IN VITRO CORROSION BEHAVIOR OF MAGNESIUM ALLOY AZ31B-HYDROXYAPATITE METALLIC MATRIX COMPOSITES PROCESSED VIA FRICTION STIR PROCESSING

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Magnesium and its alloys have been considered for load-bearing implant material due to their similar mechanical properties to the natural bone, excellent biocompatibility, good bioactivity, and biodegradation. Nevertheless, the uncontrollable corrosion rate in biological environment restrains their application. Hydroxyapatite (HA, Ca$_{10}$(PO$_4$)$_6$OH$_2$) is a widely used bio-ceramic which has bone-like mineral structure for bone fixation. Poor fracture toughness of HA makes it not suitable for load-bearing application as bulk. Thus, HA is introduced into metallic surface in various forms for improving biocompatibility. Recently friction stir processing (FSP) has emerged as a surface modification tool for surface/subsurface grain refinement and homogenization of microstructure in biomaterials. In the present efforts, Mg-nHA composite surfaces on with 5-20 wt% HA on Mg substrates were fabricated by FSP for biodegradation and bioactivity study. The results of electrochemical measurement indicated that lower amount (~5 wt%) of Ca in Mg matrix can enhance surface localized corrosion resistance. The effects of microstructure and the presence of HA precipitates on in-vitro behavior of Mg alloy were investigated by TEM, SEM, EDX, XRD, and XPS. The detailed observations will be discussed during presentation.
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CHAPTER 1

INTRODUCTION

Orthopedic biomaterials application is used to restore the function of degenerative and fractural bone and joint, and it plays an enormously influence in society medical system worldwide. In fact, in developed countries the chronic diseases have become a general problem amount people over 50 years of age. With the elderly population growing, the higher risk for osteoporosis, osteoarthritis, bone injuries, and obesity will enlarge the orthopedic device market. The statistical data of the number of total hip replacement procedure from 2000 to 2010 (Figure 1.1) revealed the increasing need of hip replacement of aged 45 and over. According to the report from Transparency Market Research, the value of global orthopedic device market was $29.2 billion in 2012 and is expected to reach $41.2 billion by 2019, the expected annual growth rate of the market will be 4.9 percentages over the next five years. (Transparency Market Research, http://www.transparencymarketresearch.com/orthopedic-devices-market.html). Beside the age effect, various reasons including high intensity labor, sport, and accident may cause of bone fractures, requiring surgery to recovery its biological functions by applying permanent, temporary, or biodegradable devices. Such the devices are meant to be implanted in body environment for fracture fixation or joint replacement purposes, in order to repair or substitute the origin ability of natural bone.
The selections of biomaterials for orthopedic application are generally limited to those that can withstand cyclic load-bearing process during implantation. Therefore, the mechanical properties play a leading role for these candidate materials\(^1\). In addition, since the human body is a complex biochemical system, during implantation several corrosion reactions occur between device surface and biological fluid, resulting the failure of implant device and other negative effects to the surrounding tissue. Thus, early concept of successful implant materials was considered as inert as possible in order to reduce the side effect of corrosion produce. Consequently, the first generation of bioimplant materials generally obtains combination properties with high strength and corrosion resistance to avoid generation of particles and
releasing ion from wear and corrosion processes. Metallic implants, such as stainless steel, Co-Cr base alloys, and Ti-6Al-4V alloys were the popular materials to provide sufficient mechanical properties and extremely low degradation rate for permanent load-bearing device\textsuperscript{2,3}. The lack of these metallic devices is that with minimal tissue response, causing rare fibrous layer forms between the implant surface and joint tissue. In order to improve the success of this kind of device, ceramic and polymer materials were used as different sections to combine with metallic material for their manufacture, for enhancing interaction of metallic implants with biological environment. As Figure 1.1 shows the standard hip replacement joint with multi-component assembly. It can include austenitic stainless steel as the stem, porous polyethylene as the acetabular cup, and ceramic as femoral head. This combination provides reasonable strength and biological bonding and gives an average lifetime for 10 years or more.

![Figure 1.1](http://orthoinfo.aaos.org/topic.cfm?topic=a00377)

Figure 1.2 Schematic of individual components of total hip replacement joint (Left), the components merged into an implant (Center), and the implant as it fits into the hip (Reprint from source: http://orthoinfo.aaos.org/topic.cfm?topic=a00377)
Although the current metallic implants have been widely used in orthopedic market, due to the poor interaction with the cell/molecule in body fluid and weak bonding between surface to tissue, patients who receive the orthopedic surgery may suffer by inflammation, infection, and discomfort during long-term healing time. To address this issue, the secondary generation implants were developed as bioactive materials to enhance the biological response in vivo. Bioactivity refers to that material surface interact or absorb cells with the aim of inducing their specific responses and behaviors\textsuperscript{1}. Mineralization reaction between material surface and bone tissue is one of the most important processes to evaluate bioactive implant. Since most of the metallic biomaterials are inert, the development of surface modification process plays a role to produce bioactive metallic implant. A popular method is to deposit a bioactive layer, such as bio-glass (BG) and calcium phosphates (CaP) coating, on metallic implant surface\textsuperscript{4, 5}. The similar composites and structure of these materials to the natural bone mineral phases are accountable for their excellent bioactive properties, enabling to attract cell/molecular and binding to the bone with fibrous connective tissue interface. However, the poor fracture toughness of these ceramic materials makes them not suitable for load-bearing applications. Thus, common solution is through bioactive ceramic coating on metallic substrate surface to produce a implant with proper biological responding and mechanical, resulting the enhancement of protein absorption and bone regeneration rate by formation of mineralization between implant and tissue.

Although metallic biomaterials are mostly suitable orthopedic surgery, they are still considered as a foreign organ to the human body. Thus except the total joint replacement
requiring permanent implant device, most of the metallic implants, such as screws, pins, and plates, are used for temporary purpose, and they need to be removed after the fully recovery of a fractural bone. The main reason for this is that to avoid the weakening process occur on the bone. The natural bone is constantly undergoing remodeling where “old” bone is resorbed and replaced by new bone, the bone-producing cells (osteoblasts) are induced by the application of stress to replenish new bone material\textsuperscript{1,6}. Since the rigid metallic implant attaches to a bone, carrying the majority loading, the surrounding tissue will experience low replenish rate due to the reducing stress effect, resulting in losing bone density. This phenomenon is so call “stress shielding effect”\textsuperscript{7,8}. Therefore, the conventional process to avoid such effect is to apply second surgery soon after the fractural bone has healed. However, repeating surgery causes increasing morbidity rate of patients, health care cost, and length for hospitalization\textsuperscript{9}. Thus, one of the critical requirements of next generation implant is to avoid removal operation. Alternative approaches have been considered for this aim, one of the solutions is the biodegradable material.

The concepts of biodegradable materials are self-dissolved and been resorbed into the surround tissue over a period of time\textsuperscript{10}. Therefore, biocompatibility and toxic-free composites are popular for this kind of application. In addition, the new generation of implants should be able to stimulate the healing responses of bone regeneration at the molecular level\textsuperscript{11}. The convention metals (stainless steel, Ti-6Al-4V, and Co-Cr base alloys) are generally inert in body environment, but even small amount of released metallic ions by corrosion could trigger the risks of toxicity, causing damage to the tissue and patient health\textsuperscript{12}. Thus, the common
Biodegradable materials are polymers such as polyglycolide (PGA), polylactide (PLA), polylactic acid (PLA), polydioxanone (PDS), and etc. They have been widely used in various applications, including surgical sutures, antibacterial coatings, drug delivery systems, fixation devices, and tissue replacement components. Still, the mechanical properties of polymer are not sufficient as metal to provide enough strength for load-bearing applications and needed to be modified.

In the past decades, the potential advantages of magnesium (Mg) as a temporary, biodegradable implant presents a promising alternative to polymers due to its unique biodegradation combined with appropriate mechanical properties as well as good bioactivity and biocompatibility. In addition, using Mg and its alloys as implant can avoid stress shield effect during implantation because of their similar elastic modulus to the natural bone. Nowadays Mg and its alloys have been developed for several bio-applications such as cardiovascular stents, bone fixation, and porous scaffolds. Although biodegradable Mg and its alloys are potentially attractive for the orthopedic field, there are numerous issues which limit and slow the development of Mg-based biomaterials. The primary issue of Mg is its prone to rapid corrosion, especially in biological environments. This challenge demands quite an effort to reduce corrosion rate of Mg in order to maintain functionable for sufficient time while injured tissue repairs. Many methodologies have been applied in literatures to address this issue. The most attention is given to exploring the development of bio-friendly coatings and surface modification. Coating for biodegradable material have the same requirement as the base substrate itself of being biocompatible and biodegradable. Numbers of researchers considered hydroxyapatite (HA, Ca$_{10}$(PO$_4$)$_6$OH$_2$) as coating material on Mg surface to enhance
corrosion resistance and bioactivity by various techniques. In view of this, in accordance with previous efforts, the current work takes a step forward by additively producing the layer structured coatings of hydroxyapatite on AZ31B Mg alloy. The following subsection discusses briefly the aim and the organization of the thesis.

To summaries, the overall aim of this thesis was to investigate the possibility of enhancement the biowettability, biocorrosion resistance, and biomineralization rate of Mg alloy by producing Mg-HA composites layer. For this purpose, the additive technique - friction stir process (FSP) was utilized to produce surface compositied layer with variable weight percentage of HA. The untreated AZ31B alloy and all FSP samples were examined for electrochemical and in vitro experiment. In addition, it is important to study the microstructure and phases in order to understand their influence to corrosion mechanisms and in vitro behavior.

