstances, the accumulation of small $H_{2(g)}$ bubbles can be safely diffused through the surrounding tissues and blood vessels [87, 144-145]. Using tubal Mg as intestine, blood vessel and nerve connector, Payr reported that $H_{2(g)}$ was shown...
to be fully absorbed within the body without significantly reducing blood flow. While
acknowledge that the gas formation was dependent on the tissue type and anatomical
location, he reported no observation of gas embolisation in any patients [73, 91-92].
Furthermore, in a study using a Mg ring to connect two blood vessels, Lespinasse reported
that the rate of \( \text{H}_2(\text{g}) \) absorbed was equal with the rate it was produced [146]. Numerous in vivo studies have found that \( \text{H}_2(\text{g}) \) bubbles are often resorbed within a few weeks of appearing [98, 147-148]. Recently, using porous AZ91 scaffold as subchondral bone plate for cartilage
repair, Witte et al. reported that subcutaneous \( \text{H}_2(\text{g}) \) bubbles were visible at 1 week following
surgery and resorbed within 2-3 weeks [89].

However, it is possible that the rate of \( \text{H}_2(\text{g}) \) accumulation results in the formation of larger
bubbles, which if enter into the blood stream can cause blockages and embolism [149].
Moreover, gas pockets forming adjacent to the implant have the potential to cause separation
of the tissues and delay the healing process [78, 143, 150]. While the volume of \( \text{H}_2(\text{g}) \)
generated depends on a number of factors, such as alloying elements, implant location and
application, \( \text{H}_2 \) evolution issues can be solved via controlling the degradation rate of Mg
alloys. Furthermore, \( \text{H}_2(\text{g}) \) pockets can be removed by drawing off the gas with a
subcutaneous needle [151].

2.3.7 In vitro corrosion testing Mg biomaterials

In vitro corrosion testing is aimed to simulate the desired implantation site and its local
environment in order to screen the performance and study corrosion mechanisms of Mg and
Mg alloys as they would occur in a given application in vivo. However, the development of
appropriate protocols for investigating Mg corrosion in vitro has presented significant
challenges to biomaterial scientists, with many different factors contributing to the corrosion
rate and behaviour of Mg [62]. It has already been established that there is a poor correlation
between results obtained from in vivo and in vitro tests [100]. In addition, corrosion rates as
determined from in vitro corrosion tests can be greatly different due to the testing set up [152-
153]. For example, testing pure Mg in 2.5% NaCl solution will provide significantly different
corrosion rates as compared to testing with Hank’s balanced salt solution (HBSS), as
discussed in more detail below.
2.3.7.1 Effect of testing media on the in vitro corrosion behaviour of Mg

Generally, in vitro test environments utilising well established simulated body fluids (SBF), in combination with accurate pH and temperature regulation at physiological levels, are recommended to achieve comparable in vivo results [154]. In regards to testing media, NaCl solutions, as adopted from corrosion testing for industrial applications, do not take into account the influence of other ions and proteins typically found in the physiological environment that are more readily accepted methods for in vitro testing of Mg biomaterials [153, 155]. Different SBF media have been designed to contain ions and proteins typically found in the physiological environment to make the in vitro test result more comparable with that of in vivo experiments [153, 155].

The choice of media was shown to contribute to the difference in corrosion behaviour and the formation of a protective passivation layer on the surface [31, 153, 155-156]. In a study by Yamamoto et al., it was found that on average over a 14-day period, the corrosion rate of pure Mg in 0.125 M NaCl solution was 100× higher than that in Earle's minimum essential medium, supplemented with foetal bovine serum (E-MEM+FBS) [155]. Furthermore, Xin et al. found that SBFs containing phosphates helped decrease corrosion rate and pitting corrosion due to the formation of magnesium phosphates on the surface, whereas the presence of hydrogen carbonate ions accelerated the corrosion rate at early stages, but later assisted in the formation of a protective magnesium carbonate layer on the surface [156]. In a more comprehensive study, Muller et al. emphasized the importance of selecting suitable electrolyte solutions to narrow the gap between in vivo and in vitro corrosion data. He suggested that high concentration of chloride and the absence of phosphate proteins in the testing media contributed to the high in vitro corrosion rate. Furthermore, localised corrosive attack was detected with size and shape of the pits affected by the electrolyte composition [153].

2.3.7.2 Effect of temperature and pH on the in vitro corrosion behaviour of Mg

Regarding the suitability of applying in vitro corrosion testing results in biomedical applications, the maintenance of a constant temperature (37 °C) and pH (7.4) is recommended to best mimic the in vivo environment. For example, studies have found that in vitro corrosion rate increases significantly with increasing temperature [157-158]. Furthermore, in
a study by Gerasimov et al., the corrosion rate of Mg in 1.0 M NaCl + 0.1 M NaOH solution increased continuously with increasing temperature (Figure 2.4). The rate of corrosion rate increase was particularly rapid as the temperature changed from 0 °C to 20 °C. After this point, the temperature continued to adversely affect the corrosion rate, however, at a slightly slower speed. As Figure 2.4 shows, the influence of temperature on corrosion rate of Mg was more obvious than on other metals, such as lead (Pb) (curve number 2) and iron (Fe) (curve number 3) when tested in the same solution.

![Figure 2.4: Effect of temperature on corrosion rate of Mg (red line) in (1.0 M NaCl + 0.1 M NaOH) solution [158]](image)

In a more recent study, Merino et al. found that corrosion attack in Mg, AZ31, AZ80 and AZ91D exposed to salt fog increased with increasing temperature. For example, the kinetic laws as calculated by multiplying mass change with time for Mg increased by 2× as temperature increased from 20 °C to 30 °C [110].

In addition, it is well-known that pH has important effects on the corrosion rate of Mg [159]. Bender et al. found that at pH of 12 or above, a stable and self-healing protective layer is formed, and this significantly reduces the corrosion rate. At a pH between 10 and 11, the
layer is between stable and unstable states [19]. Meanwhile, Ng et al. claimed that at pH of 5.5, the corrosion rate is exceptionally higher than that at pH of 7 or 8 [18]. Ng et al. suggested that pH might be as low as 5.5 at the affected site after implantation, however, this effect is temporary and the body will be able to maintain the normal pH level of 7.35-7.45 to avoid negative impacts on the surrounding cells [159].

2.3.8 In vitro corrosion testing techniques

2.3.8.1 Hydrogen evolution and mass loss

Hydrogen evolution testing is a simple and inexpensive technique, which has been widely adopted in previous studies and has become a reliable method in Mg corrosion testing [23, 140, 150, 160-161]. Generally, H$_2$(g) generated by the corrosion reaction is collected using a funnel placed directly on top of the sample, with H$_2$(g) accumulated in a burette placed vertically over the funnel (Figure 2.5).

![Figure 2.5: Hydrogen evolution test setup](image)
At the beginning of the experiment, the burette is filled with testing solution. Since the evolved \( \text{H}_2(\text{g}) \) displaces the solution inside the burette, this provides a direct correlation with the volume of \( \text{H}_2(\text{g}) \) produced. According to equation 2.1, 1 mol of corroded Mg will result in 1 mol of \( \text{H}_2(\text{g}) \). However, the stoichiometry of the redox equation that produces elemental hydrogen is not fully understood, therefore, the amount of \( \text{H}_2(\text{g}) \) generated does not directly correlate to the Mg ions [21, 62]. However, this method has several limitations due to the atmospheric pressure changing and possible \( \text{H}_2(\text{g}) \) leakage due to the set up of the experiment [62].

Immersion testing is another easy and inexpensive technique with corrosion rate derived from the total mass loss during the experiment following equation 2.2 [150, 162]. This is performed by weighing the sample before and after the test. Corrosion product on the tested samples must be removed using chemical methods such as chromic acid solution before the weight is measured [163-164].

\[
\text{corrosion rate} = \frac{\text{mass loss}}{\text{surface area} \times \text{day}} = \frac{\text{mg}}{\text{cm}^2 \times \text{day}}
\] (2.2)

Generally, it is possible to calculate mass loss from hydrogen evolution experiment by weighing the sample before and after the hydrogen evolution testing.

2.3.8.2 Electrochemical tests: EIS and PDP

Electrochemical measurements, including electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP), are the most common methods adopted in Mg corrosion testing. The principle of these techniques is based on the time-dependent changes in the metallic volume to provide information regarding the corrosion behaviour of the material. PDP tests provide both thermodynamic information, from the corrosion potential \( E_{\text{corr}} \) and kinetic information from the corrosion current density \( i_{\text{corr}} \) [165-166]. Meanwhile, in EIS experiments, corrosion resistance and capacitance values are obtained to help explain a number of phenomena and properties of the metal surface [166-167].

The principle of the EIS technique is based on the mechanism and properties of the electrical double layer (EDL). EDL is formed on the surface of a structure when it is placed in a solution (Figure 2.6A). In metal, or Mg to be more specific, this phenomenon occurs as metal
ions diffuse away from the surface under influence of water molecules and leave the negative charged electrons behind (Figure 2.6B). The surface is now negatively charged due to the electrons and begins to attract the released ions. However, these ions can come close to the surface but cannot diffuse back into the structure. Other positive charge ions in the electrolyte are also attracted to the negative charge surface. Consequently, a layer of electrolyte consisting of metal and electrolyte ions and water molecules is formed next to the surface, and this layer in combination with the negatively charged surface are referred as the EDL (Figure 2.6C). The electrical properties can be represented by an equivalent circuit program, which primarily consists of a resistor and capacitor in parallel and series with another capacitor (Figure 2.6D). The two opposite charge planes of the EDL act as an electrical capacitor, of which the level is determined by the type of metal and electrolyte composition. Meanwhile, the material’s surface will resist the transfer of its electrons into the more electrochemically active region. Displaying properties of both capacitor and resistor, the EDL is represented by a simple electrical circuit composed of a resistor and capacitor in parallel. Moreover, the solution also exhibits a resistance to the electron flow, and is expressed as a resistor connecting in series with the EDL circuit.
During the experiment, polarisation is applied and forces the ions to move to either the working or counter electrode side in order to maintain the electrical neutrality. This disrupts the equilibrium of the EDL and causes the layer to set a new equilibrium as quickly as the polarising voltage frequency changes. This process relates to the impedance of the system. EIS data can be described in a number of forms based on the vector magnitudes of the components, total impedance magnitudes, and phase angles. The three most common types are, complex plane or Nyquist plots, Bode magnitude, and Bode phase plots.

Nyquist plots contain the impedance magnitude corresponding to the real and imaginary frequency as recorded by EC-Lab software during the EIS test. It is possible to fit an appropriate circuit to the plot and determine the number of time constants and the resistance and capacitance values at each time constant. Figure 2.7 shows an example of the Nyquist plot with one time constant and one of the simple fitting circuits. More complex plots can be
fitted to determine the effect of additional coating or film layer of the corrosion. It should be noted that the value of solution resistance is a property of the solution and test cell geometry, and is not related to the corrosion mechanism.

Figure 2.7: Single time constant Nyquist plot: $W$ is the angular frequency ($s^{-1}$), $R_s$ is the resistance of the electrolyte (Ω) and $R_{EDL}$ and $C_{EDL}$ are the charge transfer resistance (Ω) and capacitance (F), respectively.

However, the Nyquist plot does not show the dependence of impedance on the frequency of the signal. Thus, in EIS data analysis, it is usually necessary to include Bode plots, in which the log values of corresponding frequencies are plotted against those of the total impedance ($\log|Z|$) for the magnitude plot (Figure 2.8A) and against the phase angle for the phase plot (Figure 2.8B).
In Bode plots for ideal cases, the detection of regions that are dominated by the resistive elements is shown by a slope of zero, and the detection of regions dominated by the capacitive elements is presented as a slope of -1. Moreover, the plots can help determine the types of corrosion that occur. For example, Bode plots on Mg were reported to allow the identification of the presence of high frequency electrochemical processes which are only present in the case of fast localized attack [27].

The principle of PDP tests is via applying over-potential to accelerate the rate of reaction at the working electrode (sample) surface and recording the ensuing current. Therefore, results from PDP experiments provide information about the electrochemical behaviour of a metal in a given electrolyte [166]. The plot of potential versus current density is known as an E-log(i) plot or Evans diagram, of which the reaction can be generally divided into oxidation (anodic) and reduction (cathodic) reactions, depending on the polarity of the polarising signal. $E_{corr}$ and $I_{corr}$ values can be analysed from the coordinate of the point where the linear regions of each reaction meets, and this method is referred to as Tafel-type analysis. An idealised schematic of a polarisation curve is as shown in Figure 2.9. The dotted lines represent collected data, and the solid lines are linear approximations which can be used to perform a Tafel-type fit to estimate the corrosion current density ($I_{corr}$).
Figure 2.9: An ideal polarisation curve with a Tafel-type fit

PDP tests are performed after the open circuit potential (OCP) is reached. OCP is the potential at which currents of the anodic and cathodic reaction are balanced. It is recorded between the working electrode and the reference electrode without any current being passed through the counter electrode. It was demonstrated that a waiting time of 15 minutes was adequate for the OCP to be stabilised but not too long for the surface to be corroded [147-148].

2.3.9  In vivo corrosion testing of Mg biomaterials

As for any biomaterial, in vivo tests are required prior to any clinical trials or the adoption of Mg for biomedical applications [168]. In vivo studies on Mg have been predominantly performed in small animals such as rats, guinea pigs and rabbits, for investigating bone remodelling behaviour [100, 169-171]. For example, Erdmann et al. compared the in vivo biomechanical properties of Mg alloy, MgCa0.8, with commonly used stainless steel (S316L). Screws made from each material were implanted in rabbit tibiae, and after 2-3 weeks, MgCa0.8 implants showed comparable biocompatibility and biomechanical properties to S316L [170]. Witte et al. performed implantation of AZ91D in the rabbit femur condyle for longer periods of 3 months and 6 months. It was found that even though the material was largely degraded and shape of the implant disappeared, AZ91D was found to have good
biocompatibility and promote appropriate inflammatory host response [87-88]. A number of large animal models have also been reported, including sheep for spinal applications [86], and pigs for cardiovascular stents [82, 172]. Waksman et al. found that after 28 days implantation in domestic pigs, Mg alloy-based stents started to degrade. However, no stent particle embolization, thrombosis, excess inflammation, or fibrin deposition was observed [82]. Mg alloys were concluded to have high potential of being used as biomaterial from these studies.

However, there are a number of disadvantages associated with in vivo testing, especially in relation to the choice of suitable animal model, cost, time and difficulty in analysis. Choosing the site for in vivo implantation in animals must fit the intended application of the device or material. This step is often problematic since the blood flow and properties of tissues are different between animals. The choice of animal model is particularly important in orthopaedic applications, in which the mechanical behaviour of the implant is one of the key evaluating factors [173-174]. For instance, small animals such as guinea pig and rabbit are not suitable for testing biomaterials aimed for spinal implants due to their small bones. Furthermore, extrapolation of experimental findings across species is difficult and not always valid [175].

While in vivo experimentation is costly, it also requires sufficient sample size for statistical accuracy, especially with assessment over multiple time points, and significantly increases the number of sample and animals per experiment. Furthermore, uncontrollable factors and variations occur during the experiment can lead to inaccurate results or even failed experiments [174]. Moreover, in situ analysis is generally challenging, and while techniques such as X-ray and µCT can be adopted, animal scarification is required for greater qualitative and quantitative analysis.

In modern culture, animal rights are well-defined and closely monitored. Ethical approval is generally required to justify the need of testing on animal versus the benefit brought to humans. Furthermore, without being properly tested prior to implantation in animals, the device or material may cause serious pain and discomfort to the animal, and therefore, most countries in the world have strict policies regarding testing protocols and ethical approvals prior to animal testing [174, 176-177].

Furthermore, results obtained from in vitro and in vivo are not directly comparable, especially
when testing the corrosion behaviour of Mg [62]. When comparing the in vivo and in vitro corrosion behaviour of Mg alloys, AZ91D and LAE442, Witte et al. found that the in vivo corrosion rate as found following implantation in femurs in guinea pig was about 4× lower than that of in vitro. Moreover, the sequence of the corrosion rates as obtained from in vitro and in vivo corrosion tests were opposite. While corrosion resistance of AZ91D was higher than that of LAE442 according to in vitro corrosion test, in vitro test results showed a completely opposite trend, in which LAE442 had better corrosion resistance than AZ91D [100].

2.3.10 Corrosion protection for Mg biomaterials

Corrosion rate and behaviour of Mg in the physiological environments can be affected by several factors, such as alloying elements, impurities, implant location, surface roughness and surface area of the structure [100]. Therefore, the development of methods to improve corrosion behaviour of Mg has generally been focussed on examining and understanding the effect of those factors. Among various strategies to improve corrosion resistance of Mg, has been the application of surface coatings. There has been significant interest in searching for a coating that is non-toxic, and reduces the corrosion rate to acceptable levels for adoption in orthopaedic applications [72]. Techniques such as alkaline treatment, heat treatment, microarc oxidation, electrodeposition and ion implantation have been investigated to increase corrosion resistance of Mg [178].

Alkali-heat treatment that introduces a biomimetic precipitation of CaP on the implant surface has shown to be a simple, yet effective method, and attracted significant attention [179]. CaP has been used widely in coating strategies for orthopaedic implants, especially in Ti. This is because CaP is biocompatible and also one of the main constituents in natural bone [126, 179]. Furthermore, CaP coatings can initiate a rapid biological response and therefore, improve adhesion between newly forming bone and the implant [179-183]. For example, synthetic CaP was successfully used for filling bone defects in various clinical indications owing to its bioactive and osteoconductive characteristics [151, 173, 175]. Taking advantage of the properties of CaP and its popular usage in biomedical fields, many studies have applied biomimetic coating methods on Mg substrates and achieved positive results [184-188]. There have also been an increasing number of studies searching for improvements
to biomimetic CaP coating techniques on pure Mg. For example, Li et al. treated high purity Mg in an alkaline solution of NaHCO$_3$-MgCO$_3$ at pH of 9.3 for 24 hr, followed by 773 K heat treatment in 10 hr. Corrosion tests in simulated body fluid over a 14-day period showed no mass loss on the sample. Meanwhile, untreated or only alkaline treated samples completely degraded during the test [188]. In a more recent study, Waterman et al. investigated the effect of pre-treatment time on the formation of biomimetic CaP coatings, and found that additional pre-treatment time was beneficial to the corrosion resistance (Figure 2.10A) [185].

![Figure 2.10](image)

**Figure 2.10: Surface morphology and structure of (A) biomimetic CaP coating on pure Mg substrate [185] and (B) HA coating on AZ91D substrate [162]**

Meanwhile, Chiu et al. employed the conversion treatment to form MgF$_2$ layer on the surface of the Mg implant. This was done by immersing the sample in hydrofluoric acid (HF) solution with 48 wt.% at room temperature. *In vitro* corrosion tests showed an increase in corrosion resistance and uniform corrosion occurred on treated samples [189].

Plasma immersion ion implantation and deposition techniques were employed by Liu et al. to plasma-implant Ti, Al and Zr into AZ91 magnesium alloys to improve the corrosion resistance. Improvement was reported for all samples, with the best corrosion protection accounted for via Al implantation mainly due to the formation of a compact Al$_2$O$_3$ layer [190]. Similar improvement was also observed in pure Mg samples coated with Ti via ion plating [191].

Electrodeposition methods have become increasingly popular, with uniform surface coatings formed offering enhanced corrosion protection. Song et al. reported that the electrodeposition
of hydroxyapatite (HA) on AZ91D substrate via decreased the degradation rate compared with as-deposited HA coating method (Figure 2.10B) [162]. Recently, Luo et al. coated Mg with poly(3,4-ethylenedioxythiophene) (PEDOT) using an ionic liquid as the solvent. This technique not only improved the corrosion resistance, but with the use of PEDOT, it also allowed the attachment of anti-inflammatory drug, dexamethasone, onto the implant [192]. While many studies have focused on developing coating methods and claimed improvements in corrosion resistance for Mg, the majority of the corrosion tests to date were performed in vitro, and little work has been carried out in vivo.

2.4 Cellular materials

Low density porous structures can be found widely in nature, such as the trabecular bone, the structure of wood and many other growing organisms (Figure 2.11) [111, 125, 193-196].

![Figure 2.11: Porous structure of (A) trabecular bone and (B) wood [194-195]]

With the development of technology and science, man-made porous materials have been manufactured in large scale and attracted significant interest. Numerous processing routes have been developed to manufacture porous structures from materials, such as Al, Ti, Mg, ceramics and polymers [197-199]. Until now, the polymer foam industry is considered to be at the mature stage and porous products are used widely in packaging, energy absorption applications, and more recently, biomedical applications [117, 200-201]. Research in the development of porous metallic structures has been steadily increasing since some of the initial reports in 2000. Figure 2.12 shows the number of publications on porous metals per
year with respect to total overall number of publications in Scopus from 1970 to 2010 [202].

![Figure 2.12: Evolution of the annual number of publications on porous metallic structures in comparison with the total amount of publications listed in Scopus [202]](image)

Developed as a new class of materials, porous structures offer properties that no other monolithic materials can. They can be low density while having properties such as high mechanical strength, stiffness and damping capacity. For certain applications where a high surface area to volume ratio is important, only porous structures can satisfy the requirements. More importantly, they can be tailored to meet design or application requirements via changing structural variables [198, 202]. Applications of porous foams are across a wide various industries, including electrical, aeronautical, automotive, building construction, military and medical fields [198, 203-205].

### 2.4.1 Manufacturing routes for random architecture metallic porous structures

To date, the manufacturing of porous cellular metals has primarily focused on the fabrication of random architectures from different materials, such as titanium (Ti), Ti alloys, tantalum and aluminium. Generally, the main routes can be classified into four groups, based on the state of the processed material. These include: liquid metal, solid metal in powdered form, metal vapour or gaseous metallic compounds, and metal ion solutions [204].

43
2.4.1.1 *Liquid metal processing technique*

With liquid state processing techniques, the porosity of metal foams can be formed by introducing gas bubbles in the molten material. Popular methods include melt gas injection (Hydro/Alcan), solid-gas eutectic solidification (Gasar), foaming of melts with blowing agents (Alporas), foaming of powder compacts, casting and spray forming [198, 203-204].

Foaming of melts by gas injection technique was first performed on Al and Al alloys by Hydro Aluminium in Norway and Cymat Aluminium Cooperation in Canada [205-206]. Two main steps involved in the process are melting the metal and injecting gases (air, nitrogen, argon) into the liquid metal, which introduces fine gas bubbles into the melt and distributes them uniformly [203]. The process has been used and reported frequently in the literature to investigate the properties of the manufactured foams, as well as methods to improve and further control the process [207-209].

The Gasar method takes advantage of the eutectic system formed by some liquid metals with hydrogen gas [210]. During the process, the metal is melted in the hydrogen environment under high pressure to form a homogenous melt charged with hydrogen. If the temperature is lowered, the molten material will undergo a eutectic transition into a heterogeneous two phase system that consists of a solid and a gas. Once the temperature drops, the melt is solidified and traps the gas inside. The resulting pore morphologies are determined by the gas content, pressure, direction and rate of heat removal, and also chemical composition of the melt [203, 210]. Figure 2.13A shows foam with elongated pores manufactured using Gasar method.

The Alporas method involves adding a blowing agent into the molten material instead of injecting it as in Hydro/Alcan method. During the process, under influence of heat, the blowing agent decomposes and releases gas, which subsequently propels the foaming process [203, 205]. The foaming method using blowing agents is considered to produce most homogenous foam available [203].

Preparing metal foam using powder begins with mixing the metal powder with blowing agent to create a dense, semi-finished product, which is subsequently put through heat treatment at temperatures close to the melting point of the metal. The blowing agent decomposes under the effect of heat and releases gas, which forces the molten metal to expand and form a porous structure (Figure 2.13B) [203, 211-212]. As opposed to other processing methods that
are limited to certain materials, metals such as tin, zinc, brass, lead, gold and other alloys can be used in this powder compact process for manufacturing porous structures [203].

Meanwhile, the infiltrating casting method involves the use of a preform, which acts as a template for the molten material to be casted against. The preform can be a plaster template that was cured by heat treatment on polymer foam impregnated with plaster slurry [204, 213-214].

Spray forming methods allow the processing of many different metals and alloys. During the process, the molten metal is continuously atomised and creates a spray of fast flying small metal droplets. The droplets are collected and grow on a substrate to generate porous structures in a given shape [204]. Metal foams manufactured by this method are low in oxide content and possess a fine grain [215].

Figure 2.13: Foam manufactured using (A) Gasar technique and (B) powder-compact foaming [203, 210]

2.4.1.2 Solid state processing technique

As the name suggests, solid state processing methods use solid metal in powdered form instead of molten metal, whereby the powder remains in solid form for the entire process [204]. While the liquid state technique normally produces closed-pore foam, the morphology of the porous structure produced by the solid state technique contains open pores. There are seven main techniques involved in the solid state processing technique, including: sintering
of metal powders and fibres, gas entrapment techniques, foaming of slurries, cellular metals based on space-holding fillers, metallic hollow sphere structures, metal powder/binder methods, and reaction sintering [204].

In the sintering technique, both metal powders and fibres can be sintered under high temperature to create porous structures. The three main steps involved in the process are: powder/fibre fractioning and preparation, compaction, and sintering [204, 216]. However, it is more difficult to use this method on Al alloys due to the dense oxide layer covering the surface that prevents the particles from sintering together.

The gas entrapment technique is similar to the powder compact melting technique but without the use of blowing agents and molten metal. During the process, powders are compressed into dense precursor materials with gas pockets trapped inside the material. This is followed by the heating process, in which pressure generated by heated gas expands the metal. The expansion occurs in the solid state [204, 217]. Aircraft manufacturer Boeing used this method to make porous Ti structures [218].

Porous metallic structures can also be manufactured using slurry of metal powders, blowing agents and reactive additives. In this method, the slurry is poured into a mould, in which it becomes viscous under the influence of additives and blowing agents, and starts to expand as the gas evolves [204, 219].

The process of producing cellular metals based on space-holding fillers is similar to the casting method. The difference being that a fine metal powder fills the space-holding material instead of liquid metal. Filler materials are employed in the process to mix the space holder and the metal powder. After compaction, which can occur at either room or elevated temperature, the filled structure is sintered [204, 220-221].

Porous structures can also be made by bonding the individual hollow spheres together via a sintering process [204]. Hollow spheres of copper, nickel, steel or Ti can be produced by various techniques, for example, by combining polymer coated spheres with a binder/metal powder suspension and subsequently sintering the metal to remove the polymer [222]. This method offers flexibility of manufacturing either open or closed porosity with ordered or random architecture [204].
2.4.1.3 Other techniques

In addition to the above methods, electro-deposition and vapour deposition techniques are also common. Deposition methods start from the ionic state of the metal. In electro-deposition methods, the metal is electrically deposited onto an open-cell polymer foam which can be removed by thermal treatment. Similarly, vapour deposition techniques involve the condensation of metal vapour on the surface of polymer precursor [204, 223]. A summary of available processes for manufacturing cellular metal foam and corresponding material and achievable porosity is as shown in Table 2.5

Table 2.5: Summary of foam manufacturing methods, the applicable metal and porosity limit [203-204, 223]

<table>
<thead>
<tr>
<th>Category</th>
<th>Process</th>
<th>Metals</th>
<th>Achievable porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid state processing</strong></td>
<td>Direct foaming by gas injection</td>
<td>Al, Zn</td>
<td>80-97.5</td>
</tr>
<tr>
<td></td>
<td>Direct foaming with blowing agents</td>
<td>Al, Zn</td>
<td>91-93</td>
</tr>
<tr>
<td></td>
<td>Gasar</td>
<td>Cu, Al, Mg, steel</td>
<td>5-75</td>
</tr>
<tr>
<td></td>
<td>Powder compact melting</td>
<td>Al, Zn, Pb</td>
<td>60-90</td>
</tr>
<tr>
<td></td>
<td>Investment casting using polymer foams</td>
<td>Al, Zn</td>
<td>80-97</td>
</tr>
<tr>
<td></td>
<td>Casting around space holders</td>
<td>Al, Zn, Pb, Cu</td>
<td>≤65</td>
</tr>
<tr>
<td></td>
<td>Spray forming</td>
<td>Steel, Cu</td>
<td>≤60</td>
</tr>
<tr>
<td><strong>Solid state processing</strong></td>
<td>Sintering of powders and fibres</td>
<td>Bronze, steel</td>
<td>20-80</td>
</tr>
<tr>
<td></td>
<td>Gas entrapment</td>
<td>Ti</td>
<td>≤45</td>
</tr>
<tr>
<td></td>
<td>Foaming of slurries</td>
<td>Al</td>
<td>≤93</td>
</tr>
<tr>
<td></td>
<td>Powder pressing around space holders</td>
<td>Ti, Al, steel</td>
<td>≤70</td>
</tr>
<tr>
<td></td>
<td>Hollow sphere structures</td>
<td>Steel</td>
<td>≤80</td>
</tr>
<tr>
<td></td>
<td>Power/binder techniques</td>
<td>Fe, Cu</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Other methods</strong></td>
<td>Electro-deposition</td>
<td>Ni, Cu</td>
<td>92-95</td>
</tr>
<tr>
<td></td>
<td>Vapour deposition</td>
<td>Ni, Ci-Cr, Ta</td>
<td>93-97.5</td>
</tr>
</tbody>
</table>
The majority of the described methods are for manufacturing porous structures with randomly oriented or distributed architecture. Of those methods described, only hollow sphere structure processing methods are capable of producing ordered architecture materials. While random porous architectures may meet mechanical requirements, they are generally not suitable for the purposes of optimising scaffold properties such as porosity, stiffness and permeability [224] because the inherent manufacturing technique for generating the pores is a random process and does not allow precise control over the size, shape and architecture if individual pores. These random porous structures typically have homogenous mechanical and biological properties at the macro level, but not at the micro level. This results in undesirable behaviour in the material, such as reduced effective stress and localised strut yielding and twisting [225]. Manufacturing routes which permit the design and fabrication of topologically-ordered porous structures allow accurate control over pore structure, which inherently provides desired characteristics in certain regions, while other regions can be tailored for other functional requirements.

2.4.2 Manufacturing of metallic topologically-ordered structures

Studies describing manufacturing methods for fabricating porous structures with random pore architectures have showed a rapid and stable development. Meanwhile, manufacturing methods for fabricating topologically-ordered porous scaffolds have received limited interest.

2.4.2.1 Rapid prototyping technique

Rapid Printing (RP) methods, which are adopted to directly print porous structures based on computer aided design (CAD) models, have become more popular and achieved significant results. RP techniques have been used widely to build porous structures for tissue engineering from other non-metallic materials such as polymers, and hydroxyapatite ceramics [224, 226-229] and offer the advantages of allowing control over size, shape and distribution of the porosity [230-231]. One principle RP technique adopted is similar to that of ink-jet printing technology, in which one layer is printed at a time on top of the previous layer, allowing the part to be created inside the cavity of a supporting material [223].

With respect to porous metals, rapid prototyped porous scaffolds made from Ti and its alloys
have been fairly common. For example, Lopez-Heredia et al. produced porous Ti scaffolds in cylindrical shape by the RP technique aimed at orthopaedic and maxillofacial applications. The structures had a pore size diameter of 800 µm and 1200 µm and porosity of approximately 60% [127].

More commonly, three-dimensional printing (3DP) techniques have been combined with other methods for ease of manufacturing, improved control over the final product and more flexibility. For instance, Li et al. combined 3DP techniques with powder sintering to manufacture porous Ti6Al4V scaffolds with interconnected pores. Five designs were generated in the study by varying design parameters, such as: layer spacing (ranging from 200-800 µm), lay down angle (0 to 90°), and layer thickness (e.g. 320 µm). The structure was implanted in goats to investigate bone formation [232-233]. Meanwhile, combining 3DP with laser-engineered net shaping (LENS™) techniques enabled Krishna et al. to make porous Ti6Al4V scaffolds for load-bearing implants with porosity up to 70% [109] (Figure 2.14A).

Electron beam melting (EBM) is an emerging method of manufacturing porous ordered architecture structures. The process selectively melts metal powder with a high energy electron beam fabricating complex structures in a layer by layer fashion. EBM technology produces implants which combine mechanical properties, which are vastly superior to metal foams and laser sintered devices, allow much greater control over pore size and regularity, and enable complete free form shaped devices. These structures can have intricate and precisely controlled porous architecture with fully dense struts giving great freedom to create optimal structures for orthopaedic bone interfacing materials. The material and manufacturing process has been extensively qualified for use in orthopaedic devices [234]. Specific porous titanium (Ti6Al4V) structures with pore sizes ranging from 500 µm to 2000 µm and porosity range of 50% - 70% were successfully manufactured using EBM technique (Figure 2.14B) [235]. Mechanical testing on the produced scaffolds showed that those structures possessed favourable mechanical properties not dissimilar from that of bone [235]. In a different study, Hrabe et al. was successful in reducing the effects of stress shielding in load-bearing applications via modifying structural properties of the porous scaffold. Namely, the architecture followed the crystal structure of diamond and five structures were produced with varying relative densities, pore sizes, and strut sizes [236]. There has been a great deal of work performed that demonstrates the efficacy of this family of materials [237]. Notable recent studies have demonstrated that titanium scaffold structures
allow significant bone in-growth [127, 238]. For example, a porous Ti6Al4V scaffold manufactured using an EBM technique with a pore size range of 45 µm to 100 µm was implanted in domestic pigs. It was found that the bone volume inside the implants reached 30% and 46% after 30 days and 60 days, respectively [238].

2.4.2.2 Other methods

The technique of using hollow spheres as a casting template was employed in several studies and various methods were developed for preparing the templates. For example, Jinnapat et al. prepared the template by mixing rice flour with NaCl while Covaciuc et al. employed the rapid prototyping (RP) technique to make the mould from CaP [239-240]. Shin et al. fabricated highly porous Ti scaffolds using HA as supporting structure (Figure 2.14C) [241]. In a different study, Covaciuc et al. was successful in using RP technique together with powder technology to generate controlled open pore geometry and cell arrangements from Zn powder [240].

Orderly oriented wire mesh methods have been employed to create a porous coating for orthopaedic implants. However, its application is currently limited to generating the coating layer only, not an entire structure [223, 242-243].

