Corrosion Behavior of Magnesium Based Foam Structure in Hank’s Solution

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Abstract. Metal foam is a new class of materials with promising applications and a unique combination of physical, chemical, and mechanical properties. The purpose of biodegradable implants is to support tissue regeneration and healing in a particular application by material degradation and implant replacement through the surrounding tissue. Magnesium alloys are expected to be degraded in the body and its corrosion products not deleterious to the surrounding tissue. In the present study, the foam metal was manufactured via powder metallurgy with a different variation of sintering temperature and TiH₂ used as a foaming agent which are added to Mg-1Ca-3Zn alloy as much 3% wt TiH₂. The sintering temperatures were 500, 550 and 600 °C with a constant holding time of 5 hours. It’s critical that the sintering temperature is carefully selected in consideration of their corrosion behavior. This paper reports the study of the behavior of the Mg-Ca-Zn alloy metal foam which evaluated by SEM, EDX, and electrochemical corrosion test in Hank’s solutions. After exposure, the SEM result of Mg-Ca-Zn-3TiH₂ to Hank’s solution, a volcano-like structure is formed. The streams of H₂ bubbles form at local sites on the Mg alloy surface where electrochemical reactions are taking place, leading to the particular structure with around shape and often with a hole in the center. The corresponding EDS result maps reveal enrichment of O, Ca, P and Mg as corrosion product. Potentiodynamic polarization experiments conducted at 37 °C and pH 7.4 indicated the increased biodegradation rates resulted from porous structure of foam samples. Corrosion rate in 500°C sintering temperature were 1.99 millimiles per year (mmpy) with corrosion current density ($I_{corr}$) 87.3.10⁻⁶ A/cm², corrosion rate in 550 °C sintering temperature were 2.16 mmpy with $I_{corr}$ 94.4.10⁻⁶ A/cm² and rate in 600 °C sintering temperature were 2.41 mmpy with $I_{corr}$ 105.10⁻⁶ A/cm². The results showed that the increasing of sintering temperature could influence the corrosion resistance of Mg alloy.

Keyword: magnesium, alloy, corrosion, in vitro, Hank’s solution

1. Introduction

Research and development work on magnesium and magnesium-based alloys for bio-implant applications have increased significantly in recent years [1-3]. Magnesium (Mg) and magnesium alloys as a new kind of biomedical material have attracted increasing attention due to their unique advantages. The mechanical properties of Mg and its alloys such as Young’s modulus of elasticity ($E$ = 41-45 GPa) and density (1.74-1.84 g/cm³) are known to be similar that of bone ($E$ = 15-25 GPa and density = 1.8-2.1 g/cm³). This is lower than other biodegradable materials such as iron-manganese (Fe-
Mn) and zinc (Zn) based alloys [4]. Corrosion of metal implants is critical due to it can adversely affect the mechanical properties and biocompatibility. Simultaneously, the materials used should not cause any adverse biological reaction in the body, and they must be stable retaining their functional properties. Mg element is the fourth most abundant in the human body, and Mg\(^{2+}\) is an essential element for the human body and the daily intake of Mg\(^{2+}\) for a normal adult is about of 300-400 mg. A high content of Mg is naturally found in the skeleton [5]. Excess magnesium ions are harmless and can be excreted in the urine, while toxic element releases lead to metal allergy and skin disease, such as Ni in 316L. Magnesium alloys can be biodegraded in the human body by corrosion, which can eliminate second surgery for implant removal. Some in vivo studies showed that the degradation of the magnesium alloy is harmless [3,6,7]. Additionally, it has been reported that magnesium stents can be successfully degraded and have a minimal effect on the surrounding tissue [8,9].

As bone regeneration increases, the resorption of the implant material introduces an augmented load transmission to the bone. A period of 6–18 months is desired for the remodeling process to be completed [10]. Since the stiffness of metals greatly exceeds the stiffness of bones, the cellular metals with low young’s modulus have been proposed to avoid the resulting problems of stress shielding [11-13]. Cellular metals typically fall within the stiffness range of cancellous bone [14]. Metal foams enable bone cells in growth and blood vessels incorporation promoting implant stabilization [10,11,15]. In the ideal case, progressive osteointegration on the one hand and degradation of the implant, on the other hand, guarantee an optimal adaptation to the corresponding strength state at any time [10].

