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The role of solution heat treatment on corrosion and mechanical behaviour of Mg–Zn biodegradable alloys

A. Fereidouni Lotfabadi*1,2, H. R. Bakhsheshi-Rad1,3, M. H. Idris1, E. Hamzah1 and M. Kasiri-Asgarani3

The mechanical properties and bio-corrosion behaviours of T4 solid solution heat-treated Mg–1.5Zn and Mg–9Zn alloys at 340°C under different heat treatment durations were investigated. In vitro corrosion behaviour of the heat-treated alloys immersed in simulated body fluid (SBF) were measured by electrochemical, hydrogen evolution and mass loss tests. Surface examination and analytical studies were carried out using optical and scanning electron microscopy, EDX, and X-ray diffractometry. The results show that the grains size of both the alloys apparently remained unchanged after T4 treatment. T4 treatment at 340°C for 6 h slightly increased the strength and elongation of Mg–1.5Zn alloy while it significantly improved the strength and elongation of the Mg–9Zn alloy because of the presence of residual Mg51Zn20 and Mg12Zn13 secondary phase at the grain boundary. The results of electrochemical tests show that the corrosion rate of both the alloys decrease with increasing treatment temperature. The result also shows corrosion resistance of both the T4 treated alloys much better than that of as-cast samples. The corrosion mechanism exhibited that the occurrence of galvanic and pitting corrosion, which varied with the alloy composition and treatment time.

On a examiné les propriétés mécaniques et le comportement à la corrosion biologique des alliages Mg-1.5Zn et Mg-9Zn avec traitement thermique de solution solide T4, à 340°C et à différentes durées du traitement thermique. On a évalué in vitro le comportement à la corrosion des alliages traités thermiquement et immergés dans un liquide organique simulé (SBF) au moyen de mesures électrochimiques, de l'évolution d'hydrogène et de la perte de masse. On a effectué un examen de la surface et des études analytiques en utilisant la microscopie optique et la microscopie électronique à balayage, ainsi que les techniques EDX et XRD. Les résultats montrent que la taille de grain des deux alliages est demeurée apparemment inchangée après le traitement T4. Le traitement T4 à 340°C pendant 6 h a légèrement augmenté la résistance à la sollicitation et l'allongement de l'alliage Mg-1.5Zn alors qu'il a amélioré significativement la résistance à la sollicitation et l'allongement de l'alliage Mg-9Zn, grâce à la présence de phases résiduelles secondaires de Mg51Zn20 et de Mg12Zn13 dans les joints de grain. Les résultats des mesures électrochimiques montrent que la vitesse de corrosion des deux alliages diminue avec l'augmentation de la température de traitement. Les résultats montrent également une meilleure résistance à la corrosion des deux alliages avec traitement T4 par rapport aux échantillons de
brut de coulée. Le mécanisme de corrosion a montré que l’occurrence de corrosion galvanique et de corrosion par piqûres variait en fonction de la composition de l’alliage et de la durée de traitement.

Keywords: Mg alloy, Solution treatment, Corrosion behaviour, Mechanical properties

Introduction

The development of biodegradable materials has attracted a great deal of attention in recent years. The idea of using biodegradable implants is to assist tissue revival and healing in a particular request; this will take place by degradation of specific materials and replacement of current implants through the nearby tissue. Compared with present biodegradable materials such as polymers, ceramics, or bioactive glasses, biodegradable metallic materials represent enhanced behaviour in load bearing applications because of their higher tensile strength and Young’s modulus. Among biodegradable metallic materials, Mg-based alloys are physiologically compatible and they are biodegradable in the human body and also they can stimulate bone formation. Mg as a lightweight metal has closer elastic modulus (44 GPa) to natural bone (17 GPa) than the traditional metallic implant materials such as stainless steel, titanium alloys and cobalt chromium alloys. Fracture toughness and compressive yield strength (YS) of Mg is more comparable to the natural bone than the other metallic biomaterials like Ti alloys. However, its poor corrosion resistance and high degradation rate not only affects the implantation service duration before healing but also considerably decreases its mechanical properties, which cause failure of bone healing. Therefore, it is essential that the corrosion resistance of magnesium alloys be enhanced to better suit the alloys for biomedical application. Alloymg and heat treatment are the main tools to enhance the corrosion resistance of Mg alloy. To guarantee the biosafety of biodegradable materials, the constitutional elements of magnesium-based alloys should be toxic free. As far as the effects of rare earth (RE) elements on the human body is unknown and based on various investigations, the existence of RE (Pr, Ce, Y, etc.) elements could cause hepatotoxicity study of Mg–Zn binary alloys and their improvement is on demand. Zn is one of the most abundant nutrition essential elements in the human body. It appears in all enzyme classes and has basic safety for biomedical applications. Zn is known to increase age hardening response as it produces intermetallic compounds and refine the grain size. Zn addition because of solid solution strengthening can improve alloy strength. In addition, the ability for casting also can be improved by Zn addition. Heat treatments can cause microstructural changes and redistribution of metal elements, which have significant effect on the corrosion behaviour of the alloy. The effect of T4 and T6 treatment on the corrosion behaviour of Mg–5Zn alloy was investigated by Song et al., and their result indicated that the best corrosion resistance was obtained after T4 treatment. Chang et al. investigated corrosion and electrochemical behaviours of NZ30K alloy after heat treatment, and their result revealed that T4 treated sample showed lower corrosion rate because of the dissolution of cathodic compound and higher Nd content in x matrix. However, Liu et al. showed that solution treatment followed by aging leads to formation of homogeneous microstructure, which enhances the corrosion resistance of the AZ63 alloy. Several studies have investigated the effect of Zn concentration on the corrosion behaviour of Mg–xZn alloys. However, the effect of the T4 heat treatment on the corrosion resistance of binary Mg–Zn alloys with low and high concentration of Zn in a simulated body environment has been seldom probed. Therefore, the main aim of the present study is preparation of two binary Mg–xZn alloys (x=1.5 and 9) and investigated the effect of T4 treatment on the microstructure, mechanical property and corrosion behaviour of the alloy.