![Porous structures produced using (A)3DP [113], (B) EBM method [235] and (C) hollow sphere casting method [241]](image)

*Figure 2.14: Porous structures produced using (A)3DP [113], (B) EBM method [235] and (C) hollow sphere casting method [241]*

2.4.3 Porous metallic structures for biomedical applications

While many of these porous metallic structures (or foams) are commercially available, it is their application in orthopaedic devices and tissue engineering fields that has attracted more recent attention [237, 244]. The applications of metallic foams in joint replacements and the
development of porous Ti for dental applications were reported thoroughly [245-246]. As biomaterials, porous metals have advantages of being sufficiently strong to provide suitable mechanical properties for the implanted site, while remaining lightweight. More importantly, the porous architecture is known to facilitate tissue growth and implant fixation, as well as support flow of tissue fluid carrying nutrients [247-250].

Similar to all other orthopaedic biomaterials, porous scaffolds need to meet certain basic requirements, such as being biocompatible, sterilisable and preferably radiolucent. In addition, as a tissue engineering scaffold, the structure is required to provide a space that shapes the regenerating tissue, provide temporary function at the affected site while tissues regenerate, and encourages tissue growth [250-251]. While the first requirement can be satisfied by producing the implant with shape and size following that of the defect site, there are a number of factors that can affect the fulfilment of the second and third requirements.

For scaffolds to be used in load bearing applications, the structure needs to possess suitable mechanical properties to support the affected area, to promote tissue growth, and allow integration and remodelling with host tissue to be established. The desirable mechanical properties should match those of the implanted region in terms of stiffness and strength to prevent stress-shielding problems. For non-degradable porous implants, the fatigue strength also needs to be considered since the structure is subjected to cyclic loading during the rest of the patient’s life.

In addition, surface properties of the porous structure such as surface roughness, surface area, and surface wettability need to be considered. Surface roughness has been shown to affect cell morphology and growth. The surface macro- and microtopography of bone-interfacing implants plays a critical role in osteoconduction, osseointegration, and de novo bone formation in a range of biomaterials including titanium (Ti) alloys, ceramics and coatings [252-257]. For example, micro-topographies generated on Ti substrates in the range of $S_a > 1-2 \, \mu m$ have been suggested to be the predominant factor for platelet factor activation during early de novo bone formation, resulting in enhanced osteoconduction and bone contact [256, 258-259]. It was also reported that materials coated with a porous surface showed less fibrous capsule formation than monolithic materials [260]. Meanwhile, larger surface area means more sites for new tissue to grow on, and therefore is a desirable property of the scaffold. Similarly, intermediate surface wettability is known to be advantageous for initial
cell adhesion, inherently further affects the cell proliferation [261-262].

Structural parameters such as pore size, distribution and interconnectivity should be designed to suit the cell seeding, migration, vascularisation and nutrient transportation requirements [247, 251]. For instance, pore size has been reported to affect the type of cell that penetrates and proliferates inside the structure, and also the volume of materials and nutrients that can be transported in and out of the structure [237]. Previous studies suggested that pore sizes ranging from 100-500µm in cellular foams was optimum for bone growth [263-264].

Meanwhile, in a study by Hollister et al., hydroxyapatite scaffold with ordered porous architectures were manufactured and implanted in mandibles of minipigs. Significant bone regeneration was observed in all pore sizes that ranged from 400 µm to 1200 µm; no pore size was more advantageous for bone growth than the others [265]. In a different study, a solid free form fabrication technique was employed to produce ordered architecture scaffolds from polylactic-co-glycolic acid (PLGA) polymer. Following the implantation in rabbit calvarial defects, no significant difference in bone growth was observed for 500 µm and 1600 µm pores [266-267]. These findings suggested that while random architecture scaffolds have a range of pore sizes, which can be as small as few microns, determination of pore size range that is suitable for bone growth is important. Whereas, with ordered porous scaffolds, the pore architecture can be accurately designed and reliably controlled to be completely interconnecting throughout. This helps promote nutrient diffusion as well as cell and vascular infiltration, resulting in an improved bone formation over a broad range of pore sizes [247, 265]. This further confirms the advantages for developing topologically-ordered porous structures.

2.4.4 Manufacturing of porous magnesium scaffolds

While reasonable attention has been paid to manufacturing materials such as Ti, Al, ceramics and polymers in ordered porous form [268-273], porous Mg scaffolds reported in the literature have been limited, mainly because of the difficulties in powder processing or sintering of Mg. Very few studies have focussed on developing reliable, safe and relatively low cost methods for manufacturing ordered porous Mg scaffolds. Since Mg is highly flammable, processing the material is normally performed in a vacuum or inert gas environment. This makes applying current manufacturing methods to Mg difficult and
requires modifications to the equipment and processes. Most of the techniques for manufacturing porous Mg structures have relied on existing foam fabrication methods. For example, Gu and colleagues manufactured lotus-type porous pure Mg using metal/gas eutectic unidirectional solidification method (GASAR process) [274]. Ho et al. adopted a lost foam casting method to produce a micro-truss sandwich core foam from Mg alloy AZ91 [275], whereas Wen et al. made porous pure Mg scaffolds using a powder metallurgical process [276]. The infiltration process was used by Yamada et al. to manufacture highly porous AZ91D scaffolds (Figure 2.15A) [277]. Recently, Tan et al. used a mechanical perforation technique to produce porous Mg structures with controllable pore size, pore arrangement and hence, porosity [278]. However, the manufacturing method was limited by pore shape and regional optimisation (Figure 2.15B).

![Figure 2.15: Mg porous structures with (A) random architecture [277] and (B) controlled architecture [278]](image)

### 2.4.5 Mechanical properties of porous structures

Since the majority of metallic porous structures are aimed at load-bearing orthopaedic applications, obtaining suitable mechanical properties is one of the most important criteria in evaluating the success of any porous scaffold. Table 2.6 summaries mechanical properties of metallic porous structures found in the literature. Generally, the stiffness and compressive strength of these porous structures are varied and dependent on the manufacturing process adopted. For example, Ti foams with 78% porosity produced by powder metallurgical methods showed a stiffness of 5.3 GPa [279], which was more than 3× higher than that of 74% porous Ti-alloy foam made from a space-holder sintering method [280]. However, the relationship between structural strength and the architecture, i.e. random or ordered, was not
clear. For instance, Ti scaffolds with 60% porosity consisting of an ordered architecture had a stiffness of 2.7 GPa [281], which was 2× lower than that of a 59% porous Ti foam with a random architecture [280]. Meanwhile, pure Mg scaffolds with optimised architecture, manufactured via mechanical perforation method resulted in 70% porosity and 14.93 GPa in stiffness [278], was significantly stronger than pure Mg foams produced from powder metallurgical method with 55% porosity and 3.6 GPa in stiffness [282].

Table 2.6: Properties of porous metallic scaffolds: type of architecture, porosity, stiffness and compressive strength

<table>
<thead>
<tr>
<th>Material</th>
<th>Architecture</th>
<th>Porosity</th>
<th>Stiffness (GPa)</th>
<th>Compressive Strength (MPa)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Random</td>
<td>78%</td>
<td>5.3</td>
<td>35</td>
<td>[279]</td>
</tr>
<tr>
<td>Ti10Nb10Zr</td>
<td>Random</td>
<td>42-74%</td>
<td>21-1.6</td>
<td>368-27</td>
<td>[280]</td>
</tr>
<tr>
<td>Ti</td>
<td>Ordered</td>
<td>25%-60%</td>
<td>30-1</td>
<td>-</td>
<td>[283]</td>
</tr>
<tr>
<td>Ti</td>
<td>Ordered</td>
<td>66.8%</td>
<td>4.35-20.5</td>
<td>23.5-104.4</td>
<td>[268]</td>
</tr>
<tr>
<td>TiAl6V4</td>
<td>Ordered</td>
<td>52%</td>
<td>2.97</td>
<td>794</td>
<td>[284]</td>
</tr>
<tr>
<td>Ti</td>
<td>Ordered</td>
<td>60%</td>
<td>2.7</td>
<td>80</td>
<td>[281]</td>
</tr>
<tr>
<td>TiAl6V4</td>
<td>Ordered</td>
<td>49.75%-70.32%</td>
<td>2.92-0.57</td>
<td>163.02-7.8</td>
<td>[235]</td>
</tr>
<tr>
<td>TiAl6V4</td>
<td>Ordered</td>
<td>66%</td>
<td>2.5</td>
<td>116</td>
<td>[285]</td>
</tr>
<tr>
<td>Pure Mg</td>
<td>Random</td>
<td>50%</td>
<td>0.35</td>
<td>2.33</td>
<td>[279]</td>
</tr>
<tr>
<td>Pure Mg</td>
<td>Random</td>
<td>36%-55%</td>
<td>18.1-3.6</td>
<td>15-31</td>
<td>[282]</td>
</tr>
<tr>
<td>Pure Mg</td>
<td>Ordered</td>
<td>70%</td>
<td>14.93</td>
<td>92</td>
<td>[278]</td>
</tr>
</tbody>
</table>

2.4.6 Topology optimisation for ordered porous scaffolds

With the development of manufacturing techniques for fabricating scaffolds with almost any geometry of ordered pore architecture, it opens the possibilities to produce structures for
biomedical applications that are optimised to meet certain requirements, such as maximising porosity while maintaining the stiffness of the structure and vice versa [247]. Using topology optimisation techniques in the design process provides optimal distribution of material while also satisfying the objectives of stiffness, porosity and pore size [284, 286-287]. The optimisation process is particularly important for structures in load-bearing applications, whereby the structure can be optimised to minimise stress shielding, while be porous enough to facilitate nutrient transportation and provide sites for tissue growth [247, 284].

Utilising homogenisation theory has been one of the most popular techniques in topology optimisation. The technique allows “homogenisation at a macro level, of a heterogeneous system at a micro level” [288]. In structural mechanics, homogenisation is employed as a tool to compute a material’s effective mechanical properties in relation to the local voids [288-290]. For example, using homogenisation theory to relate density to stiffness, Bendsoe et al. could define a topology that had maximum stiffness with a fixed volume [286]. In a similar study, Sigmund et al. reported employing homogenisation topology optimisation approach to design both 2D and 3D microstructures with desired stiffness with fixed volume [291]. More recently, utilising homogenisation theory to relate pore diameters to stiffness and porosity, Hollister et al. successfully matched the Young’s modulus for minipig mandibular and trabecular bone with ceramic and polymer scaffolds [251]. Lin et al. went further with applying topology optimisation into define the structural layout and inner microstructure for lumbar spine interbody fusion cage in order to enhance stability, biofactor delivery and arthrodesis [284, 292] (Figure 2.16A).

Wettergreen et al. took a different optimisation approach by creating a unit block library of architectures. Each structure was designed using Computer Aided Design (CAD) and mechanical properties were studied using Finite Element Analysis (FEA). The library of architectures with known properties allowed merging of each unit structure to the site according to the requirements of mechanical properties, porosity or surface area [293]. A vertebral bone was designed using the library with the allocation of unit structure based on the material and mechanical properties demands of the vertebral body [294] (Figure 2.16B).
2.5 Orthopaedic applications: Spinal fusion device

2.5.1 Introduction

Due to a number of factors, especially age, daily and sport activities, a number of problems can occur in human joints and bones, such as degeneration and inflammatory diseases. These problems affect millions of people, who may require surgery for treatment, which often involve permanent, temporary and/or biodegradable devices or prostheses [120]. The development of orthopaedic medical devices represents both an active research area and a significant market. Among total joint prostheses for knee and hip replacement, spinal fusion devices (SFDs) for treating vertebral degenerative spine diseases and spine trauma are also one of the more regularly implanted orthopaedic devices [292]. The device has been developed with the primary purposes of relieving pain for the patient and stabilising the affected spine segment [295].

2.5.2 Anatomy and physiology of the human spine

The vertebral column consists of 26 bones, including 7 cervical vertebrae, 12 thoracic vertebrae, 5 lumbar vertebrae, the sacrum and the coccyx (Figure 2.17A). Between the
vertebral bones is the intervertebral disc (IVD), which consists of a nucleus pulposus and annulus fibrosus (Figure 2.17B). In addition to connecting the vertebrae, the disc has an important role of allowing flexible movement of the vertebral column. The nucleus pulposus in the centre of the disc acts as a shock absorber, with its jelly-like structure helping to absorb compressive loads on the spine. Meanwhile, the annulus fibrosus surrounding the nucleus pulposus consists of several layers of fibrocartilage. This structure of the disc allows movements such as bending and rotating the neck and back, and bending in the lumbar spinal region [296-297].

Figure 2.17: Anatomy of the (A) human spine and (B) vertebral bone and intervertebral disc [297]

However, the IVD may be damaged or diseased due to aging, injury, infection or tumours, leading to limited movement and causing pain. The pain is generally referred as back pain, which is one of the most common diseases in the world and suggested to affect up to 80% of the United States population at some point during their lives. Back pain can be the symptom of diseases such as spinal disc herniation, degenerative disc disease and spondylolisthesis [298].
2.5.3  Spinal fusion

Spinal fusion is a common treatment for spinal problems and is used to fuse or immobilise two or more vertebrae. During the surgery, the intervertebral disc is removed partially or completely, depending on its condition. This is followed by placing an implant between the affected vertebrae to maintain or reinstate the vertebral spacing, as well as the physiological size and shape of the spine. Generally, with the use of fusion cage, the formation of new bone tissue is promoted with the use of autograft bone or stimulatory factors to gradually fuse the two vertebrae together [295, 299]. As Lin et al. proposed, a suitable SFD needs to meet three main criteria, namely: limited displacement for stability; sufficient strain energy density transfer to ingrown bone to reduce stress shielding; and required porosity for tissue ingrowth and biofactor delivery [284].

In recent years, there has been a significant increase in the number of spinal fusion surgeries. Rutkow reported over 70,000 spinal fusions performed each year during the 1979-1983 period [300]. A report in 1999 estimated 350,000 spinal fusion operations per year in the United States [301]. In a national survey also in the United States, the annual number of spinal fusion surgeries increased by 77% between 1996 and 2001 [302]. There are several reasons for the increasing number of spinal fusion treatments, such as people living longer and more active lives [298].

Supplementary bone grafting is often required for SFDs to encourage bone growth and fusion. Traditionally, autogenous bone graft was favoured and widely used, however, it was shown to have major drawbacks, such as the risk of chronic donor site pain, hematoma, limited availability, variable quality, infection and increased operative time [303-304]. Consequently, synthetic bone graft substitutes were investigated. To date, there have been numerous studies investigating materials such as demineralised bone matrix, collagens, calcium phosphate biomaterials, biphasic calcium phosphates, collagen/calcium phosphate composites, calcium sulphate biomaterials and biodegradable polymers [303, 305-307]. Bone grafting materials are required to deliver and retain osteoinductive and osteogenic agents to the site requiring bone development. The system needs to be osteogenic, osteoinductive and osteoconductive to encourage the fusion [303-304].

The most common surgical approach in SFD implantation is anterior cervical disectomy and fusion (ACDF). Compared with posterior cervical disectomy and fusion (PCDF), ACDF
provides broader access to the disc space and potentially avoids injury to the nerve roots and spinal cord caused by over-retraction [295, 308]. However, ACDF has its own disadvantages. In addition to the general risks of surgery, the soft tissue structures at the neck may be affected with common complications include dysphagia and voice disorders [309].

2.5.3.1 Current SFDs design

Current fusion devices aim mainly to maintain the disc height and provide space for bone grafting materials. Most of the designs are either cylindrical or wedged shape with thick outer shells to provide the necessary mechanical properties and hollow interior space to contain bone graft. Based on the anchorage mechanism for fixation, the cage design can be further classified by threaded or non-threaded. Threads are placed along the whole body of the cylindrical cage and only on the upper and lower surfaces in the wedge cage [292].

Similar to other orthopaedic applications, Ti and its alloys are commonly adopted biomaterials in SFDs. For example, BAK/C® is a cervical interbody fusion system made from Ti alloy. With V-shaped threads, the cylindrical device is designed to collect bone locally into the implant’s chamber during implantation to create local autograft (Figure 2.18A) [310-311]. Meanwhile, the PEEK Prevail cervical interbody device from Medtronic is made from polyetheretherketone (PEEK) polymer in an I-Beam shape and requires autograft (Figure 2.18B) [312]. Another device by Medtronic is the InFUSE™ Bone Graft/LT-CAGE™ Lumbar Tapered Fusion device. The implant is composed of a Ti metallic tapered cage to be filled with bone graft (Figure 2.18C) [313].
2.5.3.2 Issues with current SFDs

In ideal cases, the SFD facilitates rapid bone in-growth to produce a completely fused joint. However, it was reported that up to 45% of the ~1 million annual worldwide SF procedures failed as a result of device fracture or bony non-union [314-315]. Failure of SF procedures results in complicated and costly (up to $50,000) [316] revision surgery.

Supplementary bone grafting is often required for SFDs to encourage bone growth and fusion. Traditionally, autogenous bone graft was favoured and widely used, however, it was shown to have major drawbacks, such as the risk of chronic donor site pain, hematoma, limited availability, variable quality, infection and increased operative time [303-304]. Furthermore the mechanical strength of the autogenous bone grafting material is generally inadequate for interbody loading initially and can lead to immediately collapse or extrude [317-319]. Allograft (donor) bone grafts are the most common grafting material for spinal fusion but do not resorb quickly or promote rapid bone growth, as well as presenting the possibility of disease transfer [303].

Another of the major challenges faced by current SFDs is the stress shielding caused by differences in stiffness of the vertebral bone and the device. Stress shielding is one of the biggest concerns for load-bearing biomaterials and occurs when the stiffness of the orthopaedic device is different from that of bone, leading to uneven stress distribution between bone and implant [118-120]. This in turn affects bone remodelling and healing processes since under-loaded bone will adapt to the low stress environment and become more porous and weak [121]. Stress shielding-related problems were observed in orthopaedic
devices based on non-degradable biometals, such as stainless steel and Ti [121-122].

In studying spinal interbody fusion, Van Dijk et al. found that in goat model, the reduced stiffness of the interbody fusion cages made of biodegradable poly-(L-lactic acid) increased the bone fusion rate as compared to the Ti cage [320]. It was suggested that the loss of cage’s stiffness introduced by degradation of the bioresorbable cage helped increase the load on grafting material, thus stimulated the bone growth [321-322]. Therefore, while Ti alloy is a good choice with excellent biocompatibility, the stiffness of Ti alloy is approximately 6× higher than that of cortical bone. Furthermore, post-operation analysis has been problematic with Ti cages due to Ti being non-radiolucent [323]. While PEEK was claimed to replace Ti in spinal fusion as it is radiolucent, stiffness of PEEK (3-4 GPa) [131] is potentially inadequate for the high load-bearing application. In addition, both Ti and PEEK are not degradable, therefore, the device will remain permanently in the spine and potentially cause loosening as a result of stress shielding and painful inflammatory responses in the long term. Ceramic materials can be bone conducting, bone bonding and bioresorbable, however, ceramic cages have not been successful in SF as they suffer from low fracture toughness, subjecting them to fatigue fractures, collapse and/or extrusion [324]. For these reasons, Mg with favourable mechanical properties (Young’s modulus) close to that of native bone compared may help alleviate some of the issues with current SFD designs, as well as minimise the risk of stress shielding [72-73, 87-88].

Furthermore, via measuring intra-cage pressure, Kanayama et al. found that the stress shielding was more dependent on the pore size than the total porous area [325]. However, increase pore size potentially lead to reduction in overall stiffness of the structure and introduce deformation and instability into the device [292].

Therefore, there is a need of a porous degradable device that is capable of provide mechanical strength comparable to bone, reliable joint fusion via rapid bone growth and biodegradation over time leaving fused vertebral bone without remnant of the SFD. With the development of manufacturing techniques for ordered porous structures, topology optimisation research, and investigation into the use of Mg for biomedical applications, an Mg-based SFD with optimised architecture may offer significant potential as an alternative device. With the structure designed to match bone’s properties, other structural properties could be optimised to encourage bone growth and lead to rapid fusion. Furthermore, being biodegradable, Mg-based SFDs could be designed to degrade while natural bone tissue is developing, and still
provide sufficient mechanical support for the site. Once the healing process is completed, the SFD could completely disappear and leave only natural tissue at the fusion site. Furthermore, other fixation devices such as screws and rods can also be made from Mg alloys instead of Ti at the present. With the use of Mg for fixation, advantages include eliminating the necessity for additional surgeries to remove the device and potentially limit the stress shielding effect.

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CHAPTER 3

Synthesis of TOPM structures from pure Mg
3.1 Chapter Preface

In this chapter, a solid free form (SFF) fabrication manufacturing process for topologically ordered porous magnesium (Mg) (TOPM) scaffolds is described. Given that the ultimate goal was to fabricate porous Mg implants directly from three-dimensional (3D) computer-aided design (CAD) models, the resolution limits of each step of the manufacturing process was systematically characterised to compare the final dimensions and architecture of as-produced Mg structures with those parameters from the original CAD design. The capability of manufacturing process was further examined by producing complicated architectures.

Section 3.2 to 3.4 in this chapter was part of the following publications:


3.2 Abstract

The use of porous metal foams as biomaterial scaffolds has been widely adopted, however, many of these porous structures are manufactured with pore architectures that are inherently random. This makes structural optimisation for a specific purpose challenging. Scaffolds containing ordered pore architectures can be fabricated to meet design criteria, such as porosity, stiffness, and volume fraction. Mg and its alloys offer potential as a new class of degradable metallic orthopaedic biomaterials. In comparison with current metallic orthopaedic implant materials, Mg offers advantages such as closer-to-bone stiffness and biodegradability, thereby eliminating the need for a second surgery to remove hardware. Currently there are few methods described in the literature to manufacture ordered porous Mg.

The aim of this chapter was to determine the resolution of a novel indirect SFF process for
producing TOPM structures. The multi-step method involved the printing of an RP mould, NaCl infiltration and liquid Mg casting techniques. Using a range of characterisation methods, it was demonstrated that the selected structures were manufactured with a high level of accuracy. Differences in dimensions from CAD models to Mg scaffolds ranged from 2.5% to a maximum of 8.33%. Similarly, there was a maximum of 6.1% reduction in porosity in Mg scaffolds compared with the initial design. Meanwhile, with surface roughness of 10.17 ± 1.75 µm, there was an average of 70% increase in surface area. This chapter demonstrates a simple, reliable and safe route to manufacture TOPM scaffolds for potential application in medical device design.

3.3 Introduction

Porous metals have applications across a wide variety of industries, including lightweight composites, electrical screening, filtration systems and medical devices. While many of these porous metal structures (or foams) are commercially available, their application in orthopaedic devices and tissue engineering fields has recently attracted significant attention [1-2]. As biomaterials, porous metals have advantages of being strong enough to provide suitable mechanical properties for the implanted site while remaining lightweight. More importantly, the porous architecture helps facilitate tissue growth and anchoring of the implant to the recipient tissue (e.g. bone), as well as supporting flow of tissue fluid carrying nutrient, which are two of the most important requirements for successful application of porous biomaterial scaffolds in the repair or replacement of damaged or diseased tissues [3].

To date, the manufacturing of porous cellular metals has primarily focused on the fabrication of random architectures (e.g. cellular foams) from different materials, such as titanium (Ti), Ti alloys, tantalum (Ta) and aluminium (Al). For example, a 3D fibre deposition and powder sintering method was used to produce porous Ti6Al4V structures with interconnected pores and a porosity of up to 90% [4]. Laser-engineered net shaping (LENS™) techniques have been used by Krishna et al. to make porous Ti6Al4V scaffolds for load-bearing implants [5], whereas in a different study, a multi-stage rapid prototyping technique together with a powder sintering process produced porous Ti scaffolds aimed for orthopaedic applications [6]. However, while these random porous architectures may meet mechanical requirements, they are generally not suitable for the purposes of optimising scaffold properties such as
porosity, stiffness and permeability [7] and do not allow precise control over pore architecture. These random porous structures typically have homogenous mechanical and biological properties at the macro level, but not at the micro level. This results in undesirable behaviour of the material, such as reduced effective stress and strut bending and twisting [8]. Manufacturing routes which permit the design and fabrication of topologically-ordered porous structures allows accurate control over pore structure, which inherently provides desired characteristics in certain regions while other regions can be tailored for other functional requirements.

While reasonable attention has been paid to manufacturing materials such as Ti, Al, ceramics and polymers in ordered porous form [6, 15-19], most porous Mg scaffolds reported in the literature have relied on existing foam fabrication methods resulting in random porous architectures. For example, Gu et al. manufactured lotus-type porous pure Mg using metal/gas eutectic unidirectional solidification method (GASAR process) [20]. Ho et al. adopted a lost foam casting method to produce a micro-truss sandwich core foam from Mg alloy AZ91 [21], whereas Wen et al. made porous pure Mg scaffolds using a powder metallurgical process [22]. Recently, Tan et al. used a mechanical perforation technique to produce porous Mg structures with controllable pore size, pore arrangement and hence, porosity [23], however, the manufacturing method was limited by pore shape and regional optimisation.

SFF fabrication methods, which adopt a layer-by-layer fabrication process from CAD models, have been shown as an ideal solution for manufacturing complex 3D porous structures by accurate control of pore topology. Different techniques are available, such as fibre deposition, laser sintering and 3D printing techniques [1]. However, due to the difficulties in powder processing or sintering of Mg, very few studies have focussed on developing reliable, safe and relatively low cost methods for manufacturing TOPM scaffolds.

Therefore, the aim of this study was to develop a SFF fabrication process for manufacturing TOPM scaffolds, which allows for the precise control of pore size and shape to meet specific biological requirements. Furthermore, given that the ultimate goal was to fabricate porous Mg implants directly from 3D CAD models, the resolution limits of each step of the manufacturing process were systematically characterised to compare the final dimensions and architecture of as-produced Mg structures with those parameters from the original CAD design.
3.4 Fabrication route

3.4.1 Introduction

Six steps were implemented for the synthesis of TOPM as illustrated in Figure 3.1. Briefly, these steps involved: (1) the use of computer-aided design (CAD) to create a 3D model with the desired architecture; (2) rapid prototyping (RP) printing of a positive polymeric mould of the CAD model; (3) infiltration of the polymeric mould with a NaCl paste; (4) burn-out of polymeric materials and sintering of NaCl; (5) pressure-assisted infiltration of the negative NaCl template with liquid Mg; and finally (6) removal of the NaCl template.

Figure 3.1: Illustration of the six-step SFF method for manufacturing TOPM scaffolds. (1) 3D CAD model with the desired architecture; (2) RP model of a positive polymeric mould of the CAD model; (3) infiltration of the polymeric mould with a NaCl paste; (4) negative NaCl template after sintering process; (5) pressure-assisted infiltration of the negative NaCl template with liquid Mg; and finally (6) Mg scaffold after removal of the NaCl template.
3.4.2 **CAD model design and RP model printing**

CAD models were generated using 3D solid modelling software (Rhinoceros 3D, McNeel Associates, WA). Each CAD model was designed with overall dimensions of Ø20 × 20 mm. The final CAD design was converted to stereolithography (STL) format, and was subsequently printed into RP moulds using a ProJet™ HD 3000 Professional 3D Printer (3D Systems, USA) at the ultra-high definition (UHD) mode. The RP mould material used was either VisiJet HR200 or EX200 as they both provided a sufficient high level of accuracy and suitable compression strength required to prevent deformation during NaCl infiltration process. Most importantly, both materials could be burnt out without leaving any residual via the sintering process. Since the product was aimed to be used in biomedical applications, it was important that all materials used in the manufacturing process were biocompatible for human use.

3.4.3 **NaCl infiltration**

The NaCl paste was prepared by mixing NaCl with laboratory grade gelatine and a supersaturated NaCl solution. NaCl in powder form was prepared by grinding high purity (99.5%) NaCl (Biolab, Biolab Ltd, Australia) in a Retsch Model ZM100 Centrifugal Grinding Mill (Krackeler Scientific Inc., USA). NaCl powder preparation was performed at a humidity of 75% or less to prevent the NaCl from absorbing moisture. The NaCl was dried at 60 °C for at least 24 hr before grinding. Particles sized between 45 – 63 µm were separated and collected using a vibratory sieve shaker Analysette (Fritsch GmbH - Milling and Sizing); sieve pore sizes were 120 µm, 90 µm, 63 µm and 45 µm.

Gelatine powder (Biolab, Biolab Ltd, Australia) was used as a binding agent and was added at a ratio 9:1 of NaCl to gelatine by mass. A supersaturated NaCl solution helped lubricate the paste without significantly changing the concentration of NaCl powder, with 5.3 ml of supersaturated NaCl solution added for every 24 g of NaCl powder. The paste preparation and mixing processes were performed under temperature-controlled conditions (20 °C) using an automatic mixer (Caframo RZR2-64, Canada) for consistency. The mixer speed was kept between 60 – 80 rpm in order to mitigate heat production. Total mixing time for 24 g NaCl, 2.6 g gelatine and 5.3 ml supersaturated NaCl solution was 20 min, and the produced NaCl
paste was sufficient for two RP moulds with overall dimensions of Ø20 × 20 mm. It was noted that the viscosity of the paste changed significantly during the mixing process, from dry and viscous at the beginning, to smooth and less viscous at the end (Figure 3.2).

A custom designed uniaxial compression apparatus and filter system was fabricated (Figure 3.3), consisting of a Perspex sandwich mould, which was held together using high-grade stainless steel screws and bolts, a piston and valve for pressing the NaCl paste into the RP mould, and a pipe to connect to the vacuum pump. With an overall RP mould diameter of 20 mm, the slot inside the sandwich mould was designed to have a corresponding diameter of 20 + 0.1 mm so that the RP mould could be held tightly and vertically inside. The detailed set up is shown in Figure 3.3. The RP mould was placed between two layers of O-ring seals, paper filter and mesh filter. The NaCl paste was fed from the top of the RP mould just prior to placing the filters. This set up ensured a uniform infiltration and distribution of NaCl paste throughout the RP mould.

Figure 3.2: Changes in viscosity of NaCl paste: before mixing, at 0, 5 and 20 min
To help distribute the NaCl paste evenly along the RP mould, both pressing and vacuuming steps were performed inside a 50 – 60 °C oven, as the viscosity of gelatine increases significantly at this temperature range. During the pressure infiltration process, a 2 MPa pressure was applied to the mould for 1 hr to ensure the RP mould was thoroughly filled with NaCl paste and the NaCl particles were well-packed together. It was crucially important to make sure the NaCl was packed as densely as possible to prevent molten Mg from entering the porous spaces in the NaCl template during the casting process. This was followed by a vacuum step, in which the pressure was reduced to 0.5 MPa and excess gelatine liquid was slowly drawn out using a vacuum pump (Hitachi 3VP-C, 50 L/min). The air was let in by the filter on one end of the RP mould while the other filter allowed only liquid gelatine and water, not NaCl, to flow into the pipe and out of the sandwich mould. This process was run for at least 22 hr to ensure most of the gelatine was removed and the NaCl was dried at the end of the process.

The full set up is shown in Figure 3.4. Pressure was applied using a pneumatic system and controlled using a pressure regulator (Precision Reg, IR2000-N02, SMC Pneumatics, USA). The vacuum pump (SuperEvac™ 4, CFM Pumps, Yellow Jacket, USA) was attached to the
sandwich mould via pipes.

![Infiltration set-up](image)

*Figure 3.4: Infiltration set-up shows pressure and vacuum control*

### 3.4.4 Polymer removal and NaCl sintering

After the NaCl infiltration process, the collected NaCl-infiltrated RP mould went through a sintering process in which the polymeric RP mould was removed by heating to 680 °C at an average rate of ~3 °C/min in air after a number of repeated heating/dwell steps (Figure 3.5). More specifically, the temperature was raised from room temperature to 149 °C over 2 hr, and maintained for 1 hr. The temperature was then raised to 371 °C over 1 hr, and stayed at this level for another hr before finally heating to 680 °C in one hr. The NaCl template was left to cool down inside the furnace at a rate of ~1 °C/min. These optimal sintering conditions required to completely remove the RP polymer were determined via Thermo Gravimetric Analysis (TGA) using a Q600 TGA machine (TA instruments). TGA results for gelatin, HR200 and ER200 are as shown in Appendix C. During the sintering process, air was blown into the chamber at the rate of 1 L/min. The negative NaCl template was not removed from the furnace until the temperature was < 80 °C to prevent cracks in the mould occurring due to a rapid drop in temperature. The NaCl negative mould collected after the sintering step was ready for the Mg casting process.
3.4.5 Casting

The Mg casting was performed in a custom built 10 kW induction furnace (Induktio, Slovenia) in a high-purity (Grade 0) argon (Ar) environment. Given that the density of NaCl is lighter than that of Mg, a steel base was attached to the NaCl template using a thin steel wire (Figure 3.6A) to prevent the NaCl template from floating in the molten Mg during casting. This setup was then placed inside a cylindrical steel crucible, which was designed with dimensions of Ø55 × 160 mm to fit inside an induction furnace chamber (Figure 3.6B). A thermocouple was placed inside the crucible as shown in Figure 3.6C. The crucible together with the thermocouple was placed inside the refractory, with the setup inside the furnace chamber as shown in Figure 3.6D.
Before Ar was pumped in, the furnace chamber was placed under vacuum (-990 mBar or below) to remove as much air as possible. Initially, Ar was pumped in at the rate of 25 L/min to give a positive pressure inside the chamber. When the pressure reached 250 mBar, the Ar rate was reduced to 10 L/min and at this stage, the oxygen level in the chamber would start to decrease. The Ar flow was kept at 10 L/min while waiting for the oxygen level to drop, and the pressure in the chamber was kept below 400 mBar, which was the maximum pressure allowed for the door seals. As soon as the oxygen level was below 1%, which was safe enough to heat the Mg without risk of fire, the furnace was turned on. Meanwhile, the Ar flow was reduced to 0.3 L/min and maintained for the remainder of the process. To avoid cracking in the NaCl template, the temperature was increased slowly from room temperature to 680 °C in 12 min at an average rate of 55 °C/min. The temperature was then maintained at 680 °C for the whole process. As soon as the Mg was completely molten, a vacuum was applied to create a negative pressure inside the chamber and this pressure was held for a short period. This was one of the most crucial steps in the manufacturing process since a high pressure, or an extended holding time, would result in an over-infiltrated NaCl template (i.e. molten Mg penetrating between individual NaCl grains), whereas a low infiltration pressure or too short a holding time resulted in only partial infiltration of the template. Since these phenomena were directly linked to the desired pore architecture (i.e. strut size and shape), the corresponding pressure and holding time for each strut size were investigated in this experiment (described in section 3.5.1). During this step, the liquid Mg was stirred occasionally to remove any air bubbles trapped inside. In the last step, the pressure was
increased to be equal with atmospheric pressure and the crucible temperature was cooled down at the rate of 25 °C/min by water flow. The Ar flow was turned off when the temperature dropped below 600 °C, and for safety reasons, the furnace door was opened only when the temperature was 500 °C or below. The flow chart of the casting process, showing corresponding temperature, pressure, and times for each step, is as shown in Figure 3.7.