The current Chapter 1 introduces briefly the topic of biomaterials and provides an idea behind the current work. Chapter 2 provides a state of the art literature review related to Mg and its alloys being considered as potential biomaterials. The majority study in this thesis focused on its corrosion and biomineralization behavior of additively surface modified AZ31B Mg alloy with HA. In light if this, the literature review is mainly devoted to these two aspects. The discussion then proceeds to the experimental and analytical methodologies followed in the current work in Chapter 3. Outcomes of this work are presented in Chapter 4. Furthermore, the conclusions derived from the current research endeavor are mentioned in Chapter 5. The thesis
concludes with suggested future work that can potentially be done to build upon the understanding developed during this thesis work in Chapter 6.
CHAPTER 2

LITERATURE REVIEW

2.1 Application of Magnesium as Bio-Implant Material

There are some essential properties required for bioimplant application. Mg and its alloy as mentioned in Chapter 1 possess some such properties making it potential biomaterial for orthopedic implant. Following section review about characteristics of Mg and its alloys from bioapplication point of view.

2.1.1 Mechanical Properties

Magnesium (Mg) is the well known light-weight metallic element that is widely used nowadays for different industry areas such as automotive, aerospace, and electronic application. The density of Mg (1.74 g/cm$^3$) is 2.5 and 4.5 times less dense then Ti and steel, respectively\textsuperscript{2, 19}. In addition, the fracture toughness of Mg is greater than ceramics such as bioglass (BG) and HA. From bioapplication perspective, Mg and its alloys have elastic modulus and yield strength very similar to that of the human bone (Table 1). As a result, Mg based bioimplants have been thought to reduce stress shield effect and losing bone density\textsuperscript{20}. Additionally, due to the high damping capacity, Mg has shock and vibration absorbing properties, which is very important in heavy load bearing application\textsuperscript{21}. Moreover, Mg and its alloy are considered as the easiest structure metal for machining, and stable final dimensions are easy to achieve\textsuperscript{22}. From bioimplant application point of view the important class of Mg
alloys containing aluminum and zinc (referred to as AZ series alloys) is discussed in the following section.

Table 2.1 Mechanical properties of various biomaterials and human bone\textsuperscript{19, 23-27}.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm\textsuperscript{3})</th>
<th>Elastic Modulus (GPa)</th>
<th>Compressive Strength (MPa)</th>
<th>Fracture Toughness (MPa/m\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium alloy</td>
<td>4.4-4.5</td>
<td>110-117</td>
<td>758-1117</td>
<td>55-155</td>
</tr>
<tr>
<td>Co-Cr alloy</td>
<td>8.3-9.2</td>
<td>230</td>
<td>450-1000</td>
<td>N/A</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>7.9-8.1</td>
<td>189-205</td>
<td>170-310</td>
<td>50-200</td>
</tr>
<tr>
<td>Magnesium alloy</td>
<td>1.74-2.9</td>
<td>41-45</td>
<td>65-100</td>
<td>15-40</td>
</tr>
<tr>
<td>Sintered HA</td>
<td>3.16</td>
<td>70-90</td>
<td>120-150</td>
<td>0.7-0.9</td>
</tr>
<tr>
<td>45S5 bioglass</td>
<td>2.70</td>
<td>76.74</td>
<td>500</td>
<td>0.7-1.1</td>
</tr>
<tr>
<td>Bone</td>
<td>1.8-2.1</td>
<td>3-20</td>
<td>130-180</td>
<td>3-6</td>
</tr>
</tbody>
</table>

2.1.2 Mg-Al Alloys

Pure Mg usually performs poorly as regards the required mechanical and corrosion performance\textsuperscript{28}. Appropriate additions of alloying elements can enhance the mechanical properties, corrosion resistance, and the ease of manufacture of Mg. Mg-Al-Zn alloys is one of the major groups of Mg based alloys for biomaterial application. Al is the most common alloying for structure Mg alloys, the commercial Mg-Al alloys typically contain 2-10wt% Al with relatively low additions of zinc (Zn), for solid solution strengthening, and minor amount of manganese (Mn), for clearing away the heavy impurities from the melt resulting in enhanced corrosion resistance\textsuperscript{29, 30}. Typical Mg-Al alloys are AZ91, AZ31, AE21, calcium (Ca) modified AZ alloys, and LAE442. AZ91 and AZ31 alloys have been widely used in technical manufacturing. The benefit of Al alloying in Mg matrix is generally believed to be a result of $\beta$ (Mg$_{17}$Al$_{12}$) phase in microstructure\textsuperscript{31}. $\beta$-phase can play an important role to modify surface properties, such as
wetting ability and corrosion resistance when it form as continuous net-shaped structure along grain boundary. The corrosion resistance enhances rapidly with increasing Al up to 4%. The effect of Al in strengthening corrosion resistance appears to be due to changes in the composition of the hydroxide layer formed on the surface due to Al addition. Furthermore, β-phase obtains a passive behavior and inert reaction in the chloride solution over a wide range pH values. However, excessive fractions of β-phase may cause micro galvanic effect with α-matrix, leading acceleration of the corrosion rate. Moreover, Al is also a toxic element for body because of its quick combination rate with inorganic phosphates in the blood, leading to a lack of phosphate in the body and inducing dementia. Therefore, the alloys with large Al amounts are not recommended for long term implantation. This brings the discussion to another important point that is biocompatibility. The following section provides information about biocompatibility of Mg and its alloys.

2.1.3 Biocompatibility of Mg and Its Alloys

Mg is the fourth most abundant cation in the human body. It is estimated that 0.24 kg of Mg is stored in the body of a normal adult with 70 Kg weight. Approximately 50% of total physiological Mg is stored in bone tissue. Furthermore, Mg is a co-factor for different enzymes and assists in stabilizing the structure of DNA and RNA. In a homeostatic system the level of Mg in the extracellular fluid range is between 0.7 to 1.05 mmol/L, importantly, Mg depletion may resulting cardiac arrhythmias, development of artherosclerosis, vasoconstriction of coronary arteries, and increased blood pressure. On the contrary, an excess of Mg can be controlled by storing it in bone/muscle areas, or by excreting via the kidneys making it safer for
implant application\textsuperscript{41}. Furthermore, the US Food and Nutrition board recommended daily allowance of Mg as 420 mg per day and 320 mg per day for man and women, respectively\textsuperscript{42}. Therefore, Mg is generally considered as body-friendly metal, and toxicity is normally not an issue\textsuperscript{43}. While using Mg as a bioimplant material, the releasing ions can partake with tissue regeneration process, forming biological apatite as bone mineral\textsuperscript{44}. In summary, the main reason behind Mg and its alloys be considered as important biomaterials is that they not only provide a base for tissue attachment but also supply simulated effect for growing the new bone while the recovery process. However, the overall corrosion resistance of Mg alloys in blood environment is evaluated to be poor, which poses the main barrier in their application. Efforts are continuously ongoing to address this issue in the biomaterials community. The following section covers discusses the attributes of Mg and Mg alloy corrosion behavior in bioenvironment.

2.1.4 Corrosion Behavior of Mg in Bio Environment

Human body is a harsh environment for implant materials. It contains oxygenated saline solution with salt (NaCl) of \textasciitilde0.9wt\% at a pH of 7.4 and temperature of 37.1 °C\textsuperscript{45}. Figure 2.1 shows the electrolyte composition of blood plasma, interstitial fluid, and intracellular fluid. In such a condition, all types of metal will undergo electrochemical corrosion at the surface, leading to two major issues: (1) reducing the structural integrity and (2) reacting unfavorably with the host.
The corrosion process composed of the cathodic reaction (reduction) and anodic reaction (oxidation) occurring simultaneously. The tendency for corrosion taking place depends on the electrode potential of the material. The electrochemical series is the commonly used reference to rank the potentials of cathodic reactions of various metal in comparison to the equilibrium of $\text{H}_2$ (Table 2.1$^{46}$). The magnitude of electrode potential indicates the corrosion resistance tendency; the elements that possess large positive potential will be prone reduction reaction and hence more resistance to corrosion. These metallic materials are considered noble. On the contrary, the elements with large negative potential possess tendency of enhanced oxidation reaction and are considered as active. Since the electrical potential of Mg is $-2.372 \, \text{V}$
occupying the bottom portion of the series (Table 2.2), the aggressive corrosion of Mg is expected in harsh environment such as human body.

Table 2.2 Standard electrochemical series of metallic elements\textsuperscript{46}.

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Electrode Potential (V\textsubscript{SHE})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noble (Corrosion resistance)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>Au</td>
<td>1.692</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt</td>
<td>0.951</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag</td>
<td>0.7996</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>0.521</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>0.00</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>-0.037</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>-0.1262</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>-0.257</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>-0.28</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>-0.744</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>-0.7618</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>-1.185</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>-1.37</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Zr</td>
<td>-1.53</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>-1.662</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>-2.372</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>-2.71</td>
</tr>
<tr>
<td>Active (corrosion prone)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>-2.868</td>
</tr>
</tbody>
</table>

The potential difference also shows the driving force tendency\textsuperscript{47}. It can be revealed by a change in Gibb’s free energy, which is controlled by the potential difference as shown in Equation 2.1:

\[ \Delta G = -nFE \]

Equation 2.1

Where \( \Delta G \) is the change in Gibb’s free energy, \( n \) is the number of electrons, \( F \) is the Faraday’s constant, and \( E \) is the electrochemical potential. The greater potential difference, the stronger the driving force for corrosion take place.
The anodic reaction and cathodic reaction for Mg is shown as Equation 2.2 and Equation 2.3:

\[
\text{Mg}_\text{s} \rightarrow \text{Mg}^{2+}_{\text{aq}} + 2e^- \\
2\text{H}^+_\text{(aq)} + 2e^- \rightarrow \text{H}_2
\]

Equation 2.2
Equation 2.3

These reactions can be combined into the total reaction listed in Equation 2.4.

\[
\text{Mg}_s + 2\text{H}_2\text{O} = \text{Mg(OH)}_2 + \text{H}_2
\]

Equation 2.4

According to Equation 2.4, it reveals how magnesium hydroxide (Mg(OH)$_2$) layer and H$_2$ forms on the Mg substrate surface during corrosion.