Materials and methods

Magnesium alloys were prepared by melting 99.99% pure magnesium ingots and 99.99% pure zinc chips. The materials were melted by electrical resistance furnace under a protective atmosphere in a stainless steel crucible at 750°C. The melt was stabilised by keeping at molten state for nearly 45 min. After stabilisation, molten metal with different Zn contents (1.5 and 9 wt.%) was poured into mild steel moulds, which had been preheated at 400°C accompanied by a 30 s stirring process. Specimens 15 × 15 × 10 mm in size have been prepared from the as-cast alloy ingots, and the samples were then mechanically wet ground for microstructural observation. T4 solid solution heat treatment at 340°C for 6, 12 and 18 h was carried out followed by hot water quenching at around 70°C. For microstructure observation, a scanning electron microscope (SEM) equipped with EDS analysis was used. Phase identification also was carried out by X-ray diffractometry (XRD). For electrochemical tests, rectangular specimens, with a surface area of 1 cm², were mounted in epoxy resin. The test was conducted at 37°C in an open-air glass cell containing 350 mL Kokubo solution with a pH of 7.44, using a PARSTAT 2263 potentiostat/galvanostat (Princeton Applied Research; AMETEK; USA). A three-electrode cell was used for potentiodynamic polarisation tests. The reference electrode was a saturated calomel electrode (SCE), the counter electrode was a graphite rod, and the specimen was the working electrode. The samples were immersed in the simulated body fluid (SBF) for 1 h before the electrochemical test to establish the open-circuit potential. All experiments were carried out at a constant scan rate of 0.5 mV s⁻¹, initiated at −250 mV
relative to the open-circuit potential. The immersion test procedure was carried out based on the ASTM: G1–03. The specimens were then immersed in a beaker containing 200 mL of Kokubo SBF with a chemical composition as listed in Table 1. The SBF was not replenished during the testing period. The minimum amount of solution volume to specimen surface area is $20 \text{ mL cm}^{-2}$. The average pH of the SBF was measured ($n=3$) after an immersion time of 24 h. The hydrogen evolution rate of the specimens was also measured during the 144 h immersion in Kokubo solution. The specimens were immersed in a beaker containing 250 mL of SBF, where a funnel was located over the sample to collect evolved hydrogen in a burette (50 mL) placed above the funnel. The SBF was renewed every 24 h after recording the hydrogen evolution rate (mL cm$^{-2}$ day$^{-1}$). At least two specimens were used to verify the reproducibility of the measurements. Tensile tests were performed by using an Instron-5569 universal testing machine at a displacement rate of 2.0 mm min$^{-1}$ at ambient temperature. Specimens with a diameter of 6 mm and a gauge length of 30 mm were machined for tensile test. For each testing material, two specimens were examined.

Results and discussion

Microstructure analysis

Figure 1 shows the as-cast and T4 solution treated microstructure of Mg–$x$Zn alloys with different treatment duration. As can be seen in Fig. 1a, the as-cast microstructure of Mg–1.5Zn contained primary $\alpha$-Mg and secondary phase. Meanwhile, the microstructure of the as-cast alloy after being heat treated for 6, 12 and 18 h remained unchanged and almost similar quantity of secondary phases can be observed (Fig. 1b–d). This observation can be explained according to binary Mg–Zn alloy phase diagram$^{20}$ and thermal analysis detection of Mg–Zn alloys, which have been reported elsewhere,$^{21}$ the temperature of Mg$_{12}$Zn$_{13}$ phase formation is distinct from the solution treatment temperature. Figure 1e–h indicates the microstructure of Mg–9Zn alloys, both as-cast and T4 treated for 6, 12 and 18 hours. The as-cast Mg–9Zn alloy microstructure contained primary $\alpha$-Mg and the secondary phases (Mg$_{12}$Zn$_{13}$ and Mg$_{51}$Zn$_{20}$). However, after 6 h of T4 treatment, it can be observed that the amount of secondary phases decreased but these phases were not completely dissolved in the matrix. Also extending the T4 treatment time did not affect the microstructure significantly.