**Figure 3.7: Flow chart of the casting process**

### 3.4.6 NaCl removal

The final step in the manufacturing process was to remove the NaCl from the cast Mg structure. During this process, chloride (Cl\(^-\)) ions were released into the aqueous solution as NaCl dissolved. Cl\(^-\) ions are known to be highly aggressive, increasing Mg corrosion with increasing Cl\(^-\) concentration [1-3]. Therefore, in order to dissolve the NaCl template in this study and inhibit the corrosion effect of NaCl on Mg as much as possible, the solution needed to be changed frequently to reduce the build up of Cl\(^-\) ions. NaOH with pH above 12 has been shown to create a corrosion resistant Mg(OH)\(_2\) layer on Mg surfaces [4]. However, with the existence of Cl\(^-\) ions in solution, it was suspected that the NaOH would not be able to
form the protective layer rapidly enough before corrosion occurred. A study by Song et al. reported that in NaCl solution, Na$_2$SO$_4$ solution can reduce the corrosion effect of Cl$^-$ ions on Mg [5-6]. Therefore, an experiment was performed to compare NaOH against Na$_2$SO$_4$ for the effectiveness of removing NaCl while minimising corrosion on Mg. NaOH (pH=14) was prepared by mixing 0.4 g NaOH with 80 ml distilled water. Similarly, a supersaturated solution of Na$_2$SO$_4$ was prepared by adding 6 g of Na$_2$SO$_4$ into 80 ml of distilled water. Mg-infiltrated NaCl templates were then placed in each solution in an ultrasonic bath to accelerate the washing process. The solution was refreshed every 3 min to prevent the concentration of chloride from increasing. After 9 min in the solution, the Mg scaffold was cleaned with ethanol in an ultrasonic bath for another 2 min, and finally, air-dried and kept in a desiccator to prevent corrosion. SEM and microscopy were used to check for corrosion on the scaffold after this NaCl removal process. Energy Dispersive X-ray Spectroscopy (EDS) (JSM-7000F, Jeol Ltd.) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) techniques (Spectrometer Services Pty. Ltd., Australia) were used to verify whether the rigorous washing step left any residual NaCl on the Mg scaffold surface.

3.5 Materials and methods

3.5.1 Materials and structures

The test material used in this experiment was commercially pure Mg 99.98% (Timminco Ltd.). With the purpose of investigating the accuracy of the manufacturing process, a range of pore architectures were evaluated to assess the repeatability of the process in terms of strut and pore dimensions. The four chosen porous architectures are illustrated in Figure 3.8A, comprising of orthogonal square struts with varying thickness of 0.6, 0.8, 1.0 and 1.2 mm, with corresponding pore sizes ranging from 1.4 to 0.8 mm. This resulted in porous structures with a predicted porosity of 80%, 65%, 50% and 35%, respectively (Figure 3.8A). Each architecture was designed based on one single unit structure, with larger macrostructures achieved by assembling the single units together. An example of eight unit structures assembled together is shown in Figure 3.8. One of the aims of this study was to determine the optimal infiltration pressure and time required during the Mg casting phase for the varying strut sizes and pore architectures. Therefore, pressure values ranging from 500 mBar to 720 mBar were tested for each of the chosen strut sizes. Furthermore, to understand the
capability of the manufacturing process in replicating complicated architectures, two additional structures, namely “fire-hydrant” and “crossbar” architectures, with complex cylindrical features and intricate details were designed (Figure 3.8B). Both structures contained common interfaces at the end of each strut for ease of mating unit structures with different strut sizes. The “fire-hydrant” structure had cylindrical struts of 0.9 mm in diameter, and the main challenge in manufacturing this structure was to replicate the common interface plates that were 0.15 mm in thickness and 1.3 mm in diameter. Meanwhile, the “crossbar” architecture contained thin circular struts 0.6 mm in diameter, small pores of 0.5 mm, and a common interface plate of 0.15 mm in thickness.

<table>
<thead>
<tr>
<th>Structures (1 unit structure)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
</table>
| Structures (8 unit structures put together) | ![CAD models showing unit structures of the four porous architectures characterised in the study](image)

<table>
<thead>
<tr>
<th>Strut size (mm)</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
<th>0.9</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (mm)</td>
<td>1.4</td>
<td>1.2</td>
<td>1.0</td>
<td>0.8</td>
<td>2.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>80</td>
<td>65</td>
<td>50</td>
<td>35</td>
<td>80</td>
<td>60</td>
</tr>
</tbody>
</table>

*Figure 3.8: (A) CAD models showing unit structures of the four porous architectures characterised in the study; (B) complex fire-hydrant (left) and crossbar structures (right)*

### 3.5.2 Media for NaCl removal

The suspicion that NaOH would not be able to form the protective layer on pure Mg rapidly enough before corrosion occurred was confirmed in this study. In the NaOH solution (pH=14), noticeable corrosion was observed within the first 30 s on Mg-NaCl scaffolds. As can be seen in Figure 3.9A and B, as soon as the NaCl layer was dissolved, Mg was exposed and corrosion occurred instantly. Meanwhile after 10 min in the supersaturated Na₂SO₄ solution, no corrosion could be seen on the Mg surface (Figure 3.9C & D).
Figure 3.9: (A & B) Corrosion on Mg scaffold in NaOH (pH=14) after 30 s (A) 2× magnification (B) 7× magnification; black arrows: corroded Mg; white arrows: NaCl remaining in the structure; (C & D) Surfaces of TOPM after NaCl removal process using Na$_2$SO$_4$ for 10 min (C) 2× magnification (D) 7× magnification

Further tests using ICP-MS (Spectrometer Services Ltd., Australia) and EDS (JSM-7000F, Jeol Ltd.) techniques on the samples, washed in the Na$_2$SO$_4$ solution, displayed negligible concentrations of NaCl (< 0.03%) on the TOPM scaffold (Figure 3.10).
3.5.3 Characterisation of porous architectures

With the aims stated above, the four Square Block architectures were characterised in terms of dimensional accuracy, surface area, porosity and surface roughness. Micro-computed tomography (µCT) (Skyscan 1172, SkyScan) and Scanning Electron Microscopy (SEM) (JSM-7000F, Jeol Ltd.) were employed to sequentially measure changes in strut dimensions for each phase of the manufacturing process, from CAD models, RP moulds, NaCl templates, and finally the as-fabricated Mg scaffolds. Results from these two methods were then compared for accuracy. Measurements were performed across the full height of the sample to check for dimensional consistency in each scaffold.

To determine the surface area and volume of cast Mg scaffolds, 3D models were reconstructed from µCT data in Amira (Visage Imaging, Inc.) and compared directly with values from designed CAD models, as illustrated in Figure 3.11. In order to capture as much detail of the structures as possible, the highest scanning resolution setting of 2 µm per pixel was used. This resolution was determined based on balancing the total scan time, capability of the processing computer and achieved resolution.
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In terms of surface roughness measurement, there were several methods available, including the use of surface profilometer (Dektak 150, Veeco, Woodbury, NY, USA) and atomic force microscopy (AFM). However, due to the topography of the structures with only a small surface area available on each strut and pores existing in between struts, the tendency for the stylus of the surface profilometer to fall into the pore was high. A significant amount of time was spent trying to measure the surface roughness using the surface profilometer, however no usable results were generated. Additionally, the roughness value exceeded the limit of AFM. Therefore, a different method which did not involve direct contact was investigated. Confocal laser scanning microscopy (CLSM) has been used widely in various research fields due to its capability of scanning samples at different depths, a high signal to noise ratio, and the ability to obtain high resolution images [7-8]. Briefly, the surface data was collected using a CLSM (Leica TCS SP5) with a resolution of 512 × 512 pixels, a pixel size of 1.51 µm, and distance between images of 0.99 µm. The images were processed in ImageJ version 1.42i (National Institutes of Health, USA) to extract surface topography using the Extended Depth of Field plug in. The surface topography image was a conversion of image stacks into one single image that contained information about depth of each point (Figure 3.12). These depth values were extracted via the surface profile information, and average roughness values were calculated using a customised Matlab code that converted the depth in pixels to µm for each point. Similar to dimensional accuracy, measurements were performed at various locations throughout the height of each sample to determine consistency across the structure.
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Grain structures of the raw pure Mg, cast solid Mg and TOPM were also examined. For all samples, except the raw material, the grain analysis was performed in both longitudinal and transverse directions. Samples were prepared to have a surface size of 10 × 10 mm or below in order to fit into the mounting holder. TechCut® 5 precision sectioning machine (Allied High Tech Products Inc., USA) was used for cutting samples. A diamond blade and slow feed rate (1.25 mm/min) were used to ensure accurate cuts with minimal deformation to the subsurface. For ease of holding samples during the polishing process, all samples were mounted in EpoFix® epoxy resin (Struers Australia Pty, Milton, Australia). After pouring resin into containers with the samples, they were placed in a desiccator and a vacuum of -1 MPa was applied for 2 min to remove any trapped air. All samples were left for a minimum of 24 hr to allow complete curing of the resin. Mounted samples were then ground with 240 and 600 grit SiC paper, then 9 µm, 3 µm and final polishing of 1 µm using polishing liquid. Each polishing step was performed for at least 2 min to ensure the surface was smooth. All samples were cleaned using high purity ethanol (99.5%) in an ultrasonic bath for a minimum of 2 min between each polishing grade, then air-dried and stored in a desiccator immediately after finishing. To illuminate the alloy microstructure, etching was performed on the polished samples using solution Song’s reagent, which contained of 6 g of picric acid, 5 ml of acetic acid, and 10 ml of distilled water and 100 ml of high purity ethanol (99.5%). Each sample was exposed to the etchant for 20 s, washed with ethanol (99.5%), before being analysed under a light microscope. Further etching was carried out by repeating the same process if the grain structure was not clear enough. Grain analysis was performed primarily on a Leica DM IRM inverted microscope (Leica Microsystems GmbH, Germany). An Axiocam® MR digital camera was used to obtain images using computer-based capture software AxioVision® 4.8 (Carl Zeiss NZ Ltd., New Zealand).

Figure 3.12: (A) Actual surface; (B) Surface topology as processed in ImageJ from confocal microscope scan data; and (C) Surface profile
3.6 Results and discussion

3.6.1 Optimisation of casting pressure

As mentioned previously, the pressure and pressure-dwell time applied in the Mg casting process after Mg was completely melted had a significant effect on the produced Mg scaffold. Inadequate pressure and dwell times resulted in incomplete infiltration of the NaCl template as can be seen in Figure 3.13A. Figures 3.13B & C show the consequences of too high a pressure and a longer dwell time. The scaffold in Figure 3.13C was over-infiltrated, where molten Mg at high pressure had not only infiltrated pores of the NaCl template, but also the micro-pores between sintered NaCl particles, and it was not possible to remove all residual NaCl from these structures. Figure 3.13B shows a partially over-infiltrated scaffold, in which the general architecture was maintained but not the surfaces and strut/pore shapes, and again only residual NaCl could only be partially removed. The Mg scaffold in Figure 3.13D is an example of optimal infiltration.

![Figure 3.13: Examples of (A) under-infiltrated; (B) partly over-infiltrated; (C) completely over-infiltrated; and (D) successfully infiltrated TOPM scaffolds.](image)

The pore size of the negative NaCl template, which corresponded to the strut size of the designed model, correlated directly with the required pressure and time for complete infiltration. In other words, the larger the NaCl pore size (i.e. larger strut size in CAD
Chapter 3 – Synthesis of TOPM structures from pure Mg

model), the higher the pressure and the longer dwell time were required. The optimal corresponding pressures (controlled via the air-out valve on the furnace) and holding period for each strut size are shown in Table 3.1.

Table 3.1: Optimal pressure and pressure-dwell time required for successful Mg infiltration as a function of CAD model strut/pore size

<table>
<thead>
<tr>
<th>Strut size (mm)</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (mm)</td>
<td>1.4</td>
<td>1.2</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Pressure (mBar)</td>
<td>620 ± 5</td>
<td>640 ± 5</td>
<td>660 ± 5</td>
<td>680 ± 5</td>
</tr>
<tr>
<td>Dwell Time (seconds)</td>
<td>15 ± 1</td>
<td>5 ± 1</td>
<td>0 ± 1</td>
<td>0 ± 1</td>
</tr>
</tbody>
</table>

3.6.2 Characterisation of surface roughness

As can be seen from Figure 3.14, the cast Mg structures had relatively rough surfaces due to the nature of the casting process and the incomplete packing of NaCl with narrow particle size range (43 – 65 µm). Furthermore, after sintering, the gelatine powder in the NaCl paste was burned out leaving micro-pores (<10 µm) in the structure (Figure 3.15) and with the shrinkage of Mg upon cooling, as-produced surfaces were not expected to be smooth (Figure 3.14).
Figure 3.14: High magnification images of scaffolds’ surface under (A) SEM (150× magnification) and (B) microscope (5× magnification)

Analysis using CLSM technique further confirmed the observation with surface roughness values for all 4 architectures (Table 3.2). Since suitable casting pressure was applied for each individual structure, surface roughness values were found to be consistent across individual samples as well as between structures. As can be seen from the data, surface roughness increased with increasing strut size and decreasing pore size. Therefore, structures with 1.2 mm strut size and 0.8 mm pore size had highest roughness value of 11.15 µm, whereas structures with the smallest strut size (0.6 mm) and largest pore size (1.4 mm) had a lower surface roughness of 9.06 µm.

Table 3.2: Corresponding surface roughness values for each structure

<table>
<thead>
<tr>
<th>Strut size (CAD model) (mm)</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (CAD model) (mm)</td>
<td>1.4</td>
<td>1.2</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Surface roughness (µm)</td>
<td><strong>9.06 ± 1.4</strong></td>
<td><strong>9.71 ± 1.7</strong></td>
<td><strong>10.76 ± 1.9</strong></td>
<td><strong>11.15 ± 2.0</strong></td>
</tr>
</tbody>
</table>

The primary reason for the varying surface roughness values, given the fact that all TOPM structures were manufactured using the same process, is related to the NaCl template. It was observed that the NaCl template of the structures with a larger pore size had significantly rougher and more porous surface appearance (Figure 3.15). For example, structures with 1.2 mm strut size (0.8 mm pore size) showed a rough surface with a number of defects due to incomplete packing of NaCl grains.
Figure 3.15: Surfaces of NaCl templates under SEM: Improved in NaCl packaging with increasing porosity

The reason for this was that the larger the pore in RP model was, the easier the NaCl paste could infiltrate the pore volume. Therefore, NaCl particles were packed more tightly together and the resultant NaCl template had smoother and less porous surfaces than NaCl templates.
infiltrated into RP moulds with a smaller pore size. Subsequently, during the Mg casting process, the molten Mg under high pressure was pushed against the NaCl surface and followed the contour on the NaCl template. In other words, surface properties of the NaCl template directly affected the surface roughness of the resultant TOPM scaffold, and along with optimisation of Mg infiltration pressure and timing, provided a means for accurately controlling surface roughness of cast TOPM scaffold.

3.6.3 **Dimensional accuracy: CAD model to NaCl template and TOPM scaffold**

3.6.3.1 **SEM vs. µCT**

As illustrated in Table 3.3, there appeared to be no significant difference between the SEM and µCT dimensional analysis techniques adopted for the varying strut architectures. Therefore, data recorded using µCT techniques was reported hereafter unless mentioned otherwise.

*Table 3.3: Similar strut sizes of TOPM scaffolds as measured by SEM and µCT techniques*

<table>
<thead>
<tr>
<th>Strut size (CAD model)</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strut size of TOPM scaffolds measured using SEM (mm)</td>
<td>0.66 ± 0.02</td>
<td>0.84 ± 0.03</td>
<td>1.02 ± 0.02</td>
<td>1.23 ± 0.03</td>
</tr>
<tr>
<td>Strut size of TOPM scaffolds measured using µCT (mm)</td>
<td>0.65 ± 0.01</td>
<td>0.85 ± 0.03</td>
<td>1.03 ± 0.03</td>
<td>1.23 ± 0.03</td>
</tr>
</tbody>
</table>

3.6.3.2 **Dimensional accuracy throughout each step of the SFF process**

A critical aspect to validating the SFF manufacturing process was to determine how accurately the final TOPM scaffold could be replicated from the initial CAD design model. Therefore, dimensional accuracy was evaluated for each step of the manufacturing process, from CAD model to RP mould, NaCl template and Mg scaffold.

Overall, for the four structures evaluated, the maximum increase in strut size from the CAD design to the final Mg scaffold was 0.05 ± 0.02 mm (8.3%), and was observed in structures with the smallest strut size (0.6 mm). Structures with larger 1.2 mm struts had the least
change in strut dimensions of $0.03 \pm 0.04$ mm (2.5%). Given this, however, it was important to determine which step in the multi-step Mg scaffold fabrication process contributed to the largest errors in scaffold architecture. Provided that RP moulds were printed using the most advanced method and material available at the time, it was still crucial to check for changes from the CAD model. Given that the NaCl templates represent the negative moulds of the CAD models, RP moulds and final Mg scaffolds, the NaCl template “pore size” was compared to the “strut size” of these other structures (Figure 3.16).

<table>
<thead>
<tr>
<th>Strut size CAD model (mm)</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strut size of RP moulds (mm)</td>
<td>$0.59 \pm 0.01$</td>
<td>$0.79 \pm 0.01$</td>
<td>$0.99 \pm 0.01$</td>
<td>$1.18 \pm 0.01$</td>
</tr>
<tr>
<td>% change in strut size from CAD design to RP moulds</td>
<td>1.7%</td>
<td>1.3%</td>
<td>1.0%</td>
<td>1.7%</td>
</tr>
<tr>
<td>Pore size of NaCl mould (mm)</td>
<td>$0.63 \pm 0.02$</td>
<td>$0.83 \pm 0.01$</td>
<td>$1.02 \pm 0.01$</td>
<td>$1.21 \pm 0.01$</td>
</tr>
<tr>
<td>% change in strut size from CAD design to NaCl template</td>
<td>5.0%</td>
<td>3.8%</td>
<td>2.0%</td>
<td>0.8%</td>
</tr>
<tr>
<td>Strut size of TOPM scaffolds (mm)</td>
<td>$0.65 \pm 0.02$</td>
<td>$0.85 \pm 0.03$</td>
<td>$1.03 \pm 0.02$</td>
<td>$1.23 \pm 0.04$</td>
</tr>
<tr>
<td>% change in strut size from CAD design to TOPM scaffolds</td>
<td>8.3%</td>
<td>6.3%</td>
<td>3.0%</td>
<td>2.5%</td>
</tr>
</tbody>
</table>

Figure 3.16: Dimensional accuracy comparison of RP mould, NaCl template and Mg scaffold with CAD design for all four structures
As can be seen from Figure 3.16, there was a small reduction in strut size of the RP moulds compared with the initial CAD design. This difference was in the order of 0.02 ± 0.01 mm in 1.2 mm structures. Other structures possessed a decrease of 0.01 ± 0.01 mm between CAD and RP moulds.

In comparison, there was small increase in strut dimension between CAD models and NaCl templates for every structure. Again, the greatest change was with 0.6 mm-strut structures, of which NaCl template pore dimension was 0.03 ± 0.02 mm (or 5.0%) larger than strut size of the CAD design. The smallest change was 0.01 ± 0.01 mm (or 0.8%) and occurred with 1.2 mm strut structures. In general, the largest percentage change in dimensions occurred during this NaCl infiltration step, and was likely due to the high viscosity of the NaCl-gelatine paste and incomplete packing of NaCl particles during infiltration, leading to gaps between the NaCl paste and strut walls of the RP mould.

The Mg infiltration process also resulted in an increase in strut dimensions for all structures. Even though the amount of change was smaller overall compared to that of the previous step, inheriting the increase in dimension after NaCl infiltration process made the change at the Mg casting step appear more pronounced. The maximum increase was 0.05 ± 0.02 mm (or 8.3%) occurring with 0.6 mm strut size model. Meanwhile, structures with 1.2 mm strut size had the least change with 0.03 ± 0.04 mm (or 2.5%). This increase in strut size was a likely the result of pressure infiltration and the close conformation of molten Mg against the NaCl template during the casting phase of the process.

In general, as changes in strut size were tracked from the CAD design to RP moulds, to NaCl templates and then finally to fabricate porous Mg scaffolds, the step in which the greatest dimensional errors originated was the NaCl infiltration phase. The increase in strut size from RP model to NaCl template was 0.3 mm to 0.4 mm, while from NaCl template to Mg scaffold, the maximum increase was 0.2 mm. Since this was suspected to be the result of low filling efficiency during the NaCl infiltration process, it is suggested that an increased NaCl particle distribution size (i.e. from 20-65 µm) would improve the flow of the NaCl paste, and consequently improve the accuracy of the whole process.

It was observed that in CAD models incorporating structures with pore size smaller than 0.8 mm, it was difficult to achieve satisfactory infiltration of the NaCl paste throughout the RP mould, and therefore, the resultant strut of NaCl template was fragile, which made
handling and Mg casting difficult. Provided that the pressure applied during NaCl infiltration could not be increased due to the limited compression strength of the RP moulds, changes in NaCl particle size may bring the potential of manufacturing a wider range of strut sizes.

All TOPM structures were manufactured using the novel SFF method with a high level of accuracy, including strut sizes as small as 0.6 mm. Due to limitations in RP mould printing and the NaCl infiltration process, this manufacturing method was limited to pore size and strut size above 0.5 mm. For RP mould printing, pore size of 0.2 mm and below was not generated successfully with current the machine and printing technique. More importantly, it was relatively difficult to thoroughly remove the supporting wax from the mould. Besides, the NaCl infiltration step was limited by the RP mould’s pore size of 0.5 mm and below. The NaCl strut resulting from this pore size range tended to be fragile and unstable. Furthermore, controlling appropriate infiltrating pressure in the Mg casting process for NaCl pore sizes (i.e. RP mould strut size) below 0.5 mm was difficult. Therefore, it was recommended that the designed structure should contain strut and pore sizes of 0.5 mm and above.

3.6.4 Characterisation of surface area: CAD model to TOPM scaffold

As mentioned previously in section 4.4.2, the sintered NaCl template possessed relatively rough surfaces and this was further confirmed by surface observation under SEM. As in Figure 3.15, structures with 80% porosity showed significantly smoother surfaces compared with that of 35% porous structure. However, since the NaCl template was the negative mould of the CAD and Mg model, its surface area was not investigated in comparison with CAD model or Mg scaffold.

With rough surfaces, the surface area of Mg scaffolds was expected to increase significantly compared to that of initial idealised CAD design models with perfectly smooth surfaces, and results collected from 3D reconstructed μCT models confirmed this theory (Figure 3.17). In general, the larger the surface area of the structure, the greater the discrepancy was between the CAD model and as-produced Mg scaffold. The maximum increase in surface area (77% or 15.5 ± 1.0 mm²) was observed in structures containing 1.2 mm struts. The 0.6 mm strut size designs yielded the minimum change of 58%, corresponding to 7.1 ± 1.0 mm² (Figure 3.17).
The observed large increase in surface area due to the rough surface topography of TOPM scaffolds can be considered as an advantage from a biomaterial point of view. Since this manufacturing process was developed and aimed towards orthopaedic applications, a considerable increase in surface area along with small change in dimensions can be considered as an advantage of the process as there are more sites for cell adhesion, osteoblastic differentiation, and osteogenesis [9-16]. However, it may affect the corrosion rate, which has been shown to increase with increasing surface roughness in stainless steel [17-19] and a Mg alloy [20]. Consequently, in certain circumstances where slower corrosion rate is required rather than osteogenetic properties, a less rough surface will be preferable. The role of surface roughness on corrosion rate was investigated in more detail in Chapter 4.
3.6.5 *Characterisation of volume and porosity: CAD model to NaCl template and TOPM scaffold*

The volume of NaCl templates was calculated using the same method as for Mg scaffolds. However, since NaCl templates were negatives, the calculated volume could not be directly compared with volumes of CAD model or Mg scaffold but would first need conversion. The volume of a bounding box size of 2×2×2 mm was used to subtract the volume of the NaCl template and result was compared with volume of CAD model and Mg scaffold (Equation 3.1).

\[
V_{\text{bounding box}} = 2 \times 2 \times 2 = 8 \text{ mm}^3
\]

\[
V_{\text{CAD corresponding}} = V_{\text{bounding box}} - V_{\text{NaCl template}} \tag{3.1}
\]

The increase in strut size was reflected in an overall increase in volume of both NaCl templates and Mg scaffolds versus those predicted in CAD models (Figure 3.18) leading to a decrease in porosities (Figure 3.19). Overall, in comparison with CAD models, the increase in NaCl template volume was slightly higher than that in Mg scaffolds. The greatest percentage change occurred in 0.6 mm strut size structures with a 22.1% increase from the CAD model to the NaCl template, and a 22% increase from the CAD model to the Mg scaffold. Meanwhile, structures with larger strut sizes (1.2 mm) showed a 9.2% increase in the NaCl template and 5.2% increase in the Mg scaffold.
Correspondingly, structures containing 0.6 mm struts with the largest increase in volume showed the greatest reduction in porosity, with over 6% absolute decrease compared to CAD designs. The actual measured porosity of the 0.6 mm strut Mg structure was 73.9 ± 1.6%. Meanwhile, structures with 1.2 mm struts had the least change in porosity resulting in an actual porosity of 31.8 ± 0.6%, which was 3.2% less than that of the CAD design (Figure 3.19). In comparison, there was little change in porosity between NaCl templates and Mg scaffolds, with a maximum absolute decrease of 2.2% in porosity observed with 1.2 mm strut size structure.
Figure 3.19: Comparing porosity of TOPM scaffold and NaCl templates with CAD designs for all four structures

Increases in total scaffold volume and decreases in porosity were not significant, and followed the trend with an increase in strut size.

Furthermore, µCT scan at high resolution confirmed that there was no porosity within the struts of the TOPM scaffolds.
3.6.6 **Metallography**

During cooling, the stainless steel crucible cooled down faster than Mg and created a chill zone between the crucible’s wall and the Mg material. The grain formation in this manufacturing method became similar to that of casting via pouring molten Mg into a cold mould. This phenomenon was marked with the formation of columnar grains along the perpendicular direction from the wall toward the liquid. These grains were then interrupted by the central equiaxed region (Figure 3.20) [21-22]. This was further confirmed by long grains on the transverse direction of the casted Mg (Figure 3.20B) and short and round grains on the longitudinal direction (Figure 3.20C). Compared with raw Mg material (Figure 3.20A), there was an increase in grain size of cast Mg, from 285 µm for raw pure Mg to 3410 µm for cast pure Mg in the longitudinal direction.

However, the microstructure of the porous TOPM scaffolds did not follow the same trend of grain directions for these non-porous cylindrical samples. The grain size was relatively large (e.g. 1400 µm), but since each strut might be comprised of as little as one grain (Figure 3.20D & E), it was difficult to determine the actual grain size in TOPM structures. Due to the nature of the manufacturing method and the selected architecture, there was random grain distribution. Most often, the grains intersected at the junction between struts (Figure 3.20D & E).
Figure 3.20: Grain structures of (A) Raw material, Cast material in longitudinal (B) and transverse (C) direction, Cast TOPM scaffolds in longitudinal (D) and transverse (E) direction.

While the big grain size observed in the longitudinal direction was most likely due to the formation of uninterrupted columnar grains, the overall increase in grain size in both monolithic and porous material was mainly due to the slow cooling rate of 25 °C/min [23-24].
Findings from the metallography study suggest that these structures would not be suitable for load-bearing applications, given that the large (> 1 mm) and incomplete grains at different areas in the scaffolds would likely result in reducing stiffness, strength and introduce instability into the structure. For example, Chen et al. reported that ultimate tensile strength and hardness of a Mg alloy was reduced significantly with increasing grain size [25]. Mechanical behaviour of pure Mg as cast from the SFF method will be further discussed in detail in Section 7.4.1.

3.6.7 Complex structures

Both fire-hydrant and crossbar structures with complex pore topologies and intricate features were successfully manufactured (Figure 3.21). Small architectural details were captured and replicated in the TOPM scaffolds, including the thin (e.g. 0.15 mm) and delicate common interface plates at the end of each strut. The amount of change in strut diameter for both architectures was similar to observations for the four structures reported previously, with a maximum increase of 0.03 ± 0.04 mm (Figure 3.21). This demonstrated that with correct architecture design, the SFF process could reliably replicate complex pore architectures and replicate fine features to a resolution of 0.15 mm.
Chapter 3 – Synthesis of TOPM structures from pure Mg

<table>
<thead>
<tr>
<th>Fire Hydrant</th>
<th>Crossbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strut diameter (mm)</td>
<td>Interface diameter (mm)</td>
</tr>
<tr>
<td>CAD Model</td>
<td>0.9</td>
</tr>
<tr>
<td>Mg Scaffold</td>
<td>0.93 ± 0.02</td>
</tr>
</tbody>
</table>

*Figure 3.21: As measured dimensions and microscopic images of complex TOPM Fire Hydrant and Crossbar structures*

While manufacturing random architecture scaffolds from pure Mg has received considerable interest and have displayed significant promise [26-31], work in ordered or optimised scaffolds from Mg and Mg alloys has been limited both in number and flexibility. In a study by Tan et al., an ordered architecture scaffold was successfully manufactured using the mechanical perforation method with an overall structure fairly similar to the structures used in this study, although no structural characterisation work was reported [32]. However, compared to this SFF manufacturing route, the perforation method was limited to produce simple structures with uniform pore shape and size, not complex ones.
3.7 Conclusions

In conclusion, the described novel SFF method has been successful in manufacturing TOPM scaffolds with controllable, porous, interconnected architecture based on 3D CAD designs. Furthermore, since the materials used in the process were relatively cheap and biologically safe, the TOPM scaffolds produced in this chapter hold significant promise for biomedical applications as bone interfacing implants. The adoption of NaCl-gelatine templates as the refractory material for the casting of molten Mg, and the fact that all of these components are removed during processing further indicates a safe and biologically inert process. This helps avoid the problem of toxic solvents or materials that may remain embedded within the TOPM implant and result in undesirable inflammatory response or failure of the scaffold upon implantation in vivo.

All TOPM structures, including ones with complex architectures, were manufactured using a novel SFF method with a high level of accuracy, including strut sizes as small as 0.6 mm, and specific features replicated down to 0.15 mm. Given that, due to limitations in RP mould printing and the NaCl infiltration process, this manufacturing method is limited to pore size and strut size above 0.5 mm. Increases in total scaffold volume and decreases in porosity were not significant, and followed the trend with an increase in strut size. The observed large increase in surface area due to the rough surface topography of TOPM scaffolds can be considered as an advantage from a biomaterial point of view as a potential surface for cell adhesion, osteoblastic differentiation, and osteogenesis. The results from this study help define the capability of this SFF method for manufacturing porous, bone interfacing orthopaedic implants with high surface area, directly from CAD models with only minor variations (<50 mm or <8.3%) in as-produced Mg scaffold geometry.

References


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32. Tan, L., Gong, M., Zheng, F., Zhang, B., Yang, K., Study on compression behavior of
porous magnesium used as bone tissue engineering scaffolds. Biomedical Materials, 2009. 4.
On the role of surface roughness in the corrosion of pure Mg in vitro
4.1 Chapter preface

In this chapter, the influence of surface roughness on the in vitro corrosion behaviour of pure magnesium (Mg) will be discussed. Samples with varying surface roughness characteristics were prepared in a controlled and uniform manner using a modified approach to the topologically-ordered porous Mg (TOPM) process described previously. This approach ensured that all samples were prepared under identical casting conditions without any additional confounding surface treatment processes that may introduce variation between samples. The corrosion behaviour was evaluated using a range of techniques, including hydrogen evolution, mass loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP).

This chapter is part of the following publication:


4.2 Abstract

The fabrication route for pure Mg TOPM as described in Chapter 3 resulted in scaffolds with a relatively rough surface topography (up to 11.15 µm). The relationship between surface roughness and degradation behaviour in Mg biomaterials is still a controversial issue, with some studies suggesting that an increasing surface roughness can adversely affect the corrosion rate. This study aims to clarify the relationship between surface roughness and corrosion rate of pure Mg. Pure Mg samples with surface roughness values (Ra) of 0.59 µm, 2.68 µm and 9.12 µm were cast using an indirect solid-free form fabrication method. The corrosion behaviour in vitro was evaluated using hydrogen evolution, mass loss, PDP and EIS. It is confirmed that surface roughness has a significant influence on the corrosion rate of pure Mg, with increasing roughness resulting in an accelerated corrosion rate. However, pitting corrosion was not observed, suggesting that surface roughness does not affect the pitting potential of Mg.
4.3 Introduction

The surface macro- and microtopography of bone-interfacing implants plays a critical role in osteoconduction, osseointegration, and de novo bone formation in a range of biomaterials including titanium (Ti) alloys, ceramics and coatings [1-6]. For example, microtopographies generated on Ti substrates in the range of $S_a > 1-2 \, \mu m$ have been suggested to be the predominant factor for platelet factor activation during early de novo bone formation, resulting in enhanced osteoconduction and bone contact [5, 7-8]. As a result, one could hypothesise that the natural progression for the development of degradable bone-interfacing Mg devices, is to adopt similar surface topographies to those described for Ti above. However, for degradable metals, the timing of the desired tissue remodelling and repair processes may be adversely influenced by the presence of topologically-rough surfaces if the corrosion rate and accumulation of corrosion by-products cannot be reliably controlled. For example, previous studies on stainless steel, which can undergo corrosion in vivo, found that increasing surface roughness resulted in increasing corrosion rate and pitting potential [9-11]. However, the relationship between surface roughness and degradation behaviour of Mg is less thoroughly understood. An in vivo study on MgCa0.8 showed that the structural loss of smooth machined samples was less than that of the sand-blasted samples, however, surface roughness ($R_a$) values were not reported [12]. Alvarez et al. [13] studied the corrosion behaviour of Mg alloy AE44 with samples polished to differing degrees. Results from immersion tests showed that rougher samples corroded at a slower rate and showed less pitting corrosion and lower pitting volume than the smooth samples. However, the surface roughness value of the samples were not reported but only indicated by the grade of silicon carbide (SiC) paper and diamond paste used [13]. In a more recent study, Walter et al. [14] investigated the influence of surface roughness ($S_a = 80$ to $430 \, nm$) on the corrosion behaviour of AZ91 alloy by means of electrochemical techniques. Interestingly, the findings contradicted those of Alvarez et al., wherein the corrosion rate and pitting potential increased with increasing surface roughness [14]. Moreover, the purpose of these studies was not targeted at biomaterials applications of Mg, and the commonly adopted methods for testing in vitro biocorrosion behaviour of Mg were not used. At a minimum, the corrosion medium should be based on a simulated body fluid (SBF) that is maintained at physiological values of pH and temperature as a step toward simulation of in vivo conditions [15-17]. Furthermore, the roughness values examined in both studies was relatively narrow, ranging from
approximately 80 to 430 nm, as compared to studies comparing bone formation and osteoconduction on Ti substrates which range from less than 0.5 µm to 10 µm and above [5].