Mg and its alloys are now viewed as a potential alternative for making a scaffold for tissue regeneration application due to a combination of their excellent mechanical properties and degradability. Mg is necessary for calcium incorporation into bone, and so the release of Mg ions is expected to be beneficial for bone healing [16]. The cellular or foam structure magnesium materials have been developed and examined in clinical tests as implant materials in bone surgery [17] and cardiovascular surgery [18]. It was found that even though this material is highly biocompatible and features excellent osteoconductivity; it corrodes at such a high speed that the newly established bone is not yet able to carry the load necessary. Biodegradable Mg foam alloys are breaking the current mold in biomaterial science of developing only corrosion resistant metals. In biomedical applications, Mg alloy also ideal implants due to their outstanding comprehensive performance compared with other materials, such as stainless steel, polymers, and ceramic.

Various in vitro and in vivo tests have to be carried out in order to identify appropriate materials for use as surgical implants. It is desirable to keep the metal ion release to a minimum by the use of corrosion-resistant materials because corrosion is the first consideration for a material of any type that is to be employed in the body because metal ion release takes place mainly due to corrosion of surgical implants. Some individuals are sensitive to metals, and some may develop metal sensitivity later after receiving an implant. The environment of the body is extremely well buffered so that the pH is maintained at around 7.4 at 37 °C. Corrosion behavior of materials can be studied either in vivo or in vitro using artificial physiological fluids in which the oxygen content is controlled at a suitably low value at 37 °C. Hank’s solution is an example of an artificial solution, which has been used over a period of corrosion testing in the laboratory [19].

This work aims at examining the electrochemical degradation behavior of Mg-Ca-Zn metal foam (3 wt% of TiH\(_2\)) with variation sinter temperature (500, 550, and 600 °C) using electrochemical techniques in Hanks solution. Scanning Electron Microscope (SEM), Energy Dispersive Spectrometer (EDS) and electrochemical measurement were used for corrosion, post-corrosion and fracture surface analysis.

2. Experimental Method
Mg–Zn–Ca alloys were prepared by powder metallurgy method. The starting materials were high purity Magnesium (Merck KGaA, 98.5% pure, D 0.06-0.3 mm), Zinc (Merck KGaA, D < 45 µm), Ca granule (Merck KGaA, ≥ 98.5% pure, D < 2.6 mm) and TiH\(_2\) fine powder serving as foaming agent (98% pure)
were used to prepare foamable precursors. The TiH$_2$ was heat-treated at 450 °C for 120 min in argon in order to shift the hydrogen release range to higher temperatures, which is essential for a good foam structure [20]. The compositions were designed in this work was Mg–3Zn–1Ca with 3% TiH$_2$ in weight percentages. The powders were mixed in shaker mill for 120 min. As-milled powders were subsequently compacted at room temperature in a cylindrical die of 10 mm in diameter and 10 mm in height (green compact) under a pressure of 100 MPa for 2 min then 200 MPa for 3 min by using a hydraulic press. The green compact was sintered in an alumina crucible at the sintering temperature 500, 550, and 600 °C with constant holding time for 5 hours in argon condition and with natural cooling rate to reach ambient temperature. The heating rate was programmed to be 5 °C/minute.

For microstructural examination using optical microscopy, the specimens were prepared by standard metallographic procedures and were etched in a solution containing 3.5 g picric acid, 6.5 ml acetic acid, 20 ml water, and 100 ml ethanol. A detailed study of microstructure and the secondary phase particles distributed in the alloys was done using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analyzer for chemical microanalysis technique. SEM provides detailed high-resolution images of the sample by focusing the electron beam on the surface and detecting secondary or backscattered electron signal. An EDX is also used to provide elemental identification and quantitative compositional information.

In this study, the in vitro corrosion were carried out in the electrochemical studies were conducted using Gamry Instruments G750 potentiostat, interfaced to a computer. A three-electrode cell was used for electrochemical measurements. The counter electrode was made of carbon, and the reference electrode was saturated calomel electrode (SCE). The exposed area of the working electrode was Mg alloy foam to the solution was 1 cm$^2$. All the measurements were carried out on an electrochemical workstation at the temperature of 37 °C and pH value of 7.4 in Hank’s solution [21]. The simulated body liquid electrolyte was Hank’s solution, and composition of Hank’s solution used was in Table 1. The freshly prepared solution was used for each experiment. A constant electrolyte temperature of 37 ± 2 °C was maintained. The potentiodynamic polarization tests were carried out from -200 mV to +200 mV at a scanning rate of 0.5 mV/s. The corrosion rate was determined using the Tafel extrapolation method.

| Component        | Concentration (g/L) |
|------------------|---------------------|
| NaCl             | 8.0                 |
| KCl              | 4.0                 |
| CaCl$_2$         | 0.14                |
| MgSO$_4$.7H$_2$O | 0.1                 |
| NaHPO$_4$        | 0.048               |
| NaHCO$_3$        | 0.35                |
| Glucose          | 1.0                 |
| KH$_2$PO$_4$     | 0.6                 |
| MgCl$_2$.6H$_2$O | 0.1                 |