The SEM micrographs of Mg–1.5Zn and Mg–9Zn alloy both as-cast and T4 heat-treated specimens were shown in Fig. 2. As can be seen from the Fig. 2a, the microstructure of Mg–1.5Zn alloy consisted of $\alpha$–Mg and Mg$_{12}$Zn$_{13}$ secondary phases which indicating the formation of ($\alpha$-Mg+Mg$_{12}$Zn$_{13}$) along the grain boundaries. The corresponding EDS analysis suggested that the dark area, which is composed of Mg and Zn, is

<table>
<thead>
<tr>
<th>Solution</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>HCO$_3^-$</th>
<th>Cl$^-$</th>
<th>HPO$_4^{2-}$</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>27.0</td>
<td>103.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Kokubo (c–SBF)</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>4.2</td>
<td>147.8</td>
<td>1.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

1 Optical microscopic images of a as-cast Mg–1.5Zn and heat-treated alloys with different heat treatment times b 6 h, c 12 h, d 18 h, e as-cast Mg–9Zn and heat-treated alloys with different heat treatments time, f 6 h, g 12 h and h 18 h
related to the Mg₁₂Zn₁₃ evolution phase. However, the microstructure of the T4 heat-treated Mg–1.5Zn alloys shows no significant change. Based on the reported thermal analysis of Mg–1.5Zn alloy²¹ during solidification process of Mg–Zn alloys, Mg₁₂Zn₁₃ phase was formed around 510°C. The solid solution treatment process was carried out at 340°C, which is lower than the formation temperature of Mg₁₂Zn₁₃ phase. Therefore, the solution treatment could not affect this phase. Also, EDS analysis of the Mg–1.5Zn sample shows that the grain boundaries were enriched with Zn, which indicated the formation of Mg₁₂Zn₁₃ phase within the grain boundaries (Fig. 2b). SEM micrograph of Mg–9Zn alloy (Fig. 2c and d) in comparison with the one for the Mg–1.5Zn alloy consisted of high quantity of Mg₅₁Zn₂₀ phase in addition of Mg₁₂Zn₁₃ phase at the grain boundaries. In this situation, within the grain boundaries, the eutectic phases (α-Mg + Mg₁₂Zn₁₃ + Mg₅₁Zn₂₀) formed, also the width of the grain boundaries became thicker as Zn content increased from 1.5 to 9 wt-%. EDS analysis further confirmed bright precipitates located along the grain boundaries composed of Mg and Zn (Fig. 2c and d). For Mg–1.5Zn alloy as the molten metal solidifies, primary α-Mg forms, then rejection of alloying elements takes place from the primary magnesium at the liquid–solid interface as a result of further reduction in temperature. When the metal cools down to eutectic temperature, intermetallic phase (Mg₁₂Zn₁₃) precipitates at the grain boundary. However, by adding 9 wt-% Zn to pure Mg, solidification did not complete with the formation of Mg₁₂Zn₁₃ phase. At the final stage of the solidification process, decreasing the temperature caused the formation of Mg₅₁Zn₂₀ intermetallic phase. However, heat treatment of as-cast Mg–9Zn alloy resulted in decreasing and dissolving of Mg₅₁Zn₂₀ phase (bright colour) in the Mg matrix. Figure 2c and d shows the SEM micrographs of Mg–9Zn alloy before and after 6 h solid solution treatment. It can be seen that a considerable amount of Mg₅₁Zn₂₀ phase remained undissolved in the matrix after the treatment. This phenomenon can be described that the maximum solubility of Zn in Mg base on Mg–Zn phase diagram²² is 6.2 wt-% at 340°C; therefore, the whole Mg₅₁Zn₂₀ phase cannot be dissolved in Mg matrix in Mg–9Zn alloy and a considerable amount of this phase can be detected in the micrograph after solid solution treatment.

According to XRD pattern of solution treated and as-cast samples of Mg–1.5Zn and Mg–9Zn alloys, only the reflections of α-Mg matrix and Mg₁₂Zn₁₃ phases were observed for the Mg–1.5Zn specimen (Fig. 3a). For the Mg–9Zn alloy, the reflections of Mg₅₁Zn₂₀ intermetallic phase appear apart from the defined Mg and Mg₁₂Zn₁₃ peaks (Fig. 3b). However, with increasing the heat treatment time to 18 h, the intensity of Mg₁₂Zn₁₃ intermetallic
phase in Mg–1.5Zn alloy slightly decreased. For Mg–9Zn samples, XRD patterns indicate that during the solution treatment the Mg51Zn20 phase is dissolved into the Mg matrix but a small amount of this phase in addition to the Mg12Zn13 phase still remains in the matrix.