In this chapter, the role of surface roughness on the corrosion rate of pure Mg with a broad range of surface topographies was investigated. A well-defined *in vitro* corrosion protocol was also implemented as a step toward understanding the biodegradation of Mg-based biomaterials. The specific goal was to manufacture samples in a controlled and uniform manner *via* a solid free form (SFF) fabrication casting route, but with varying surface roughness properties to directly emulate surfaces finishes possible during the casting process. By adopting this consistent SFF route, the effect of surface roughness on the corrosion behaviour of pure Mg *in vitro* in a simulated body environment could be accurately determined given that identical surface properties could be achieved across all samples.

### 4.4 Materials and methods

#### 4.4.1 Fabrication route

Commercially pure Mg 99.98% (Timminco Ltd., Canada) was utilised for this study. An indirect SFF manufacturing method that was previously developed ([Chapter 3](#)) [18-19] was modified to suit the aims of this experiment. The advantage of adopting this controlled manufacturing approach was that cast pure Mg substrates with varying surface roughness could be generated using a consistent process. Therefore, inherent changes to surface properties as would be the case when comparing cast Mg to sand blasted Mg samples for example, could be negated. This process includes six main steps: (1) using computer-aided design (CAD) to create a three-dimensional (3D) model with the desired architecture; (2) rapid prototyping (RP) printing of a positive polymeric template of the CAD model; (3) infiltration of the polymeric template with a NaCl paste; (4) burn-out of polymeric materials and sintering of NaCl; (5) infiltration of the negative NaCl template with liquid Mg; and finally (6) removal of the NaCl template. Results from inductively coupled plasma atomic emission spectroscopy (ICP-AES) and energy dispersive X-ray spectroscopy (EDS) indicated negligible concentrations of residual NaCl (< 0.03 wt.%) were present on the final samples.

Due to the nature of the SFF manufacturing process, the surface roughness and character of the final cast Mg products (Figure 4.1B) were determined by the packing of NaCl particles.
and roughness of the NaCl template (Figure 4.1A). This was in turn directly affected by the pore size of the RP mould [19-20], with larger pore sizes promoting more efficient infiltration and packing of NaCl, resulting in a reduced surface roughness of the cast Mg.

Figure 4.1: SEM images of the surface of the (A) NaCl template and (B) pure Mg scaffold illustrating the negative imprints of the NaCl particles.

In this study, two NaCl templates were designed to generate different surface roughness values for the Mg samples whilst maintaining identical fabrication conditions. The first NaCl template was made as a solid cylindrical block by performing the NaCl infiltration process as normal but without any RP mould included. The template was subsequently hand-polished using 600 grit SiC paper to create a smooth finish. Mg cast against this NaCl template had a lower surface roughness than casting against the normal NaCl template infiltrated within the RP mould. The second NaCl template was created using an RP mould consisting of 0.4 mm thick channels between vertical plates (Figure 4.2). The surface was maintained in the original unpolished state, and Mg samples cast using this NaCl mould had a greater surface roughness than that described above. To generate a smooth surface, Mg cast on the solid NaCl template was cut using a TechCut® 5 precision sectioning machine (Allied High Tech Products Inc., USA) and diamond blade (thickness of 0.02 inch) at low speed (1000 rpm) and low feed rate (1.25 mm/min) to minimise deformation to the subsurface. All samples were rinsed in ethanol for 10 min, air-dried and stored in desiccator prior to testing. The surface roughness ($R_a$) of all samples was measured using a surface profilometer (Dektak 150, Veeco).
4.4.2 *Testing media*

To mimic the *in vivo* environment and include ions commonly found in human blood (i.e. Ca$^{2+}$ and HPO$_4^{2-}$), Hank’s balanced salt solution (HBSS, H6136, Sigma-Aldrich NZ Ltd.), buffered with 5.96 g/L of 2-(4-(2-hydroxyethyl)-1-piperazinyl) ethanesulfonic acid (HEPES, H3375, Sigma-Aldrich NZ Ltd.) was used in all experiments. HEPES has been commonly used to buffer cell culture media in air and *in vitro* Mg experiments [16, 21]. Compared with the NaCl solution, HBSS contains several other substances that are commonly found in human blood, especially Ca$^{2+}$ and HPO$_4^{2-}$. The components and corresponding concentrations of HBSS is as shown in Table 4.1.

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**Figure 4.2:** Alternative structure used in the current experiment for fabricating rough cast pure Mg plates: (1) perspective view of CAD model with outer wall and horizontal supporting struts hidden, (2) top view of the RP mould, (3) perspective view of the NaCl template and (4) top view of the Mg product with rough surfaces.
Table 4.1: Composition of HBSS

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>141.6</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>144.6</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.4</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1.3</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.9</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>0.8</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.9</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>5.5</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Temperature was maintained at 37 ± 0.5 °C and pH was controlled at the level of 7.4 ± 0.05 throughout the experiments by a SevenEasy® S20 pH/Temperature meter and LabX pH meter (Mettler-Toledo Inc., Columbus, OH, USA) (Figure 4.3).
4.4.3 \textit{Hydrogen evolution and mass loss analysis}

Hydrogen evolution tests have been used widely in previous studies and have become a reliable method in Mg corrosion testing [22-24]. In this experiment, hydrogen gas (H$_2$(g)) evolution tests were performed on samples (n=3) with an exposed surface area of 1 cm$^2$ in a beaker containing 400 ml of HBSS. Marine grade silicone (Selleys, Australia) was used to prevent corrosion on other exposed surfaces of the sample. H$_2$(g) generated by the corrosion reaction was collected using a funnel (Ø = 5 cm) place directly on top of the sample, with H$_2$(g) accumulated in a 50 ml burette placed vertically over the funnel (Figure 4.4A). The burettes were held vertically above the beakers using clamps and stands as shown in Figure 4.4B. Parafilm tape (Pechiney, USA) was wrapped around the spout outlet of the funnel to create a tight seal with the burette. At the beginning of the experiment, the burette was filled with testing solution. Since the evolved H$_2$(g) displaces the solution inside the burette, this provides a direct correlation with the volume of H$_2$(g) produced. The liquid level was read every 30 min over 6 hr with an accuracy of ± 0.1 ml. The solution was also manually stirred at each reading to reduce the likelihood of a localised increase in pH at the
sample surface. Since the total surface area and roughness of the test region increases as corrosion proceeds, the testing period was limited to 6 hr to provide adequate data while minimising the change in surface area during the test. The testing solution was maintained at 37 °C via a heated water bath. Due to the high temperature, the testing media may vaporise and reduce the volume significantly. Therefore, it was important to maintain a constant volume of solution throughout testing. This could be done via adding extra media during the test or using a lid or plastic wrap to cover the beaker so as to prevent excess water loss.

Figure 4.4: Hydrogen test setup (A) setup inside the beaker and (B) test rig

The SBF media was warmed to the required temperature (37 °C) prior to the test and was maintained throughout the experiment using a double-hulled plastic box that contained tap water and a thermo-regulator (Figure 4.4B). There were holes on the lid of the box to hold the beaker upright and water inside the box was kept at a slightly lower level than the media to prevent it from coming into the beaker. The Techne Tempette® TE-10D thermo-regulator (Bibby Scientific Ltd., Stone, UK) was placed inside the box to keep temperature for the water, hence, the testing media temperature was checked throughout the test using thermometer (Figure 4.3) and variance was at ± 0.5 °C. The double-hull design was adopted to reduce temperature loss.

Mass loss was calculated by weighing the sample before and after the H₂ evolution testing.
using a microbalance with an accuracy of 0.001 g (XP105 Analytical Balance, Mettler-Toledo Inc., Columbus, OH, USA). A 2 M chromic acid solution (200 g/L CrO$_3$, 10 g/L AgN0$_3$) was used to remove corrosion products from the sample surface before the weight was measured [25-26]. Samples were placed in the acid solution for 2 min at room temperature, followed by a rinse with 70% ethanol and stored in a desiccator after being air-dried. The mass loss was converted to a corrosion rate in units of mg/cm$^2$/day following equation 4.1.

\[
corrosion\ rate = \frac{\text{mass loss}}{\text{surface area} \times \text{day}} = \frac{\text{mg}}{\text{cm}^2 \times \text{day}}
\] (4.1)

4.4.4 Electrochemical testing

EIS and PDP experiments were performed on a BioLogic® SP-150 potentiostat, controlled by EC-Lab 10.02 software (BioLogic Inc., Knoxville, USA) and using a three electrode flat-cell containing 300 ml HBSS (K0235, Princeton Applied Research, Oak Ridge, TN, USA) (Figure 4.5). The sample had an exposed surface area of 1 cm$^2$; a minimum of 3 replicates of each sample set was tested in every experiment for reproducible results. The saturated calomel (SCE) reference electrode was kept in a separate glass well, which was inside the cell, and was directed to the surface of the working electrode using a Luggin capillary tube. The counter electrode was a platinum wire mesh and placed on the other side of the cell. To maintain a physiological temperature in the test media inside the cell at 37 °C for, a silicone pipe (Ø10 mm) with heated water running through was wrapped around the cell. With a 2 m distance that the water needed to travel before reaching the cell, the heater was set at 39.7 °C; at this temperature plus the heat lost on the way, the water was approximately 37 °C when it reached the cell. Furthermore, the media was pre-warmed to 37 °C prior to testing as use of the hot water pipe system took up to 2 hr to reach the required temperature. All experiments were performed inside a purpose built Faraday cage to minimise electrical noise, as is typically reported in previous studies [27-28].
Figure 4.5: The test cell

The working voltage ranged from -3 V to 0 V for EIS tests to cover the full range of potentials encountered while maximising the resolution of the tests (50 µV). A frequency range of 30 mHz to 10 kHz was used for the EIS scans. The first two scans were performed after samples were exposed to HBSS for 15 and 30 min. The 15 min time point was chosen since it was sufficient time for the surface to stabilise and form the typical protective oxide layer. Subsequent scans were carried out after every 30 min for 6 hr. A scan rate of 1 mV/s was used for PDP and each test was carried out in the range of -150 mV below the open circuit potential (OCP) to 500 mV above. Similar to EIS, the first PDP scan was performed after the sample was immersed in HBSS for 15 min, and subsequent scans were at 30 min intervals. Tafel-type analysis was performed at points ± 50 mV outside of the corrosion potential, which is based on best practice [29]. After corrosion testing, surface morphology and composition of pure Mg samples were analysed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively.
4.5 Results

4.5.1 Surface roughness

The surface roughness ($R_a$) of the samples was 0.59 µm (“Smooth”), 2.68 µm (“Rough 1”) and 9.1 µm (“Rough 2”). The surfaces of all 3 samples were of uniform topology with distinctly different surface roughness (Figure 4.6).

<table>
<thead>
<tr>
<th></th>
<th>A. Smooth</th>
<th>B. Rough 1</th>
<th>C. Rough 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_a$ (µm)</td>
<td>0.59 ± 0.04</td>
<td>2.68 ± 0.74</td>
<td>9.1 ± 0.44</td>
</tr>
</tbody>
</table>

Figure 4.6: Optical and SEM images of as-cast Mg surfaces.

4.5.2 Hydrogen evolution and corrosion rate

Figure 4.7A illustrates the volume of $H_2(g)$ (ml/cm$^2$) evolved over 6 hr as a function of time and surface roughness for the three samples. The Smooth samples produced an average of 0.6 ml/cm$^2$ of $H_2(g)$ after 6 hr, while Rough 1 and Rough 2 samples generated approximately 28× and 80× more $H_2(g)$, respectively (Figure 4.7A). For Rough 1 samples, 17.45 ml/cm$^2$ of $H_2(g)$ was produced after 6 hr, indicating that a 5× increase in surface roughness resulted in a 28× increase in the volume of evolved $H_2(g)$. 
Similar to total $H_2(g)$ volume generated after 6 hr, total mass loss was significantly higher in rough samples compared to smooth samples (Figure 4.7B). Rough 2 samples had a converted mass loss rate of 130.12 mg/cm$^2$/day, compared with 2.74 mg/cm$^2$/day of the Smooth sample. A linear correlation ($R^2 = 0.9979$) was observed between surface roughness and mass loss.

4.5.3 Influence of surface roughness on the corrosion resistance of pure Mg

In general, Smooth and Rough 1 samples showed a similar trend with a rapid increase in corrosion resistance in the first hour, then a gradual increase thereafter (Figure 4.8A). In contrast, Rough 2 samples showed a reduction in the corrosion resistance after 1 hr and levelled out for the remaining time. After 6 hr, the corrosion resistance of Smooth samples was approximately 2× and 12× higher than that of the Rough 1 and Rough 2 samples, respectively (Figure 4.8B). The data collected from the EIS supports the findings of $H_2$ evolution tests with a reduced corrosion resistance in samples with increasing surface roughness as illustrated by a reduced width of the loop in the Nyquist plot (Figure 4.8B). In contrast to previous studies [14], no low frequency loop that would typically indicate pitting corrosion, was observed in any of the samples in the current study.
4.5.4 Polarisation behaviour

Overall, the samples showed different trends in changes of $i_{corr}$ values over time as a function of surface roughness (Figure 4.9A). While Smooth samples showed little reduction in the corrosion current, there was a slight reduction in $i_{corr}$ values for the Rough 1 sample over the first 2 hr, however, this was followed by a sharp decrease. Rough 2 samples showed an interesting trend, in which $i_{corr}$ increased significantly after the first hr, then continued to rise slightly in the next hr, and stayed relatively stable for the remaining period. Interestingly, Rough 2 had a lower initial corrosion current compared with Rough 1, although after 6 hr the $i_{corr}$ value of Rough 2 had tripled that of Rough 1. The Smooth sample exhibited an $i_{corr}$ value of 94.52 $\mu$A/cm$^2$ after 6 hr, which was approximately 2× and 6× lower than that of the Rough 1 and Rough 2 samples respectively.
There was a strong shift in corrosion potential ($E_{corr}$) in the anodic region with an increase in surface roughness (Figure 4.9B). Having a less negative $E_{corr}$, the Smooth sample was less likely to corrode than the other two rough samples. Generally, results from PDP tests showed the same trend in influence of surface roughness on corrosion rate of pure Mg.

### 4.5.5 Examination of surfaces before and after corrosion testing

SEM images in Figure 4.10 show the corroded surfaces of all three samples after 6 hr immersed in HBSS solution. This cracked corrosion layer and morphology is commonly found in the literature of Mg corrosion studies [30-31]. Data from corrosion testing suggested that pitting corrosion did not occur in any sample, and this was visually confirmed with SEM images. Furthermore, EDS analysis showed that the base layer was composed of Mg and oxygen; this indicated that a protective Mg(OH)$_2$ layer was formed on the surface during the corrosion test. Compared with Rough 2 sample, the others showed more a uniform cracked layer (Figure 4.10).
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<table>
<thead>
<tr>
<th></th>
<th>A. Smooth</th>
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<th>C. Rough 2</th>
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<tbody>
<tr>
<td>$R_a$ (µm)</td>
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</tr>
<tr>
<td>Surface before corrosion test</td>
<td>![Image]</td>
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<td>Surface after corrosion test</td>
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\textit{Figure 4.10: SEM images of sample surfaces before and after the hydrogen evolution test.}

4.6 Discussion

This study demonstrated the possibility to accurately control changes in surface roughness of pure Mg substrates via a SFF casting technique. Furthermore, the findings in this study agreed with previous corrosion reports on metallic biomaterials [11, 32], and more specifically Mg alloys \textit{in vitro} [14] and \textit{in vivo} [12], indicating that corrosion rate increases with increasing surface roughness.

Hydrogen evolution tests have been used widely in previous studies and have become a reliable method in Mg corrosion testing [22-24]. Mass loss, hydrogen evolution and electrochemical tests indicated that increasing surface roughness leads to increasing \textit{in vitro} corrosion rate in cast pure Mg substrates. Hydrogen evolution testing showed that while $H_{2(g)}$ evolution in the Smooth samples remained relatively low and constant over the 6-hr period, a significant increase was observed in both Rough 1 and Rough 2 samples after 2 hr. As can be seen from Figure 4.7A, the curve was particularly steep in Rough 2 samples and suggested that the corrosion was accelerated. In the first hr, the rate of $H_{2(g)}$ evolved was low as a result of the formation of a protective oxide layer, which was composed mainly of Mg(OH)$_2$, following exposure of the sample to the testing media. However, unlike in Smooth samples
where this protective layer remained stable [14], it was suspected that beyond this 2 hr period, the corrosion rate reached a critical point where it was increasingly difficult to maintain this protective layer, leading to accelerated corrosion rates.

The hydrogen evolution tests clearly indicated that a significantly higher volume of $\text{H}_2(\text{g})$ and an enhanced corrosion rate was generated in samples with increasing surface roughness. Since the volume of $\text{H}_2(\text{g})$ evolved from both rough samples was relatively high, this may increase the chance of complications associated with release of $\text{H}_2(\text{g})$ following implantation if Mg is implanted in vivo. For example, the formation of $\text{H}_2(\text{g})$ pockets adjacent to the implant may separate the tissues and tissue layers, therefore slow down the healing process [23, 33]. Furthermore, while small $\text{H}_2(\text{g})$ bubbles may be absorbed in vivo, larger $\text{H}_2(\text{g})$ bubbles carry the risk of entering blood vessels and causing blockages (gas embolism) [23, 34].

Importantly, the mass loss calculation as derived from hydrogen evolution experiments agreed well with the in vivo study by Hoh et al. on MgCa0.8, whereby sand-blasted samples showed greater structural loss than both smooth machined rod and threaded cylinders following implantation into the rabbit femur [12]. To provide an indication of the levels of corrosion, a scoring system was adopted in this study. Smooth machined samples received a corrosion score of $2.6 \pm 0.5$ out of 3, which indicated that the implant maintained its original shape with only slight reduction in dimensions, and even resorption at the edges was observed. In contrast, sand-blasted samples scored $0.3 \pm 0.5$ since most of the implants were completely degraded. The score for the threaded samples was $1.1 \pm 0.8$ since only part of the structure remained with highly irregular resorption [12]. While Hoh et al. did not directly measure the surface roughness value ($R_a$) of their sand-blasted and machined surfaces, these findings in combination with results from the present study, confirm that increasing roughness increases corrosion rate of Mg in vitro as well as in vivo.

Changes in actual surface area as a result of increasing roughness value was also considered as one of the potential factors contributing to the higher corrosion rate observed on rougher surfaces in this study. Since surface topographies produced in this experiment had roughness values ($R_a$) as high as 9.1 µm, an increase in the actual surface area compared with the original CAD design was expected. As reported previously, surface roughness of the topologically-ordered porous magnesium (TOPM) scaffold with 0.6 mm strut size produced in the same manufacturing process was 9.06 µm [19], which was almost identical to that of samples with highest roughness value (Rough 2) in this experiment. Therefore, the increase
in surface area of Rough 2 samples was assumed to be similar to that of the TOPM, which was reported to be 58% [19]. In other words, the actual total surface area of Rough 2 sample was estimated to be 1.58 mm$^2$ instead of 1 mm$^2$ as with Smooth surfaces. Since the total surface area exposed to the testing media increased in these rough samples, a higher corrosion rate was expected [10].

Previous in vitro corrosion studies have demonstrated that the presence of a low frequency inductive loop in EIS Nyquist plots indicates that pitting corrosion occurs on the surface [35]. However, this was not observed in any samples prepared in this study, as was confirmed by SEM images. Song et al. [36] suggested that pitting corrosion of Mg in solutions that contained Cl$^-$ ions was mainly due to a high local concentration of Cl$^-$ that breaks down the protective film, inducing pitting corrosion. In this experiment, the solution was stirred every 30 min mainly to regulate the pH level in the testing solution, but also in part to simulate a dynamic environment as expected in vivo. The fluid flow may have helped to reduce build-up of localised Cl$^-$ on the surface of the sample. Moreover, with the use of Mg-Al alloys in previous studies [13-14], pitting corrosion was more likely to occur due to corrosion attack along the Mg$_{17}$Al$_{12}$ network [37], whereas using pure Mg in this study helped eliminate this factor. Furthermore, the pitting behaviour found in the current study agreed with the in vivo finding by Hoh et al., in which no pitting corrosion was observed in either smooth or rough sand-blasted MgCa0.8 samples, but did occur in threaded samples [23]. Given that the testing conditions were consistent, the possible reasons for this difference in pitting behaviour were likely due to the surface preparation technique. While the smooth and rough surfaces were generated via machining and sand-blasting, respectively, the threaded implants were prepared via a number of steps, including turning, which was known to result in higher and deeper residual compression stress and inherently, changed the corrosion behaviour [38]. For these reasons, the pitting behaviour of Mg is affected by a number of factors, including alloying composition and surface modification technique.

Results from this study agreed with those of Walter et al. [14] to the extent that corrosion rate was accelerated by increasing surface roughness but our results do not confer that roughness influences the pitting tendency of pure Mg. Since all corrosion tests performed in this study used a frequently stirred HBSS solution, and no pitting was observed on any sample, this finding disagreed with previous suggestions that stirring disturbs the passive film formation and hence, increases pitting corrosion [14].
Furthermore, the in vitro corrosion test protocol adopted in both above mentioned studies was relatively basic, therefore, making it difficult to interpret the results when relating to degradation profiles for biomedical applications. More specifically, in both experiments, the NaCl solution used for in vitro corrosion testing did not take into account the influence of other ions and proteins typically found in the physiological environment that are more readily accepted methods for in vitro testing of Mg biomaterials [15-16]. Yamamoto et al. suggested that the choice of media was shown to contribute to the difference in corrosion behaviour and the formation of protective passivation layer on the surface [16]. It was found that on average over a 14 day period, the corrosion rate of pure Mg in 0.125 M NaCl solution was 100× higher than that in Earle's minimum essential medium - supplemented with foetal bovine serum (E-MEM+FBS) [16]. Furthermore, Xin et al. found that SBFs containing phosphates helped decrease corrosion rate and pitting corrosion due to the formation of magnesium phosphates on the surface, whereas the presence of hydrogen carbonate ions accelerated the corrosion rate at early stages, but later assisted in formation of a protective magnesium carbonate layer on the surface [39]. In a more comprehensive study, Muller et al. emphasized the importance of selecting suitable electrolyte solutions to narrow the gap between in vivo and in vitro corrosion data [15]. He suggested that high concentration of chloride and the absence of phosphate proteins in the testing media contributed to the high in vitro corrosion rate. Furthermore, localised attach was detected with size and shape of the pits affected by the electrolyte composition [15]. In this study, HBSS, which is one of the commonly used SBFs, was used; even though it still lacks other key components, such as proteins found in blood serum. Therefore, this could be one of the factors contributing to the difference in formation of the passive film and corrosion behaviour reported in this experiment compared with ones using simple NaCl solution.

Moreover, regarding the suitability of applying in vitro corrosion testing results in biomedical applications, a constant temperature (37 °C) and pH (7.4) was maintained in the current study to best mimic the in vivo environment. Whereas in the experimental set up of Walter et al. and Alvarez et al. a constant temperature and pH were not considered. Studies have found that corrosion increases significantly with increasing temperature [40-41], and it is well-known that pH has important effect on the corrosion rate of Mg. Bender et al. found that at pH of 12 or above, a stable and self-healing protective layer is formed, and this significantly reduces the corrosion rate [42]. Meanwhile, Ng et al. claimed that at pH of 5.5, the corrosion
rate is exceptionally higher than that at pH of 7 or 8 [43]. Ng et al. suggested that pH might be as low as 5.5 at the affected site after implantation, however, this effect is temporary and the body will be able to maintain the normal pH level, which is 7.35-7.45 to avoid negative impacts on the surrounding cells [44].

Additionally, Alvarez et al. and Walter et al. prepared samples with relatively smooth surface topographies ($S_a = 80$ to $430$ nm) via grinding or polishing processes [13-14]. These do not necessarily reflect the range of surface topographies present in porous scaffolds or implants prepared via casting. For example, porous Ti prepared by powder sintering had surface roughness up to $374$ μm [45], whereas porous TiNbZr alloy scaffolds fabricated using space-holder sintering method in a study by Wang et al. showed roughness value of $2.4$ μm [46]. Similarly, previous studies on topologically ordered Mg scaffolds prepared using the SFF method introduced a surface roughness up to $11.15$ μm [19]. In this study, different surface roughness values were successfully generated with one single manufacturing process and no further surface modification was required. Furthermore, compared with study done by Walter et al., the range of surface roughness values investigated was greater (i.e. $0.59$ μm up to $9.1$ μm). Therefore, these samples were representative of bone-interfacing biomaterial substrates or scaffolds that would typically be prepared by methods other than polishing or grinding. Furthermore, with the ability to fabricate advanced 3D structures with complex pore architecture [19], this manufacturing process shows potential to produce structures whose geometry and surface properties could be optimised to meet certain design parameters, such as porosity and volume fraction ratio. More importantly, this offers the potential to tailor the degradation rate as required, via controlling the surface roughness within the structure. Further optimisation could be achieved by changing design parameters, such as pore size, strut size and shape. The observed correlation between corrosion rate and roughness value obtained from hydrogen evolution experiments reported in this study will allow the modelling of corrosion behaviour of complex porous Mg structures as part of the optimisation process.

Finally, given the results of this study, it is highly recommended that future investigations of in vitro and in vivo corrosion of Mg should include accurate surface roughness characterisation to determine $R_a$ values. Not only will this allow improved comparison between studies where surfaces of varying roughness are prepared, but also verify that all samples prepared for in vitro or in vivo analysis have similar or well-defined tolerances in roughness value. The implication being that subtle changes in roughness between samples
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and/or conditions may result in drastically different corrosion rates as well as the associated experimental outcomes.

4.7 Conclusions

Increasing the surface roughness of Mg-based implants can be expected to increase the corrosion rate, although not pitting corrosion. Furthermore, the correlation between corrosion rate and roughness value obtained from hydrogen evolution experiments allows the future development of degradable Mg devices with tailored corrosion rate based on controlled surface roughness, irrespective of the Mg or Mg alloy substrate composition.

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Controlling corrosion rate of pure Mg via coating systems
Chapter 5 – Controlling corrosion rate of pure Mg via coating systems
5.1 Chapter preface

In Chapter 4, the corrosion rate of cast pure magnesium (Mg) was shown to increase with increasing surface roughness. This finding indicated that with a rough surface finish (Ra up to 11.15 µm), improvement in corrosion resistance of topologically ordered porous magnesium (TOPM) structures needed to be investigated before further biomedical applications could be considered. In this chapter, biomimetic calcium phosphate (CaP) and electrochemically-assisted deposition (ECAD) coatings were applied on the samples with rough surfaces (Ra = 9.12 µm) in seeking for improving corrosion protection. Corrosion tests were performed on the coated samples and results were compared with uncoated samples.

This chapter is part of the following publication:


5.2 Abstract

As reported in Chapter 3, the surfaces of the manufactured pure Mg TOPM were relatively rough, with Ra ranging from 9.06 µm up to 11.15 µm. Rough surface topographies on biomaterial substrates have been shown to be advantageous for cell adhesion and osteoconduction. However, the corresponding corrosion rate, as determined in Chapter 4, suggested that the as-produced TOPM may not be directly suitable for use as s biomaterial in its present form. The mass loss rate observed for surfaces with Ra = 9.12 µm was considerable, measuring 130.12 mg/cm²/day. Therefore, it was necessary to improve the corrosion resistance of the cast material before further investigating its potential. One of the most popular solutions for improving corrosion protection for Mg is the application of coating layers to the Mg substrate. In this chapter, coating techniques presently being investigated within our group [1], were employed to improve the corrosion resistance of samples with high surface roughness (Ra = 9.12 µm). The two methods used in this study were biomimetic CaP and ECAD coatings. The effectiveness of each technique was examined in vitro using corrosion testing methods as described in Chapter 4.

It was observed that while the biomimetic CaP coating slightly improved corrosion resistance
of samples with rough surfaces, the corrosion rate was still significantly higher than that of uncoated samples with a smooth surface finish. Adopting a biomimetic ECAD coating technique, on the other hand, was effective in reducing the corrosion rate of rough samples via the formation of a stable passivation layer.

### 5.3 Introduction

The rate at which hydrogen gas ($H_2(g)$) is absorbed in the body strongly depends on the implant location, due to the blood flow and the water content of the different tissues [2]. For example, vascular stents allow higher rates of hydrogen evolution to be safely tolerated as compared to cortical bone, given the higher blood flow rate and water content in blood vessels than in bone tissue (Table 5.1) [3].

**Table 5.1: Comparison of the water content and the average blood flow of the specific organ in human** [2]

<table>
<thead>
<tr>
<th>Water content (%)</th>
<th>Blood flow (ml/min/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heart</td>
<td>71.2-80.3</td>
</tr>
<tr>
<td>Muscle</td>
<td>76</td>
</tr>
<tr>
<td>Brain</td>
<td>76-78</td>
</tr>
<tr>
<td>Liver</td>
<td>72.9-77.3</td>
</tr>
<tr>
<td>Spleen</td>
<td>76.5-81.1</td>
</tr>
<tr>
<td>Intestine</td>
<td>71-72.7</td>
</tr>
<tr>
<td>Skin</td>
<td>67.8-75.8</td>
</tr>
<tr>
<td>Bone</td>
<td>43.9</td>
</tr>
</tbody>
</table>

In Chapter 4, the volume of $H_2(g)$ evolution over a 6 hr period for pure Mg samples with $R_a = 9.12 \, \mu m$ was calculated to be equivalent to 195.48 ml/cm$^2$/day, while the suggested theoretical limit for the human body is 2.25 ml/cm$^2$/day [4]. Song et al. went further to set a conservative level of 0.01 ml/cm$^2$/day [5]. Compared with both limits, the volume of hydrogen gas generated from rough pure Mg samples was too high. Therefore, increasing the
corrosion resistance of Mg with rough surface finish to an acceptable level is crucial before further investigating the material for other purposes.

The application of surface coatings is one of the various strategies adopted to improve corrosion resistance of Mg. There has been significant interest in the development of a coating that is non-toxic, and reduces the corrosion rate to acceptable levels for adoption in orthopaedic applications [6]. Alkali-heat treatment that introduces a biomimetic precipitation of CaP on the implant surface has shown to be a simple, yet effective method, and attracted significant attention [7]. CaP has been used widely in coating strategies for orthopaedic implants, especially in Ti. This is because CaP is biocompatible and also one of the main constituents in natural bone [7-8]. Furthermore, CaP coatings can initiate a rapid biological response and therefore, improve adhesion between newly forming bone and the implant [7, 9-12]. Taking advantage of the properties of CaP and its popular usage in biomedical fields, many studies have applied biomimetic coating methods on Mg substrates and achieved positive results [1, 13-16]. There have also been an increasing number of studies searching for improvements to biomimetic CaP coating techniques on pure Mg. For example, Li et al. treated high purity Mg in an alkaline solution of NaHCO\(_3\)-MgCO\(_3\) at pH of 9.3 for 24 hr, followed by 773 K heat treatment in 10 hr. Corrosion tests in simulated body fluid over a 14-day period showed no mass loss occurred to the sample. Meanwhile, untreated or only alkaline treated samples completely degraded during the test [16]. In a more recent study, Waterman et al. investigated the effect of pre-treatment time on the formation of biomimetic CaP coatings. Prior to coating process, the samples were treated in pure H\(_2\)O at 100°C for 0, 10 and 30 min to form a Mg(OH)\(_2\) layer; it was found that additional pre-treatment time was beneficial to the corrosion resistance [1].

In addition to CaP coating techniques, biomimetic ECAD coating methods also have become increasingly popular, with uniform surface coatings formed offering enhanced corrosion protection [17]. Recently, Luo et al. coated Mg with poly(3,4-ethylenedioxythiophene) (PEDOT) using an ionic liquid as the solvent. This technique not only improved the corrosion resistance, but with the use of PEDOT, it allowed the attachment of anti-inflammatory drug, dexamethasone, onto the implant [18].

In this study, both biomimetic CaP and ECAD coating techniques were employed to increase the corrosion resistance of rough pure Mg samples (R\(_a\) = 9.12 µm). The changes in corrosion behaviour were studied via a range of corrosion testing techniques, including hydrogen...
evolution, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP), as previously described and used in Chapter 4. Corrosion behaviour as determined from this experiment were compared with that of uncoated smooth ($R_a = 0.59 \, \mu m$) and rough ($R_a = 9.12 \, \mu m$) samples as determined in Chapter 4.

5.4 Materials and methods

5.4.1 Material

In this study, samples with surface roughness of 9.12 $\mu m$ were prepared by the indirect solid free form (SFF) manufacturing method as described in Section 3.4 using commercially pure Mg 99.98% (Timminco Ltd., Canada) [19-20]. As shown in Chapter 4, the RP mould consisting of 0.4 mm thick channels between vertical plates was used to generate samples with required surface roughness ($R_a = 9.12 \, \mu m$).

5.4.2 Biomimetic calcium phosphate coating

The biomimetic CaP coating process was performed as described in the publication by Waterman et al. [1]. It followed the process as described by Habibovic et al. [12] with a few modifications to suit Mg. The coating technique was shown to improve corrosion resistance of raw (i.e. as-sourced non-cast) pure Mg with smooth surface preparation [1].