In general, Mg(OH)$_2$ is considered as passive layer providing surface protection in the moist air. However, Mg(OH)$_2$ layer cannot offer sufficient corrosion protection to underlying surface in biological environment. Unlike Al which forms a continuous inert oxide layer on the surface, Mg(OH)$_2$ layer is discontinuous. The main reason for this is that the hexagonal close-packed (HCP) unit cell of Mg creates a volumetric mismatch between substrate and the oxide layer. This is quantified using a ratio termed as Pilling-Bedworth ratio ($R_{P-B}$). $R_{P-B}$ is the ratio of volume of the unit cell of metal oxide to that of the corresponding metal substrate. The $R_{P-B}$ of Mg is 0.81, which is much smaller than the $R_{P-B}$ of Al (1.38). Another reason for poor corrosion protection of Mg(OH)$_2$ is that it does not form at pH value under 11 and potential value higher than -2.7 V, as depicted in Pourbaix diagram (Figure 2.2). Mg(OH)$_2$ layer in solution has an equilibrium pH at 10.4, and forms semi-protective layer between 8.5 to 11.5. Nevertheless, the pH value of human is about 7.4, suggesting Mg(OH)$_2$ will experience continued dissolution. In addition, Mg(OH)$_2$ is susceptible in chloride solution. The reaction with chloride environment
leads to formation of halide magnesium chloride (MgCl₂) more favorably because of the larger electronegativity of Cl⁻ ion compared to (OH)⁻ ion. Equation 2.5 presents the chemical process to form MgCl₂.

\[2\text{Cl}^- + \text{Mg(OH)}_2 \rightarrow 2\text{OH}^- + \text{MgCl}_2\]  

Equation 2.5

MgCl₂ is highly soluble in water due to its strong tendency to form hydrogen bonds, causing the consumption of Mg(OH)₂ and the releasing of the chloride ions back into solution where it can repeat the same process thus accelerating the dissolution. Another important point which has to be reiterated here is that the human bold does contain considerable concentration of Cl⁻ ions.

Figure 2.2 Pourbaix diagram for pure Mg in water at 25°C

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Hydrogen gas formation is another issue that needs to be considered for Mg bioimplant application. Gas pockets may form next to the implant that lead separation of tissue and tissue layers\textsuperscript{36}. Thus H\textsubscript{2} bubbles may delay healing at the joint of implant and tissue leading to necrosis (permanent death) of surrounding tissue\textsuperscript{49}. It could be a threat to patient’s life as large amount of H\textsubscript{2} bubbles might even block the blood stream\textsuperscript{3}. Although H\textsubscript{2} could be fully absorbed by the body\textsuperscript{50}, the rapid degradation behavior still needs to be controlled to reduce such the risks. On this note, the following subsections goes into the details of mechanism of biocorrosion of Mg and its alloys.

2.1.5 Corrosion Mechanisms of Mg in Body Fluid

The failure of Mg implants during implantation usually results from experience of several different types of corrosion reactions simultaneously; each process contributes acceleration of degradation to Mg substrate. In general corrosion can be classified into eight typical forms as shown in Table 2.3\textsuperscript{51}. It has been reported that the common corrosion occur on Mg and its alloy in biological fluid may be galvanic corrosion, pitting corrosion, corrosion fatigue, and erosion corrosion as presented in the following discussion.
Table 2.3 The various corrosion and its general concept

<table>
<thead>
<tr>
<th>Type of corrosion</th>
<th>General Concept</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform corrosion</td>
<td>Chemical/electrochemical reaction proceeds over the entire exposed surface</td>
</tr>
<tr>
<td>Galvanic corrosion</td>
<td>Occur due to the potential difference between two metals</td>
</tr>
<tr>
<td>Crevice corrosion</td>
<td>Take place with crevices or shielded areas on metal surface exposed to corrosives</td>
</tr>
<tr>
<td>Pitting corrosion</td>
<td>Several anodic sites on the metal surface causes localized corrosion</td>
</tr>
<tr>
<td>Intergranular corrosion</td>
<td>Localized attack at grain boundaries with little corrosion of the grains</td>
</tr>
<tr>
<td>Erosion corrosion</td>
<td>Happen at the metal surface with relative rapid movement between corrosive fluid and metal surface</td>
</tr>
<tr>
<td>Stress corrosion</td>
<td>Cracking occurs by the simultaneous presence of tensile stress and a specific corrosive medium</td>
</tr>
<tr>
<td>Selective leaching</td>
<td>A process of removal of one element from alloy, i.e. remove zinc in brass alloys</td>
</tr>
</tbody>
</table>

2.1.5.1 Galvanic Corrosion

Galvanic corrosion takes place when two metals with different electrochemical potentials are in physical contact to each other and are surrounded by the ionic conducting fluid. The metal with lower electrochemical potential is referred as anode part and undergoes oxidation reaction. On the other hand, the metal with higher electrochemical potential is referred as cathode and undergoes reduction reaction. Galvanic corrosion rate is affected by several factors such as high conductivity of the surrounding medium, large potential difference between anode and cathode, low polarizability of anode and cathode, large area ratio of cathode to anode, and small distance from anode to cathode. Mg and its alloys are especially susceptible to galvanic corrosion because of the lower electrochemical potential compared to most metals (see Table 2.2). Cathodes not only can be an external ones such as other metals in
contact with Mg, but also can be an internal as secondary phases and impurity phases. Figure 2.3 illustrates these two types of galvanic corrosion.

![Diagram of galvanic corrosion](image)

**Figure 2.3** (a) External galvanic corrosion and (b) Internal galvanic corrosion of Mg-Al alloy

### 2.1.5.2 Pitting Corrosion

Pitting corrosion is observed as discontinuous areas of a material that undergo rapid corrosion attack while the vast majority of the surface remains unaffected. This type of corrosion, which is also referred as localized corrosion, commonly occurs in Mg alloys. For instance, Mg-Al alloys generally consist of α-matrix, β (Mg₁₇Al₁₂) phase, and other intermetallic particles like Al₈Mn₅, pitting corrosion generally occurs and nucleates at the interface between these particles and α-matrix. The reason behind such a phenomenon is thought to be their relatively higher electrochemical potentials compared to the α-matrix. Corrosion pit sites generally manifested as a cavity or hole with small area (Figure 2.4), and they can be further developed leading to crack initiation during corrosion fatigue and stress corrosion cracking.
2.1.5.3 Corrosion Fatigue

Corrosion fatigue occurs when metals experience accumulated cyclic-load load in an aggressive environment. It manifests from the interaction of irreversible cyclic plastic deformation with localized electrochemical reactions. Corrosion fatigue is an important factor while estimating the life of metallic implants as they go through a substantial and long term cyclic mechanical loading. The materials for long term implant, such as total hip replacement, are required to be corrosion fatigue resistant. Aqueous solutions including the blood can significantly reduce the fatigue life of Mg alloys. In addition, it has been reported that the Mg surface with defects, such as oxide and pores tends to suffer shorter fatigue life, and easily nucleate the cracks ultimately resulting in failure\textsuperscript{53}.

2.1.5.4 Erosion Corrosion

The definition of erosion corrosion is that the acceleration in rate of degradation on metal due to relative movement between a surrounding solution and the metal surface\textsuperscript{51}. This

Figure 2.4 SEM image of AZ91 Mg corroded surface after 2 hours immersion in m-SBF\textsuperscript{52}
process is usually rapid, and mechanical wear effects are also involved. When metal is removed from the surface as dissolved ion or solid corrosion product, these get mechanically swept over the metal surface by the movement of the fluid, resulting several surface features such as grooves, gullies, waves rounded holes, and valleys. The damage of erosion corrosion can be prevented via forming a protective thin layer on metal surface. Examples are Al and stainless steel which easily form such an inert layer forming during immersion. However, the passive layer of Mg is not stable in biological fluid, making it more susceptible to erosion corrosion. Few works have discussed the erosion corrosion effect on Mg in biological environment, Chen et al. used artificial test platform to simulate the environment encountered by stents in coronary arteries for investigation of erosion corrosion of Mg-9wt%Zn alloy in simulated body fluid (SBF). Wang et al. reported that polymer base 1,3-trimethylene carbonate (PTMC) coating of pure Mg exhibited 10 times less weight loss than pure Mg in dynamic degradation test, indicating the improvement of erosion resistance of Mg. They also studied the effect of the fluid flow to erosion corrosion on Mg-Al alloy, and found that high flow-induced shear stress (FISS) could directly cause increased uniform corrosion, localized corrosion coverage ratio and depth, as well as erosion corrosion of pure Mg and AZ31 Mg alloy. These studies pointed towards the need for surface modification of Mg based implant material to improve its overall electrochemical performance.

2.2 Calcium Phosphate (Ca-P) Bio-Ceramic Coating

Ceramic materials are compounds of metallic or nonmetallic element with ionic or covalent bonding. While such materials are used for skeletal or hard tissue repair referred to
bioceramics. These bioceramics can be inert (alumina, zirconia), bioresorbable (tricalcium phosphate), bioactive (hydroxyapatite, bioglass), and porous and have been used for various implant applications\textsuperscript{5, 57, 58}. Unlike metallic implants, their success depends on the ability to induce cell/tissue regeneration at implant surface without the intermediate fibrous tissue layer. Nowadays calcium phosphate (Ca-P) is considered as one of the important bioactive ceramics for load-bearing implant application. The primary reason for such an increased attention is that Ca-P forms a major constituent of the bone. Brushite (DCP, CaHPO\textsubscript{4}∙2H\textsubscript{2}O), octacalcium phosphate (OCP, Ca\textsubscript{8}H\textsubscript{2}(PO\textsubscript{4})\textsubscript{6}∙5H\textsubscript{2}O), Tricalcium phosphate (TCP, Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}), and calcium hydroxyapatite (HA, Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}OH\textsubscript{2}) are the prominent Ca-P salts found in the bone\textsuperscript{59}. Table 2.4 shows the vary Ca-P base ceramics in formula, name, and Ca/P ratio. Among these materials HA is the dominant constituent of body hard tissue, making it to quickly adapts to the biological environment and reacts smoothly to make a strong bonding to tissue. Furthermore, HA is also reported to exhibit low solvability at neutral pH\textsuperscript{60}. It also displays an osteoconductivity, which is capable to encourage bone already being formed to adhere to HA surface\textsuperscript{61}. This is an extremely useful property when fast bone growth is required. HA can be produced from biological skeletal carbonate by hydrothermal exchange as shown in Equation 2.6\textsuperscript{59}.