Electrochemical measurements

Figure 4 shows the potentiodynamic polarisation test results of the as-cast and solution treated Mg–1.5Zn and Mg–9Zn alloys, which were recorded after 1 h exposure to Kokubo solution. From the graphs, it can be seen that Mg–9Zn alloy compared to Mg–1.5Zn alloy shows more negative corrosion potential; this phenomenon indicates that the secondary phases significantly affect the corrosion behaviour of the alloy. Mg–1.5Zn alloy showed more positive corrosion potential (−1.740 V_{SCE}) in comparison with the Mg–9Zn alloy (−1.856 V_{SCE}). This is ascribed to the higher Zn content that results in increasing amounts of the intermetallic phases, which precipitated along the grain boundaries. Owing to higher galvanic corrosion that occurs between the primary magnesium (α–Mg) and secondary precipitated phases, the corrosion rate of the Mg–9Zn alloy accelerated. For the Mg–9Zn alloy, the secondary phases act as a micro-cathode and play an important role to increase the corrosion rate. Heat treatment of Mg–1.5Zn alloy for verity of solution treatment duration has a less considerable effect on corrosion behaviour. From the polarisation curves can be seen that all solution treated Mg–1.5Zn have similar corrosion potential (E_{corr}, V_{SCE}) to the as-cast Mg–1.5Zn alloy as the amount of the secondary phases after treatment remains unchanged.

The corrosion current density (i_{corr}) of as-cast Mg–1.5Zn alloy was 109 μA cm^{-2}, this value is slightly higher than the treated alloy for 6 h (140 μA cm^{-2}) and treated alloy for 12 h (135 μA cm^{-2}). The electrochemical measurement for 18 h solution treated alloy is also similar to other treated samples. In the as-cast Mg–1.5Zn alloy, a galvanic couple can be suggested between the α–Mg phase and Mg12Zn13 intermetallic phase. In this galvanic couple, the α–Mg phase plays the anode and the Mg12Zn13 phase performs the cathode.
role, while the largest amount of the Mg₁₂Zn₁₃ secondary phase as cathode exhibits the highest hydrogen evolution rate. The corrosion potential value for the as-cast Mg–9Zn is −1.856 V SCE. While the corrosion current density is 157 μA cm−². However, after performing solution treatment, the corrosion potential value increased to −1.712 V SCE and the value of corrosion current density is decreased to 98 μA cm−². In general, cathodic polarisation curves were presumed to show hydrogen evolution via water reduction; however, Mg dissolution can be indicated by using anodic polarisation curves. In the as-cast Mg–9Zn alloy, the cathode reaction kinetics is faster compared to the solution treated Mg–9Zn alloy for 6 h. This indicates that based on kinetic aspect, the cathodic reaction was more difficult in the as-cast alloys in contrast with that based on kinetic aspect, the cathodic reaction was more difficult in the as-cast alloys in contrast with treated alloy. When the solution treatment duration increased to 12 and 18 h, the value of potential shifted to −1.706 V SCE and −1.704 V SCE, and the corrosion current density decreased to 96 and 93 μA cm−², respectively. Table 2 shows the electrochemical parameters of as-cast in comparison with heat-treated alloys. According to the following equation, the corrosion rate (P) of samples can be obtained from the corrosion current density.

\[ P = \frac{22.85 \cdot i_{corr}}{A \cdot c} \quad (1) \]

Calculated values of corrosion rate for as-cast and solution treated Mg–1.5Zn alloy were in the similar range of 3.02–3.19 mm year−¹. However, Mg–1.5Zn treated alloys showed a lower corrosion rate compared to as-cast Mg–9Zn alloy. It can be because of larger amount of the secondary phase, which leads to acceleration in hydrogen generation rate; consequently, the as-cast alloys indicated higher corrosion rate than the solution treated alloys. Additionally, dissolution of the Mg₅₁Zn₂₀ secondary phase in the structure of the Mg–9Zn alloy occurred because of solution treatment. Therefore, lesser galvanic couples can be occurred between Mg₅₁Zn₂₀ and α-Mg phases. As a result, the solution treated Mg–9Zn sample presented lower corrosion rate compared to the as-cast one. The corrosion rate of Mg–9Zn solution treated sample decreased from 4.79 to 3.36 mm year−¹ with increasing treatment time, regarding the role of the reduced Mg₅₁Zn₂₀ secondary phase as micro-cathodes to increase the corrosion rate. Overall, solution treated Mg–9Zn alloys represent lower corrosion rate than the solution treated Mg–1.5Zn alloys. This can be related to the protective film, which covers the surface of Zn-containing magnesium alloys. This surface film can act as a good barrier to suppress the penetration of chloride anions into the magnesium hydroxide and improve the corrosion resistance of the alloy. Relatively similar value in the range of 0.30–0.52 kΩ cm² can be seen for the polarisation resistance value of the as-cast and solution treated Mg–1.5Zn alloy. The similarity of the Rp values indicated that the solution treatment does not have a considerable effect on the corrosion behaviour of the Mg–1.5Zn alloy because of similar volume fraction of the precipitation phases in the crystal grains. However, T₄ treatment enhanced the polarisation resistance of the as-cast Mg–9Zn alloy because of the dissolving of Mg₅₁Zn₂₁ phase. The Rp value of T₄ treated alloy for 6 h was 0.518 kΩ cm², which slightly increased to 0.519 and 0.527 kΩ cm² for the samples heat treated 12 and 18 h, respectively. This indicated that secondary phases have a considerable effect on the corrosion behaviour of as-cast and solution treated alloys.