In the previous study, Waterman et al. treated all the samples in pure H$_2$O at 100 °C for different amounts of time to form a Mg(OH)$_2$ layer. However, due to the low corrosion resistance of the rough samples, no pre-treatment was performed in this study. The coating process had two separate stages, in which different modified simulated body fluids (SBF) were prepared. To prevent corrosion on Mg substrates during the coating process, both solutions were designed with reduced chloride ions (Cl$^-$). Both solutions contained ions present in the physiological environment but at higher concentrations to promote CaP formation. The compositions of each SBF solution are shown in Table 5.2.
Table 5.2: Chemical compositions of two modified SBF solutions used in the biomimetic CaP coating process

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Solution 1 (g/L)</th>
<th>Solution 2 (g/L)</th>
<th>Ion concentrations</th>
<th>Solution 1 (ppm)</th>
<th>Solution 2 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>1.65</td>
<td>1.65</td>
<td>Cl⁻</td>
<td>3300</td>
<td>10300</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.3</td>
<td>0.3</td>
<td>PO₄²⁻</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>1.8</td>
<td>–</td>
<td>SO₄²⁻</td>
<td>1800</td>
<td>0</td>
</tr>
<tr>
<td>Na₂HPO₄·4H₂O</td>
<td>0.4</td>
<td>0.4</td>
<td>CO₃²⁻</td>
<td>2270</td>
<td>350</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>2.27</td>
<td>0.35</td>
<td>Ca²⁺</td>
<td>1650</td>
<td>1650</td>
</tr>
<tr>
<td>NaCl</td>
<td>–</td>
<td>7.0</td>
<td>Na⁺</td>
<td>3070</td>
<td>8150</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mg²⁺</td>
<td>1800</td>
<td>0</td>
</tr>
</tbody>
</table>

Solution 1 had a higher concentration of carbonate ions (CO₃²⁻) to promote formation of amorphous CaP with good coverage, while solution 2 was designed to have a low Mg²⁺ ion concentration to promote crystalline apatite formation [10, 21]. Each solution was heated to 37 °C before carbon dioxide gas (CO₂(g)) was dissolved to generate a pH of 6 for the solution. When the desired pH was reached, CO₂(g) was removed from the solution and air was bubbled through. In the first stage, Mg samples were immersed in solution 1 for 24 hr. During this process, a magnetic stirrer was employed to mix the solution and consequently, generate a uniform ionic concentration. After 24 hr, the samples were removed and rinsed in distilled water before being put into solution 2 for another 24 hr. The pH of solution 2 was also controlled by the same application of CO₂(g) and air.

5.4.3 Biomimetic ECAD coating

The biomimetic ECAD coating could be considered as a more advanced biomimetic coating technique. Instead of having only a single passivating CaP layer on the surface, a secondary calcium hydroxide (Ca(OH)₂) under-layer to the biomimetic coating was added in an attempt
to improve the corrosion resistance. The Ca$^{2+}$ ions released from Ca(OH)$_2$ help promote formation of additional CaP nucleation on the CaP layer, especially in regions containing cracks and defects, thereby generating a potentially more stable and effective coating layer. A convenient method for forming dense and adherent Ca(OH)$_2$ is using the biomimetic ECAD process. This technique was employed by Song et al. to create a hydroxyapatite coating on AZ91D samples with a smooth surface preparation, and resulted in a considerable reduction in the corrosion rate [17]. In this study, the rough Mg samples were coated with the biomimetic ECAD system using platinum (Pt) as a counter electrode in 2 M Ca(NO$_3$)$_2$ solution. This was performed by attaching a copper wire to the sample for electrical connectivity, with the surface to be coated facing the Pt electrode. The initial pH of the solution at 4.9 was adjusted using NaOH and HNO$_3$. Electrostatic coating was performed with -5.1 V between the Mg and a Pt counter electrode during the deposition. The timing of the process was optimised at 10 min in order to obtain a consistent, smooth coating. This step resulted in a calcium hydroxide layer on the surface of the material. Reactions occurring during the electrostatic coating step are as shown in equations 6.1 – 6.3.

Cathodic reactions:

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- \quad (6.1)
\]
\[
\text{Ca}^{2+} + 2\text{OH}^- \rightarrow \text{Ca(OH)}_2(\text{s}) \quad (6.2)
\]

Anodic reaction:

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4 \text{e}^- \quad (6.3)
\]

This was followed by the CaP coating steps as described earlier in Section 5.4.2. The second coating step was performed to create the outer CaP layer on top of the Ca(OH)$_2$ to increase protection. Once the Ca(OH)$_2$ layer is exposed to the media or physiological environment, this coating layer will begin to dissolve into Ca$^{2+}$ and OH$^-$. The Ca$^{2+}$ will combine with the phosphate ions in the physiological fluid resulting in deposition of calcium phosphate at the defect site. This inherent re-passivation will provide corrosion protection for the site. An illustration of how the protective layer formed from the calcium hydroxide is as shown in Figure 5.1.
5.4.4 Corrosion testing methods

Corrosion tests performed on the both biomimetic CaP and ECAD coated samples included hydrogen evolution, EIS and PDP, testing in Hank’s balanced salt solution (HBSS) at $37 \pm 1 \, ^\circ C$ and pH of $7.4 \pm 0.1$. It was not possible to calculate the mass loss from hydrogen...
evolution tests as described in Chapter 4 since the mass added to the sample by the coating layer was difficult to determine. In addition, Mg substrates may have corroded and lost mass during the coating process. All the corrosion tests were set up and performed as described in Chapter 4. However, the test period was increased to 24 hr and 72 hr for the CaP and ECAD coated samples, respectively, instead of 6 hr as for the uncoated samples. This was because with the extra corrosion protection from the coating layer, the sample was expected to withstand a longer corrosion testing period. Surfaces of the coated material before and after corrosion testing were examined under light microscopy and SEM. Results were compared against that of uncoated rough and smooth cast pure Mg samples (Chapter 4). Due to the difference in material processing technique, the corrosion behaviour of raw (i.e. as-sourced non-cast) smooth CaP coated Mg sample in [1] could not be compared to findings on cast Mg in this experiment.

5.5 Results and Discussion

5.5.1 Surface examination

Surfaces of CaP coated (Figure 5.2D & E) and biomimetic ECAD coated samples (Figure 5.2G & H) were examined under SEM after the coating process and compared with the rough uncoated surface (Figure 5.6A & B).
Figure 5.2: Surface of rough uncoated sample under (A) microscope and (B) SEM, and (C) after corrosion testing; biomimetic CaP and ECAD coated sample after coating process (D&G) under the microscope and (E&H) SEM, and (F&I) after corrosion testing

Even though the biomimetic CaP coating method successfully formed a uniform and even coating layer on the smooth pure Mg [1], it did not perform as well when applied on rough Mg surfaces. The CaP coating layer on the $R_a = 9.12$ $\mu$m was relatively inconsistent with thick CaP flakes in some regions, and with thin layers elsewhere (Figure 5.2D). At the microscopic level, cracks and defects (as shown by the arrows) were found in both smooth [1] and rough coated samples (Figure 5.3).
Surface examination on samples after corrosion testing showed cracks and defects occurring on the CaP coating layer (Figure 5.2F). This suggested an inconsistent and unstable coating layer allowing ongoing corrosion to occur.

Furthermore, it was observed that during the coating process, some samples were corroded severely and could not be used. On average, the success rate in coating rough as-cast pure Mg samples was 80% while it was 100% for smooth raw pure Mg substrates [1]. This observation was mainly due to the low corrosion resistance of the uncoated rough Mg as reported in Chapter 4. Given that the coating media was modified with reduced Cl\(^-\) ion concentration, immersing a material that was highly susceptible to corrosion for a total of 48 hr still introduced significant corrosion to the sample.

Unlike the biomimetic CaP coating, samples coated with the biomimetic ECAD process did not show any signs of corrosion during the coating process, such as cracks and an uneven surface. All samples were coated successfully with a uniform layer observed on the surface, which appeared to be more even than uncoated samples (Figure 5.2A & G). It can easily be seen that the coating layer was more uniform and did not change noticeably after the corrosion test (Figure 5.2I). This was mainly a result of the continuous formation of CaP repassivation layer as Ca\(^{2+}\) ions, which was released from the dissolved Ca(OH)\(_2\) layer, combined with phosphate ions in the SBF.

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**Figure 5.3:** Cracks and defects on the biomimetic CaP (A) smooth [1] and (B) rough samples.
From surface analysis observations and the successful coating rate, the biomimetic ECAD coating method appeared to increase the effectiveness of the biomimetic coating technique.

5.5.2 **Hydrogen evolution**

The volume of $H_2(g)$ generated over the 6-hr period for the rough uncoated sample was compared to that of smooth uncoated and rough biomimetic CaP and ECAD coated samples over 24 hr as shown in Figure 5.4. As previously explained in Chapter 4, given that the total surface area and roughness of test samples increases as corrosion occurs, the testing period was limited to 6 hr for rough uncoated samples. For rough samples, both coating methods helped reduce the volume of hydrogen evolved considerably. For example, while the uncoated sample produced up to 48.87 ± 0.5 ml/cm$^2$ of $H_2(g)$ after 6 hr (equivalent to approximately 195.48 ml/cm$^2$/day), the biomimetic CaP and ECAD coating decreased that figure down to 25.63 ± 4 ml/cm$^2$/day and 2.22 ± 0.7 ml/cm$^2$/day, or more than $7\times$ and $88\times$ reduction, respectively.

![Graph showing hydrogen evolution](image_url)

*Figure 5.4: $H_2(g)$ evolution for rough uncoated sample over 6-hr period and for biomimetic CaP, ECAD coated and smooth uncoated samples over 24 hr.*
However, in comparison with smooth uncoated samples ($R_a = 0.59 \ \mu m$), which produced $1.8 \pm 0.5 \ \text{ml/cm}^2/\text{day}$ of hydrogen, CaP coated samples had approximately $14\times$ higher volume of hydrogen gas evolved. Results from hydrogen evolution tests suggested that the CaP coating improved the corrosion resistance of Mg with rough surfaces. Given the volume of hydrogen generated on the coated sample was lower than that of the uncoated version, the CaP coating did provide certain protection to the Mg substrate. However, since the $H_2(g)$ volume from the rough coated sample was still considerably higher than the theoretical limit of $2.25 \ \text{ml/cm}^2/\text{day}$ [4], the improvement in corrosion protection introduced by the CaP coating could be considered as being insufficient for biomedical applications. With an inconsistent coating, hence, inconsistent passivation layer formed on the Mg substrate, the corrosion reaction may continue to occur as a result of defects and cracks in the CaP layer [1], and therefore, continue to evolve $H_2(g)$ in a linear fashion over time. Combining the observation on the change in surface after corrosion with the trend of increasing $H_2(g)$ evolution of CaP coated samples, it is suspected that continuing the test for over 24 hr, the surface area and roughness of the sample would change too significantly to produce reliable data. Given that after the 8th hour, the change in $H_2(g)$ volume could be expressed as a straight line, it can be expected that gas evolution would continue to increase at the same rate beyond 24 hr.

Comparing the biomimetic ECAD coated sample with smooth uncoated samples ($R_a = 0.59 \ \mu m$), coated samples showed a higher rate of hydrogen gas increase than the smooth uncoated sample in the first 12 hr. However, after 12 hr, the generation of $H_2(g)$ was considerably reduced in the coated sample compared with smooth uncoated samples. This led to a similar $H_2(g)$ formation between two samples, i.e. $2.22 \pm 0.7 \ \text{ml/cm}^2/\text{day}$ for the biomimetic ECAD coated sample and $1.8 \pm 0.5 \ \text{ml/cm}^2/\text{day}$ for the smooth uncoated sample. Given that the original surface roughness of the Mg substrate was approximately $15\times$ greater ($R_a = 0.59$ and $9.12 \ \mu m$), the biomimetic ECAD coating system considerably reduced the corrosion rate of the samples with rough surfaces.

Furthermore, the reduction in the rate of $H_2(g)$ volume evolution in the biomimetic ECAD coated samples after 12 hr suggested that a stable protective layer was formed on the substrate. This was in contrast with the trend of $H_2(g)$ generation in both uncoated samples and CaP coated samples, which was relatively unchanged over time. The reason for this difference could be due to the protective layer CaP continuously formed on the surface as the
Ca(OH)$_2$ was broken down. The released Ca$^{2+}$ ions combined with the phosphate ions in the physiological fluid to allow deposition of CaP at the defect site. Therefore, while for the uncoated samples, the protective layer (Mg(OH)$_2$) was formed and corroded at an equal rate, the stability of the CaP protecting layer in biomimetic ECAD coated samples increased with time. After 72 hr testing in HBSS solution, a total of 3.2 ± 0.8 ml/cm$^2$ of hydrogen was generated by the biomimetic ECAD coated samples (Figure 5.5).

![Figure 5.5: Change in hydrogen gas level in the biomimetic ECAD coated sample over 72 hr](image)

Therefore, using the theoretical limit for tolerable H$_2$(g) evolution of 2.25 ml/cm$^2$/day, the biomimetic ECAD coating technique reduced the H$_2$(g) evolution of rough as-cast pure Mg samples ($R_a = 9.12$ µm) to a potentially physiologically acceptable level. However, given that the H$_2$(g) diffusion is dependent on the implant location [2], it is still important to further investigate the in vivo behaviour of biomimetic ECAD coated samples in future studies.

**5.5.3 Corrosion resistance**

The change in corrosion resistance over 6 hr following EIS testing for all four samples; uncoated smooth ($R_a = 0.59$ µm), uncoated rough ($R_a = 9.12$ µm), rough biomimetic CaP and ECAD coated samples, is shown in Figure 5.6A. In the first hr, rough CaP coated samples
showed a slightly higher corrosion resistance than the uncoated rough version. However, the difference became insignificant after 1 hr, with corrosion resistance of 40.94 Ω and 33.05 Ω for the rough CaP coated and uncoated samples, respectively, after 6 hr. Both uncoated and CaP coated samples shared a similar trend in the resulting corrosion resistance values. The initial corrosion resistance was high at the start of the test, but decreased after 2 hr and remained at this level for the duration of the testing period. Meanwhile, a similar trend was also observed between rough biomimetic ECAD coated and smooth (R_a= 0.59 µm) uncoated samples. However, the trend was opposite to the rough uncoated and CaP coated versions, with the corrosion resistance increasing gradually with time. At the 6 hr time point, total corrosion resistance of the biomimetic ECAD coated sample was 360.8 Ω, which was close to that of smooth uncoated samples (412.3 Ω). With this corrosion resistance value, the biomimetic ECAD coatings improved the corrosion resistance for rough samples by approximately 11×.

The initial corrosion resistance reading on smooth uncoated samples was slightly higher (222.7 Ω) than that of the rough CaP coated samples (150 Ω). However, after 2 hr when both samples reached a stable state, the difference in resistance values became significant. At the 6 hr time point, corrosion resistance for the smooth uncoated and rough CaP coated sample was 388.9 Ω and 40.87 Ω respectively, and corresponded to approximately 9× difference. In other words, the corrosion resistance of the rough CaP coated samples was considerably lower in comparison with smooth uncoated samples.

Figure 5.6B shows the Nyquist plot of all the samples after 6 hr. The second time constant, which represents the resistance of the coating layer, could be observed for the biomimetic ECAD coated sample (red stars), but not others.
Over 24 hr, two completely opposite trends in corrosion resistance were observed on the biomimetic ECAD and CaP samples (Figure 5.7A). In general, biomimetic ECAD coated samples showed a 10× greater corrosion resistance than the CaP coated samples. For biomimetic ECAD samples, there was a steep increase within the first 6 hr, with the total corrosion resistance value of 360.8 Ω reached. This was followed by a plateau region, in
which the total resistance stayed at approximately 360 Ω for 14 hr. After 14 hr, the resistance continued to gradually increase and reached 660 Ω after 72 hr (Figure 5.7B). While the initial corrosion resistance reading for CaP coated samples was similar to that of biomimetic ECAD coated samples (150 Ω), corrosion resistance reduced dramatically in the first 2 hr, dropping to approximately 50 Ω, and remained constant at this resistance level for the duration of the test.

Figure 5.7: Change in corrosion resistance of (A) the rough CaP coated versus rough biomimetic coated sample over 24 hr and (B) the rough biomimetic ECAD coated sample over 72 hr
Results from EIS tests confirmed the findings observed in the hydrogen evolution tests, whereby the corrosion resistance of rough CaP coated samples was slightly higher than that of its uncoated version, and significantly lower than that of smooth uncoated samples ($R_a = 0.59$ µm). The decrease in corrosion resistance as observed on CaP coated samples (particular in the first 2 hr) could be attributed to the previously described defects in the coating layer. Corrosion occurring beneath the coating as the result of cracks may undercut the coating layer and decrease its adhesion to the sample. In other words, the Mg substrate in some regions may be left exposed to the solution due to the failure of the coating layer [1].

As reported in previous studies, additional precipitation of CaP on the surface may result due to the existing elements in the HBSS and local pH rise, especially at defects in the coating layer where corrosion proceeds [1-2, 22]. However, since the corrosion resistance of the CaP coated sample was observed to decrease, and remained unchanged over time, this re-passivation phenomenon did not appear to occur, or did not occur rapidly enough on Mg samples coated with CaP techniques in this study.

On the other hand, biomimetic ECAD coatings significantly improved the resistance of Mg samples with rough surfaces. With an ECAD coating, the corrosion resistance of rough samples increased considerably (11×), and was similar to that of smooth uncoated samples after 6 hr (Figure 5.6A). Furthermore, while the resistance of the uncoated samples stayed relatively constant over time, a continuously increasing trend was observed in biomimetic ECAD coated samples (Figure 5.7). This suggested that the coating layer was stable and the CaP continued to form at the defect sites as a result of the reaction between Ca$^{2+}$ and phosphate in the test media. Thus, as corrosion occurred, the coating repaired itself and the corrosion resistance increased with time.

### 5.5.4 Polarisation behaviour

Similar to corrosion resistance observations, changes in $i_{corr}$ value could be put into two groups. Group one contained rough uncoated and CaP coated sample with increasing $i_{corr}$ value, and the other group included the smooth uncoated and rough biomimetic ECAD coated samples, whose $i_{corr}$ value decreased with time (Figure 5.8).

Rough uncoated samples showed a significant increase in $i_{corr}$ values within the first 2 hr, from 368.4 $\mu$A/cm$^2$ to 511.9 $\mu$A/cm$^2$, and then subsequently increased at a slightly slower
rate. Similarly, the resulting current density measured on the rough CaP coated sample was 256 µA/cm² initial, and then gradually increased to 343 µA/cm² after 6 hr, which was nearly 2× lower than that of the rough uncoated samples. Meanwhile, \( i_{corr} \) value of smooth uncoated samples (\( R_a = 0.59 \) µm) decreased slightly after 1 hr and then remained unchanged at approximately 100 µA/cm². In other words, after 6 hr the \( i_{corr} \) value of the rough CaP coated samples was approximately 3× higher than that of smooth uncoated samples.

Interestingly, \( i_{corr} \) value of the biomimetic ECAD coated samples reduced considerably within the first 2 hr, from 113.6 µA/cm² to 31.4 µA/cm², showed a similar trend to that of the smooth uncoated samples. This was nearly a 4× reduction in the current density after 2 hr, followed by relatively constant \( i_{corr} \) reading for the remainder of the test. After 6 hr, the large drop in \( i_{corr} \) value of biomimetic ECAD coated samples resulted in a 3× lower corrosion resistance than that of smooth uncoated samples. Meanwhile, the difference in \( i_{corr} \) value between the rough uncoated and biomimetic ECAD coated samples increased from 3× in the first reading to 20× after 6 hr.

![Figure 5.8: Change in \( i_{corr} \) value over 6 hr for uncoated smooth and rough samples, rough CaP and biomimetic ECAD coated sample](image-url)

The current density of both rough CaP and biomimetic ECAD coated samples remained relatively constant beyond 6 hr. At the beginning of the PDP testing, the \( i_{corr} \) value of biomimetic ECAD coated samples was approximately 2× higher than that of CaP coated
samples. However, after 24 hr, the difference increased significantly to more than $11\times$ (Figure 5.9A).

More importantly, the $i_{\text{corr}}$ value of the biomimetic ECAD coated samples remained low after 72 hr (Figure 5.9B), and this suggested a stable protective layer formed on the Mg substrate.

Figure 5.9: (A) Change in $i_{\text{corr}}$ value over 24 hr for rough CaP and biomimetic ECAD coated sample and (B) over 72 hr for biomimetic ECAD coated sample
PDP test results further supported the findings of both hydrogen evolution and EIS experiments. With lower $i_{\text{corr}}$ values than rough uncoated samples, the CaP coated samples were less vulnerable to corrosion. However, since the current density was still approximately 3× higher than that of smooth uncoated samples after 6 hr, the CaP coating layer did not sufficiently improve the corrosion protection for Mg with rough surfaces. Meanwhile, the biomimetic ECAD coating method reduced the current density for the rough samples by 20×. Moreover, the $i_{\text{corr}}$ value of the biomimetic ECAD coated sample was not only stable over time, but also was considerably lower than that of smooth uncoated samples, indicating a stable and effective protective CaP layer formed on the Mg substrate.

5.6 Conclusions

Generally, the biomimetic CaP coating method was shown to improve the corrosion resistance in as-cast pure Mg sample with rough surfaces (Rₐ= 9.12 µm). In comparison with rough uncoated samples, a higher corrosion resistance and lower current density were observed in coated samples. However, compared with smooth uncoated samples, rough CaP coated samples showed a higher corrosion rate. With 25.63 ml/cm²/day of hydrogen gas generated after 24 hr, the potential in vivo application of rough CaP coated Mg or TOPM samples needs to be carefully considered. Furthermore, the biomimetic CaP coating was a less suitable method for Mg samples with high surface roughness due to the fact that corrosion occurred on samples during the actual coating process. Therefore, the resulting coating layer was inconsistent, with cracks and defects observed on the surface, allowing corrosion to occur at these sites.

Meanwhile, the use of biomimetic ECAD coating techniques was more suitable for use on samples with rough surfaces. No corrosion was observed on rough Mg samples during the coating process, and the corrosion behaviour of the material was significantly improved. Furthermore, with relatively unchanged corrosion resistance and current density over time, the protective re-passivating layer formed on the substrate was shown to be stable. The rate of hydrogen gas evolution of 2.22 ± 0.7 ml/cm²/day for biomimetic ECAD coated samples was within theoretical tolerable physiological limits [4]. However, further in vivo testing is required to confirm the suitability of using the ECAD coated Mg materials for biomedical applications. In addition, the pure Mg TOPM scaffolds as manufactured via the SFF method
inherently exhibit in rougher surface topographies than those structures produced via commonly adopted machined or polished techniques. Therefore, to further improve the corrosion resistance of the pure Mg TOPM structures, future work should evaluate CaP and ECAD coatings on cast candidate Mg alloys instead of pure Mg to assess their further ability to enhance corrosion resistance.

Finally, full characterisation of the coating layers needs to be undertaken but this was beyond the scope of this study. This includes testing coatings parameters, such as thickness, strength, morphology and composition (i.e. via EDS and Fourier transform infrared spectrometry (FTIR) analysis). It was unclear whether the coating layer followed the surface contour or simply filled the pits and pores of the rough Mg substrate. This can be determined via studying the cross-cut section of the coated sample. Moreover, since the ultimate goal will be the application of the described CaP and ECAD coatings systems on 3D TOPM scaffolds, further investigation on achieving successful coatings on porous Mg and Mg alloy structures is required.

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Tesinova, Editor. 2011, InTech.


CHAPTER 6

Synthesis of TOPM structures from Mg Alloys
6.1 **Chapter preface**

Given the eventual goal of fabricating a range of prototype medical devices with controlled porous architecture from a range of magnesium (Mg) alloys, it was necessary to investigate methods for optimising the casting process using Mg alloys instead of pure Mg. In this chapter, an optimised method for manufacturing and characterisation of topologically ordered porous magnesium (TOPM) scaffolds from Mg alloy, AZ91D, is reported and compared against that of the pure Mg structures described previously. Similar solid free-form (SFF) methods and scaffold characterisation techniques as described in *Chapter 3* were employed.

6.2 **Abstract**

Due to the disadvantageous microstructure of the pure Mg TOPM (described in *Chapter 3*), AZ91D was employed to produce TOPM structures which seek to improve the surface roughness and grain size compared with pure Mg. Furthermore, it was important to confirm the feasibility of applying and optimising TOPM manufacturing process for Mg alloys.

The changes in dimensions, surface roughness, surface area, volume and porosity compared with the computer-aided design (CAD) model, was shown to be considerably lower in the AZ91D TOPM scaffold than in the pure Mg version. Most importantly, surface roughness was reduced by approximately 5× compared with that of pure Mg TOPM.

6.3 **Introduction**

As described in *Chapter 3*, the microstructure of pure Mg TOPM structures might be disadvantageous for its mechanical performance. It was found that due to the large grain size, a majority of the 0.8 – 1.2 mm thick struts in TOPM were composed of one incomplete grain, and that the grain boundary was usually found at the junction between struts or in the middle of a strut (see Figure 3.20 in *Chapter 3*). Furthermore, according to the ASTM standard for compression test sample preparation [1], the sample needs to consist at least 15 grains in the cross section for reproducible and reliable results. Given that the average grain size of the pure Mg TOPM scaffold was 1.4 mm as reported in *Chapter 3*, the inherent cross section of the sample for compression tests would need to be at least 21×21 mm. Given the physical
constraints of the TOPM casting moulds, crucibles and induction furnace, it was not possible to prepare pure Mg samples of with these dimensions without completely modifying the entire TOPM manufacturing process.

Furthermore, results from Chapter 4 indicated that the surface roughness values of the produced pure Mg TOPM scaffolds (Rₐ of 11.5 µm) were potentially less suitable for in vivo investigation in bone due to the high corrosion rate and volume of evolved hydrogen gas. Despite being able to significantly enhance the corrosion resistance of rough pure Mg samples via surface coatings, findings in Chapter 5 suggested that further reduction in surface roughness of the TOPM structures would be beneficial.

Moreover, it was necessary to analyse the performance of the developed fabrication route in producing pure Mg TOPM structures to include those from Mg alloys. Therefore, AZ91D, one of the most popular Mg casting alloys, was selected. AZ91D has been used widely in various industries such as automotive, computer construction, household, sport equipment and many other applications [2]. AZ91D has been known to possess relatively high fatigue strength and at high grade of purity, it shows a high corrosion resistant [3-4]. More recently, a number of studies have been investigating the potential of using AZ91D for biomedical applications [5-10].

Regarding the use of AZ91D for biomedical applications, even though biocompatibility of aluminium (Al) is limited and not well-understood [11], AZ91 alloy has been recently investigated for use in biomedical purposes. Al is known as a neurotoxic agent and can cause various neurological disorders such as dementia, senile dementia and Alzheimer disease [12]. Safe level of Al permissible in serum is suggested to be from 0.5 to 10 micrograms per litre. Toxicity can be expected at a concentration of 100 micrograms per litre, while neurological disorders can be expected at 250 micrograms per litre [13].

A number of in vitro corrosion tests have been performed on AZ91 aimed at orthopaedic applications [5, 9-10, 14-16], and several studies aimed at improving corrosion resistance have used AZ91D as material substrate [17-19]. While finding no negative cellular response in AZ91D, Gu et al. suggested that Al would be an alloying element for stent and orthopaedic applications given that Al ions could be carefully monitored and considered as another source of metal ions supply to the body [20]. Recently, using porous AZ91 scaffolds for cartilage repair, Witte et al. implanted the subchondral bone plate in rabbits’ knee [21]. Witte et al.
also implanted AZ91 rods into the distal femoral condyle of guinea pigs to observe material degradation and bone growth around the implant [7-8]. It was claimed that the presence of Al increased the osteoblastic activity and the amount of Al released during the corrosion was tolerable [6]. Therefore, while thorough understanding about the tolerance limit of Al in the body and the rate it is released after implantation, investigating AZ91D as a biomaterial should not be completely ignored. However, the use of AZ91D in this study was solely as a model Mg alloy biomaterial to further assess, characterise and optimise the TOPM manufacturing route.

In order to compare the structural accuracy of the TOPM structures made of AZ91D and pure Mg, the same architectures consisting of orthogonal square struts studied previously in Chapter 3 were selected. Strut sizes of 0.8 mm and 1.0 mm were chosen with corresponding pore size of 1.2 mm and 1.0 mm and porosity of 65% and 50%. The manufacturing process was performed as described in Chapter 3. Changes and improvements as observed were recorded and reported accordingly. Structural characterisation techniques adopted in Chapter 3 were employed in this chapter on AZ91D TOPM for direct comparison with data for pure Mg TOPM.

### 6.4 Materials and methods

#### 6.4.1 Materials

AZ91D used in this work was manufactured by Dead Sea Magnesium (Dead Sea Magnesium Ltd, Israel). Table 6.1 presents the chemical composition of the raw material as shown by the manufacturer. In addition, inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Spectrometer Services Pty. Ltd., Australia) was performed to accurately determine the composition of the sample.
Table 6.1: Chemical composition of AZ91D as reported in the data sheet of manufacturer [22] and from ICP-AES test.

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>Manufacturer</th>
<th>ICP-AES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>8.5-9.5</td>
<td>9.14</td>
</tr>
<tr>
<td>Mn</td>
<td>0.17-0.4</td>
<td>0.23</td>
</tr>
<tr>
<td>Zn</td>
<td>0.45-0.9</td>
<td>0.75</td>
</tr>
<tr>
<td>Si</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.025</td>
<td>0.0006</td>
</tr>
<tr>
<td>Ni</td>
<td>0.001</td>
<td>0.0002</td>
</tr>
<tr>
<td>Fe</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>Be</td>
<td>6-12</td>
<td>0.0009</td>
</tr>
<tr>
<td>Mg</td>
<td>Balanced</td>
<td>Balanced</td>
</tr>
</tbody>
</table>

Table 6.2 shows the properties of AZ91D in comparison with that of pure Mg. The density of AZ91D is slightly higher than that of pure Mg and its melting temperature was approximately 55 °C lower than that of pure Mg. Furthermore, being one of the Mg alloys with the highest strength as mentioned previously, AZ91D has a Young’s modulus and strength higher than that of pure Mg (Table 6.2).
Table 6.2: Properties of die cast pure Mg and sand cast AZ91D [2, 23]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Pure Mg</th>
<th>AZ91D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.74</td>
<td>1.81</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>650</td>
<td>595</td>
</tr>
<tr>
<td>Specific heat at 20°C (J/(kg K))</td>
<td>1030</td>
<td>1050</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>44</td>
<td>45</td>
</tr>
<tr>
<td>Compressive Yield Strength (MPa)</td>
<td>21</td>
<td>160</td>
</tr>
<tr>
<td>Ultimate tensile Strength (MPa)</td>
<td>90</td>
<td>250</td>
</tr>
</tbody>
</table>

6.4.2 Optimisation of the casting process for Mg alloys

The TOPM manufacturing process was performed exactly as described previously for pure Mg in Chapter 3. However, several differences in the casting process were observed when replacing pure Mg with AZ91D, as follows.

Compared with casting pure Mg, working with AZ91D was considerably easier for several reasons. For example, due to the low melting point of AZ91D (Table 6.1), the total waiting time for the alloy to melt was reduced from 7 min down to 3 min. Furthermore, the casting pressure error margin as reported in Table 3.2 of Chapter 3 was ±5 mBar for casting pure Mg, which increased to ±15 mBar as for AZ91D casting. As shown in Figure 6.1, in the last step, a positive pressure (+100 mBar) was maintained rather than atmospheric pressure at the end of the casting process. This change was found to help decrease the risk of over-infiltrating of the NaCl template due to the improved flow of AZ91D over pure Mg. With a lower melting point, the furnace door was opened when the temperature dropped below 420 °C for AZ91D casting, instead of 500 °C as for pure Mg casting.
The most significant advantage of employing AZ91D as casting material was the ease in removal of NaCl from the cast product without incurring significant corrosion. Given that pure Mg was extremely vulnerable to corrosion in an environment containing Cl\(^-\) ions, the chosen chemical and the time for TOPM sample to stay in the solution must be carefully monitored. In contrast, AZ91D possessed better corrosion resistance and, therefore, the manufactured TOPM scaffolds could be left in the solution for NaCl removal as long as it required.

6.4.3 Statistical analysis

Statistical analysis was performed to test for significance difference between structural parameters of pure Mg and AZ91D TOPM structures. Student t-tests were performed using Microsoft Excel (Microsoft Corporation) and a confidence interval of \( p < 0.05 \) considered as statistically significant.
6.5 Results

6.5.1 Dimensional changes from CAD design to AZ91D TOPM scaffold

Using similar methods for characterisation of pure Mg TOPM scaffolds, µCT techniques were employed to check dimensional accuracy of AZ91D TOPM. The result showed slight differences in strut size between the CAD design and the AZ91D TOPM (Figure 6.2). There was a slight increase of 0.9% or 0.01 mm in strut dimensions observed in structures with 1.0 mm struts, while the 0.8 mm structure showed negligible change.

In comparison with pure Mg, the accuracy in casting AZ91D was significantly enhanced. For structures with 0.8 mm strut size, the improvement was significant (p=0.0001) with the percentage of difference between the CAD model and the actual product reduced from 6.3% for pure Mg to as low as 0.5% for AZ91D. Similarly, the dimensional accuracy significantly improved by 2.1% for 1.0 mm strut size structures (p=0.0365) as compared to pure Mg TOPM.
6.5.2 Surface characterisation

6.5.2.1 Surface roughness of AZ91D TOPM scaffold in comparison with pure Mg version

The AZ91D TOPM casting showed a visible reduction in surface roughness. Surface profilometry measurements indicated that the surface roughness of AZ91D scaffolds was $2.1 \pm 0.5 \, \mu m$, which was approximately $5\times$ lower than that of pure Mg scaffolds ($11.15 \pm 2 \, \mu m$ as observed on $1.2 \, mm$ strut size structure) ($p=0.0045$). Further examination
using SEM and microscopic techniques confirmed the finding (Figure 6.3).

<table>
<thead>
<tr>
<th></th>
<th>Under SEM</th>
<th>Under Microscope</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NaCl template</strong></td>
<td><img src="image" alt="A" /></td>
<td><img src="image" alt="B" /></td>
</tr>
<tr>
<td><strong>Pure Mg</strong></td>
<td><img src="image" alt="C" /></td>
<td><img src="image" alt="D" /></td>
</tr>
<tr>
<td><strong>AZ91D</strong></td>
<td><img src="image" alt="E" /></td>
<td><img src="image" alt="F" /></td>
</tr>
</tbody>
</table>

*Figure 6.3: SEM and microscopic images of the surface of the (A) NaCl template, (B) pure Mg TOPM and (C) AZ91D TOPM scaffold illustrating the negative imprints of the NaCl particles on the TOPM’s surface*

On the surface of pure Mg TOPM scaffold, the imprint of the NaCl mould on the Mg product was obvious with Figure 6.3C showing cubic features in the TOPM surface resembling NaCl crystals from the NaCl template (Figure 6.3A). The rough texture on the Mg surface was a result of molten Mg imprinting the shape and size of NaCl particles precisely (Figure
6.3A&D). While this phenomenon was observed in a few small regions in AZ91D scaffolds, the remainder of the surface appeared smooth (Figure 6.3E&F).