3. Results and Discussion

3.1. EDX and SEM before corrosion process

The EDX spectra of the corresponding microstructures of the three sintering temperatures of Mg metal foam alloys are shown in Figure 1. Quantitative EDX data of the spot composition are given in Table 1. The increasing of the sintering temperature of Mg alloy foam have increased the pore size of magnesium alloy. The thermal pre-treatment of TiH$_2$ with argon was a useful property since it improves metal foam generation. The effect was attributed to oxide layers around the cores of TiH$_2$ particles which build up during heat treatment and act as diffusion barriers to hydrogen [22]. Oxide layers on titanium hydride particles modify their hydrogen desorption behavior because they form an efficient diffusion barrier [23, 24].
Table 2. Spot element of mg alloys before electrochemical reaction.

| Temperature sinter (°C) | Mg   | Ca   | Zn   | Ti   |
|-------------------------|------|------|------|------|
| 500                     | 79.78| 5.79 | 6.61 | 7.82 |
| 550                     | 80.89| 5.18 | 6.76 | 7.17 |
| 600                     | 82.87| 5.05 | 6.19 | 5.89 |

Figure 1. EDX spectra of Mg-Ca-Zn-TiH₂ at sintering temperatures of (left) 500 °C, (right) 550 °C and (center) 600 °C. The corresponding optical microstructures are presented as insets.

The oxide layer in TiH₂ foaming agent make the foam more stable, so that need the higher sinter temperature can make the layer break, which resulted in the release of hydrogen in Ti and formed the foam structure [25]. It correlates with the pore diameter changed significantly with an increasing in higher sinter temperature. The higher heat of reaction seems to make the viscosity of the molten or semi-solid specimen lower. Under this condition, the growth of pores (the growth of small pores or coalescence of pores) becomes easier, and the size of pores becomes larger. The EDX quantitative spot element composition analysis shows in Mg-Ca-Zn-TiH₂ alloy shift is not significant substantially changes with increasing the sintering temperature.

3.2. Electrochemical measurement

The increasing of biodegradable or corrodible alloys for medical become higher because the degradation or decomposition the material which was corroded in the body’s solution has a potential for orthopedic or cardiovascular application. Corrosion potential (E_{corr}) and current density (I_{corr}) is calculated by extrapolation intersection from anode and cathode of line Tafel. The electrochemical polarization curves of the alloy with three different sinter temperatures, as shown in Figure 2. The corresponding electrochemical data are given in Table 3.
The corrosion rate values show that the increasing sintering temperature to magnesium alloy shifts the corrosion potential towards more corroded. The anodic polarization curves show a passivation-like region in all the alloys. However, the current density in this region is substantially lower in lower sintering temperature. All the alloys showed a similar break-down potential at 1.5 V. The increasing of sinter temperature, as generally resulted in the increasing of porosity, so that can decrease the corrosion potential. The positive line in Tafel diagram indicated any decreasing the corrosion rate. Significant value occurred at sinter temperature 500 °C and 600 °C. At sinter temperature 500 °C, produce lower foam in Mg alloy foam. It can be formed the passive layer in Mg material that exposed in atmosphere condition and becomes a protective layer [26]. Song etc. reported that magnesium oxide layer could hinder the direct contact with a solution [27]. Ca/P compound precipitated on hydroxide layer from hank solution as corrosion product. The increasing corrosion rate in Mg alloy was association with potential corrosion become more negative. Cl⁻ ion can be penetrated from corrosion layer, distract the layer structure and reacted with the metal substrate.

However, pores are inherent defects that make the materials mechanically weak while electrochemically active; there is a decrease in corrosion resistance due to the larger surface area exposed to the electrolyte compared to non-porous materials. A previous study [25] has shown that the sintered porous Mg alloy with a higher porosity ratio underwent more severe corrosion than the
sample with a lower porosity because of the larger real surface area. With higher porosity and larger pore size have poorer corrosion resistance.

3.3. SEM and EDS investigation after electrochemical process

In Figure 3, showed the details foam material surface after corrosion. Foam material surfaces were rough and damage. Corrosion propagation was seen in Figure 3 (b) and (c) because of the highest sintering temperature. In a small pore, the solution can become acidic or oxygen deficient, resulting in an autocatalytic process by which localized corrosion accelerates. From Figure 3, an increase of the porosity, many pores exhibit irregular shape. And the inner walls of the pores are generally unsmooth. These features may also be vulnerable sites and imperfections in any passive films. When the porosity increases, the interconnectivity of larger pores is clearly increased. For the samples with a lower porosity, the majority of the pores are the middle pores and small pores, which are unlikely to have trapped appreciable volumes of solution. This causes the samples relative resistance to induce corrosion. When the porosity increases, the interconnectivity of the larger pores is markedly improved. The interconnected channels allow the free flow of the liquid and fewer sites are available to induce corrosion.