\[ 10\text{CaCO}_3 + 6(\text{NH}_4)_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 6(\text{NH}_4)_2\text{CO}_3 + 4\text{H}_2\text{CO}_3 \]  

Equation 2.6

<table>
<thead>
<tr>
<th>Ca/P ratio</th>
<th>Chemical name</th>
<th>Mineral name</th>
<th>Formula</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>Hydrated calcium phosphate/ Brushite</td>
<td>CaHPO\textsubscript{4}∙2H\textsubscript{2}O</td>
<td>DCP</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>Anhydrous calcium phosphate/Monetite</td>
<td>CaHPO\textsubscript{4}</td>
<td>ADCP</td>
<td></td>
</tr>
<tr>
<td>1.33</td>
<td>Octacalcium phosphate</td>
<td>Ca\textsubscript{8}H\textsubscript{2}(PO\textsubscript{4})\textsubscript{6}∙5H\textsubscript{2}O</td>
<td>OCP</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>Tricalcium phosphate/Whitlockite</td>
<td>Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}</td>
<td>TCP</td>
<td></td>
</tr>
<tr>
<td>1.67</td>
<td>Flourapatite</td>
<td>Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2}</td>
<td>FA</td>
<td></td>
</tr>
<tr>
<td>1.67</td>
<td>Hydroxyapatite</td>
<td>Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2}</td>
<td>HA</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>Tetracalcium phosphate/Hilgenstockite</td>
<td>CaO·Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}</td>
<td>TTCP</td>
<td></td>
</tr>
</tbody>
</table>
In spite of its remarkable biocompatibility and bioactivity, it suffers from brittleness, low tensile strength (~38 MPa)\textsuperscript{62}, and poor impact restricting its usage as a bulk for load-bearing application. Thus, the usage of HA has been explored in the form of surface coating on metallic implant in order to combine the good strength and ductility of the substrate with the excellent bioreaction of the HA\textsuperscript{5,16}. In addition, it has been reported that the benefits of using HA coating includes abating the diffusion of toxic elements from implant substrate into body and reducing the friction coefficient between implant and joint tissue\textsuperscript{63}.

Since mid-1980s the HA coatings were first used for enhanced fixation between implant and tissue\textsuperscript{64}, Various methods have been explored to synthesize HA coating on various metals surface for orthopedic application. When designing HA coating processing, several quality specifications are considered, including purity (phase composition), crystallinity, Ca/P ratio, microstructure, porosity, surface roughness, thickness, surface texture, implant type, cohesive and bond strength, tensile and shear strength, Young’s modulus, residual stress, and fatigue life\textsuperscript{65}. The ideal conditions of a good HA coating for implant were recommended to be low porosity, strong cohesive strength, good adhesion to the substrate, high chemical and phase stability, and a high degree of crystallinity\textsuperscript{66}. These properties need to be combined harmonically to each other through processing techniques and parameters. Next section will focus on reviewing vary HA surface modification methodologies on Mg and its alloy.
2.3 Surface Modification Methodologies

As mentioned in the previous paragraph, HA is generally used as a surface coating on metallic implant surface. The common coating methodologies can be divided into two classes: conversion coating and deposited coating. Conversion coatings are in situ grown coating, which are formed by chemical reaction between the substrate and the immersed liquid\textsuperscript{16}. The produced layer is generally inorganic with ceramic like structure. On the contrary, Deposited coatings are most constituted by organic biopolymer base material, such as polylactic-co-glycolic acid (PLGA) coating. Other than these two major methods several other techniques were also tried for CaP-coating synthesis\textsuperscript{16} (Table 2.5). Most of the techniques are aimed to improve corrosion resistance of Mg implant by providing fixation for sufficient time before total degradation. However, they suffer from several drawbacks such as poor adherence between coating and substrate, lack of uniformity, corrosion damage on substrate during process, long time process, and toxic by-product. Hence, to address these issue, laser surface modification and friction stir processing which usually result in minimal chemical reaction processes and quick process have been utilized to synthesize Mg implant. Furthermore these processes are also quick in nature. The laser process technique has already been proven to be useful during the Master’s thesis work of the present candidate\textsuperscript{32}. In a continuation, the focus was given to the friction stir processing. In light of this, the next section provides the review of friction stir processing (FSP) technique for implant application.
Table 2.5 CaP-base surface modification by various techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Method</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion coating</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical conversion</td>
<td>Immersion in SBF at 37 °C for period of time</td>
<td>Controllable phase composition of CaP coating via adjusting immerse solution composition</td>
</tr>
<tr>
<td>Anodization</td>
<td>Plasma electrolytic oxidation in NaOH/Na₂SiO₃/CaOH₂ + (NaPO₃)₆ + Ca(H₂PO₂)₂ solution</td>
<td>Adjustable Ca/P ratio through operating reaction time, voltage, and additional element in electrolytic</td>
</tr>
<tr>
<td>Deposited coating</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electro deposition (ED)</td>
<td>ED in Ca(NO₃)₂ + NH₄H₂PO₄ solution and immersion in NaOH solution at 80 °C</td>
<td>Multiple step processing produced various CaP-base phases</td>
</tr>
<tr>
<td>Sol-gel</td>
<td>Using calcium nitrate and phosphorus pentoxide for heat treatment at 450 °C for 24 h. Additional tetraethyl orthosilicate was applied to synthesis Si containing coating</td>
<td>Different elements can be included in the gel formation process and this can be incorporated in the final structure of CaP coating</td>
</tr>
<tr>
<td>Laser</td>
<td>Rapid laser melting and cooling on HA pre-coating on Mg</td>
<td>Surface roughness, coating thickness, and microstructure can be controlled by laser process parameters (power, scanning rate, pattern spacing)</td>
</tr>
<tr>
<td>Surface composite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Friction stir process (FSP)</td>
<td>The friction movement between pin and substrate causes localized heat and soften to stir CaP powder into Stir Zone within metallic matrix</td>
<td>Refined grains can be achieved in Stir Zone with Mg-HA composite.</td>
</tr>
</tbody>
</table>
2.3.1 Friction Stir Processing

Friction stir processing (FSP) is a solid-state joint technique, which was developed from friction stir welding (FSW) at The Welding Institute (TWI, Cambridge, United Kingdom) in 1991. The welding process is illustrated in Figure 2.5 that a non-consumable rotating tool with pin and shoulder is inserted into the adjoined edges of plates, to be joined and then move along the line of joint while the shoulder contacts the plate surface. The friction between the tool and contact surface causes the rise of the temperature, resulting localized heat to soften the material surrounding the pin. FSW has been widely used for different material systems, such as high-strength aerospace aluminum alloys, stainless steel, and other metallic alloys that are hard to weld by the traditional fusion welding techniques. Mishra et al. applied this technique to develop FSP for microstructure modification on 7075Al alloy. After FSP the fine-grained microstructure for high-strain-rate superplasticity was achieved in commercial 7075Al alloy. It has been reported that plastic deformation played a critical role in the processing material, thereby resulting in the occurrence of dynamic recrystallization in the stirred zone (SZ). In this condition, fine and recrystallized grains of quite uniform size were produced in the SZ. Moreover, the true strain during FSP was as high as 40%. In addition, the possibility of incorporating the ceramic particles into metallic substrate to form the surface composites was also demonstrated. For the first time, Mishra et al. successfully fabricated the SiC surface composite with ~100 μm thickness on 5083Al alloy by FSP. Another example is that Lee et al. demonstrated using FSP to produce nano-SiO$_2$ into AZ61 Mg alloy for enhancement of mechanical properties.
Several remarkable advantages of FSP as suggested in the literature\textsuperscript{67} include (1) solid-state technique with one step processing that achieves refined, densified, and homogeneous microstructure. (2) Controllable mechanical properties of the processed area by tool design. (3) Extensive applications for various purpose. (4) Energy-efficient technique with low outsource requirement.

Although FSP has been well studied for microstructural evolution, mechanical properties, and corrosion resistance of common structural alloys, in biomaterial field, however, there were few efforts utilizing this technique for implant applications. Farnoush et al. used FSP and electrophoretic deposition to fabricate nano-HA coatings on Ti-CaP nanocomposite layer\textsuperscript{75}. They reported that the refined, homogeneous Ti-CaP layer acts as barrier to block the penetration of Cl$^-$ ion and water molecules into substrate, resulting in improvement of corrosion resistance in SBF. For Mg biomaterial application, in particular, Sunil et al.\textsuperscript{76},
produced Mg-HA surface composite on AZ31B Mg alloy. Grain refined Mg via FSP was evaluated for bio wettability, weight loss during immersion, corrosion during electrochemical measurement, cytotoxicity, and cell adhesion tests. They demonstrated the predeposition method consisting of one or two grooves cut along the FSP travel direction, and then filled with ceramic powder in the grooves, as illustrated in Figure 2.6. It is even possible to obtain bulk composites with deeper grooves in the processing plate and proper choice of pin dimensions. Ma et al. used the similar method to produce FSP on pure Mg and Mg-HA metallic matrix nanocomposites and reported improvement in corrosion resistance in SBF. Kannan et al. focused on corrosion behavior study of FSP AZ31B Mg by electrochemical impedance spectroscopy (EIS). Their results revealed that the galvanic effect could be reduced due to the homogenization by dissolution of grain boundary precipitates. All these efforts pointed towards the merits of FSP for bio implant application. Therefore, FSP can be considered as the potential technique to enhance Mg implant performance.