6.5.2.2 Surface area changes from CAD design to AZ91D TOPM scaffold

A reduction in the surface area of AZ91D structures was predicted given the results of dimensional changes and surface roughness. For the 1.0 mm strut size structure, while there was a 75.1% increase in surface area from CAD model to pure Mg TOPM scaffold, the difference was reduced to 34.4% in AZ91D scaffolds (p=0.0001). A similar trend was observed in 0.8 mm strut size structures where the percent increase in surface area reduced to 36.5% for AZ91D from 68.7% for pure Mg (Figure 6.4) (p=0.0068).
6.5.3 Volume and porosity changes from CAD design to AZ91D TOPM scaffold

Reflecting the small change in strut dimension and a smoother surface, there was an approximately 2% increase in volume for both structures compared with the CAD design (Figure 6.5). For 0.8 mm strut size structures, the volume increased from 2.82 mm$^3$ in CAD models to 2.89 mm$^3$ in the TOPM, and was equivalent to a 2.5% change. Similarly, the
difference for 1.0 mm strut size structures was 0.09 mm$^3$ or 2.3%. In comparison with pure Mg, a significant improvement ($p=0.0112$) was observed in structures with 0.8 mm strut size, where the increase in volume from CAD model to pure Mg scaffold was 12.9%, it was only 2.5% in AZ91D scaffolds.

Corresponding to the trend of volume change, there was a slight reduction in porosity of the produced structures compared with the original design (Figure 6.6). AZ91D structures with
1.0 mm strut size showed a 1.2% absolute reduction in porosity from 50% as originally designed, whereas it was 3.5% for pure Mg TOPM. Similarly, the 0.8 mm strut size structure had final porosity of 63.9% in AZ91D, corresponding to a 1.1% absolute decrease from the original 65% design and was noticeably lower than the 4.7% absolute decrease (or 60.3% porosity) of the pure Mg TOPM.

<table>
<thead>
<tr>
<th>Strut size CAD model (mm)</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Porosity of CAD design (mm³)</strong></td>
<td>65</td>
<td>50</td>
</tr>
<tr>
<td><strong>Porosity of AZ91D TOPM scaffold (mm³)</strong></td>
<td>63.9 ± 1.9</td>
<td>48.8 ± 1.8</td>
</tr>
<tr>
<td><strong>Difference in porosity between CAD design and AZ91D TOPM scaffold</strong></td>
<td>1.1%</td>
<td>1.2%</td>
</tr>
<tr>
<td><strong>Porosity of pure Mg TOPM scaffold (mm³)</strong></td>
<td>60.3 ± 1.6</td>
<td>46.5 ± 2.4</td>
</tr>
<tr>
<td><strong>Difference in porosity between CAD design and pure Mg TOPM scaffold</strong></td>
<td>4.7%</td>
<td>3.5%</td>
</tr>
</tbody>
</table>

Figure 6.6: Changes in porosity from CAD model to TOPM structures made of pure Mg and AZ91D

6.5.4 **Metallography**
Polished cross sections of both the monolithic and porous cast AZ91D showed dendritic grain structures. Since the same casting method was used for AZ91D as for pure Mg, there was a similar formation of columnar grains on the longitudinal direction of the sample (see Figure 3.20 in Chapter 3). These columnar grains developed in the dendritic form with secondary arms (Figure 6.7B), however this was not observed in the transverse direction. Grain size measurements performed at equiaxed regions using a line intercept method resulted in an average grain size of 654 µm, which was approximately half of that of pure Mg (1400 µm). With this grain size, each strut of AZ91D TOPM scaffold was composed of one or more grains instead of one incomplete grain as in pure Mg TOPM structures (Figure 6.7F&G). Grain boundaries of AZ91D TOPM scaffold could be observed at the middle of the strut and junction of struts (Figure 6.7D&E).
Figure 6.7: Grain structures of (A) Raw AZ91D; Cast AZ91D material in longitudinal (B) and transverse (C) direction; Cast AZ91D TOPM scaffold in longitudinal (D) and transverse (E) direction; Cast pure Mg TOPM scaffold in longitudinal (F) and transverse (G) direction.
6.6 Discussions

Using the same manufacturing route, TOPM structures made of AZ91D material had considerably higher accuracy than that of pure Mg. The changes in strut dimensions, volume and porosity between the AZ91D TOPM scaffold and the original CAD model were not significant. Notably, the 0.8 mm strut size structures showed literally no change in strut size and 1.1% absolute reduction in overall porosity. Moreover, the surface roughness of the TOPM structure was reduced up to 5× with use of AZ91D instead of pure Mg. Considering the manufacturing and scaffold characterisation process were performed identically for both materials, the likely reason behind this improvement was accounted for by the properties of the material used.

Viscosity of a material is one of the main factors that influence the success of casting techniques [24], and relates to the ability of a molten metal to flow through and to fill a mould cavity before solidification occurs [25]. It is known to be affected by a number of factors, including composition of the material and casting parameters [24], with fluidity of pure metal often being better than that of its alloys [26-27]. Therefore, with the casting parameters kept consistent for both pure Mg and AZ91D, pure Mg was more likely to flow into small pores and cavities within the porous NaCl template than AZ91D under a given infiltration pressure. Inherently, the surface finish of AZ91D TOPM structures were less rough than that of pure Mg and smaller changes in dimensions, surface area and volume were observed with AZ91D TOPM scaffolds.

Furthermore, with the advantage of being highly corrosion resistant compared with pure Mg, AZ91D was easier to work with during the NaCl dissolution phase of the process. The AZ91D scaffold could be left in the cleaning solution for longer periods for thorough NaCl removal without being corroded.

The microstructure of the AZ91D TOPM scaffold was more advantageous than that of pure Mg TOPM, with smaller grain size and a greater number of grains per strut. Hence, it could be considered as a more ideal candidate for the detailed study of mechanical properties of various TOPM architectures.

Despite limited understanding about the interaction of AZ91D and the human body, AZ91D has been used in a number of studies for manufacturing porous structures aiming for biomedical applications. For example, Yamada et al. fabricated open-cell AZ91 scaffolds
with density of 0.05 g/cm$^3$ using polyurethane foam and mechanical testing showed that produced structure had a low plateau stress of 0.11 MPa [28-29] (Figure 6.8A). In a study by Ho et al., AZ91 micro-truss structures were made with specific strength up to 98 MPa/(g/cm$^3$) and it was found that the specific strength increased with relative density [30]. More recently, Xu et al. employed a powder sintering method to produce porous AZ91 scaffolds aimed at biomedical applications [31] (Figure 6.8B).

![Figure 6.8: (A) SEM image of the open-cellular AZ91 by Yamada et al. [28]; (B) Sintered AZ91 foam with 55.1% porosity [31]](image)

However, in comparison with the described SFF method, none of these studies investigated scaffolds with ordered or controlled porous architectures. Furthermore, the use of AZ91D in this study was not necessarily as a biomaterial, but to show the benefits and changes in the properties of TOPM scaffolds, and to confirm the capability of the SFF process in casting with other Mg alloys, not just pure Mg.

In addition, work on the development of other binary and ternary Mg alloys using Zn, Ca and Zr as alloying elements within our group has developed a number of candidate alloys with good biocompatibility and corrosion resistance. Other properties of the alloys are being investigated, especially the mechanical properties, microstructure and casting properties. In the future, this work will offer an alternative to AZ91D.

### 6.7 Conclusions

In this chapter, the TOPM structure was successfully manufactured from Mg alloy (AZ91D) material via the developed SFF route. In comparison with casting from pure Mg, use of
AZ91D in the manufacturing process was easier and more importantly, the structural accuracy, microstructure and surface roughness of the TOPM scaffold was improved considerably. In comparison with pure Mg TOPM, scaffolds made from AZ91D had a 5x reduction in surface roughness, and dimensional change from CAD design to final TOPM scaffold was as low as 0.5%, allowing excellent replication of CAD design to as produced final TOPM scaffolds. This is important in relation to the adoption of FEA models on CAD designs to predict mechanical properties and performance based on physiological loads in vivo. Poor structural replication and inconsistencies in the manufacture of final TOPM scaffolds would likely result in significant differences between the modelled and actual mechanical properties of desired structures or implants. Furthermore, the findings in this chapter suggest that using Mg alloys rather than pure Mg as a casting material would help generate TOPM structure with properties suitable for use as a biomaterial.

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Chapter 6 – Synthesis of TOPM structures from Mg alloys


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CHAPTER 7

Mechanical properties of AZ91D TOPM based on FEA prediction and actual compression testing
7.1 Chapter preface

In this chapter, mechanical properties of the AZ91D topologically ordered porous magnesium (TOPM) scaffolds, manufactured as in Chapter 6, are examined via finite element analysis (FEA) and compression testing. Findings from the two techniques are analysed and compared with each other. Finally, options to reduce stress concentrations at the strut intersection were investigated using FEA.

7.2 Abstract

Given that the mechanical properties of the TOPM structures could be predicted via techniques such as FEA, and that scaffolds could be accurately manufactured with high resolution to replicate computer-aid design (CAD) models used in FEA, it was important to confirm the relationship between designed and actual mechanical properties. This would further help validate the TOPM scaffolds manufactured using the indirect solid-free form (SFF) fabrication method in terms of having predictable mechanical properties.

In this chapter, FEA was employed to predict the stiffness and the corresponding stress distribution of the AZ91D TOPM structures, as reported in Chapter 6. Meanwhile, compression tests were performed on the manufactured product to determine actual stiffness, ultimate compressive strength and stress-strain curves. Stiffness values found in FEA were compared with results from compression tests to determine the accuracy of the prediction. It was found that while the FEA techniques gave a reliable prediction of the mechanical behaviour of TOPM scaffolds, it underestimated the stiffness of the investigated design by approximately 2x. Results from actual compression testing showed that the structures with 0.8 mm and 1.0 mm strut size had stiffness values of 24.1 GPa and 30.5 GPa, respectively, which were close to that of human bone.

The results from this chapter will allow advanced implant design with architectures generated from the topology optimisation process to be fabricated to meet a range of key criteria including mechanical properties, as well as porosity and surface area.
7.3 Introduction

Developed as a new class of materials, porous structures offer properties that no other monolithic materials can. They can be low density while having properties such as high mechanical strength, stiffness and damping capacity. For certain applications where a high surface area to volume ratio is important, only porous structures can satisfy the requirements. More importantly, they can be tailored to meet design or application requirements via changing structural variables or even the introduction of gradients in structural variables throughout the three-dimensional (3D) pore architecture [1-2]. An increasing number of studies have looked at the development of ordered porous structures with mechanical properties optimised for specific purposes. For example, porous titanium (Ti6Al4V) scaffolds aimed for reconstruction of craniofacial defects with pore sizes range of 500 µm - 2000 µm and porosity range of 50% - 70% were successfully manufactured using electron beam melted (EBM) techniques [3]. Mechanical testing on the produced scaffolds showed that those structures possessed stiffness values of 0.57 - 2.92 GPa and compressive strengths of 7.28 – 163.02 MPa, which were not dissimilar from that of the bone [3].

Furthermore, with the development of manufacturing techniques for fabricating scaffolds with almost any geometry of ordered pore architecture, it opens the possibilities to produce structures for biomedical applications that are optimised to meet certain requirements, such as maximising porosity while maintaining the stiffness of the structure and vice versa [4]. Using topology optimisation techniques in the design process provides optimal distribution of material while also satisfying the objectives of stiffness, porosity and pore size [5-7]. The optimisation process is particularly important for structures in load-bearing applications, whereby the structure can be optimised to minimise stress shielding, while be porous enough to facilitate nutrient transportation and provide sites for tissue growth [4, 7]. Wettergreen et al. performed optimisation via creating a unit block library of architectures. Each structure was designed using CAD and mechanical properties were studied using FEA. The library of architectures with known properties allowed merging of each unit structure to the site according to the requirements of mechanical properties, porosity or surface area [8]. However, none of these model structures were fabricated and tested to confirm the feasibility of manufacturing the designed architectures and their actual properties.

While ordered porous Mg scaffolds reported in the literature have been limited, mainly
because of the difficulties in powder processing or sintering of Mg, optimised porous Mg scaffolds for certain applications have not attracted interest yet, and represents a totally novel area of biomaterials research. Therefore, given that the TOPM scaffolds could be successfully manufactured with high accuracy, an important step of the characterisation process was to evaluate the relationship between the designed and actual mechanical properties of the structures. In this chapter, FEA was employed to predict the stiffness and mechanical behaviour of the AZ91D TOPM scaffolds. Findings from FEA were compared with results from actual compression test on the produced scaffold.

7.4 Materials and methods

7.4.1 Sample preparation

Machining can be considered as one of the most standard and popular methods in preparing samples for mechanical testing since it is capable of generating parallel surfaces and achieving a good surface finish. The method allows samples made to desirable dimensions and tolerances. Therefore, for all monolithic test samples in this experiment, machining was employed to prepare samples with a smooth surface finish.

Meanwhile, given the delicate features of the TOPM structure and the relatively low inherent stiffness of Mg, techniques used to prepare samples for compression testing needed to be carefully considered. Similar to machining technique, adopting the use of a low speed circular diamond sectioning saw gave excellent surface finishes. However, challenges exist with the use of both machining and low speed diamond saw, and were related to deformation arising from clamping the sample during sectioning. Using other types of saw, such as band saw or hand saw, was considered to be not appropriate due to blade thickness, low precision and poor surface finish [1]. Hand polishing to the desired size appeared to be a more suitable method because it could avoid the disadvantages associated with other methods. The hand-polishing technique minimised the damage to the sample, especially on the surfaces, since the load acting on the sample during polishing was small and adjustable (Figure 7.1). This method also allowed good control over the final dimensions of the sample.
Therefore, all samples for compression testing were prepared via hand polishing using silicon carbide paper in a series of 240 grit, 400 grit, and 600 grit. The sample size and shape followed ASTM standard (ASTM-E9-89a) [9]. Standards recommend that samples for compression testing can be either cylindrical or rectangular, and that porous samples be prepared with an aspect ratio of height to thickness of 1.5 or above [1]. Due to the difficulties in preparing sample via machining and cylindrical sample via polishing, TOPM samples with a rectangular shape were chosen for this study.

### 7.4.2 Design of compression plates

One disadvantage of the hand polishing technique was the difficulty in generating samples with perfectly parallel top and bottom faces. This led to an uneven stress distribution during compression testing, and the potential to introduce inaccurate stiffness data. To minimise this effect, a set of custom-designed compression plates were fabricated. The design was adopted from compression plates designs from MTS Systems Corporation [10].

The compression plates consisted of three parts: (1) the top plate, which was gripped by the upper jaw of the testing machine and had a flat cylindrical plate with surface orthogonal to the test axis, while (2) the bottom plate, gripped by the lower jaw, had a matching cylindrical platen surface and (3) a self-locating central rotating block consisting of a ball-bearing fitting (Figure 7.2). Two sets of compression plates were manufactured to accommodate samples...
with different sizes. Figure 7.2A shows a design that was suitable for samples with a width ranging from 11 mm to 14 mm, whereas the design in Figure 7.2B could be used for samples with a width less than 11 mm. For samples with cross sectional area significantly smaller than that of the compression plates, their corresponding length, in order to keep a desired aspect ratio of 1.5, was close to the height limit of the extensometer (i.e. 16 mm), which was employed to accurately measure strain (described in Section 8.5.4.3). Hence, these smaller samples needed to be placed adjacent to the outer edge of the compression plates in the design illustrated in Figure 7.2A, to avoid any damage that may occur to the extensometer during the test. However, this led to another challenge, given that the sample was offset from the vertical test axis through the centre of the compression plate, and, therefore, unbalanced the central block. For this reason, an additional compression plate set was designed (Figure 7.2B) by chamfering the edge of the upper plate and central block to accommodate these smaller samples and allowed the samples to be centrally located.

Figure 7.2: Two sets of compression plates for testing samples with width (A) 11-14 mm and (B) 11 mm or less
Figure 7.3A illustrates the design of the articulation ball-bearing joint at higher magnification. The design provides limited rotation for the middle block when the top and bottom surfaces of the test sample are perfectly parallel. The set up in Figure 7.3C illustrates the condition where the sample does not have completely parallel surfaces. As can be seen in the figure, the self-adjusting rotation of the middle block on the bottom plate accommodates for the imperfection of the sample, ensuring both faces of the sample are in contact with the compression plates and thereby limiting any point, or non-uniform load distribution to both top and bottom surface of the test samples. Lubricant was applied at the bearing surface to allow for low friction movement.

Figure 7.3: Articulating bearing surface of the compression plates (A), and magnified example of sample placement when (B) two faces are perfectly parallel and (C) two faces are not perfectly parallel.

7.4.3 Preliminary compression tests

7.4.3.1 Compression testing of cast monolithic pure Mg

Several pilot mechanical tests were performed on cast pure Mg to determine the suitable testing parameters, such as strain rate and data acquisition rate, and to validate the test protocol through appropriate implementation of an extensometer and compression plate...
design. The sample size was 18×12×12 ± 0.1 mm. These preliminary tests were performed on cast, monolithic pure Mg samples with an MTS858 Desktop load frame with 2.5 kN load cell. The setup parameters included: a test rate of 10^{-3} per min; a data acquisition rate of 1 Hz and no extensometer. Typical resulting stress-strain curves for these monolithic pure Mg samples are illustrated in Figure 7.4.

As shown in the inset of Figure 7.4, the collected data was not suitable for accurately determining the elastic modulus due to the noise and inadequate sampling rate. The elastic modulus calculated by the slope of the stress/strain curves was 2.8 GPa, which was approximately 15× lower than the theoretical elastic modulus of pure Mg (41-45 GPa) [11]. Machine compliance is a well-established contributing factor resulting in incorrect displacement readings, particularly for compression testing and when relying on crosshead displacement for recording strain [12]. In this case, the recorded strain was overestimated and included the sample deformation, as well as the compliance displacement inherent to the
loading system. Due to the small sample size and relatively low strains involved in compression testing of Mg, compliance errors were likely to be significant.

Therefore, the compliance of the MTS858 Desktop load testing system was tested by placing the two compression plates against each other without any sample in place, and performing a compression test. The recorded displacement corresponding to the applied load indicated the compliance level of the machine (Figure 7.5). For the load range up to 2.5 kN, the compliance level was up to $2.76 \times 10^{-2}$ mm/kN.

![Figure 7.5: The recorded compliance level of the MTS858 Desktop load](image)

Given the outcome of this test, the use of an extensometer was deemed to be crucial for accurately determining strain readings independent of crosshead motion and associated machine compliance. Additionally, the data acquisition rate was changed to increase the number of data points available for analysis.

Additional tests were performed on the same material with an extensometer attached to the sample and data acquisition rate of 100 Hz. Results from both experiments are plotted in the same graph below for comparison (Figure 7.6).
As can be seen in Figure 7.6, the elastic modulus of monolithic pure Mg (13.3 GPa) was closer to the theoretical value compared with that of the initial test. However, it was still 3× lower than the theoretical elastic modulus for monolithic pure Mg. According to the ASTM standard for compression test sample preparation [13], the sample needs to consist of at least 15 grains in the cross-section for reproducible and reliable results. Given that the average grain size of the cast pure Mg was 3.41 mm, as reported in Chapter 3, the samples used in these compression tests contained approximately 3-4 grains over the entire sample cross section. In other words, the samples did not satisfy requirements for sufficient numbers of grains. However, with the reported grain size, the inherent cross section of the sample for compression tests would need to be at least 52×52 mm. Given the physical constraints of the TOPM casting moulds, crucibles and induction furnace, it was not possible to prepare pure Mg samples greater than approximately Ø20 x 20 mm without completely modifying the entire TOPM process and equipment.

Furthermore, it is important to examine the finding from a microstructural point of view. The formation of twins, in which the atoms are located in mirror-image positions of atoms on the...
other side of the twin boundary, is caused by applied mechanical forces [14]. Twining has been known to cause early failure of pure Mg material during compression deformation, i.e. micro-yielding behaviour. Twin boundary phenomena occur when the strain is localised in a few shear bands [15-16] and is an important mode of strain accommodation in hexagonal close packed (HCP) metals, such as Mg, Zr, Ti, Zn and Cd [16-19]. In pure Mg, twins have been observed to develop from grain boundaries during compression deformation [20] and were reported to be associated with increasing average grain size [21-22]. Given the grain size of cast pure Mg used in this experiment (1400 µm), this helps further explain the low compressive strength in the early stage of compression testing.

As a result of the numerous issues mentioned above utilising, pure Mg as a model composition for fabrication and mechanical testing of TOPM structures, samples made from pure Mg were excluded from compression tests.

7.4.3.2 Compression testing of cast monolithic AZ91D

In this experiment, a set of cast, monolithic AZ91D samples (n=4) were prepared using a low speed diamond saw with a rectangular shape. Given the grain size of cast AZ91D was 654 µm as reported in Chapter 6, the dimensions of the sample were chosen to be 10×10×20 ± 0.1 mm and ensured a sufficient number of grains over the sample cross-section. The testing setup was then exactly the same as performed for cast pure Mg (Section 8.3.2). Stress-strain curves for the monolithic cast AZ91D material are as shown in Figure 7.7.
The elastic modulus was found to be 41.1 ± 2.2 GPa, which was close to the theoretical value of 45 GPa [24]. Furthermore, the grain size of 654 µm of cast AZ91D helped eliminate the necessity for very large sample dimensions as for pure Mg. For these reasons, TOPM structures cast from AZ91D were selected for subsequent investigation of mechanical properties.

7.4.3.3 Non-contact strain measurement

The major disadvantage with using an extensometer for compression testing at present is the limitation of the sample’s size caused by the height limit of the extensometer, which is currently available at 10 mm and above. Furthermore, while testing with the extensometer on porous samples, it was crucial to prepare flat surfaces for the “knife edges” of the device to move in accordance with the samples and provide accurate strain readings. This limitation, therefore, restricted the types of certain porous structures that could be tested using the extensometer. Given that the displacement reading from the test machine crosshead was inaccurate due to machine compliance (Section 8.3.3.1), testing without the extensometer would not yield correct strain data.

Therefore, in order to obtain correct strain readings during compression testing for small
samples, non-contact strain measurement (NCSM) systems have been developed. Several commercial systems have been developed and used widely, including: camera-based ARAMIS [25] and AVE systems [26]; and a laser speckle extensometer [27]. However, the cost of these systems is considerable and was not available in our group or within industry. Therefore, a side project was established aiming to develop a low cost NCSM system. Initial testing was promising, however, more work is required to further validate the system, especially for porous materials in compression (Appendix D). For this reason, the developed NCSM prototype system could not be used in this study.

7.4.4 Materials

As discussed previously, TOPM made from pure Mg materials was not suitable for mechanical testing due to its microstructural properties. Therefore, mechanical tests were performed on AZ91D TOPM of 0.8 mm and 1.0 mm strut size structures. For testing of porous TOPM scaffolds, sample dimensions were prepared to have an aspect ratio of 1.5, as recommended for compression testing of porous structures [1]. To determine the stiffness, an accurate strain reading using an extensometer was required. The actual sample size and shape are as shown in Table 7.1. Each TOPM sample contained 6×6 struts in the cross section, and 9 struts in the longitudinal direction.
The surfaces of the manufactured TOPM scaffold were not smooth due to the orthogonal struts (Table 7.1). These struts needed to be removed via polishing prior to testing to generate smooth surfaces for attachment and proper function of the extensometer. For this reason, the actual porosity of the prepared sample was lower than that of original design. Actual porosity values of the tested sample were reported in Table 7.1 with 59.1% and 44% for 0.8 mm and 1.0 mm strut size structure, respectively. Overall, both structures had a reduction of approximately 6% in porosity.

Table 7.1: Actual shape and size of samples for compression test

<table>
<thead>
<tr>
<th>Structure</th>
<th>0.8 mm strut size</th>
<th>1.0 mm strut size</th>
<th>Before polishing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>![Model Image]</td>
<td>![Model Image]</td>
<td>![Model Image]</td>
</tr>
<tr>
<td>Actual size (mm)</td>
<td>10.8×10.8×16.8</td>
<td>11×11×17</td>
<td>–</td>
</tr>
<tr>
<td>Designed porosity</td>
<td>65%</td>
<td>50%</td>
<td>–</td>
</tr>
<tr>
<td>Actual porosity</td>
<td>59.1%</td>
<td>44%</td>
<td>–</td>
</tr>
</tbody>
</table>
7.4.5 Methods

7.4.5.1 Finite element analysis (FEA)

Prediction of the elastic modulus and stress distribution in the structure was performed using FEA. CAD models were generated in Rhinoceros 3D software (McNeel Associates, WA) and saved in STEP (.stp or .step) format. The finite element analysis (FEA) was performed using ABAQUS CAE (AB AQUS Inc., Pawtucket, RI).

The elastic modulus of the material was imported from actual compression testing on cast AZ91D material while the Possions’ ratio was taken from the literature (Table 7.2).

Table 7.2: Elastic modulus and Poissons’ ratio of AZ91D as in theory and in the FEA

<table>
<thead>
<tr>
<th></th>
<th>Elastic modulus (GPa)</th>
<th>Poissons’ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical value</td>
<td>45</td>
<td>0.35</td>
</tr>
<tr>
<td>Used in FEA model</td>
<td>41.1</td>
<td>0.35</td>
</tr>
</tbody>
</table>

In the compression test, grease was applied to both top and bottom faces of the sample to reduce friction with the compression plates. Therefore, to mimic the actual compression test conditions for more comparable results, the boundary conditions applied in FEA were a fixed translation in the y direction for the bottom surface, and an axial displacement in y-direction on the top surface (Figure 7.8).
The applied displacement was calculated using formula 7.1 for a pre-selected strain value, where \( L \) was the total length of sample. Output from FEA models recorded the total reaction force acting on the nodes of the top surface. The compressive stiffness (\( E \)) of each structure was calculated by dividing the total reaction force (\( F \)) over the bounding box area (\( A \)) by the strain (\( \varepsilon \)) as shown in equation 7.2. This technique has been used widely in the literature [8, 28].

\[
\Delta L = L \times \varepsilon \quad (7.1)
\]
\[
E = \frac{\sum F}{A \times \varepsilon} \quad (7.2)
\]

The total reaction force (\( F \)) increased with increasing strain (\( \varepsilon \)) applied, therefore, according to equation 7.2, the stiffness of the structure is independent from the applied strain. For this reason, the strain of 0.05% selected in this study was mainly chosen for later comparison with values from actual compression tests.

The architecture was meshed with tetrahedral elements and subjected to linear perturbation test. Since mesh density or number of elements for the FEA model can significantly affect the outcome [8] and computational time, convergence tests were performed on a small model of
0.8 mm strut size structure to determine the appropriate mesh size. The model was designed to be small to reduce computational time, with overall size of 2.8×2.8×4.8 mm³, or 2 struts in the cross section and 3 struts in the longitudinal direction. A mesh density range of 8×10⁻³ to 4×10⁻⁵ was tested and a strain of 0.05% was applied. The corresponding stiffness was calculated and plotted against the number of elements.

7.4.5.2 Convergence test

With the size of the sample (6×6×9 struts), the total analysis time and computational power required were significant if a high mesh density was applied. A low mesh density could reduce the computational time considerably, however, the accuracy was compromised. Therefore, this convergence test was performed to determine the appropriate mesh density without compromising the result. With 0.05% strain applied, the total displacement acting on the sample was 24×10⁻⁴ mm. With the mesh density ranging from 8×10⁻³ to 4×10⁻⁵, the corresponding number of elements ranged from 618 to 1419871.

The corresponding compressive stiffness was calculated using equation 8.2 with a total surface area of 7.84 mm². The relationship between the number of elements and stiffness is illustrated in Figure 7.9. As shown in the graph, the difference in resultant stiffness with varying mesh size was significant, ranging from 17.18 GPa to 15.06 GPa; a difference of more than 12%. The results emphasized the importance of choosing an appropriate mesh size for the model to achieve sufficiently accurate results. Regarding the total computational processing time, Figure 7.9 shows an increase in time with higher number of elements. It was found that while models with 618 elements took less than one min to analyse, the model with highest number of elements took over two hr to be analysed. Convergence was achieved when the stiffness error was less than 1% compared to the highest mesh density. In this study, it occurred at 232955 elements or a mesh density of 8×10⁻⁵.
Moreover, stress distribution was observed to be affected by the number of elements (Figure 7.10). With a coarse mesh, the stress appeared to be highly concentrated in a wide area (Figure 7.10A). Looking at the cross section of the strut, the highest stress level was shown in approximately half the strut (Figure 7.10C&E). Meanwhile, with a finer mesh, high stresses were localised in small regions rather than distributed across the vertical strut (Figure 7.10B). Furthermore, high stress was observed mainly at the intersecting corners of struts, not in the middle of the struts as observed in the coarse mesh case (Figure 7.10D&F). In both cases, horizontal struts exhibited minimal stress. Similar stress profile on the structure with higher mesh density agreed with findings in previous studies [8, 29-30].

**Figure 7.9: Relationship between number of elements with stiffness of the structure and computational processing time**
Figure 7.10: Difference in stress distribution in the same structure with varying number of elements

Based on these outcomes and the relative size of the sample used in the convergence test compared with the actual sample, a mesh density of $8 \times 10^{-4}$ was applied for ongoing FEA analysis of porous TOPM architectures.

7.4.5.3 Experimental compression tests

Compression tests were performed on either an MTS858 Desktop load frame with 2.5 kN load cell or an MTS810 servo-hydraulic load frame with 50 kN load cell. An MTS 8 mm extensometer was employed (MTS, Minnesota, USA). With the use of the extensometer, all four sides of the sample needed to be flat and smooth, and due to the 15 mm total thickness of the extensometer unit, all samples needed to have a length greater than 16 mm to avoid
damage to the extensometer during testing. Three sets (n=3) of samples were prepared and tested, including monolithic cast AZ91D, 0.8 mm and 1.0 mm AZ91D TOPM.

In order to determine the elastic modulus of all three structures, the samples were tested with the extensometer on the MTS858 Desktop load frame with a 2.5 kN load cell and a maximum 1 kN applied load. The crosshead speed was 0.01 mm/min and the data acquisition rate was 100 Hz. To determine the full stress-strain curve and ultimate compressive strength of the two porous structures, the MTS810 Servo-hydraulic load frame with 50 kN load cell was employed. No extensometer was used as the sample was compressed beyond its plastic deformation region, which exceeded the capacity of the extensometer. The test rate was increased to 1 mm/min and the data acquisition rate was kept at 100 Hz. Actual test setups with and without the extensometer are as shown in Figure 7.11.

Figure 7.11: Actual compression test setup (A) without and (B) with the extensometer
7.5 Results

7.5.1 Results from FEA

Results from FEA are reported in Table 7.3. Being 15% less porous, structures with 1.0 mm strut size were predicted to have stiffness of 15.14 GPa, which was more than 35% greater than the 0.8 mm structure, with a stiffness of 9.75 GPa.

Table 7.3: Results from computational analysis for both structures

<table>
<thead>
<tr>
<th>Strut size (mm)</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>59.1%</td>
<td>44%</td>
</tr>
<tr>
<td>Number of elements</td>
<td>680156</td>
<td>1358658</td>
</tr>
<tr>
<td>Applied displacement (mm)</td>
<td>8.4×10^{-4}</td>
<td>8.5×10^{-4}</td>
</tr>
<tr>
<td>Total surface area (mm²)</td>
<td>116.64</td>
<td>121</td>
</tr>
<tr>
<td>Predicted stiffness (GPa)</td>
<td>9.75</td>
<td>15.14</td>
</tr>
</tbody>
</table>

In addition to comparing the effective stiffness of varying TOPM structures, FEA stress profiles on the various architectures also helped to explain how the structures were deformed during compression testing. Both structures showed similar stress patterns since they had the same architecture. Figure 7.12 shows the stress profile within different regions of the sample with 1.0 mm strut size, from general stress distribution to local stress concentrations. As can be seen in Figures 7.12C, the highest stress concentration could be found at the corners of the vertical struts, close to the intersection between struts. While the vertical struts absorbed the majority of the axial compressive load, horizontal struts did share a small amount of stress. Minimal stress concentrations were found in the middle of the horizontal struts (Figure 7.12D).
Figure 7.12: Stress profile in the 1.0 mm strut size structure

Overall, vertical struts in the four surrounding surfaces showed lower stress on the outer surface (green regions). Meanwhile, the stress on the vertical struts inside the structure was more uniform (red and orange regions) (Figure 7.12C). For individual vertical inner struts, stress was highest at the corners and reduced in magnitude in the middle of the strut (Figure 7.12D). With high stress concentrations at the intersecting corners between struts, the structures were predicted to start failing at the corners of weakest strut.

7.5.2 Results from actual compression test

The stiffness of the AZ91D TOPM structures is as presented in Table 7.4. Compression tests
showed 0.8 mm and 1.0 mm strut size structures possessed stiffness values of 24.1 ± 2.6 GPa and 30.5 ± 2.5 GPa, respectively. Being nearly 15% less porous, the 1.0 mm strut size structure was approximately 21% stiffer than the 0.8 mm structure. In comparison between actual and predicted stiffness values, the actual stiffness was higher than FEA predicted values for both structures. The difference was as high as 60% for structures with 0.8 mm struts and 50% for the 1.0 mm structure.