**Immersion test**

Figure 5 shows the corresponding SEM morphology of the formed corrosion products on the surface of the as-cast and solution treated Mg–1.5Zn and Mg–9Zn samples during immersion test in Kokubo solution for 144 h. For the as-cast Mg–1.5Zn specimen, the formation of cracks as well as precipitation of a large number of white particles on the crack layer can be seen (Fig. 5a and b). Dehydration of the layer after drying in the ambient atmosphere is the main reason for the crack formation. As can be seen from Fig. 5a and b, solution treated Mg–1.5Zn sample was observed to present similar morphology to the as-cast sample. This similar observation happens because of the formation of galvanic couples between the present Mg₅₁Zn₁₃ secondary phase and the Mg alloy matrix. In this condition, the second phase acts as a micro-anode, which decreased the corrosion rate. Increasing the Zn content to 9 wt-% results in the precipitation of more quantity of bright particles on the crack layer as shown in Fig. 5c and d. However, solution treated alloys represented lesser

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sample condition</th>
<th>Ecorr (V SCE)</th>
<th>icorr (μA cm⁻²)</th>
<th>b₀ (V SCE decade⁻¹)</th>
<th>b₄ (V SCE decade⁻¹)</th>
<th>Corrosion rate, P (mm year⁻¹)</th>
<th>Rp (kΩ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg–1.5Zn</td>
<td>As-cast</td>
<td>−1.74</td>
<td>135</td>
<td>361.42</td>
<td>282.32</td>
<td>3.08</td>
<td>0.510</td>
</tr>
<tr>
<td>T₄-6 h</td>
<td>−1.761</td>
<td>140</td>
<td>383.17</td>
<td>295.84</td>
<td>3.19</td>
<td>0.518</td>
<td></td>
</tr>
<tr>
<td>T₄-12 h</td>
<td>−1.741</td>
<td>137</td>
<td>381.24</td>
<td>286.38</td>
<td>3.13</td>
<td>0.519</td>
<td></td>
</tr>
<tr>
<td>T₄-18 h</td>
<td>−1.751</td>
<td>132</td>
<td>374.55</td>
<td>279.62</td>
<td>3.02</td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>Mg–9Zn</td>
<td>As-cast</td>
<td>−1.856</td>
<td>210</td>
<td>383.12</td>
<td>235.37</td>
<td>4.79</td>
<td>0.301</td>
</tr>
<tr>
<td>T₄-6 h</td>
<td>−1.712</td>
<td>154.5</td>
<td>383.12</td>
<td>235.37</td>
<td>3.53</td>
<td>0.417</td>
<td></td>
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<tr>
<td>T₄-12 h</td>
<td>−1.706</td>
<td>152.7</td>
<td>388.47</td>
<td>239.72</td>
<td>3.49</td>
<td>0.401</td>
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<tr>
<td>T₄-18 h</td>
<td>−1.704</td>
<td>147.3</td>
<td>374.63</td>
<td>226.53</td>
<td>3.36</td>
<td>0.490</td>
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</tr>
</tbody>
</table>

**Table 2** Electrochemical parameters obtained from the polarisation curves for the as-cast and solid solution treated (T₄) Mg–1.5Zn and Mg–9Zn alloys
corrosion products on the sample surface resulting in higher corrosion resistance. This phenomenon can be described as a result of reduced galvanic corrosion, which carried out because of dissolution of Mg$_{51}$Zn$_{20}$ precipitates in the alloy matrix during solution treatment process, consequently, the corrosion resistance of the alloy improved.$^{26}$

Based on the corrosion mechanism during the immersion of the Mg alloys in a SBF solution, initially Mg element is being dissolved and simultaneously a
corrosion layer begins to deposit on the substrate surface.\(^\text{27}\) The formation of corrosion products pursues the following reactions:

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Mg}^{2+} + 2e^- \quad \text{Anodic reaction} \\
2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{Cathodic reaction} \\
\text{Mg}^{2+} + 2\text{OH}^- & \rightarrow \text{Mg(OH)}_2 \\
\text{Mg(OH)}_2 + \text{Cl}^- & \rightarrow \text{MgCl}_2 + 2\text{OH}^-
\end{align*}
\]