Figure 2.6 Schematic of FSP of Mg-HA surface composite.
CHAPTER 3
EXPERIMENTAL METHODS

3.1 Materials and Sample Preparation

Commercially available AZ31B Mg alloy (Yin Xun Co., Taiwan) sheets (3.0wt% Al, 1.0wt% Zn, 0.5wt% Mn, and Mg balance) of size 120 mm x 1030 mm x 1.3 mm and 330 mm x 3330 mm x 2.3 mm (width x length x thickness) were used for performing FSP. Prior to the processing, the sheets were cut into 20 mm x 127 mm x 1.3 mm and 20 mm x 127 mm x 2.3 mm. Pure Hydroxyapatite powder (97.9-99.9%, ACROS ORGANICS Inc.) with average particle size of 10 μm was used to form Mg-HA metallic matrix composite in this study. Three different weight percentages of HA powder, which are 5wt%, 10wt%, and 20wt%, were prepared to pack upon Mg sheets layer by layer, as shown schematically in Figure 3.1(a).

3.2 Friction Stir Processing

The FSP was utilized to incorporate and disperse HA powder into AZ31B Mg matrix in solid state. Figure 3.1(b) shows the schematic of FSP. The tool is made of nitrided high-speed steel consisting a tapered pin (6 mm in diameter and 6 mm in length) and shoulder (16 mm in diameter). The rotating tool was traversed at a speed of 30 mm/min with a rotation speed 900 rpm along the traverse axis of the processing sample. A 3° traversed angle was applied to the tool. Multiple passes of FSP were processed back and forth along the traversed axis to disperse the powder. Figure 3.2 displays the appearance of finished FSP sample, which coded as FSP Mg-HA, and it cross-section.
Figure 3.1 Schematic of (a) sample preparation and (b) FSP

(a) AZ31B Mg plate (Thickness: 2.3mm)
AZ31B Mg plate (Thickness: 1.3mm)
HA Powder

(b) Machine axis
Normal Direction
Processing Direction
HA Layer
Tool Rotation
Shoulder
Pin
Stirred Zone
Retreating Side
Advancing Side
Tilt Angle = 3°
3.3 Phase Identification

Phases formed in the FSP Mg-HA composite and untreated AZ31B Mg alloy were primarily evaluated by using a Rigaku III Ultima X-ray diffractometer (XRD) with Cu Kα radiation (wavelength=0.15418 nm). The XRD system was operated at 40 kV and 44 mA in a 2θ range of 20-90° using a step size of 0.025° and a scan rate of 2.5°/min. The XRD analysis software JADE was used for phase identification and background correction. The phases present in the resulting pattern were identified by comparing the XRD pattern with standard International Center for Diffraction Data (ICDD) files obtained from the Joint committee of Powder Diffraction Standards (JCPDS).
3.4 Microstructure

To study microstructure and elemental distribution within stir zone of FSP Mg-HA composites, the samples were initially cut into 6 mm x 6 mm x 5 mm coupons by using slow speed diamond saw. The sectioned coupons and untreated AZ31B Mg were mounted in epoxy and then polished with SiC papers of different grit size (from 600 to 1200 grit) followed by disk polishing with alcohol base diamond suspension (from 1 to 0.2 μm) to get a scratch free surface. In order to remove the foreign particles from SiC paper and diamond suspension on the polished surface, the coupons were then ultrasonically cleaned with methanol for 2-3 minutes. To reveal the microstructure features, FSP Mg-HA and untreated AZ31B Mg coupons were etched the etchant constituting of mixture of 5mL acetic acid, 6 g picric acid, 10mL H₂O, and 100mL ethanol (95%) for approximately 5 s by immersion etching. The microstructural observation was carried out by using FEI Quanta 200 environmental scanning electron microscope (ESEM) and Energy-Dispersive X-ray Spectroscopy (EDS) detector, respectively.

Moreover, to have a clear idea about precipitate distribution at nano scale, transmission electron microscopy was performed on the FSP samples. Philips EM420 field emission gun transmission electron microscope (TEM) was used for this purpose. TEM was operated at an accelerating voltage of 120 kV. The sample preparation for TEM observation was carried out by following steps:

1. Convention polishing (180, 400, 600, and 1200 grit SiC paper) until sample thickness reached ~70 μm.
2. Ion milling PIPS ion milling machine with 4.5 kV and 4 rpm rotation to obtain electron transparent region.

These prepared samples were loaded in the TEM column and observed at various magnifications in bright field and dark field modes. The selected area diffraction (SAD) patterns were also extracted from various locations to identify the phases present and to capture the centered dark field images. All the TEM micrographs were then quantified using ImageJ™ software for various microstructural attributes.

3.5 Corrosion Evaluation

Effect of various microstructural developments on corrosion behavior was examined using electrochemical methods and weight loss tests. All the tests were carried out in simulated body fluid (SBF) medium as described below.

3.5.1 Electrolyte Preparation

Simulated body fluid (SBF) solution was used in this present study to understand the corrosion behavior and corrosion resistance evaluation of FSP Mg-HA composites and untreated AZ31B Mg alloy. The chemical composites of SBF includes:

(1) Sodium chloride (NaCl, 8.035 g)

(2) Sodium hydrogen carbonate (NaHCO₃, 0.355 g)

(3) Potassium chloride (KCl, 0.225 g)

(4) Di-potassium hydrogen phosphate trihydrate (K₂HPO₄·3H₂O, 0.231 g)
(5) Magnesium chloride hexahydrate (MgCl$_2$$\cdot$6H$_2$O, 0.311 g)

(6) Calcium chloride (CaCl$_2$, 0.292 g)

(7) Sodium sulfate (Na$_2$SO$_4$, 0.072 g)

(8) D.I water (700 mL)

The buffer solutions that controlled the pH value of SBF were HCl (1.0 M) and Tris-hydroxymethyl aminomethane ((HOCH$_2$)$_3$CNH$_2$). The SBF solution preparation detail were followed the process, which was described by Kokubo et al.$^{80}$ Table 3.1 is the comparison of ion concentrations of SFB white human blood plasma, and the final pH of SBF is 7.40 at 36.5°C.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ion concentration (mM)</th>
<th>SBF</th>
<th>Blood plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>142.0</td>
<td>142.0</td>
<td>142.0</td>
</tr>
<tr>
<td>K$^+$</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Mg$^+$</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Ca$^+$</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Cl$^+$</td>
<td>147.8</td>
<td>103.0</td>
<td>103.0</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>4.2</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td>HPO$_4^{2-}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.40</td>
<td>7.2-7.4</td>
<td>7.2-7.4</td>
</tr>
</tbody>
</table>

3.5.2 Electrochemical Experiment

The testing FSP Mg-HA and untreated AZ31B Mg coupons were cut into 6 mm x 6 mm x 5 mm then mounted in the cold epoxy. All the samples were polished unto 1200 girt SiC paper followed by ultrasonically cleaned with methanol for 2-3 minutes. All electrochemical corrosion measurements were performed by using a three electrode flat cell with water jacket (EL-FLAT-3,
Bio-Logic, Inc., Knoxville, TN, USA) as schematic in Figure 3.3. The cell contained 250 mL of medium and had an exposed working electrode area of 1 cm². The reference electrode used for these measurements was a saturated calomel electrode (SCE), and the counter electrode was platinum gauze counter electrode.

![Figure 3.3 The schematic of three electrodes cell in this present thesis](image)

The linear potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were carried out for all FSP Mg-HA and untreated AZ31B Mg coupons in SBF at constant temperature of 36.5°C a temperature close normal human body temperature. A BioLogic® SP-300 potentiostat/galvanostat and EC-Lab 10.40 software (BioLogic Inc., Knoxville, TN, USA). Prior starting the test, the sample surface was exposed in SBF for relaxation period of 1 hour to stabilize initial conditions. The polarization scan was started at a potential 150 mV below the corrosion potential measured, and the voltage scan rate was 1 mV/s. The EIS
measurements were performed at the corrosion potential with AC amplitude of 5 mV over the frequency range $10^5 \text{ Hz}$ to $10^1 \text{ Hz}$.

3.6 Immersion Tests

Immersion tests included weight loss measurement and biomineralization evaluation. All three FSP Mg-HA conditions and untreated AZ31B Mg coupons were mounted and vertically placed in SBF at constant temperature (36.5°C), as shown in Figure 3.4, to avoid gravity effect on corrosion behavior. The volume of SBF that was used for testing is calculated by Equation 3.1:

$$V_s = \frac{S_a}{10}$$

where $V_s$ is the volume of SBF (mL) and $S_a$ is the apparent surface area of coupon (mm$^2$).

![Figure 3.4 The schematic of immersion test](image)

In weight loss experiment the glass beakers were used to immerse testing coupons in SBF for different time periods (1 day, 4 day, 8 day, and 12 day). The pH value was monitored before and after the immersion. The coupons were removed from SBF and cleaned using boiling solution of 180 g/l chromic acid to remove the surface corrosion layer ($\text{Mg(OH)}_2$) and
then rinsed with methanol and dried in atmosphere prior measuring weight loss as suggested in the literature\textsuperscript{77}. The weight loss and corrosion rate were calculated according to Equation\textsuperscript{81, 82}:

\[
\text{Weight loss} = \frac{\text{Weight before immersion}}{\text{(Weight after cleaning/surface area)}} \\
\text{Corrosion rate} = \frac{8.76 \times 10^4 W}{\text{ATD}} 
\]

Where \( W \) is the weight loss (g), \( A \) is the original surface area of the coupon (cm\(^2\)), \( T \) is the immersion time (hour) and \( D \) is the density of the coupons (g/cm\(^3\))

The process of biomineralization test was similar to weight loss experiment, except that the SBF solution was refreshed every 24 hours to maintain a pH of 7.4. The coupons were removed from SBF and rinsed with D.I water and then dried in air. The mineralized surface morphology was observed by ESEM, and the element analysis of the mineralized coupons was conducted by VersaProbe\textsuperscript{TM} 5000 Scanning X-ray photoelectron spectroscopy (XPS) Microprobe. The monochromatic X-ray beam source at 1486.6 eV, 49.3 W, and 200 \( \mu \)m beam diameter was operated to scan upon the coupon surface. The vacuum condition was \( 5 \times 10^{-6} \) Pascal for the analysis.