Table 7.4: Mechanical properties of TOPM

<table>
<thead>
<tr>
<th>Strut size (mm)</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit structure porosity</td>
<td>65%</td>
<td>50%</td>
</tr>
<tr>
<td>Actual porosity</td>
<td>59.1%</td>
<td>44%</td>
</tr>
<tr>
<td>Predicted stiffness (GPa)</td>
<td>9.75</td>
<td>15.14</td>
</tr>
<tr>
<td>Actual stiffness (GPa)</td>
<td>24.1 ± 2.6</td>
<td>30.5 ± 2.5</td>
</tr>
<tr>
<td>Yield strength (MPa)</td>
<td>13.5 ± 2.1</td>
<td>30.9 ± 4.3</td>
</tr>
<tr>
<td>Ultimate compressive strength (MPa)</td>
<td>40.5 ± 4.8</td>
<td>93.9 ± 12.7</td>
</tr>
</tbody>
</table>

Figure 7.13 shows the full stress-strain curves of both structures under compression until failure. Overall, no definite elastic region was observed in any structures, however, the curve could be divided into three sections with: (1) a steep initial increase; then (2) a more gradual increasing trend; and finally, (3) after reaching the ultimate strength, the stress magnitude quickly decreased. Generally, 1.0 mm strut size structures showed a more rapid decrease in stress after reaching the ultimate strength (section (3)) compared with 0.8 mm strut size structures.

As shown in Table 7.4, the yield strength for each structure as determined from compression tests was 13.5 ± 2.1 MPa and 30.9 ± 4.3 MPa for the 0.8 mm and 1.0 mm strut size structure, respectively. Being 15% less porous, the structure with 1.0 mm strut size had a yield strength approximately 2× higher than that of the structure with 0.8 mm strut. Similarly, the ultimate compressive strength for structures with 1.0 mm struts was 93.9 ± 12.7 MPa, which was more than 2× greater than for 0.8 mm strut structures.
Figure 7.13: Full stress-strain curve of compression test on porous structures: (A) 0.8 mm strut size and (B) 1.0 mm strut size

Figure 7.14 shows the sample before and after compression testing to failure. By observation, the deformation was in the diagonal direction along lines of maximum shear stress as indicated by the red arrow, and occurred at the intersection between struts. Interestingly, none of the struts in the transverse or longitudinal plane was fractured.

Figure 7.14: Sample (1.0 mm strut size) before and after compression test: red arrow shows deformation mode
Further investigation using the microscope confirmed these findings (Figure 7.15). The red arrows indicate the cracks and slips within the struts. As in Figure 7.15A, the cracks started and ended at the corners of the pores and followed a diagonal direction. A similar pattern was observed inside the struts, with crack initiation and slipping at an angle of approximately 45° (Figure 7.15B).

![Figure 7.15: High magnification (5×) images of the deformation in TOPM after compression testing (A) at the pore and (B) inside the strut](image)

7.6 Discussion

AZ91D materials investigated in other studies, or manufactured commercially, typically have a compressive elastic modulus ranging from 44-46 GPa [31], and this was slightly higher than the elastic modulus of 41.1 GPa of cast AZ91D determined via compression testing and used in FEA in this study. There are several reasons for this difference. Factors such as the specific casting method and casting temperature used, grain size, sample size, and strain rate have been known to affect the mechanical properties of magnesium alloys [32-37].

In comparison with previous studies of porous structures with randomly oriented pore architectures, the manufactured AZ91D TOPM showed significantly higher stiffness values (see Table 7.5). Interestingly, in a study done by Wen et al., [38], the Young’s modulus of a 50% porous Mg structures with random pore architecture was 0.35 GPa, whereas a TOPM structure with 0.8 mm strut size, and a porosity of 59.1%, was nearly 70 times stiffer at 24.1 GPa. Similarly, a 59% porous structure with random architecture made from Ti had a stiffness of 5.6 GPa and was approximately 4.5 times less stiff than that of an 0.8 mm strut.
In comparison with other reports on ordered porous scaffolds, the TOPM produced in this study showed a relatively similar stiffness. For example, a pure Mg 70% porous scaffold made by a mechanical perforation method had a Young’s modulus of 14.93 GPa, which was comparable to properties of the AZ91D TOPM made in this study [28]. However, in terms of capability of the manufacturing process such as mechanical or laser perforation, the current TOPM method allowed significantly greater control over complex and complicated 3D architectures [43]. For example, the mechanical perforation method allowed only generation of straight cylindrical channels of fixed diameter, not gradients in pore size or any other complex features or pore architectures [28].

In comparison to other reports on optimised porous structures made from Ti or Ti alloys, the TOPM in this study possessed a considerably higher compression modulus. For instance, the Ti-Al6-V4 optimised architecture scaffold manufactured using selective laser melting method was 52% porous and had an average stiffness of 2.97 GPa.
Taking into consideration the stiffness values observed in the compression tests in this study, both TOPM structures could be considered as suitable candidates for use as biomaterial scaffolds, especially in orthopaedic load bearing applications. With the elastic modulus of cortical bone ranging from 3 GPa to 20 GPa depending on the location [11, 44-46], these structures with stiffness of 24.1 GPa and 30.5 GPa would provide sufficient mechanical strength for the affected area and most importantly, with Young’s modulus close to that of bone, common problems associated with stiff materials, such as stress shielding could potentially be avoided [7, 46-47].

The stress-strain curve could be separated into three distinct sections due to the way the TOPM structures deformed and underwent failure (Figure 7.13). Section (1) was noticeably steeper than section (2) since at this point, a majority of the struts were behaving in a linear-elastic manner and had not started to undergo plastic deformation. In section (2), crack initiation in weaker struts resulted in the onset of plastic deformation, while stronger struts were able to support the remaining load. When the majority of vertical struts in the structure had plastically deformed or failed with increasing strain (above 10%), there was a noticeable drop in the stress level, which was represented by section (3). At this point, the entire structure was beyond plastic deformation limits and continued compression would not reveal further information about the mechanical behaviour of the structure, other than the eventual increase in stress associated with the complete densification of the samples under compression. The stress-strain curves described for pure Mg foams by Wen et al. also showed a similar trend when strain was below 10% (Figure 7.16), particularly with the sudden drop in stress magnitude after reaching ultimate compressive strength [38]. In that study, sample densification could also be observed after approximately 40-50% strain.
When comparing the results between FEA and actual mechanical test data for the compressive stiffness of TOPM structures, FEA under-estimated the stiffness by up to 60% compared to actual compression test data (Table 7.4). While FEA was found to over-predict the mechanical properties of the porous structures in some cases [7, 30], under-predicted FEA results were also reported in a number of studies.

There are several factors that could contribute to the observed differences. For example, in FEA, the microstructure was not considered while micro-structural parameters such as grain size and phases have been shown to significantly affect the mechanical properties of AZ91D [32, 37, 48]. The effect was potentially more significant in porous structures where each strut contained only a few grains (see Chapter 6). Furthermore, the FEA model conditions were assumed to be ideal with smooth and completely frictionless surfaces, and the models exactly replicated the shape and size exactly as designed. However, while the as-manufactured TOPM structures used for compression testing accurately replicated most features and resolution of the initial CAD designs (Chapter 6), they did contain several imperfections, such as chamfered angles (Figure 7.17A) and non-uniform strut size (Figure 7.17B). As illustrated later in Section 7.7, structures with chamfered angles reduced the stress magnitude and concentration significantly compared to structures with 90° angles. Therefore, future
studies should consider perform FEA on 3D reconstructed model of the final product rather than on CAD model. This would potentially reduce the difference between FEA and actual mechanical tests. Furthermore, given that the boundary conditions applied in FEA were in perfect alignment, the horizontal struts shared a minor amount of load (Figure 7.12). Meanwhile, misalignment may occur during actual testing and in combination with the effect of chamfered angle, this may have resulted in considerable stress being shared by the horizontal struts and inherently increased the effective stiffness of the structure.

![Figure 7.17: (A) Chamfered angles and (B) Non-uniform struts as illustrated by the red lines observed on the TOPM scaffolds](image)

In one study, Cahill et al. manufactured ordered porous structures from polyamide materials and found that the effective modulus predicted by FEA was significantly higher than the results from actual compression test by 67% [30]. Meanwhile, Eshraghi et al. compared results from FEA and mechanical tests on different porous architectures made from polycaprolactone (PCL) and found different correlations for each structure. Depending on the pore architecture, FEA either under-estimated or over-estimated the compressive modulus, with an overall average difference of 30% between FEA and actual compression results. Among three investigated structures, two had an elastic moduli predicted via FEA that were lower than those determined following actual compression testing. Importantly, the porous lattice structure that had a similar architecture to TOPM scaffolds (Figure 7.18-3D) showed the same trend with a lower predicted stiffness [29].
Consequently, while FEA can be a useful and correct tool to predict the compression modulus of a structure, the accuracy is dependent on the assumptions made in the FEA model and several other factors, such as: architecture, design parameters and material properties. In this particular case, FEA underestimated the stiffness of these AZ91D TOPMs.

Meanwhile, the stress profile from FEA supported the observations on the deformation and failure of TOPM samples during compression testing. With high stress concentrations observed at the corners close to the intersection of orthogonal struts, these regions were expected to be the weakest points of the structure. Therefore, crack initiation and deformation was likely to occur here first. Once a strut or corner was deformed, the stress propagated to nearby struts or corners. However, this was not necessarily on the strut or corner directly below the deformed strut, but propagated to the diagonally opposite strut or corner. In this mechanism, the deformation appeared to occur at the weakest site in the structure. In some cases, samples had multiple sites of weakness. Figure 7.19 shows deformation in different
samples with red arrows pointing at strut intersections that have failed. The failure mechanism could start either at the sides of the structure from the top left strut then gradually propagate to the right side (Figure 7.19A), or occur at random weak sites in the middle of the sample (Figure 7.19B & D). Figure 7.19C shows a different situation where the deformation started from the top of the sample then moved sideways in a leftward direction.

![Figure 7.19: Different deformation locations on the samples](image)

### 7.7 Reduction of stress concentrations in TOPM

A simple experiment using FEA to analyse the modified architectures was performed to suggest alternative structural solutions to reduce the stress concentration in the vertical struts. The concept involved the implementation of cylindrical struts instead of rectangular struts, and to reduce the sharp 90° angle corners at strut intersections via a fillet radius. Figure 7.20 shows the three investigated structures, all of which were similar to the original designs but with cylindrical struts, 0.8 mm in diameter. The first architecture was not modified any
further (Figure 7.20A) while the second and third structure had a fillet radius of 0.1 mm and 0.4 mm, respectively (Figure 7.20B & C) added at the corners.

Similar FEA was performed on each structure to determine the stress distribution. As can be seen in Figure 7.20D, the architecture without filleting showed a stress profile with high stress concentrations adjacent to the strut intersections. However, the stress was still heavily concentrated compared with the other two structures. Structure 2 showed a slight improvement in stress distribution with high stress regions spreading along the vertical strut (Figure 7.20E & H). Structure 3 with a 0.4 mm fillet had a more preferable stress profile with high stress appearing in a wider region around and inside vertical struts (Figure 7.20F & K). Furthermore, the maximum stress observed in the structure decreased from 4.6 MPa to 3.7 MPa with the increase of fillet radius (Figure 7.20).

<table>
<thead>
<tr>
<th>Fillet radius (mm)</th>
<th>0</th>
<th>0.1</th>
<th>0.4</th>
<th>Key</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume (mm³)</td>
<td>2.29</td>
<td>2.3</td>
<td>2.48</td>
<td></td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>71.4</td>
<td>71.3</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>Max stress (MPa)</td>
<td>4.6</td>
<td>4.2</td>
<td>3.7</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 7.20: Three structures with modified architecture and the corresponding stress profile*
Given that all structures had the same strut size, adding a fillet radius slightly reduced the porosity by up to 2.4% absolute difference. With the observed benefits, it is recommended that a round fillet be included in future designs to avoid high local stress concentrations at strut intersections. In terms of strut geometry, cylindrical struts were more advantageous than the rectangular struts as a result of their improved stress distribution and also higher porosity. As mentioned in Section 4.5.7, the cylindrical strut was successfully manufactured by the developed manufacturing route. Furthermore, given that the feature replication of the TOPM process had a resolution of 0.15 mm (Chapter 3), and that struts could be replicated accurately at 90° to one another but with slightly rounded or chamfered corners (Figure 7.17), the desired fillet radius would likely be manufactured successfully.

7.8 Conclusions

FEA was shown to be an effective technique in predicting the mechanical properties of the selected TOPM structures. While the difference between predicted and actual stiffness value is dependent on various factors, especially the architecture, FEA results underestimated the stiffness value by approximately two times for the model TOPM design investigated. The inherent benefit from this finding was a high factor-of-safety for future structural optimisation experiments, particularly with respect to the mechanical performance of TOPM architectures designed to meet specific loading conditions in vivo. This is a highly important benefit, given that the suitable control of corrosion rate in Mg alloys has been a major issue, and certainly any corrosion would act to decrease mechanical properties in TOPM structures over time. Furthermore, the technique has provided a good prediction over the failure behaviour and was a useful tool in optimising the architecture for certain purposes, such as reducing localised stress.

The compression test data in this study confirmed that the AZ91D TOPM structures had stiffness close to that of human bone. Compared with most Mg- and Ti-based porous structures in the literature, the current TOPM scaffold showed significantly higher stiffness values for a given porosity.

The results from this study will allow advanced implant designs to be made, which meet a range of key criteria, including mechanical properties to match those of bone as well as
porosity and surface area to control desired corrosion rate.

References:


CHAPTER 8

Proof of concept: Development of prototype TOPM biomedical devices
Chapter 8 – Proof of concept: Development of prototype TOPM biomedical devices
8.1 Chapter preface

In this chapter, the capability of the solid free form (SFF) manufacturing route and proof-of-concept for design of topologically-ordered porous magnesium (Mg) (TOPM) porous implants was investigated to produce prototypes of biodegradable cervical spinal fusion device (SFD) and screw. Mechanical properties of the SFD were studied using finite element analysis (FEA) and mechanical compression tests.

8.2 Abstract

As biomaterials, TOPM has the potential for use in a wide range of applications, from bone grafting to orthopaedic devices [1-2]. There are a number of advantages that TOPM-based orthopaedic devices offer. For example, with a Young’s modulus close to that of human bone, the likelihood for stress shielding can be reduced. Furthermore, by combining the biodegradability of Mg with the flexibility of the manufacturing process, the TOPM-based device could be designed to gradually degrade whilst also promoting new bone growth until it is completely osseointegrated or replaced by new bone tissue, as well as achieving reliable bone fusion.

Therefore, in this chapter, the TOPM manufacturing process was employed to produce a prototype SFD with the aim of utilising TOPM as the internal structure. Two investigated porous architectures were designed to be relatively simple with no structural optimisation. FEA and compression tests were performed to determine the mechanical properties of each design. Results confirmed that both structures had mechanical properties suitable for the intended purpose. Additionally, one screw design was generated and manufactured primarily to test the capability of the manufacturing method.

This experiment was considered a proof-of-concept and a pilot study. Experience and conclusions drawn from this study would contribute to future work in adopting the manufacturing process for making orthopaedic devices from Mg and its alloys.
8.3 Introduction

Spinal fusion is a common treatment for spinal problems and is used to fuse or immobilise two or more vertebrae. During the surgery, the intervertebral disc is removed partially or completely, depending on its condition. This is followed by placing an implant between the affected vertebrae to maintain or reinstate the vertebral spacing, as well as the physiological size and shape of the spine. Generally, with the use of fusion cage, the formation of new bone tissue is promoted with the use of autograft bone or stimulatory factors to gradually fuse the two vertebrae together [3-4]. In ideal cases, the SFD facilitates rapid bone in-growth to produce a completely fused joint. However, it was reported that up to 45% of the ~1 million annual worldwide SF procedures failed as a result of device fracture or bony non-union [5-6]. Failure of SF procedures results in complicated and costly (up to $50,000) [7] revision surgery.

Supplementary bone grafting is often required for SFDs to encourage bone growth and fusion. Traditionally, autogenous bone graft was favoured and widely used, however, it was shown to have major drawbacks, such as the risk of chronic donor site pain, hematoma, limited availability, variable quality, infection and increased operative time [8-9]. Furthermore the mechanical strength of the autogenous bone grafting material is generally inadequate for interbody loading initially and can lead to immediately collapse or extrude [10-12]. Allograft (donor) bone grafts are the most common grafting material for spinal fusion but do not resorb quickly or promote rapid bone growth, as well as presenting the possibility of disease transfer [8].

Another of the major challenges faced by current SFDs is the stress shielding caused by differences in stiffness of the vertebral bone and the device. Stress shielding is one of the biggest concerns for load-bearing biomaterials and occurs when the stiffness of the orthopaedic device is different from that of bone, leading to uneven stress distribution between bone and implant [13-15]. This in turn affects bone remodelling and healing processes since under-loaded bone will adapt to the low stress environment and become more porous and weak [16]. Stress shielding-related problems were observed in orthopaedic devices based on non-degradable biometals, such as stainless steel and Ti [16-17].

In studying spinal interbody fusion, Van Dijk et al. found that in goat model, the reduced stiffness of the interbody fusion cages made of biodegradable poly-(L-lactic acid) increased
the bone fusion rate as compared to the Ti cage [18]. It was suggested that the loss of cage’s stiffness introduced by degradation of the bioresorbable cage helped increase the load on grafting material, thus stimulated the bone growth [19-20]. Therefore, while Ti alloy is a good choice with excellent biocompatibility, the stiffness of Ti alloy is approximately 6× higher than that of cortical bone. Furthermore, post-operation analysis has been problematic with Ti cages due to Ti being non-radiolucent [21]. While polyether-ether-ketone (PEEK) was claimed to replace Ti in spinal fusion as it is radiolucent, stiffness of PEEK (3-4 GPa) [22] is potentially inadequate for the high load-bearing application. In addition, both Ti and PEEK are not biodegradable, therefore, the device will remain permanently in the spine and potentially cause loosening as a result of stress shielding and painful inflammatory responses in the long term. Ceramic materials can be bone conducting, bone bonding and bioresorbable, however, ceramic cages have not been successful in SF as they suffer from low fracture toughness, subjecting them to fatigue fractures, collapse and/or extrusion [23]. For these reasons, Mg with favourable mechanical properties (Young’s modulus) close to that of native bone compared may help alleviate some of the issues with current SFD designs, as well as minimise the risk of stress shielding [24-27].

Furthermore, via measuring intra-cage pressure, Kanayama et al. found that the stress shielding was more dependent on the pore size than the total porous area [28]. However, increase pore size potentially lead to reduction in overall stiffness of the structure and introduce deformation and instability into the device [29].

Therefore, there is a need of a porous degradable device that is capable of provide mechanical strength comparable to bone, reliable joint fusion via rapid bone growth and biodegradation over time leaving fused vertebral bone without remnant of the SFD. With the development of manufacturing techniques for fabricating topologically-ordered structures and the advantageous properties of Mg, an Mg-based SFD with optimised architecture is a potential candidate. With the structure designed to match bone’s properties, other structural properties could be optimised to encourage bone growth and lead to rapid fusion. Furthermore, being biodegradable, Mg-based SFDs could be designed to degrade while natural bone tissue is developing, and still provide sufficient mechanical support for the site. Once the healing process is completed, the SFD could completely disappear and leave only natural tissue at the fusion site. Furthermore, other fixation devices such as screws and rods can also be made from Mg alloys instead of Ti at the present. With the use of Mg for fixation, advantages
include eliminating the necessity for additional surgeries to remove the device and potentially limit the stress shielding effect.

In this chapter, combining knowledge of the fabrication route and mechanical characterisation of AZ91D TOPM structures (Chapter 6 and 7), the capability of the SFF process will be investigated in manufacturing SFEs with homogenous and gradient internal architectures. The outcome will help determine the ability to translate an optimised structure from CAD design to an actual TOPM implants with known features. Mechanical testing will be performed on the produced devices to check their suitability for the intended purpose. Results from this experiment will help prove the practicality of the SFF method in manufacturing TOPM structures.

8.4 Material and methods

8.4.1 SFD and screw design and material

Given the advantages and ease of casting AZ91D compared with pure Mg, as shown in Chapter 6, AZ91D was selected as the casting material for this experiment. The TOPM manufacturing process was performed as described in Chapter 3. The overall shape and size of the SFD followed a commercial polymer PLDLLA/PGA cervical interbody fusion cage [19]. The original design had an anatomical wedge shape, and consisted of a large central cavity and four smaller peripheral holes to provide space for bone growth and fusion between vertebral endplates (Figure 8.1).

![Figure 8.1: The commercial cervical interbody fusion cage [19]](image-url)
The device in this chapter was designed to have a 1.6mm thick solid peripheral rim and a customisable internal porous cavity for testing various TOPM designs (Figure 8.2). Compared with the commercial design (Figure 8.1), this arrangement provided a large surface area for bone in-growth and osteoconduction, and also reduced the overall porosity, while also providing sufficient mechanical properties. The proposed surgical route for the device would be via an anterior cervical interbody fusion (ACIF) introduced in Chapter 2. Therefore, a backing plate was added to the main cage to provide fixation to proximal and distal vertebral endplates during anterior implantation. To simplify the design, screw holes could be drilled in the backing plate at a later date post casting, and so were not included in the original design. The dimensions of the device were designed to fit into current TOPM manufacturing moulds, NaCl infiltration rigs, and casting crucibles with minimal alteration required. The overall shape and specific dimensions are as shown in Figure 8.2. The cage had a maximum width of 17 mm and thickness of 7 mm, typical of current anterior cervical SFDs on the market. The solid peripheral wall had average thickness of 1 mm. The backing plate was 3 mm thick at the thickest point, 11 mm wide and 24 mm long. Given the average diameter of the cervical spinal C3 to C6 ranging between 17 and 18 mm, and 15 mm at C7 [20], the dimensions of this design was best suited for cervical SFD, but could be upscaled to lumbar SFD applications.

**Figure 8.2: Anterior cervical interbody fusion cage design (A) Overall shape, (B) Side view and (C) top view with dimensions**

Two porous internal structures with different architectures but similar porosity were selected in this experiment. The first structure had a homogenous pore distribution with an orthogonal
square struts and pore sizes of 1.0 mm. This structure was chosen due to its consistent and reproducible architecture as previously investigated and characterised in Chapter 3 and Chapter 6. The other more complex structure consisted of a gradient in strut and pore sizes assembled as basic unit structures. All unit structures had a surrounding box dimension of 2×2×2 mm and strut size range from 0.8 mm to 1.2 mm. With this arrangement, the pore size varied depending on the strut size of the unit structure. The gradient structure was selected to confirm the feasibility of applying complex and gradient architecture into production of orthopaedic devices to meet design requirements such as pore size, strut size, porosity and mechanical properties. Table 8.1 shows a summary of design parameters for both architectures.
Table 8.1: Design properties of two SFD models

<table>
<thead>
<tr>
<th></th>
<th>Homogenous design</th>
<th>Gradient design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strut size (mm)</td>
<td>1.0</td>
<td>0.8 – 1.2</td>
</tr>
<tr>
<td>Surface area (mm$^2$)</td>
<td>2014.8</td>
<td>1965.8</td>
</tr>
<tr>
<td>Volume (mm$^3$)</td>
<td>905.7</td>
<td>947.9</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>29.9</td>
<td>26.6</td>
</tr>
</tbody>
</table>

Strut distribution

The gradient structure throughout the total height of the implant consisted of 0.8 mm strut size in the central core, then 1.0 mm struts immediately adjacent to the 0.8 mm struts, and similarly, 1.2 mm struts adjacent to the 1.0 mm struts (Figure 8.3). Therefore, the porosity and pore size decreased from the centre towards the periphery of the gradient SFD prototype.
The 7 mm thickness of the cage was generated by assembling four layers of the homogeneous 1.0 mm and gradient architectures in CAD to build up the total height of the SFD. With 1.0 mm and 1.2 mm struts dominating, the gradient structure had a slightly lower porosity than the homogenous 1 mm structure. The theoretical porosity for both designs was less than 30%, with 29.9% and 26.6% for the homogenous and gradient structures respectively. The basic model homogenous structure with 1.0 mm strut and pore size had a porosity of 50% (Chapter 3 and Chapter 6). However, due to the solid peripheral wall required for the SFD design, the actual porosity of the SFD was reduced to 29.9%. Similarly, the SFD with a gradient architecture had a porosity of 26.6% instead of 42.6% for the basic model homogenous structure.

For actual device manufacture, RP moulds based on the CAD design as shown in Figure 8.4B & D were produced. Since the pressure applied during the NaCl infiltration process was relatively high for the RP mould, a supporting plate was added below the cage to increase strength of the mould (Figure 8.4D). The thickness and contour of the plate followed
that of the peripheral wall. For the actual strength of the cage, mechanical testing was to be performed on samples with the backing plate removed since the function of the plate was not to provide structural strength to the SFD. Therefore, an additional CAD model that excluded the back plate was generated for each structure (Figure 8.4A&C). Each CAD model was designed to be 20 mm in height; in that way, each produced Mg structure could be cut in half horizontally, and provide two samples for compression testing. For both CAD models, a 1mm thick plate was included at the bottom to secure the RP mould during NaCl infiltration process, which contained holes to allow for easy removal of liquid gelatine during NaCl infiltration. These extra features could be removed after casting easily by polishing or machining.

![Figure 8.4: CAD models for compression testing samples (A & C) and actual device (B & D)](image)

The design of the prototype porous screw was designed with high surface area by creating a porous shank (Figure 8.5). The head was round in shape with an overall diameter of 5.85 mm,
and included a square shaped socket for use of standard orthopaedic tool for screwing into bone. The total length of the screw was 15 mm and tapered at a 4.4° angle. The blade was 1.3 mm in width and the step between blades was 2.9 mm. With the small size of the screw, each RP mould could accommodate two screws as shown in Figure 8.5. Similar to other rapid prototyping (RP) designs, the base of the RP mould had holes to drain gelatine during the NaCl infiltration process.

Figure 8.5: CAD models of the screw in top and side view, as well as the RP model consisting of 2 screw mould for TOPM manufacture.

8.4.2 Testing methods

In this study, compression tests were performed to determine the actual mechanical behaviour, and FEA was employed to determine the stress profile of each design. For mechanical testing, to avoid damage to the extensometer during compression test, samples were required to be at least 17 mm long (Section 7.3.3). Therefore, given that both prototype SFD samples were only 7 mm in height, the extensometer could not be used in this experiment. All compression tests were performed on the MTS810 Servo-hydraulic load frame with 50 kN load cell without extensometer. Each structure was tested up to a maximum load of 25 kN with a crosshead speed of 0.5 mm/min.

In FEA, the setup described in Chapter 7 was followed with $2e^{-4}$ mesh density. In this study, only compression behaviour of the models was investigated. Therefore, simplified boundary conditions were applied to the model, which included fixing the movement of the bottom
surface in the y-direction, and applying a displacement of \(35 \times 10^{-4}\) mm, which was equivalent to 0.05\% strain, on the top surface. As mentioned in Section 7.4.5.1, the selected strain value does not affect the final effective stiffness of the structure; therefore, value of 0.05\% was chosen for consistency with Chapter 7.

8.5 Results and discussions

8.5.1 Manufacturing

Producing samples for compression testing was easily implemented and successful given that the design was similar to the previous model TOPM architectures described in Chapter 3 and Chapter 6. Figure 8.6 D and E show samples prepared for compression testing, which did not include the backing plate. The as-produced prototype implant is as shown in Figure 8.6F. The CAD designs are presented to illustrate the accuracy of the process in replicating architectures of the design onto the actual SFD prototype. Both homogenous and gradient structures were produced with fine details in the gradient design successfully replicated. With AZ91D TOPM structure manufactured with high accuracy (Chapter 6) and given that the manufacturing process was performed consistently in both experiments, the structures as manufactured in this chapter were expected to possess an accuracy similar to that of the AZ91D TOPM scaffold.
Given the high success rate (100%) of manufacturing samples for compression testing, the actual device displayed a lower success rate of 30% with the most common problem being over-infiltration of the bottom half of the mould (Figure 8.7A). The bottom surface of the cage was completely filled with AZ91D and only the top pores of the structure had the desired replication in pore architecture (Figure 8.7B).
However, the mechanisms of the over-infiltration in this case and in manufacturing the TOPM scaffolds as described in Section 4.5.1 were not similar. With the TOPM structures, the over-infiltration normally occurred when excessive infiltration pressures were used, whereby, Mg over-infiltrated the whole NaCl template from the top to the bottom pores. Meanwhile for the SFD, over-infiltration occurred only at the lower sections of the implant. This suggested that the problem was with the NaCl mould, not with the Mg casting process. Investigation of the negative NaCl mould under the microscope revealed that while packing of NaCl particles in the top half was dense and uniform, the bottom section was extremely porous and variable (Figure 8.8). This indicated that the pressure in the lower half of the mould during NaCl infiltration was not high enough to generate a well-packed NaCl template throughout. This was likely due to the design of the RP mould, in which the thick supporting plate below the cage took the majority of the pressure (Figure 8.8). This led to inadequate infiltration pressure acting on the NaCl paste below the cage, and a poorly packed NaCl template. As a result, this more porous NaCl region was easily filled by molten Mg during the casting process, thus creating an over-infiltrated product.
To solve this problem and increase the success rate in manufacturing the SFD, it is suggested that the supporting structure under the cage be optimised to be strong enough to support the cage but also weak enough to share the pressure with the NaCl paste. For example, the supporting plate could be made thinner than 1 mm or porous with orderly distributed pores.

Meanwhile, over-infiltration did not occur when casting of the porous screw design, with the overall shape and design being well replicated, except only for the porous architecture on the shank (Figure 8.9). As previously reported in Chapter 3, pore size of the RP mould to be used in this SFF manufacturing process was limited to 0.5 mm and below. Hence, the pores on the shank of the screw, which had maximum width of 0.5 mm (Figure 8.9D), exceeded this limit and were completely filled (Figure 8.9C).
8.5.2 Mechanical testing

Stress-strain curves for both the homogenous and gradient structures are as shown in Figure 8.10. In general, the homogeneous strut size (1 mm) structures showed considerably lower stress than structures with a gradient strut size at the same strain level. For example, at strain of 5%, the stress acting on the gradient strut size structure was 104.1 MPa, which was nearly twice the stress value of 57.6 MPa on the 1 mm structure.

Given that the displacement reading from the MTS machine was not highly accurate as illustrated in Section 7.4.3 [21], and usage of the extensometer was not applicable, the stiffness of each structure was calculated for indicative purposes and for relative comparison between the two structures only. The slope of the stress-strain curve showed that the compression modulus of homogenous and gradient structures were 15.7 ± 2.2 GPa and 27.7 ± 1.7 GPa, respectively. While the gradient structure was 3.3% less porous, it was 43.3%
stronger than structures with homogenous 1.0 mm struts.

A significant difference in the trend of increasing stress for the two structures was noticed. In gradient structures, the stress magnitude displayed a steep increase just before reaching a strain of 4%, resulting in a high stiffness value (Figure 8.10). After the elastic limit, the stress magnitude continued to increase but at a considerably slower rate. Meanwhile, stress in the homogenous 1mm structures showed a gradual increase during testing. There was a difference in the slope before and after the elastic limit, however, it was not as obvious as that of the homogenous structure. The elastic limit for each homogenous and gradient structure was 103.6 ± 20.1 MPa and 95.42 ± 13.2 MPa respectively, with corresponding load of 16.6 kN and 15.8 kN, respectively.

![Stress-strain curve of homogenous and gradient structure](image)

*Figure 8.10: Stress-strain curve of homogenous and gradient structure*

With a higher stiffness, yield strength and stress magnitude for the same amount of strain (Table 8.2), structures with variable strut size appeared to be more favourable than 1mm structures in term of mechanical properties.
Table 8.2: Properties of the SFDs

<table>
<thead>
<tr>
<th></th>
<th>Homogenous design</th>
<th>Gradient design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strut size (mm)</td>
<td>1.0</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Effective porosity (%)</td>
<td>29.9</td>
<td>26.6</td>
</tr>
<tr>
<td>Stiffness (GPa)</td>
<td>15.7 ± 2.2</td>
<td>27.7 ± 1.7</td>
</tr>
<tr>
<td>Elastic limit (MPa)</td>
<td>103.6 ± 20.1</td>
<td>95.4 ± 13.2</td>
</tr>
</tbody>
</table>

Regarding the mechanical requirements of cervical SFD in vivo, loads acting on the cervical spine due to daily living activities range from 120 N to 1200 N [22], which was approximately 13× lower than the yield load of both structures. From the stress strain curve, at 1200 N load, stress values were 6.5 MPa and 6.64 MPa for homogenous and gradient structures, respectively. These stress values were considerably lower than the elastic limit of the structures. For these reasons, these designs could be confidently used as cervical SFD with a minimum factor-of-safety of 13×. It should be stressed however that this is not taking into account any deterioration in mechanical properties due to in vivo degradation.

Across all vertebrae, it has been shown that under compression, trabecular bone has a higher risk of initial failure within the vertebral body, compared with cortical endplates, cortical shell and corner regions [23]. Therefore, it is crucial for any SFD to have adequate strength so not to damage the trabecular bone tissue of the adjacent vertebral bodies. While mechanical properties of trabecular bone is dependent on the bone density and anatomical site [24-25], the stiffness and yield strength of trabecular bone at the lumbar region have been reported to be 0.344 ± 0.148 GPa and 2.02 ± 0.92 MPa, respectively [24]. With such properties, the two SFDs in this study would easily satisfy mechanical property requirements for trabecular bone in the spine.

Moreover, with the compressive strength of cortical bone being as high as 100 MPa [26], the elastic limit of 103.6 ± 20.1 MPa of the gradient structure was high enough for this application. While the yield strength of the homogenous structure (95.42 ± 13.2 MPa) was slightly lower than the maximum compression strength of cortical bone, the strut size could be increased to improve strength. Therefore, both structures investigated in this study can be
suitable for the intended application.

Furthermore, with dimensional modifications, such as increasing the overall size while maintaining the size and shape of the internal architecture, these structures could be used for other regions of the spine, such as in the lumbar section, where \textit{in vivo} loads of 3400 N have been reported for heavy lifting conditions [27].

### 8.5.3 FEA results

Stress profiles for each structure were investigated at different levels, from whole structure to cross sections in both transverse and longitudinal directions. Overall, a high stress was observed at the peripheral wall for both designs (Figure 8.11A&B). Meanwhile, moving to the horizontal mid-plane, the stress magnitude as observed on the struts was higher than those as observed from the top surface (Figure 8.11C&D). The stress distribution in the homogenous structure was similar to that of the AZ91D TOPM scaffold due to the similarity of the internal architecture of both designs (Section 7.4.1). More specifically, a high stress concentration was observed at the corners of the vertical struts, whereas horizontal struts of the SFD shared a small amount of loading (Figure 8.11E&G). In the horizontal cross section, the homogenous structure had an even stress distribution on all vertical struts throughout the implant.