According to reactions 2 and 3, at the first stage, Mg transforms to stable Mg\(^{2+}\) ion; the cathodic reaction occurs simultaneously with hydroxide ion formation. Afterwards magnesium hydroxide forms as a result of the reaction of the Mg\(^{2+}\) and hydroxide ions.\(^\text{27}\) Owing to the formation of Mg(OH)\(_2\) corrosion product as a barrier layer, the degradation rate of the samples decline. In addition, the presence of CO\(_3^{2-}\), PO\(_4^{3-}\) and Cl\(^-\) ions in the media result in precipitation of some other corrosion products on the surface of the specimens. Formation of these corrosion products according to reaction 4 begins with the reaction of chloride ions with the decomposed Mg(OH)\(_2\) on the surface of the specimens. As a result, MgCl\(_2\) forms, which has higher solubility compared to Mg(OH)\(_2\). It was known that the existence of Cl\(^-\) ion can decrease the corrosion resistance of the specimens because of its small radius, Cl\(^-\) ions can easily penetrate to the formed deposition layers and cause the preferential adsorption and replacement of the OH\(^-\) ion by the Cl\(^-\) ion.\(^\text{28}\) As the reactions progressed (2–5), larger amounts of Mg\(^{2+}\) ion are being dissolved in the solution, consequently more HCO\(_3^-\), HPO\(_4^{2-}\) and Ca\(^{2+}\) ions react with OH\(^-\) ions and form hydroxyapatite, which causes a decrease in the corrosion rate.

The XRD results of the solution treated Mg–1.5Zn and Mg–9Zn specimens being immersed in Kokubo solution for 144 h is shown in Fig. 5c. The XRD results confirm the presence of Mg(OH)\(_2\) along with Mg and HA on the surface of the specimens. Broader peaks of Mg(OH)\(_2\) as the main corrosion product can be observed for the as-cast Mg–6Zn sample compared to those of other specimens. Moreover, it can be seen that the diffraction intensities of Mg(OH)\(_2\) phases in both treated alloys are lower than the as-cast alloys (Fig. 5c). This phenomenon is because of lesser corrosion attack in solution treated alloys. Also, for the aforementioned alloys, the XRD pattern shows lesser presence of HA. At the early stage of the corrosion process, Mg(OH)\(_2\) layer formed on the surface of the specimens, which acts as a protective film that prevents the precipitation of Ca and P. However, the presence of Cl\(^-\) ions in the Kokubo solution contributes to the breakdown of the Mg(OH)\(_2\) film, therefore motivating the formation of corrosion pits.

The variation of pH values of the Kokubo solution for the as-cast and solution treated Mg–1.5Zn and Mg–9Zn alloys as a function of immersion time is shown in Fig. 6a and b. The pH values of all the specimens rapidly increased from 7.34 to 8.6 in the initial 24 h of immersion. Subsequently, the pH value slowly increased with immersion time and stabilised at 9.4 after 72 h. As indicated in Fig. 6a for the as-cast and solution treated T4 Mg–1.5Zn, the pH values for all the specimens increased rapidly at the early stage of immersion time. This value increased from the initial value of 7.34–8.5 in the first 24 h of immersion time. Figure 6b shows the pH variation of Kokubo solution as a function of immersion time for Mg–9Zn samples, for as-cast and solid solution treated for 6, 12 and 18 h samples. The pH values for the as-cast sample increased quickly from 7.34 to 8.5 for the alloy. At the first 24 h of immersion time, this value for Mg–9Zn increased to 8.8 for solid solution treated samples. For Mg–9Zn heat-treated T4 samples, the pH value of the immersion environment increased slower than that of the as-cast specimen and the pH value stabilised after 72 h of immersion duration. Based on the obtained results, extending the solid solution treatment period from 6 h to 18 h has no significant effect on pH variation. Therefore, solid solution treated Mg–9Zn alloys presented similar behaviour in the SBF. An early increased in the pH values for the specimens was because of OH\(^-\) ion accumulation as a result of anodic and cathodic reactions (Reactions 3 and 4), which leads to the formation of Mg(OH)\(_2\) on the specimens surface.\(^\text{29}\) This high pH value accelerates the precipitation of magnesium phosphate and carbonate, and also stabilises the magnesium hydroxide. In implantation, local alkalisation can unfavourably affect the pH dependent physiological reaction balances in the vicinity of the magnesium implant and may even lead to an alkaline poisoning effect if the local in vivo pH value exceeds 7.8 in that region.\(^\text{15}\) By increasing immersion time to 144 h, the pH value of as-cast Mg–1.5Zn and Mg–9Zn alloys gradually increased to around 9.70 representing a steady trend. This phenomenon is because of the formation of Mg(OH)\(_2\) as the inner layer and the precipitation of calcium phosphate deposited as a top layer on the Mg(OH)\(_2\).\(^\text{30}\) Simultaneously, by consuming the calcium phosphate from the solution, the amount of hydroxyapatite precipitation on the surface increased. A similar trend is also observed for T4 heat-treated alloys where the pH values steadily increased to the range of 9.50–9.80.