![Image of Figure 3](image.png)

**Figure 3.** Corrosion morphology after electrochemical process at sintering temperatures of (a) 500 °C, (b) 550 °C, and (c) 600 °C.

It would be expected that Mg and Mg alloys be vulnerable to general corrosive attack because they are highly reactive. The corrosive attack on Mg is local rather than general although Mg is highly reactive. After exposure of Mg-Ca-Zn-TiH₂ to Hank solution, a volcano-like structure formed. It is clearly evident that the localized corrosion occurs, as shown in Figure 3. The spherical corrosion
morphology suggests that H2 bubbles form at the corrosion sites. The Mg dissolution is accompanied by H2 evolution. The H2 evolution occurs in the form of bubbles. The steams of H2 bubbles form at local sites on the Mg alloy surface where electrochemical reactions are taking place, leading to the peculiar structure with a round shape and often with a hole in the center as shown in Figure 4. H2 evolution is always from cathodic sites. Thus the second phases within the spherical structure are the water reduction areas which act as cathodes [28].

Figure 4 presents the genesis of the volcano-like corrosion morphology in Mg alloy schematically, showing the micro-galvanic corrosion process suffered by Mg alloys. The Mg dissolution results in the formation of Mg oxide products (Mg(OH)2) on the Mg surface, according to the reaction 5.1 to 5.3.

\[
\text{Anodic: } \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad (1)
\]
\[
\text{Cathodic: } 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (2)
\]
\[
\text{Product: } \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad (3)
\]

According to the cathodic reaction (in Equation 2), the local pH increases due to local generation of OH\(^-\) ions. Consequently, corrosion products (such as Mg(OH)2) are easily formed at areas adjacent to the second phases. The volcanic-like structure adjacent to the cathodic is accumulated by the Mg(OH)2. The formation of Mg(OH)2 is stimulated by the cathodic water reduction releasing OH\(^-\) and by anodic Mg corrosion releasing Mg\(^{2+}\).

Besides the formation of Mg(OH)2, other corrosion products are generated during exposure to the complex electrolyte (Hank’s solution). The presence of OH\(^-\) near the Mg surface promotes the transformation of HPO\(_4^{2-}\) in Hank’s solution into PO\(_4^{3-}\). It is expected that Ca\(^{2+}\) and PO\(_4^{3-}\) ions diffuse from Hank’s solution towards the Mg surface and are incorporated in the corrosion layer Mg(OH)2 as corrosion products. The solubility product constant of Ca\(_5\)(PO\(_4\))\(_3\)(OH) and Mg\(_3\)(PO\(_4\))\(_2\) is smaller than for Mg(OH)2 [29]. Thermodynamically, Ca\(_5\)(PO\(_4\))\(_3\)(OH) and Mg\(_3\)(PO\(_4\))\(_2\) are more stable than Mg(OH)2. Thus, the final products are Mg(OH)2, Ca\(_5\)(PO\(_4\))\(_3\)(OH) and Mg\(_3\)(PO\(_4\))\(_2\) [30].

Yu Lu reported that the localized corrosion has occurred in the Mg matrix rather than in the second phase, and the elemental distribution at a localized corrosion site in Mg alloy suggesting an enrichment of O, P, Ca and Mg. From EDS result in Figure 5 after electrochemical test also produced O, Mg, Ca, P also Zn and Ti. The cluster of corrosion products is because the increase of local pH around the corroded site promotes their formation. The water reduction at the cathodic particle results in a locally increased pH.

**Volcano-like morphology**

![Volcano-like morphology](image)

**Figure 4.** Schematic of volcano-like corrosion mechanism of Mg Alloy Mg-Ca-Zn-TiH\(_2\) metal foam volcano-like morphology.
Figure 5. EDS Spectra on Mg-Ca-Zn-TiH₂ alloy foam at sintering temperatures of (a) 500 °C, (b) 550 °C, and (c) 600 °C.

4. Conclusion
The corrosion behavior of Mg-Ca-Zn alloy foam in hanks solution showed that the corrosion resistances magnesium alloy, in generally, decrease as the increasing the sintering temperature. Higher sintering temperatures resulted in the higher pores in metal foam and the samples with higher porosities suffer severer corrosion than the ones with lower porosities because the real surface areas of
porous generally increase with the increasing porosities. The localized corrosion is observed in all Mg-Ca-Zn alloy foam in 3 different sinter temperature. There are prominent volcano-shaped corrosion pits indicated by the accumulation of corrosion products locally. The volcano-shaped structure is formed around central which act as cathodes.

5. References
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