Meanwhile, in the gradient structure, high stress levels were observed in bigger struts, particularly the ones closer to the solid peripheral wall (Figure 8.11F&H). With larger structural elements, the gradient structure was able to withstand a higher load at the same strain level compared with the homogenous design. With the square shape, the struts showed a high stress concentration at the corners.
Using the anatomical finite element models based on medical imaging via CT and MRI to analyse biomechanics of the spine, Li et al. found that the stress magnitude of the intervertebral disc was higher at the annulus fibre than at the nucleus pulposus region [28] (Figure 8.12A). This stress distribution was similar to that observed for the two SFDs.
investigated in this study. The gradient design showed a particularly better fit with the low porosity 0.8 mm strut architecture in the central core of the SFD resulting in low stress magnitude in this region (Figure 8.12B).

Figure 8.12: stress distribution of (A) inter-vertebral disc at 1000 N axial compressed load [28] and (B) gradient design SFD

8.6 Conclusions

This experiment has confirmed the possibility of using a novel SFF method for manufacturing structures for potential orthopaedic applications, such as a cervical SFD. Two designs of the SFD with homogenous and gradient pore architectures were manufactured and evaluated in this study. While the success rate for manufacturing the full prototype including backing plate was low as a result of micro-pores inside the NaCl template, it was 100% for the cage without backing plate. It is suggested that the RP mould and the sandwich mould used in the NaCl infiltration process be modified to increase the success rate and also to accommodate manufacture of larger devices for use in other areas of the spine, such as lumbar fusion.

While both designs showed suitable mechanical properties for the intended purpose, both FEA and mechanical testing suggested that the gradient structure had more preferable mechanical behaviour and properties compared to the homogeneous structures. Not only had the stress profile matched well to that of the intervertebral disc, the gradient structure offered a porous lattice interior for bone growth and increasing bone fusion rate.

Further work is needed to determine the actual stiffness of these structures. Since it was not possible to use the extensometer due to the length of the sample, other non-contact strain
measurement systems can be employed. Furthermore, since Mg is degradable, its mechanical properties will change as it corrodes. While the safety factor was estimated to be 13×, further work is still required to understand and model the change in mechanical properties of these SFDs over time with degradation. Such experiments could be performed in *in vitro* corrosion tests and *in vivo*, and would help predict the performance of the TOPM devices in the long term. In addition, the FEA boundary conditions applied in this experiment were relatively simple, with bottom implant surfaces constrained while applying a uniform strain to the upper surface. More realistic boundary conditions and non-uniform physiological strains should be considered in future studies. For example, the effect of ligaments and adjacent components of the vertebral anatomy need to be included in the FEA as in previous studies on fusion cages [17-18, 29-30]. Findings from these analyses can be used to perform topology optimisation for the device in seeking an optimal structure and stress distribution. Furthermore, as mentioned previously (Chapter 6), there are limitations in the use of AZ91D as a biomaterial, and the selection of a more appropriate Mg alloy that is well tolerated *in vivo*, has good corrosion resistance as well as possessing suitable mechanical properties will be beneficial.

**References**


Chapter 8 – Proof of concept: Development of prototype TOPM biomedical devices

CHAPTER 9

Conclusions and future work
Chapter 9 – Conclusions and future work

9.1 Conclusions

This chapter presents a summary of conclusions derived from the research described herein, and discusses areas for future work.

9.1.1 Synthesis of TOPM structures

- The novel solid-free form fabrication (SFF) process was successfully developed. The processing route included six main steps: (1) using computer-aided design (CAD) to create a 3D model with the desired architecture; (2) rapid prototyping (RP) printing of a positive polymeric template of the CAD model; (3) infiltration of the polymeric template with a NaCl paste; (4) burn-out of polymeric materials and sintering of NaCl; (5) infiltration of the negative NaCl template with liquid Mg; and finally (6) removal of the NaCl template.

- The topologically ordered open-cell porous magnesium (TOPM) scaffolds were successfully fabricated from pure magnesium (Mg) and AZ91D via the SFF technique.

- The micro-computed tomography (µCT) and Scanning Electron Microscopy (SEM) techniques were employed to determine structural changes from CAD models to the as-fabricated Mg scaffolds.

- Dimensional change from CAD models to pure Mg TOPM scaffolds ranged from 2.5% (1.2 mm strut size structure) to a maximum of 8.33% (0.8 mm strut size structure). Using AZ91D as casting material, this dimensional change was significantly reduced to as low as 0.5% as observed in structure with 0.8 mm strut size.

- The increase in volume of the TOPM structure compared with CAD design followed the same trend with the increase in strut size. The highest change in pure Mg TOPM scaffold volume was 21% with 0.6 mm strut size structure. The structure with 1.2 mm strut had the lowest volume increase with 5.2%. Meanwhile, the AZ91D TOPM scaffold showed a considerable reduction in volume changes with maximum of 2.5% increase from the CAD model to the TOPM structure.
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- Corresponding to the volume increase, the porosity of the produced scaffold was slightly lower than that of the CAD design. While the AZ91D TOPM structures showed approximately 1% reduction in porosity, the scaffold made of pure Mg had a maximum of 6.1% change with 0.6 mm strut size structure and a minimum of 3.2% change with the 1.2 mm strut size structure.

- The resultant surface of the pure Mg TOPM structure was relatively rough with maximum surface roughness value ($R_a$) of 11.15 ± 2.0 μm. This value was significantly higher ($p = 0.0045$) than that of the AZ91D TOPM scaffold ($R_a = 2.1 ± 0.5$ μm). With the rough cast surface and increase in strut size, the change in surface area of the cast TOPM scaffold compared with the CAD design was high. The maximum increase in surface area was 77.1% and 36.5% for the pure Mg and AZ91D TOPM structure, respectively.

- It was observed that the ease in preparing the sample was considerably improved by using AZ91D. While the error in casting pressure was maintained at ± 5 mBar for pure Mg, this was increased to ± 15 mBar with AZ91D.

- With better corrosion resistance, the AZ91D scaffold could be left in the cleaning solution for longer period for thorough NaCl removal without being corroded as with the pure Mg TOPM structure. Therefore, using Mg alloy instead of pure Mg in the developed SFF process is recommended in order to achieve smoother cast surface and higher structural accuracy.

- Regarding the microstructure of the cast scaffold, TOPM structures possessed relatively large grain sizes, with 1400 μm and 654 μm for the pure Mg and AZ91D TOPM structures, respectively. The grain size of cast pure Mg TOPM structures resulted in difficulties in preparing compression test samples to meet the requirement of at least 15 grains in the cross section. Furthermore, pure Mg TOPM struts were predominantly composed of one incomplete grain. For both structures, the grain boundaries were mostly located at the strut intersection.
The processing route was shown to be capable of producing both simple and complex architectures with a high level of accuracy, including strut sizes as small as 0.6 mm and specific features replicated down to 0.15 mm. This capability of the SFF method will allow greater flexibility in scaffold design with a broad range of architectures possible. Moreover, complex features can be implemented to offer enhanced biological function or control over specific features, such as surface area, mechanical properties or corrosion rate.

Due to limitations in RP mould printing and the NaCl infiltration process, this manufacturing method is limited to pore and strut sizes no less than 0.5 mm. However, in comparison with other techniques for manufacturing porous structures, the current manufacturing route allowed casting of structures with ordered as well as topologically optimised pore architectures.

9.1.2 Effect of surface roughness on the corrosion behaviour of pure Mg

- Pure Mg samples for in vitro corrosion studies were successfully cast using the indirect SFF fabrication method with surface roughness value (Rₐ) ranging from 0.59 µm to 2.68 µm and 9.12 µm.
- All in vitro corrosion tests, including hydrogen evolution, mass loss, PDP and EIS, were performed in SBF with controlled pH and temperature. Such conditions are critical to evaluate the bioactivity of Mg biomaterials, and to achieve results relevant to in vivo applications.
- The findings confirmed that increasing roughness resulted in an accelerated corrosion rate. For example, the total H₂(g) volume as produced by smooth samples (Rₐ = 0.59 µm) was 28× higher than that of rough samples (Rₐ = 9.12 µm). However, pitting corrosion was not observed, suggesting that surface roughness does not affect the pitting potential of Mg. Results from this study suggested that the pure Mg TOPM scaffold exhibiting a rough surface from the SFF manufacturing process would not be suitable for further in vivo testing in bone due to the high corrosion rate, unless the
corrosion resistance of the structure could be improved.

- However, it is important to note that the correlation between corrosion rate and roughness value obtained from $H_2$ evolution experiments allows the development of degradable Mg devices with tailored corrosion rate based on controlled surface roughness.

### 9.1.3 Improving corrosion resistance via coating techniques

- Biomimetic calcium phosphate (CaP) and electrochemically-assisted deposition (ECAD) coatings were applied to investigate whether the corrosion resistance for samples with rough surface ($R_a = 9.12 \mu m$) could be improved. It was found that the CaP biomimetic coating was not a suitable method for Mg samples with high surface roughness given that corrosion occurred on samples during the coating process. Furthermore, the resulting coating layer was inconsistent, with cracks and defects on the surface, allowing on-going corrosion to occur at these sites.

- The biomimetic ECAD coating method was shown to reduce the corrosion rate and improve corrosion resistance of the material considerably, by introducing a Ca(OH)$_2$ layer underneath the biomimetic CaP coating. More specifically, after 24 hr, the CaP coated sample produced 25.63 ml of $H_2(g)$, which was nearly $12 \times$ higher than that of biomimetic ECAD coated samples. Similarly, results from EIS tests showed that the corrosion resistance of biomimetic ECAD coated samples was $10 \times$ higher than samples coated by biomimetic CaP method. An approximate $11 \times$ decrease in current density was also observed in the biomimetic ECAD coated samples compared with that of the CaP coated samples after 24 hr.

### 9.1.4 Mechanical properties of TOPM scaffolds

- Results from compression testing showed that the AZ91D TOPM structures with 0.8 mm and 1.0 mm strut size had stiffness values of 24.1 GPa and 30.5 GPa, respectively. Being nearly 15% less porous, the 1.0 mm strut size
structure was approximately 21% stiffer than the 0.8 mm structure.

- Finite element analysis (FEA), which was employed as a tool to predict the mechanical behaviour of the TOPM designs, underestimated the stiffness of the TOPM scaffold by approximately 2×. However, this underestimation can be considered as a major advantage for the optimisation process by indicating a higher actual stiffness. Furthermore, FEA provided a reliable stress profile of the various TOPM structures, and was important in predicting the failure mechanism of the structure.

- In comparison to Mg or Ti scaffolds fabricated with random pore architectures, the produced TOPM structures showed significantly higher stiffness values. More importantly, the stiffness of these scaffolds was close to that of human cortical bone (E = 3 – 27 GPa) [1] and therefore, potentially improves bone ingrowth and remodelling through enhanced load sharing, as well as help eliminate problems relating to stress shielding.

9.1.5 Cervical spinal fusion device

- Prototypes of a cervical SFD were successfully manufactured with two model architectures designed for the internal structures. One was with a homogenous 1.0 mm strut size and the other had gradient pore structure with strut size ranging from 0.8 mm towards the periphery of the SFD and 1.2 mm towards the centre.

- Yield strength data obtained from compression tests were 103.6 ± 20.1 MPa and 95.42 ± 13.2 MPa for the gradient and homogenous structures respectively. The strength values of both SFD designs were close to that of human bone, with compressive strength of cortical bone ranging from 80 - 190 MPa, and trabecular bone ranging from 0.1 - 100 MPa [2, 3].

- In addition to its higher strength, FEA analysis showed that the gradient structure had a higher stress magnitude for the same amount of strain than the homogenous structure. Therefore, it was considered to be more favourable than homogenous structures in term of mechanical properties.

- Stress analysis via FEA showed that both SFD designs had a similar stress
pattern as observed in FEA studies on intervertebral disc in literature, especially the gradient structure. Both FEA and mechanical testing confirmed that the gradient structure had preferable mechanical behaviour and properties to the homogenous structure. Furthermore, with the reported mechanical properties, the gradient SFD design investigated in this study had significant potential for future *in vivo* work.

- This experiment has confirmed the possibility of using the novel SFF method for manufacturing structures for other practical applications with both simple and complex internal architecture.
9.2 Concluding remarks

The aim of manufacturing and characterising the topologically-ordered porous scaffold from Mg and alloy was successfully fulfilled in this thesis. In addition to the high level of accuracy of the produced scaffolds, the technique was capable of generating structures from CAD models with different levels of complexity, including structures with high resolution and fine feature replication, as well as and prototypes for degradable, TOPM SFD and screw designs. Given that most current Mg studies have been focused on fabricating structures with random pore architecture, the SFF method and novel TOPM manufacturing route described in this thesis – capable of replicating architectures directly from CAD models and producing ordered and/or optimised architecture scaffolds from Mg – is totally unique. Moreover, since all the materials used in the process were biologically safe, the TOPM scaffolds hold significant promise for biomedical applications.

Furthermore, the TOPM structures offered prediction over mechanical properties and corrosion properties based on the relationship between surface roughness and corrosion rate, therefore, can be designed and produced with specific pore architectures to meet requirements of the device. These advantages of the SFF method and TOPM scaffold show the potential of developing a new class of degradable biomaterials. For example, the structure could be optimised to have high surface area, by adding thin steps of 0.15 mm to the strut of the main structure, while maintaining the overall volume and stiffness. Moreover, small grooves could be added to the structure to guide tissue growth while maintain the overall structure and properties. These above mentioned architectural features could be applied in a homogeneous fashion, or more advantageously, in an anisotropic fashion, or as gradients, in a specific orientation to promote tissue growth or enhance mechanical properties in a specific direction. Many human tissues, including bone, have anisotropic architecture and mechanical properties, and the ability to emulate these properties in degradable TOPM scaffolds would be a significant advantage. The investigation in SFDs and screw in Chapter 8 presented the potential of a new degradable device. While further work is required, the gradient structure showed good mechanical properties and matched well to the in vivo stress profile in the intervertebral disc.

The limitation of the SFF process resulting in a rough surface finish in pure Mg TOPM scaffolds was shown to be solved via the application of coatings and/or use of cast Mg alloys.
Chapter 9 – Conclusions and future work

The biomimetic ECAD coating technique has great potential to be further investigated and used in the future. In contrast to the CaP coating technique, which was limited by samples with rough surfaces, the biomimetic ECAD method effectively increased the corrosion resistance of pure Mg samples with rough surface.

While most of the studies in the literature tested the corrosion properties of Mg on samples with relatively low surface roughness value, work in Chapter 4 and Chapter 5 aimed to study samples with rough surface finish, which is common in porous structures produced via casting. With the issues raised from the effect of surface roughness on corrosion rate in pure Mg and ineffectiveness of CaP coating technique on rough samples, this thesis has emphasised the importance of including a wide range of surface roughness in Mg corrosion study.

9.3 Future work

While the capability of the SFF method was thoroughly examined in this thesis, the application of manufacturing topologically optimised Mg scaffolds is yet to be performed. Since the model porous architectures included in this thesis to validate the TOPM process were constructed from unit structure, it is possible to assign each unit structure with known properties to the suitable in vivo location to meet design requirement, as proposed by Wettergreen et al. [5, 6]. The SFD with gradient internal architecture described in Chapter 8 illustrated an example of this optimisation method. For future work, it is suggested that the unit structure library be expanded with more complex structures and variable strut/pore sizes. For more advanced optimisation, approaches such as homogenous topology optimisation as reported by Lin et al. [4] could be followed to generate a library of unit structures with topology optimised for set purposes. The limitation and capability of the TOPM manufacturing process could be included as constraints in the optimisation process. Furthermore, providing the more advantageous mechanical properties of the gradient structure compared to that of the homogenous structure, it is beneficial to investigate the anisotropic properties of the gradient TOPM structure. This will help understand the effect of pore and strut size on the anisotropic mechanical properties of the TOPM scaffold in 3D, to better reflect the anisotropic properties of human tissues, such as bone.
Given that the mechanical properties of the AZ91D TOPM scaffolds have been established as part of this thesis, it would be beneficial to undertake *in vitro* corrosion testing to investigate the structural changes due to degradation of the porous TOPM scaffold as well as the important corresponding change in mechanical properties over time to predict *in vivo* behaviour. Such understanding will aid the future development of topology optimisation models, in which the *in vitro* degradation and mechanical properties of the structure could be fully understood and included as parameters for the process. This would allow for the development of computational models of the TOPM implants with specific control of architecture, mechanical properties, and corrosion rate for a given purpose *in vivo*.

While CaP coating methods have been shown as a reliable technique for improving corrosion resistance in Mg, little attention has been paid to investigate the technique on samples with rough surfaces. As the results in Chapter 5 shows, the effectiveness of the coating technique was strongly influenced by the properties of the substrate’s surface. Furthermore, the range of surface topographies presented in porous scaffolds or implants prepared via casting are relatively high. For example, porous Ti prepared by powder sintering had surface roughness up to 374 μm [7], whereas porous TiNbZr alloy scaffolds fabricated using space-holder sintering method in a study by Wang *et al.* showed roughness value of 2.4 μm [8]. For these reasons, it is suggested that future studies on coating techniques for Mg should consider different and more realistic surface topographies that better emulate eventual implants, rather than on idealised smooth or polished surfaces.

In addition, corrosion testing on rough surfaces was analysed on 2D substrates while the actual corrosion that occurs in TOPM scaffold is in 3D. Similarly, both coating methods applied in this study were on 2D substrates, which did not necessarily reflect the true conditions in the TOPM structures. For these reasons, it is important to perform coating and corrosion testing on 3D samples in order to achieve more relevant data for future potential *in vivo* work. Moreover, it will allow a better understanding of the mechanism of how corrosion occurs in 3D TOPM structures in terms of uniform or localised corrosion, and importantly what the subsequent effect is on mechanical properties over time.

In addition, the development of *in vitro* corrosion models linked to TOPM implant mass, surface roughness, surface area, and porosity, and corresponding loss of mechanical properties over time, could lead to the future development of computational models aimed at predicting corrosion and mechanical properties of specific TOPM architectures *in vivo*. 
However, it should be noted that techniques such as EIS and PDP cannot be performed on porous samples due to a number of factors, including leaking of testing media out from the pores on the test sample (Figure 5.4) and more importantly, difficulties in determining the actual surface area exposed to the testing media. Therefore, hydrogen evolution and mass loss possibly are the two reliable techniques for examining corrosion properties of porous structures.

As discussed in Chapter 7 and 8, AZ91D is a popular Mg alloy with advantageous mechanical properties and high corrosion resistance. However, due to the aluminium content, AZ91D generally has not been accepted for in vivo use [9]. Therefore, further work is required to develop Mg alloys with excellent mechanical and corrosion properties and subsequently be used in manufacturing TOPM scaffolds. It is well-known that reducing grain size would increase corrosion resistance and mechanical properties of Mg [10, 11]. Based on research in our group, calcium (Ca) showed a great potential of being an alloying element that could enhance corrosion resistance of Mg alloy if added below the solubility limit [12]. Similarly, Zr is an excellent grain refining agent and can be used with other elements, such as Zn, Al, Tm and other REs [13-16] to also enhance mechanical properties. Further work is required to investigate the optimum percentage of added Ca and Zr to produce Mg alloys with excellent microstructure, mechanical properties, corrosion resistance and importantly, biocompatibility.

In regards to the architecture of the TOPM structures, all the designs used in this study had architectures chosen solely for the purpose of examining the capability of the fabrication technique described herein. Therefore, none of the architectures were optimised for any specific purpose. Given that, as a result of this thesis, the manufacturing process has been well-characterised and understood, TOPM scaffold architectures in the future can, and should be, better optimised to suit specific purposes, such as specific strength and surface area to balance required mechanical properties with surfaces that support nucleation, growth and remodelling of new tissue. This could be achieved by adopting the computational models as studied by Lin et al., of which homogenisation-based topology optimisation algorithm was employed to generate optimised 3D models matching stiffness of human trabecular bone anisotropic [4].

In the design and manufacture of prototype SFDs, the casting efficiency was relatively low due to inadequate pressure on the NaCl paste during the infiltration step. To solve this
problem, there should be modifications made to the CAD model to better support NaCl infiltration in large complex RP moulds. For example, a decrease in the thickness of the supporting plate would reduce its strength, therefore, increase the pressure in the NaCl paste and inherently, result in NaCl template well-packed NaCl particles. Furthermore, the current equipment for the TOPM fabrication process is not capable of producing SFDs for other spinal regions (i.e. lumbar), due to limitations imposed by the Ø20 mm moulds and casts used. For this reason, future work should include scale-up in the size of moulds, infiltration and casting equipment used during the TOPM manufacturing process.

In addition, given that the surface roughness of the produced TOPM scaffold was directly affected by the pore size and packing of NaCl particles, further reduction in the particle size of NaCl will be beneficial. In this thesis, the range of NaCl particle size was 45 – 63 µm, therefore, by adding particles with size of 45 µm and below, the smaller particles can fill in the existing pores on the surface of the current NaCl template. This will potentially generate a smoother surface for the NaCl template, and inherently, reduce surface roughness of the TOPM structure.

As reported in Chapter 7, there was limit to the height of samples for compression testing due to the use of an extensometer. Moreover, in Chapter 8, the SFD was produced but full mechanical properties could not be obtained due to the compliance problem. Therefore, the use of non-contact strain measurement system is highly recommended to achieve reliable compression test data, especially when testing porous samples.

The FEA in this study, especially in analysing stress profiles in the SFDs, employed simplified boundary conditions, which may not reflect the true biological situation [17-20]. Further studies in the future may look into performing FEA on TOPM implants with more physiologically relevant loads and constraints as defined from validated FEA models of the spine, for example. These physiological models will be critical to providing accurate boundary conditions so that optimised TOPM scaffolds can be developed to specifically meet the local loading conditions whilst also taking into account the biocorrosion kinetics in conjunction with supporting new tissue growth.

This future work will contribute significantly to the modelling and development of degradable Mg devices for biomedical applications with topology optimised architecture, with predictable and reliable mechanical and corrosion properties.
Chapter 9 – Conclusions and future work

References


APPENDIX A

Mg casting manual
The process as described below is for pure Mg, 1.0 mm strut size structure. Change casting parameters according to structure and material (Chapter 3)

**Vacuum Chamber – Basic Set-Up in Argon Atmosphere**

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Place dried materials into <strong>Chamber</strong>, ensuring <strong>Thermocouple</strong> is secured, and close the <strong>Chamber Door</strong>. <em>Turn the machine on.</em></td>
</tr>
<tr>
<td>2</td>
<td>Ensure the top <strong>Gate Lock</strong> is closed. Also ensure <strong>Linked Chambers Valve</strong> (2), and <strong>Vacuum Load-Lock Valve</strong> (3) are closed.</td>
</tr>
<tr>
<td>3</td>
<td>The crucible should be tilted several times all the way to ensure the mold is in the right place, and that the tilting action does not “pull” on wires causing problems later.</td>
</tr>
<tr>
<td>4</td>
<td>Close <strong>Argon Main Chamber Valve</strong> (1), Open <strong>Vacuum Main Chamber Valve</strong> (4).</td>
</tr>
<tr>
<td>5</td>
<td>Turn on <strong>Vacuum Pump</strong>.</td>
</tr>
<tr>
<td>6</td>
<td>Keep <strong>Vacuum Pump</strong> on until <strong>990 mBar</strong> or more is reached.</td>
</tr>
<tr>
<td>7</td>
<td>While the <strong>Vacuum Pump</strong> is running, start the <strong>Labview Software</strong> and press “Run”.</td>
</tr>
<tr>
<td>8</td>
<td>Record the time of start appropriately, along with any other appropriate factors.</td>
</tr>
<tr>
<td>9</td>
<td>Open <strong>Argon Bottle</strong> fully. The flow meter attached to the argon bottle should be <strong>25 L/min</strong>. Set the <strong>Argon Flow Rate Controller</strong> to <strong>MAX</strong>.</td>
</tr>
<tr>
<td>10</td>
<td>Once <strong>990 mBar</strong> or more is reached, close <strong>Vacuum Main Chamber Valve</strong> (4). Open <strong>Argon Main Chamber Valve</strong> (1) and turn <strong>Vacuum Pump</strong> off.</td>
</tr>
<tr>
<td>11</td>
<td>Watch the pressure on the computer screen. When this reaches <strong>-250 mBar</strong> turn down the flow meter attached to the argon bottle to just above <strong>10 L/min</strong>.</td>
</tr>
<tr>
<td>12</td>
<td>When the oxygen reading starts to drop rapidly, change the <strong>Argon Flow Rate Controller</strong> to <strong>CONTROLLED</strong>. This should happen at around <strong>260 mBar</strong> but can vary; the pressure can be allowed to reach <strong>400 mBar</strong>, which is the limit of the door seal.</td>
</tr>
<tr>
<td>13</td>
<td>It may be desired to change the <strong>Argon Flow Rate Controller</strong> to <strong>MAX</strong> again if the oxygen is taking a long time to reach below 1%. Just make sure it is on <strong>CONTROLLED</strong> for the furnace run. The flow should be around <strong>0.3 L/min</strong>.</td>
</tr>
<tr>
<td>14</td>
<td>Turn on the water</td>
</tr>
<tr>
<td>15</td>
<td>Turn on the machine</td>
</tr>
</tbody>
</table>
### Magnesium Infiltration Runs

<table>
<thead>
<tr>
<th>Step</th>
<th>Instruction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As temperature is reaching 680 °C, start <strong>Vacuum Pump</strong>. The pump should reach <strong>620 mBar</strong>.</td>
</tr>
<tr>
<td>2</td>
<td>Ensure that the <strong>flow meter</strong> attached to the argon bottle is set to <strong>25 L/min</strong> and the <strong>Argon Flow Rate Controller</strong> to <strong>MAX</strong>.</td>
</tr>
<tr>
<td>3</td>
<td>Waiting for the Mg melts completely (~2mins), start stirring, and increase the pressure to <strong>680 mBar</strong>, maintain this pressure for 5s</td>
</tr>
<tr>
<td>4</td>
<td>Close the <strong>Vacuum Main Chamber Valve (4)</strong>, open <strong>Argon Main Chamber Valve (1)</strong> and turn off the <strong>Vacuum Pump</strong>. Fill the chamber until the pressure is <strong>0 mBar</strong>.</td>
</tr>
<tr>
<td>5</td>
<td>Close the <strong>Argon Main Chamber Valve (1)</strong> and turn the <strong>Vacuum Pump</strong> on. Open the <strong>Vacuum Main Chamber Valve (4)</strong>.</td>
</tr>
<tr>
<td>6</td>
<td>When the pressure reaches <strong>680 mBar</strong>, close the <strong>Vacuum Main Chamber Valve (4)</strong>, open <strong>Argon Main Chamber Valve (1)</strong> and turn off the <strong>Vacuum Pump</strong>.</td>
</tr>
<tr>
<td>7</td>
<td>Flow on bottle meter should STILL be <strong>25 L/min</strong>.</td>
</tr>
<tr>
<td>8</td>
<td>As the pressure reaches <strong>100 mBar</strong>, turn the <strong>flow meter</strong> down to <strong>10 L/min</strong>.</td>
</tr>
<tr>
<td>9</td>
<td>As the pressure reaches <strong>-100 mBar</strong> set <strong>Argon Flow Rate Controller</strong> to <strong>CONTROLLED</strong>.</td>
</tr>
<tr>
<td>10</td>
<td>Try and maintain a small positive pressure in the chamber and turn the furnace off</td>
</tr>
<tr>
<td>11</td>
<td>When the temperature drops below <strong>600 °C</strong>, close the <strong>Argon Main Chamber Valve (1)</strong> and make sure all valves are closed.</td>
</tr>
<tr>
<td>12</td>
<td>Do not open furnace door until temperature is 500 °C or below for pure Mg and 420 °C or below for AZ91D</td>
</tr>
</tbody>
</table>
APPENDIX B

Design drawings
1. Scaffold holder drawings
   a. Bolt
Appendix B

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b. Piston

DETAIL B
SCALE 4 : 1

SECTION A-A
SCALE 2 : 1

Piston
c. Holder
d. Holder with tunnel
e. Crucible
2. Drawings for compression plates
   
a. Top block – set 1
b. Top plate – set 2
c. Central block – set 1
Appendix B

d. Central block – set 2

[Diagram of a compression plate bottom with dimensions and notes: Ø20, Ø16, 10, 5, 3, R10, R2, turned]
Appendix B

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e. Bottom plate

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Compression Plate

Top

SECTION A-A

turned
APPENDIX C

TGA Results
1. TGA-gelatine
2. TGA-HR200
3. TGA-EX200
APPENDIX D

Development of the non-contact strain measurement system
The non-contact strain measurement (NCSM) method was investigated in a Final year student project at the University of Canterbury. The aim was to develop a low cost and accurate NSCM system for use in mechanical testing on the TOPM scaffold. The system utilizes a Canon G10 PowerShot camera, CompactDAQ with two modules, a customised mounting system, a customised camera trigger system, a standalone PC, and LabView and MATLAB software. Full report is available through the Department of Mechanical Engineering:


A number of mechanical tests were performed using the developed system. However, no reliable compression data has been generated yet, hence, the NSCM system could not be employed to test the TOPM scaffold in this thesis. My role in this project was to advise on the testing procedure, requirements and result analysis, and provide testing samples.

Appendix D describes the setting of the system and results of initial compression tests.

1. MATLAB/NCC Code

   a. **Background Theory**

   The MATLAB code is based upon an image processing technique called Normalised Cross Correlation (NCC). This technique involves dividing an initial image into a set of sub-images called search windows. The second image is then divided into template windows that are each contained in the search windows of the initial image. A cross correlation is performed between each template and the corresponding search window to determine the best match. The differences between the coordinates of the search windows in the first image and templates in the second image are then recorded in the horizontal and vertical directions.

   b. **Strain measurement**

   The displacements measured with the NCC method are used to measure the strain in the sample. This is done by taking the measured vertical displacements and dividing by the vertical length (in pixels) between the two displacements according to the conventional strain equation:
These strains are calculated between top and bottom for each template window and then averaged over the entire image to give the total vertical strain between the two images. Horizontal strain is also calculated, however, displacement in this direction is almost negligible for most materials and hence results can be unreliable. The strain measurements between each pair of images are added sequentially in order to give the strain from the first photo consecutively through to the final photo. This information along with the loads captured from the MTS machine can be plotted to give a stress-strain graph. The coordinates of the stress strain graph are saved to a .txt file for easy importation into Excel or another data processing program.

2. System Integration
   a. Background

Integration of the NCSM system components was required in order to provide a largely automated system that allows for virtually anyone to operate the system. The integration requires:

- Acquisition of the load and displacement signals from the MTS testing machine
- Sending a signal to trigger the cameras at set displacement intervals
- Image transfer to a base computer
- Requesting, receiving, and processing user inputs
- Processing images and data to give the required outputs

b. Camera mounting system

To accurately track the displacement of surface features on a test sample, the camera must remain in a fixed and stable position throughout the entire test. The mounting system was a large, flat metal plate placed on the main bed of the MTS testing machine with an adjustable magnetic base unit (Figure D.1). The magnetic base unit allows the camera to be positioned anywhere on the base plate and movements in all directions.
c. **Load and Displacement Acquisition**

The controller for the MTS 858 Testing Machine that the Materials Group uses for tests is an MTS Testar II. This controller has two analogue outputs with BNC connectors, and each of these outputs can be set to output any one of a range of signals, including the load and axial displacement. A CompactDAQ combined with LabVIEW provided the means to effectively and accurately read the data signals, and the components were readily available from the stock within the Mechanical Engineering Department.

The Testar Controller is located in a room separate to the MTS Machine and NCSM system. Therefore, 2 × 12 m coaxial cables with BNC connectors were constructed to connect the Testar Controller to an NI 9205 analogue input module for the load and displacement data feeds. Due to the length of the cables, there is an effect of electrical noise from the operating environments. This effect has been mitigated by increasing the gain from the Testar Controller to the maximum 100×, but this approach limits the displacement that can be read by the NCSM system to 1 mm. However, as no samples are expected to be any longer than 25 mm, this provides a minimum strain limit of 4% which is sufficient to obtain information on the elastic behaviour of the samples.
d. **Camera triggering**

Canon G10 PowerShot cameras can be triggered remotely through connecting contacts from the 2.5 mm stereo jack. In order to utilize this remote trigger feature of the camera, a circuit box was manufactured and connected to an NI 9401 digital input/output module such that when the digital signal is output at the set 0.064 mm displacement intervals, the cameras are triggered to operate the shutter and record an image. This circuit box has been developed to have two outputs in order to allow for the rapid addition of a second camera in the future. An LED has been built into each digital trigger line to provide a visual indication that the trigger signal has been activated.

e. **Image transfer**

The image transfer can only be performed when the camera is not in use, due to the internal settings of the camera. To effectively perform the image transfer, a Windows Visual Basic script file was created in collaboration with Sheng Feng from the Mechanical Engineering Department. Once the material loading cycle has completed, the camera is connected to the NCSM computer and the script file is started. The script file determines how many cameras are connected to the computer, transfers the images into a folder specified within the script, then empties the connected cameras so they are ready for the next test.

f. **System operation**

A LabVIEW virtual instrument program was created to read in the load and displacement voltages and convert these measurements to Newton and Millimetre values respectively. Once the stand alone MTS machine and the camera are setup for the material test, the first step in the NCSM program requires that the user enters the cross sectional dimensions of the test sample before the program will initiate. This step ensures that the sample is not deformed before the correct measurements are stored. The user then switches the program to compression or tension, and instructs the program to record the ‘First Image’ (Figure D.2). This step in the program triggers the camera and records the initial load value, which will be very close to 0 N. From this point the MTS machine is set to run, and as the displacement reaches the pre-set displacement values internal to the program, the load is recorded and the
There are two options for completion of a test – either the program stops once the load reaches the maximum setting for the load cell (± 2280 N), or the user is satisfied with the data gathered and clicks the ‘STOP’ button. Either way the NCSM program automatically runs a MATLAB program developed by the NCSM team which requests user input and processes the data. The MATLAB program requests the camera to be plugged into the computer, runs the image transfer script file, requests the target test folder for data to be stored in, and requests the area of the image the user wants to analyse. The program then automatically detects the number of files, transfers the files to the target test location, and un-distorts the images using the Modified Brown’s Distortion Model. The program processes the ‘clean’ images using the NCC code, and then combines the load data, cross section dimensions and the strain data obtained from the NCC code together to output the stress vs. strain data and figures. The user can then read the outputted data to easily calculate the elastic modulus of the test sample.