Figure 6c and d indicates the evolution of hydrogen gas for the as-cast and solution treated Mg–1.5Zn and Mg–9Zn alloys for 144 h. As can be seen in Fig. 6c and d, the hydrogen evolution increasing trend of both alloy samples are similar in the initial stage. While with increasing immersion time, the rate of hydrogen evolution decreased. During the early stage of the immersion period, intensive corrosion occurs because of the larger area of the fresh surface and lesser protection of the corrosion products. Subsequently, the corrosion rate of the Mg alloys decelerated because of the passivation of the active surface and the accumulation of the corrosion products. After adequately long time of immersion, equilibrium between the formation and dissolution of the corrosion products is launched, leading to a stable degradation rate.\(^\text{21}\) It can also be seen that for Mg–1.5Zn alloy the hydrogen gas evolution for as-cast and heat-
treated T4 alloys are similar to each other. This can be because of the remaining Mg12Zn13 intermetallic phase during T4 treatment. As indicated in Fig. 6c with increasing immersion time, the rate of hydrogen evolution decreased. The precipitation of insoluble corrosion products such as magnesium hydroxide on the alloy surface can be a reason for the decreased hydrogen evolution rates. From Fig. 6d, it can be seen that after T4 treatment of Mg–9Zn alloy, the evolution of hydrogen gas decreased. This can be because of dissolved Mg51Zn20 phase after T4 treatment. Solution treatment of particularly Mg–9Zn alloys leads to slow down their initial corrosion rate, which allows the implant to maintain mechanical integrity in the bone healing procedure. Subsequently, the implant is expected to degrade similar to the biodegradable materials. Figure 7 shows calculated average corrosion rates of the as-cast and solid solution treated Mg–1.5Zn and Mg–9Zn alloys obtained by using weight loss experiment by using equation (2). Maximum corrosion rate of 7.78 mm year$^{-1}$ was observed for as-cast Mg–9Zn sample attributing the role of more Mg51Zn20 phases present in the metal matrix. According to Fig. 7 can be seen for Mg–9Zn alloy corrosion rate decreased from 7.78 to 3.25 mm year$^{-1}$ after 6 h solid solution treatment. Moreover, it is evident from Fig. 7 that lengthening the solid solution treatment from 6 to 12 and 18 h did not improve corrosion resistance of Mg–9Zn alloy. Figure 7 also reveals that no significant improvement was achieved by performing solid solution treatment on Mg–1.5Zn alloys.

**Mechanical tests**

Quantitative summary of the mechanical test results for Mg–1.5Zn and Mg–9Zn samples as-cast and after various solution treatment (T4) durations are indicated in
Table 3 and Fig. 8. Also the relative strain–stress curves of Mg1.5Zn and Mg–9Zn as-cast and after 6 h T4 treatment is presented in Fig. 9. Based on the mechanical test results, solution treatment did not significantly affect the mechanical properties of Mg–1.5Zn alloy because of less effect of solution treatment on the structure of the alloy. However, in Mg–9Zn alloy YS value increased from 82.3 to 103.4 MPa, also the tensile strength value increased from 112.4 to 179.7 MPa. Elongation value of Mg–9Zn alloy also increased from 5.6% to 14.1%. The microhardness value for the Mg–1.5Zn alloy did not change considerably after solution treatment, while this value for Mg–9Zn treated alloy increased from 46.2 to 51.5.

Table 3 Summary of mechanical properties of as-cast and solution treated (T4) after 6 h Mg–1.5Zn and Mg–9Zn samples

<table>
<thead>
<tr>
<th>Material</th>
<th>Alloy condition</th>
<th>Yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation%</th>
<th>Vickers’s hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg–1.5Zn</td>
<td>As-cast</td>
<td>45.3</td>
<td>122.3</td>
<td>8.05</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td>T4-6 h</td>
<td>39.6</td>
<td>116.6</td>
<td>7.33</td>
<td>32.1</td>
</tr>
<tr>
<td></td>
<td>T4-12 h</td>
<td>41.5</td>
<td>119.2</td>
<td>7.52</td>
<td>38.42</td>
</tr>
<tr>
<td></td>
<td>T4-18 h</td>
<td>42.8</td>
<td>121.5</td>
<td>7.90</td>
<td>32.98</td>
</tr>
<tr>
<td>Mg–9Zn</td>
<td>As-cast</td>
<td>82.3</td>
<td>112.4</td>
<td>5.6</td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td>T4-6 h</td>
<td>103.4</td>
<td>179.7</td>
<td>14.1</td>
<td>47.28</td>
</tr>
<tr>
<td></td>
<td>T4-12 h</td>
<td>101.2</td>
<td>180.8</td>
<td>14.22</td>
<td>53.1</td>
</tr>
<tr>
<td></td>
<td>T4-18 h</td>
<td>107.4</td>
<td>182.1</td>
<td>14.30</td>
<td>51.5</td>
</tr>
</tbody>
</table>

8 Effect of different solution treatment duration at 340°C on mechanical properties of Mg–1.5Zn and Mg–9Zn alloys: a yield strength; b tensile strength; c elongation%
This phenomenon can be attributed to the solid solution strengthening mechanism of Mg$_{51}$Zn$_{20}$ phase dissolved in Mg–9Zn alloy metal matrix. For this alloy, residual secondary Mg$_{51}$Zn$_{20}$ phase at the grain boundary after solution treatment and additionally the presence of Mg$_{12}$Zn$_{13}$ intermetallic phase, can also contribute to enhance the hardness.\textsuperscript{31}