3.7 Contact Angle Measurement

The surface wettability evaluation was carried out by a static sessile drop technique (contact angle measurement) by using CAM-Plus\textsuperscript{R} contact angle goniometer (Cheminstruments, Inc. Fairfiled, OH), equipped with a fiber optic light source. A liquid droplet of volume 3 \( \mu \)l
(droplet diameter of 2 mm) was placed on the thoroughly cleaned surface by a hypodermic syringe. The liquid droplet was placed on the surface for approximately 10 s to stabilize before the reading was taken. The measurement was carried out at room temperature (25°C) and a minimum of ten contact angle readings were taken on each testing surface to minimize errors in the measurement. In order to eliminate the error associated with the arbitrary tangential alignment, the contact angle was measured based on the patented half angle method (US Patent 5 268 733).

According to the Van Oss approach, the surface energy can be calculated by the following Equation:

\[(1 + \cos \theta) \gamma_L = 2 \left\{ (\gamma_{SL}^{LW} \gamma_{LL}^{LW})^{1/2} + (\gamma_{SL}^+ \gamma_{LL}^-)^{1/2} + (\gamma_{SL}^- \gamma_{LL}^+)^{1/2} \right\} \]

Equation 3.4

In this approach the \( \gamma \) is the surface energy, surface energy can be divided into the Lifshitz – van der waals surface energy (\( \gamma^{LW} \)) and Lewis acid-base surface energy (\( \gamma^{AB} \)) components as in the following Equations:

\[ \gamma = \gamma^{LW} + \gamma^{AB} \]

Equation 3.5

\[ \gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-} \]

Equation 3.6

Here \( \gamma^+ \) is the Lewis acidic or the electron-acceptor component, \( \gamma^- \) is the Lewis basic or the electron-donor component, \( \theta \) is the contact angle of liquid and solid, a subscript \( S \) is the solid, and subscript \( L \) is the liquid. To solve three unknown components, \( \gamma_{SL}^{LW}, \gamma_{SL}^+, \) and \( \gamma_{SL}^- \), in Equation 3.4, there were needed three well-characterized test liquids for calculation. One polar (1-Bromonaphthalene) and two polar liquids (water and Formamide) were used in the test, and
their surface energy is listed in Table 3.2. In order to correlate the surface energy calculation to bio-wettability of the sample, contact angle measurement was also performed for SBF solution.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( \gamma )</th>
<th>( \gamma^{LW} )</th>
<th>( \gamma^+ )</th>
<th>( \gamma^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Bromonaphthalen</td>
<td>44.4</td>
<td>44.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Formamide</td>
<td>58.0</td>
<td>39.0</td>
<td>2.28</td>
<td>39.6</td>
</tr>
</tbody>
</table>
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Phase Identification

The results of XRD pattern of all FSP Mg-HA composite samples and untreated AZ31B alloy are shown in Figure 4.1. The analysis revealed that the predominant phase in all FSP samples and untreated AZ31B alloy was α phase. HA peaks were the secondary phase exhibited in XRD pattern of all FSP Mg-HA samples, indicating that processes successfully introduced HA power into Mg matrix. Under a varying processing wt% of HA, it can be observed that there was no major phase change in the Mg and HA. It has been reported that the processing temperature is lower than the melting point of Mg (650 °C)\textsuperscript{86}, and HA is stable at this temperature\textsuperscript{87}. Thus, the chemical reaction between Mg matrix and HA powder for forming additional phase were minimal. However, from the variation in peaks intensities, it can be seen that the increasing in the amount of HA peaks at (300), (202), (302), and (401). Furthermore, with the increased processing HA amount from 5wt% to 20wt% the intensity of these peaks increased, and the highest intensity of HA peaks in XRD pattern can be found in Mg-20wt% HA sample. Although β-phase (Mg\textsubscript{17}Al\textsubscript{12}) as the intermetallic phase should be found in Mg-Al alloys, due to the low volume fraction of Al in AZ31B alloy the amount of β-phase is expected to be small (% by lever rule) and hence could be beyond the resolution of the XRD technique. Thus, the peaks corresponding to β-phase were absent in XRD pattern of all processing conditions.
Figure 4.1 XRD pattern of untreated AZ31B alloy and all various FSP Mg-HA composites samples

4.2 Microstructure

4.2.1 Scanning Electron Microscopy

Figure 4.2 shows the SEM secondary electron (SE) images of microstructure of untreated AZ31B alloy and SZ of FSP Mg-HA composite sample. Before FSP, the average grain size of AZ31B alloy that used in this thesis was measured as ~ 10 μm (Figure 4.2(a)). Comparing to untreated AZ31B alloy, Figure 4.2(b) clearly indicates that FSP resulted in refined equi-axed grains with average grain sizes ranging from 2 to 6 μm of SZ in FSP samples, indicating the occurrence of dynamic recrystallization during FSP. Although the various HA concentration
(5wt%, 10wt%, and 20wt%) was processed in Mg matrix, there were not significant different grain size between these FSP samples. The small grain size can provide beneficial effect for reducing the intensity of galvanic couple between grain interior and grain boundary. Figure 4.3(a) reveals the SEM Secondary electron (SE) image of the section area from FSP Mg-5wt%HA and Figure 4.3(b) to (e) demonstrates the elemental maps corresponding to the selected area obtained by EDS. The elemental maps confirm that the white particles appearing in the SE image are composed of Ca and P which signify HA. These observations indicate that through FSP the HA power was successfully incorporated into Mg matrix with fine and uniform distribution.

Figure 4.2 SEM SE images of (a) untreated AZ31B alloy and (b) SZ of FSP Mg-5wt%HA composite sample
4.2.2 Transmission Electron Microscopy

The study of nanoprecipitate was conducted by TEM, and Figure 4.4 (a) to (f) displays the refined grain images in bright field mode and precipitates images in dark field mode form 5wt%, 10wt%, and 20wt% HA samples. From Figure 4.4 (a) to (c) the α-Mg matrix grains can be confirmed by the HCP diffraction pattern, and black particles with ~ 1 μm in size are referred as HA since HA is harder than Mg for milling to become electron transparent. This size was also confirmed in SEM analysis (Fig. 4.2). It clearly shows that the population density of HA particles become larger in the high amount HA condition. Figure 4.4 (d) to (f) reveals the present of nanoprecipitates within Mg matrix. According to Mg-Ca binary phase diagram, intermetallic phase Mg$_2$Ca forms under 789.5 K. Due to the friction movement between tool and substrate,
stress and localized heat were introduced into Mg matrix and HA powder, which may cause decomposition of CaP from base HA\(^{73}\), then further resulting in the nucleation of \(\text{Mg}_2\text{Ca}\) within SZ. In addition, the corresponding diffraction ring patterns were indexed (Figure 4.4 (d) to (f)) and this confirms the presence of nano \(\text{Mg}_2\text{Ca}\) precipitates along with Mg. In addition, these precipitates were distributed within the grain. This is due to entrapped \(\text{Mg}_2\text{Ca}\) during the evolution of new grains during dynamic recrystallization in FSP\(^{77}\). Moreover, the area fraction of \(\text{Mg}_2\text{Ca}\) for FSP Mg-5wt%HA, Mg-10wt%HA, and Mg-20wt%HA was calculated by ImageJ\(^\text{tm}\) software and obtained 4.58 ± 1.28%, 6.69 ± 1.04%, and 11.65 ± 1.35%, respectively.
Figure 4.4 TEM images of (a) FSP Mg-5wt%HA, (b) FSP Mg-10wt%HA, (c) FSP Mg-20wt%HA in low magnification and precipitates images of (d) FSP Mg-5wt%HA, (e) FSP Mg-10wt%HA, and (f) FSP Mg-20wt%HA in high magnification
4.3 In Vitro Evaluation

The effect microstructure and phases discussed before was investigated on in vitro behavior namely electrochemical corrosion resistance, weight loss, bio mineralization and contact angle. These results are presented below.

4.3.1 Linear Potentiodynamic Polarization

Figure 4.5 shows the linear potentiodynamic polarization curves of untreated AZ31B alloy and FSP Mg-HA composites samples in SBF at 36.5 °C, and the corresponding parameters are listed in Table 4.1. All testing samples exhibited similar corrosion potential (E_{corr}) and appearing curve. However, due to the shifting of cathodic and anodic curves toward to more negative direction, the corrosion current density (i_{corr}) of all three FSP Mg-HA samples (1.95±0.60, 2.31 ± 0.13, and 5.15 ± 1.42 μA/cm², respectively) were lower than untreated AZ31B alloy (11.35±2.74 μA/cm²), manifesting the improvement in corrosion resistance because of the low chemical reaction rate while corrosion process. It can also be seen that all testing samples possessed passive region when scanning potential was between corrosion potential and pitting potential. This is generally believed that the Mg(OH)₂ passive layer formed during corrosion occur. Since the FSP only modified the grain structure and no essential change in substrate, E_{corr} are nearly the same as untreated AZ31B alloy (from -1.56 to -1.60 V).

Figure 4.6(a) to (d) displays the SEM SE images of corroded surface of untreated AZ31B alloy and all FSP Mg-HA composite samples, all corroded surfaces exhibited pit sits on the surface signifying the pitting corrosion was the predominated corrosion in SBF, which also was
reflected on pitting behavior in potentiodynamic polarization curves. Untreated AZ31B alloy experienced severely pitting corrosion during the measurement, which can be observed in the irregular pitting morphology from the corroded surface (Figure 4.6(a)). In addition, the pit size of the corroded surface of all FSP samples was smaller than on untreated AZ31B alloy, and pit morphology formed like circular-like cluster (Figure 4.6(b) to (d)) instead of irregular cavity. The reason for such a behavior is not clear at this point and further investigation is going to identify the reasons behind circular morphology.