Several factors affect the YS of the as-cast and solution treated Mg–Zn alloys. Equation (6) indicates the relationship between the factors that affect the YS of the Mg–Zn alloys

\[
\sigma_{YS} = \sigma_{sp} + \sigma_{ss} + \sigma_{gb} + \sigma_{ppt}
\]  

These factors include secondary phase (eutectic compounds) strengthening ($\sigma_{sp}$), solid solution strengthening ($\sigma_{ss}$), grain boundary strengthening ($\sigma_{gb}$) and precipitation strengthening ($\sigma_{ppt}$).\textsuperscript{32–35} YS of pure Mg is 27.5 MPa, while for Mg–1.5Zn and Mg–9Zn alloys this value was increased to 39.6 and 82.3 MPa because of the refining effect of Zn addition. The increased YS value was because of the decrease of grain sizes from 114 $\mu$m in pure Mg to between 92 and 51 $\mu$m in Mg–1.5Zn and Mg–9Zn, respectively. Therefore, because of the grain boundary strengthening, the YS value of Mg–Zn samples increased with Zn addition. Additionally, the microstructure of both as-cast Mg–1.5Zn and Mg–9Zn alloys consist of $\alpha$-Mg matrix, Mg$_{12}$Zn$_{13}$ intermetallic phase and eutectic Mg$_{51}$Zn$_{20}$ compounds. Consequently, grain boundary strengthening ($\sigma_{gb}$) and second phase-strengthening ($\sigma_{sp}$) has noticeable role on the alloy strengthening. Both the as-cast Mg–1.5Zn and Mg–9Zn alloys presented higher YS values compared to the pure Mg because of the above reasons as indicated in Fig. 8 and Table 2. As a result, YS of Mg–Zn alloys follow equation (7)

\[
\sigma_{YS} = \sigma_{sp} + \sigma_{gb}
\]

For Mg–9Zn alloy after solution treatment, the eutectic Mg$_{51}$Zn$_{20}$ phases along the grain boundaries were partially dissolved. Although in the solution-treated Mg–9Zn alloy, the amount of secondary phase (Mg$_{51}$Zn$_{20}$) decreased but Mg$_{12}$Zn$_{13}$ phase still remained in the microstructure (Fig. 2d). Therefore, the second-phase strengthening ($\sigma_{sp}$) still can contribute to YS for Mg–9Zn solution treated alloy but its role may be declined. Also, based on the microstructure observation (Fig. 1b and 2d), the grains were not coarsened during solution treatment, hence the $\sigma_{gb}$ values should be similar to the as-cast $\sigma_{gb}$ values. Consequently, for solution treated Mg–Zn alloys in addition to grain boundary strengthening and second phase strengthening, solid solution strengthening ($\sigma_{ss}$) also contributes to the alloy strength and YS of the solid solution treated Mg–Zn alloys following equation (8)

\[
\sigma_{YS} = \sigma_{sp} + \sigma_{gb} + \sigma_{ss}
\]
The eutectic phases are complex in shape with large aspect ratio and are prone to fracture under local stress concentration during tensile test. This result has a good agreement with the finding of Qian et al. which shows large Si particles in Al–Si alloy, and also Cao and Wessen indicating that Mg17Al12 compounds in Mg–Al alloys lead to local stress concentration during tensile test. Micro-cracks were mentioned as forming easily through the eutectic compounds. Hence, the as-cast Mg–9Zn alloy showed lower fracture strength than that of Mg–6Zn alloy. In solution-treated condition, the initiation and propagation of cracks may become more difficult than that of as-cast condition for two reasons: (1) as the eutectic Mg51Zn20 phase reduced, micro-cracks would not initiate easily by the fracture of eutectics; (2) the grain interior is strengthened by solid atoms; therefore, there would be more resistance for the cracks to cross the grains. Hence, solution treated Mg–9Zn alloy shows higher elongation than that of as-cast alloys. Also as can be seen in Fig. 10, the fracture surface morphology of Mg–9Zn alloy after solution treatment shows more ductile fracture compared to as-cast condition.

Conclusions

In the present study, the effects of solution treatments on the degradation behaviour and mechanical properties of bio-degradable Mg–Zn alloy in low and high Zn concentration have been investigated. The solid solution is observed to reduce the amount of Mg12Zn13 and Mg51Zn20 precipitates. The YS and ultimate tensile strength of Mg–9Zn alloy is significantly increased after solution treatment at 340°C for 18 h compared with that of Mg–1.5Zn alloy, which is because of the precipitation strengthening. The result also showed corrosion resistance of both solution the tread alloys much better than that of as-cast samples. In addition, the corrosion resistance of both the samples increased with increasing solution treatment time, which is attributed to reduction of micro-galvanic effect of secondary phases. Solution treatment has more effect on the micro-cathodes of Mg–9Zn alloy compared to the Mg–1.5Zn alloy, which can be attributed to the dissolution of the high amount of Mg51Zn20 phase into the α-Mg phase grains.

References