Figure 4.5 Linear potentiodynamic polarization curves for untreated AZ31B alloy and all FSP Mg-HA composite samples, corroded surface morphology of (b) untreated AZ31B alloy and (c) FSP Mg-5wt%HHA sample
Figure 4.6 The SEM SE images of corroded surface morphology of (a) untreated AZ31B alloy, (b) FSP Mg-5wt%HA, (c) FSP Mg-10wt%HA, and (d) FSP Mg-20wt%HA
Table 4.1 Potentiodynamic polarization parameters for untreated AZ31B alloy and all FSP Mg-HA composite samples

<table>
<thead>
<tr>
<th>Processing condition</th>
<th>Corrosion potential ((E_{corr}, V))</th>
<th>(I_{corr}) (μA/cm²)</th>
<th>(\beta_a) (mV)</th>
<th>(\beta_c) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated AZ31B alloy</td>
<td>-1.57 ± 0.01</td>
<td>11.35 ± 2.74</td>
<td>131.40 ± 8.71</td>
<td>106.03 ± 1.09</td>
</tr>
<tr>
<td>FSP Mg-5wt%HA</td>
<td>-1.60 ± 0.01</td>
<td>1.95 ± 0.58</td>
<td>137.48 ± 8.16</td>
<td>111.7 ± 9.46</td>
</tr>
<tr>
<td>FSP Mg-10wt%HA</td>
<td>-1.58 ± 0.03</td>
<td>2.31 ± 0.13</td>
<td>129.0 ± 4.53</td>
<td>109.35 ± 5.63</td>
</tr>
<tr>
<td>FSP Mg-20wt%HA</td>
<td>-1.56 ± 0.01</td>
<td>5.15 ± 1.42</td>
<td>129.30 ± 8.90</td>
<td>106.30 ± 2.70</td>
</tr>
</tbody>
</table>

4.3.2 Electrochemical Impedance Spectroscopy

Figure 4.7 displays Nyquist plots of the untreated AZ31B alloy and FSP Mg-HA composite samples and the equivalent circuit used for fitting and analysis the curves, where \(R_s\) corresponds to electrolyte resistance, \(R_{CT}\) is charge transfer resistance, \(R_f\) is thin film resistance, and \(CPE_f\) and \(CPE_{CT}\) is constant phase element of thin film and charge transfer. CPE was used to replace the pure capacitors to offset the non-homogeneity of the system. The fitting data is presented in Table 4.2. The untreated AZ31B alloy and all FSP Mg-HA composite samples clearly exhibit a single capacitive loop in Nyquist plots, and the radius of each loop can be referred to the resist ability of sample to electrolyte. It can be observed that all three FSP Mg-HA composite samples obtained larger capacitive loop as well as the \(R_{CT}\) value compared to untreated AZ31B alloy. Also, the polarization resistance \((R_p = R_f + R_{CT})\) for FSP Mg-HA composite samples \((5.18±0.60, 4.57±0.63, \text{ and } 2.76±0.38 \times 10^4 \text{ ohm, respectively})\) was greater than untreated AZ31B alloy \((1.89±0.23 \times 10^4 \text{ ohm})\), indicating the enhancement of corrosion resistance in SBF via FSP. Nevertheless, it is clearly to see that with the HA weight percentage increasing, the value of \(I_{corr}\) increased and \(R_p\) reduced. Amount the FSP samples Mg-5wt% HA
performed better corrosion resistance ($i_{\text{corr}}$:1.95±0.60 μA/cm$^2$, $R_p$:5.18±0.60 ×10$^4$ ohm) compared to Mg-10wt%HA and Mg-20wt%HA. The similar results can be found from the previous works$^{89-91}$. Kirkland et al.$^{89}$ gave a statement to explain this kind of behavior. When alloying elements are added below their solubility limit, they tend to retard anodic kinetics in Mg matrix. Therefore it has been reported that addition of Ca into Mg leading the reduction in anodically active areas and improvement of corrosion resistance$^{90}$. Nevertheless, this effect reduces when the solubility limit is reached, and the alloying elements from intermetallic phase. In most case these intermetallic phase with higher potential than Mg will play as local cathodic site in matrix, resulting faster dissolution of Mg matrix. The increasing volume fraction of intermetallic phase will have accelerated the micro galvanic effect and hence the higher corrosion rate. The Mg$_2$Ca was reported as electrochemically active phase with corrosion potential $\sim$ -1.75 V in 1.0 M NaCl solution and large $i_{\text{corr}}$, and it obtains slightly higher $E_{\text{corr}}$ compared to pure Mg$^{45,92}$. In the present case, the existence of Mg$_2$Ca precipitate within FSP Mg-HA composite samples was confirmed by TEM, and the increasing volume fraction of the precipitate in SZ with large amount HA containing samples condition was also observed. Consequently, the micro galvanic effect within Mg matrix was enhanced, thereby causing the increasing of $i_{\text{corr}}$ when corrosion occurs.
Figure 4.7 EIS Nyquist plots and curve fitting equivalent circuit for untreated AZ31B alloy and all FSP Mg-HA samples

Table 4.2 EIS parameters of untreated AZ31B alloy and all FSP Mg-HA composite samples

<table>
<thead>
<tr>
<th>Sample Conditions</th>
<th>Rs (ohm)</th>
<th>Rf (×10^3 ohm)</th>
<th>RCT (×10^4 ohm)</th>
<th>Rp = Rf + RCT (×10^4 ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated AZ31B alloy</td>
<td>32.46±3.77</td>
<td>1.16±0.55</td>
<td>1.77±0.17</td>
<td>1.89±0.23</td>
</tr>
<tr>
<td>FSP Mg – 5% HA</td>
<td>35.52±8.42</td>
<td>1.34±0.31</td>
<td>5.05±0.58</td>
<td>5.18±0.60</td>
</tr>
<tr>
<td>FSP Mg – 10% HA</td>
<td>29.19±4.03</td>
<td>1.58±0.66</td>
<td>4.40±0.60</td>
<td>4.57±0.63</td>
</tr>
<tr>
<td>FSP Mg – 20% HA</td>
<td>24.89±3.59</td>
<td>0.78±0.04</td>
<td>2.68±0.39</td>
<td>2.76±0.38</td>
</tr>
</tbody>
</table>

4.3.3 Weight Loss and pH Measurement

The weight loss and pH change record after different intervals of time for all testing samples are shown in Figure 4.8. FSP Mg-20wt%HA obtained the highest corrosion rate through 1 to 12 days immersion. FSP Mg-10wt%HA showed higher corrosion rate in the early immersion stage and then similar corrosion rate in the late immersion stage compared to untreated AZ31B alloy. FSP Mg-5wt%HA exhibited the lowest corrosion rate among all the testing samples.
through all the immersion stage. It can be seen that the slope of the corrosion curves of all FSP Mg-HA composite samples were reducing (Figure 4.8(a)). It can be attributed to the formation of HA apatite layer on the surface during immersion. Such a layer usually has a low solubility in SBF, providing protection to the substrate surface\(^6\). On the contrary, the slope of curve for untreated AZ31B alloy was constant (Figure 4.8(a)), which means the acceleration of the degradation with the immersion time increase. This observation also reflected in pH change curve (Figure 4.8 (b)), which revealed the linear slope for untreated AZ31B alloy and the reducing slope for all FSP Mg-HA composite samples as the function of time. It has been reported that the consumption of hydrogen ions and releasing OH\(^-\) ions from Mg(OH)\(_2\) cause the alkalization of the solution \(^9^3, 9^4\). According to Equation 2.2, 2.3 and 2.4, the oxidation reaction and reduction reaction need to occur simultaneously in order to process the total reaction. Therefore, Mg ion concentration between surface and surrounding solution play a role to the formation rate of Mg(OH)\(_2\). In other words, the releasing Mg ions during corrosion influence the pH change indirectly. Thus, the results of pH change plots show that the releasing rate of Mg ions from substrate reduced with immersion time for all FSP samples, signifying the delay of degradation reaction on the surface.
Figure 4.8 SBF immersion test results: (a) corrosion rate and (b) pH change
4.3.4 Biomineralization

Table 4.3 displays the photographs of the testing samples before and after immersion test carried out in SBF for 1 day, 4 day, 8 day, and 12 day. Untreated AZ31B alloy and FSP Mg-20wt%HA underwent rapid mineralization in the initial immersion stage, compared to FSP Mg-5wt% and -10wt%HA samples. With increasing the immersion time, all testing samples formed various level of mineralization precipitates on the surface. It can be observed that untreated AZ31B alloy and FSP Mg-20wt%HA samples obtained porous surface and large mineralization area, and 5wt%HA and 10wt%HA samples surfaces appeared to be smooth. Although FSP Mg-10wt% HA sample seems to appear better corrosion resistance than FSP Mg-5wt%HA sample, it was due to the coverage of mineral and corrosion product layer. Figure 4.9 presents the SEM SE images of all testing samples after 12 day immersion and the corresponding EDS analysis of the chemical composition of the mineral phases. The mineral morphology of untreated AZ31B alloy appeared to be globular shape with petal-like surface structure (Figure 4.9 (a)) constituted by Mg, O, Ca, and P elements. Different from untreated AZ31B alloy, the mineralized phase which formed on all FSP Mg-HA samples were globular morphology (Figure 4.9 (b) to (d)) with same elements as be found on untreated AZ31B alloy. However, the results of EDS plots revealed that the predominated phase of mineral on untreated AZ31B alloy was Mg-based compound. Furthermore, in case of FSP Mg-HA samples as the intensities of Ca and P were much higher suggesting presence of CaP-based mineral. Although EDS analysis can provide the beginning estimation of the chemical elements, it does not give exact atomic ratio and information of type of compound of the mineralized phases. In light of that, XPS was carried out on the mineralized samples to analysis the chemical compounds and to quantify the elements in order to fill the
gap. XPS spectra of all test samples exhibited Mg2p, Mg 2s, Mg KLL, Ca 2p$_{3/2}$, Ca 2p$_{1/2}$, P 2p, P 2s, O 2s, and O1s peaks, Figure 4.10 displays Mg2p, Ca 2p$_{3/2}$, P 2p, and O 1s peaks of for each testing samples for study compound condition. The mineral phase on untreated AZ31 alloy appeared that shifting binding energy of Mg2p from 50 to 49.32 eV, signifying the tendency of forming Mg(OH)$_2$ compound within the mineralized phase. It could be the reason for causing the petal-like surface structure of the mineral surface morphology. On the contrary, it is clearly shown that the Mg 2p peak for all FSP Mg-HA samples were low intensity with minimal shift in binding energy, indicating that the mineral phase was mainly constituted by CaP based phase. The P 2p plot also indicates that the existence of phosphate (P$_2$O$_7^{4-}$) compound within mineral for all testing samples. Table 4.4 lists the semi-quantitative Ca and P atomic concentration and its ratio (Ca/P). Ca/P ratio range of 1.42 -1.60 for FSP Mg-HA samples, and hence is very close to the Ca/P atomic ratio of stoichiometric HA (1.64), This indicates that Mg-HA composite layer can provide good quality of mineral phase formation for bioactivity.
Table 4.3 Photographs of untreated AZ31B alloy and all FSP after immersed in SBF for 1 Day, 4 Day, 8 Day, and 12 Day

<table>
<thead>
<tr>
<th>Processing Condition</th>
<th>Before immersion</th>
<th>1 Day immersion</th>
<th>4 Day immersion</th>
<th>8 Day immersion</th>
<th>12 Day immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated AZ31B alloy</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
</tr>
<tr>
<td>FSP Mg-5wt% HA</td>
<td><img src="image6" alt="Image" /></td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
</tr>
<tr>
<td>FSP Mg-10wt% HA</td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
<td><img src="image15" alt="Image" /></td>
</tr>
<tr>
<td>FSP Mg-20wt% HA</td>
<td><img src="image16" alt="Image" /></td>
<td><img src="image17" alt="Image" /></td>
<td><img src="image18" alt="Image" /></td>
<td><img src="image19" alt="Image" /></td>
<td><img src="image20" alt="Image" /></td>
</tr>
</tbody>
</table>
Figure 4.9 SEM surface morphologies and corresponding EDS of the (a) untreated AZ31B alloy, (b) FSP Mg-5wt% HA, (c) FSP Mg-10wt% HA, and (d) FSP Mg-20wt% HA after 12 days immersion in SBF
Figure 4.10 XPS spectra of various elements of untreated AZ31B alloy and all FSP Mg-HA composite samples

Table 4.4 Elemental composition and semi-quantitative analysis of Ca and P in terms of atomic concentration for the untreated AZ31B alloy and FSP Mg-HA composite samples

<table>
<thead>
<tr>
<th>Processing Condition</th>
<th>Elements present</th>
<th>Ca atomic concentration (%)</th>
<th>P atomic concentration (%)</th>
<th>Ca/P atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated AZ31B alloy</td>
<td>O, Mg, Ca, P</td>
<td>5.2</td>
<td>1.06</td>
<td>4.91</td>
</tr>
<tr>
<td>FSP Mg-5wt% HA</td>
<td>O, Mg, Ca, P</td>
<td>11.99</td>
<td>7.51</td>
<td>1.60</td>
</tr>
<tr>
<td>FSP Mg-10wt% HA</td>
<td>O, Mg, Ca, P</td>
<td>9.8</td>
<td>6.89</td>
<td>1.42</td>
</tr>
<tr>
<td>FSP Mg-20wt% HA</td>
<td>O, Mg, Ca, P</td>
<td>10.00</td>
<td>6.51</td>
<td>1.54</td>
</tr>
</tbody>
</table>
4.3.5 Contact Angle Measurement  

Surface wettability play a critical role in the nucleation and crystal formation of apatite during mineralization process, especially at low pH condition. Table 4.5 displays the experimental contact angles measurement and corresponding surface energy calculation by D.I water, Formamide, and 1-Bromonaphthalen for untreated AZ31B alloy and all FSP Mg-HA composite samples. All FSP Mg-HA composite samples possessed the higher surface energy (43.02, 44.33, and 46.81 mJ/m², respectively) and lower SBF contact angle (Figure 4.11) than untreated AZ31B alloy (37.91 mJ/m²). The statistic data indicated the decreasing tendency of SBF contact angle with increasing HA contain in Mg matrix, indicating the improvement of surface wettability. Furthermore, Ca element is electrochemically very reactive, thereby the present of HA facilitates heterogeneous nucleation and increases the rate of HA apatite crystal formation and grow. Hence, the results of contact angle can correlate to the biomineralization observation (table 4.3), and it is clearly shows that FSP Mg-20wt%HA obtained highest surface energy (46.81 mJ/m²) and rapidly mineral formation on the surface compared to other FSP Mg-HA samples. Although untreated AZ31B alloy exhibited low surface energy (37.92 mJ/m²) and also rapid mineral formation, the quality of mineral was poor due to the over excess Ca/P atomic ratio (4.91). In addition, the quick formation process of it mineral phase was contributed by Mg(OH)₂ compound instead of Ca and P compound. Therefore, the surface wettability not only affects the rate of formation HA apatite, but also influence the quality of the mineralization.
Table 4.5 The contact angle measurement and resultant total surface energy of untreated AZ31B alloy and FSP Mg-HA composite samples

<table>
<thead>
<tr>
<th>Processing condition</th>
<th>Contact angle measurement</th>
<th>Surface energy components</th>
<th>Total surface energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D.I water</td>
<td>Formamide</td>
<td>Bromonaphthalene</td>
</tr>
<tr>
<td>Untreated AZ31B</td>
<td>72.90±3.01</td>
<td>59.60±2.62</td>
<td>35.00±2.12</td>
</tr>
<tr>
<td>FSP Mg-5%HA</td>
<td>49.50±1.50</td>
<td>44.20±5.19</td>
<td>18.20±3.68</td>
</tr>
<tr>
<td>FSP Mg-10%HA</td>
<td>49.20±1.25</td>
<td>42.40±3.44</td>
<td>21.00±1.73</td>
</tr>
<tr>
<td>FSP Mg-20%HA</td>
<td>48.50±2.65</td>
<td>48.80±2.09</td>
<td>16.71±3.37</td>
</tr>
</tbody>
</table>

Figure 4.11 SBF contact angle observation and measurement of untreated AZ31B alloy and all FSP Mg-HA composite samples
Additive technique friction stir processing was used to fabricate Mg-HA surface composite layer structure with various weight percentage (5wt%, 10wt%, and 20wt%) for enhancement of biocorrosion and biomineralization of AZ31B Mg bioimplant alloy. The results of XRD, SEM, and TEM showed the refined, equi-axed microstructures with heterogeneous chemical composition of predominately α-Mg phase in grain matrix, fine HA particles and Mg$_2$Ca nano-precipitates within the stir zone (SZ). There was no significant difference in grain size between FSP conditions (average grain size 2~6 μm). In addition, the volume fraction of HA and Mg$_2$Ca within SZ increased with increasing the processing HA weight percentage.

The results of potentiodynamic polarization (PDP) experiments showed that pitting corrosion was the predominant corrosion mechanism for all FSP Mg-HA composite samples and untreated AZ31B alloy. Three FSP Mg-HA composite samples exhibited the similar corrosion potential (-1.60, -1.58, and -1.56 V, respectively) compared to untreated AZ31B alloy (-1.57 V). The corrosion current density (1.95, 2.31, 5.15 μA/cm$^2$, respectively) of FSP Mg-HA composite samples was smaller than untreated AZ31B alloy (11.35 μA/cm$^2$). The fitting analysis of electrochemical impedance spectroscopy (EIS) plots revealed that the polarization resistance (5.18, 4.57, and 2.76 ×10$^4$ ohm, respectively) of three FSP Mg-HA samples and these values were larger than untreated AZ31B alloy (1.77×10$^4$ ohm). The analyzed data also shows that the
corrosion resistance of FSP Mg-HA sample decreased with increasing processing HA weight percentage into Mg matrix.

The results of weight loss and pH change indicated the stabilization of the corrosion rate on FSP Mg-HA samples during immersion. On the contrary, the corrosion rate of untreated AZ31B Mg constantly increased with the immersion increase in time. The mineral morphology formed on untreated AZ31B alloy appeared to be petal-like structure which contained consisting majority of Mg(OH)$_2$ compound. The feathery sphere morphology with highly pure CaP base of mineral was found on FSP Mg-HA samples after biomineralization. The Ca/P atomic ratio (1.60, 1.42, and 1.54, respectively) of the mineral phase on FSP Mg-HA samples confirmed the formation of HA apatite layer.

The results of contact angle measurement and surface energy calculation signified the improvement of biomineralization rate of FSP Mg-HA samples with increasing processing HA weight percentage.

The overall key conclusions of this work are as listed below.

1. The presence of HA particles, Mg$_2$Ca precipitates, and refined grain structure provided an enhancement of corrosion resistance of AZ31B.
2. The larger volume fraction of Mg$_2$Ca accelerated the galvanic effects with Mg matrix resulting in increase in overall corrosion rate.
3. The present of HA particles in Mg matrix provided improvement in surface wettability and process of biomineralization.

4. As a result it can be concluded that FSP with addition of appropriate amounts of HA can improve biocorrosion and bioactivity of AZ31B alloy for orthopedic implant application.
CHAPTER 6

FUTURE WORK

6.1 The Effect of Biominalization on Corrosion Behavior

Since the results of immersion experiments revealed that the formation of mineral provide protection to undersurface layer, resulting in stabilization the corrosion process. Therefore, it is possible to improve corrosion resistance of Mg alloy by controlling the formation rate of biominalization. Furthermore, the mineral phase also play a critical role for this matter. Thus, studying the effect of biominalization of corrosion behavior is the interesting issues to investigate.

6.2 Biocompatibility

One of the purposes to form HA apatite layer on Mg is to enhance the bonding between implant surface and cell in the blood for reduction of bone regeneration time. Therefore, cell attachment and cell absorption are most important characteristics to evaluate the interaction of mineralized surface to living cell.

6.3 Corroded Surface Morphology Investigation

It can be observed that the pitting sits formed as circles pattern on corroded surface on FSP Mg-HA samples. So far there is no similar observation been reported in the literatures. The
reasons behind such a pattern are not clear yet. Hence, the investigation for corrosion behavior of FSP Mg-HA sample is suggested to be done in the future work.
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