An insight into the effect of buffer layer on the electrochemical performance of MgF₂ coated magnesium alloy ZK60

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ABSTRACT

Magnesium (Mg) has emerged as potential implant material owing to its property of biodegradation. The roadblock to the commercial use of Mg as implant material is its fast degradation in body fluids. The degradation of the Mg and its alloys can be retarded by surface coatings. In this work, the potential of MgF₂ coating on the surface of Mg alloy ZK60 (Mg-6.9Zn-0.8Zr) was evaluated for its corrosion properties. Two-step chemical conversion process was used to coat MgF₂ on the surface of ZK60 alloy. In the first step, a secondary layer of Mg(OH)₂ was introduced by boiling the samples in NaOH solution. In the second step, these samples were immersed in hydrofluoric acid to obtain MgF₂ coating. SEM, IR Spectroscopy, and XRD were employed to confirm the formation of Mg(OH)₂ and MgF₂. The wettability tests showed an increase in surface hydrophobicity as a result of conversion treatment. The potentiodynamic polarization tests exhibited an improvement in the corrosion potential from −1.52 V vs. SCE to −1.49 V vs. SCE after two-step conversion treatment. Moreover, coated sample witnessed a noticeable drop in hydrogen evolution compared to untreated ZK60. For a better insight, the results were compared to the MgF₂ coatings achieved on the surface of ZK60 without any buffer layer. The coating of MgF₂ with a buffer layer of Mg(OH)₂ on the surface of ZK60 exhibited a noble corrosion potential, controlled degradation, and nominal hydrogen evolution compared to the untreated ZK60.

1. Introduction

The potential of magnesium (Mg) and its alloys as biodegradable implant material has been an attraction for the researchers looking for an optimized biocompatible and biodegradable material for implant applications. The density of Mg is 1.74 g/cm³ making it the lightest of all the engineering metals [1,2]. Mg has better strength/density ratio than stainless steel and titanium alloys that are commonly used implant materials [3]. The elastic modulus of Mg (45 GPa) is slightly higher than the elastic modulus of bone (3–20 GPa) [4], significantly reducing the possibility of stress shielding of bone [4]. On the other hand, the elastic modulus of iron (Fe) is 211.4 GPa making it and its alloys much stiffer than bone and vulnerable to stress shielding [4]. The property of Mg that set it apart from other implant materials is biodegradation [4]. Mg implants possess the unique property of biodegradation in the physiological conditions reducing the risk of secondary surgery to remove the implant and long-term undesirable interactions between the implant and tissues [5,6]. Mg has been under investigation for the cardiovascular applications in the form of stents [7–11] and orthopedic applications in the form of rods, plates, pins, and screws [12–15]. The issue associated with the Mg implants is the fast degradation in physiological conditions and subsequent loss of mechanical strength leading to implant failure [4,16–18]. Apart from losing mechanical strength, another issue related to the fast degradation of Mg is the evolution of Hydrogen (H₂) gas [19,20]. The evolution of H₂ with the degradation in an aqueous solution is governed by the given reaction.

\[ 	ext{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \]

The anodic and cathodic reactions are following:

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \]

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]

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

The H₂ gas accumulated in the gas pockets can severely damage the tissues close to the implant [20]. In addition to the tissue damages, the gas bubbles can block the regular flow of blood that put the life of the patient at risk [20]. The rapid degradation of Mg and H₂ evolution

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needs to be addressed before the commercial use of Mg in implant applications.

The surface treatment and alloy formation are common methods to improve the properties of Mg alloys. The surface treatment of Mg and its alloys is a relatively simple method as compared to alloying to control the rapid degradation. In surface treatment, the aim is to achieve a protective coating on the surface of Mg to slow down the degradation process and increase the corrosion resistance. Several coating methods are currently in practice to improve the corrosion resistance of magnesium. These methods include chemical conversion [21–23], micro arc oxidation [24,25], anodization [26,27], ion implantation [28], electrochemical deposition [17] and physical vapor deposition [29].

In chemical conversion, the specimens to be coated are immersed in a treating solution. The surface of the specimen reacts with the species solution and forms Mg compounds on the surface. The layer of Mg compounds acts as a protective film to decelerate corrosion. The quality of protective film depends on multiple factors including the composition of treating solution, alloy type, and experimental parameters such as temperature, pre-treatments, and post-treatment [30,31]. Calcium Phosphate (Ca-P) [22,23,32,33] and fluors [34–39] based surfaces are the most common coatings achieved by this method.

Magnesium fluoride (MgF2) coatings are formed on the surface of Mg by immersing the Mg specimen in hydrofluoric acid (HF) [36]. The resistive nature of MgF2 coating has been proved in the literature [37,40]. Additionally, the daily recommended intake of fluorine in the body is 2–5 mg [40] reducing the risk of the adverse effects of degradation of the MgF2 layer [40]. The biocompatibility of MgF2 coating on Mg-Nd-Zn-Zr was studied by the cytotoxicity evaluation of human umbilical vein endothelial cells (HUVEC) in endothelial basal medium (EBM). The MgF2 treated sample extracts exhibited better cell viability than untreated samples [41]. The corrosion resistance, non-toxic nature and a simple method of treating are the main attractions of MgF2 coatings by the conversion process.

The effects of MgF2 protective layers on Mg-Zn-Zr alloys have been of great interest in recent years [36,38,40]. Mg-3.2Zn-0.8Zr screws coated with MgF2 were evaluated for their corrosion resistance, mechanical properties, and biocompatibility. The MgF2 coated screws experienced an improvement in corrosion rate at the initial stage, higher yield and ultimate tensile strengths as compared to uncoated samples without producing any adverse biological effect [42]. Similarly, MgF2 coated Mg-3Zn-0.5Zr alloy was evaluated for its biological activity and the results suggested an improvement in the osteoblastic activity and bone formation [36]. In both these methods, Mg alloys were coated with MgF2 without any pre-treatment or buffer layer. Recently Mg-0.5Zn-0.45Zr (commonly known as ZK60) coated with HF acid with an etching pre-treatment was studied and the coated specimens exhibited lower current densities and hydrogen evolution than that of untreated ZK60 [38].

In this work, the MgF2 layer was formed on the surface of Mg alloy ZK60 in a dual treatment process by first introducing a buffer layer of Mg(OH)2. To compare the results, MgF2 coating without a buffer layer was also investigated in this study. Although, the pretreatment by boiling Mg alloy samples in sodium hydroxide (NaOH) solution to achieve magnesium hydroxide (Mg(OH)2) layer has been widely studied in the literature but the effects of the intermediate layer of Mg(OH)2 on the surface properties of ZK60 haven’t been investigated in the literature. The aim of this work is to not only study the properties of the final MgF2 layer but also evaluate the buffer Mg(OH)2 layer. The coatings were characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The evolution of hydrogen gas was tested in phosphate buffer saline (PBS). The biodegradation was evaluated by the electrochemical testing in the PBS at 37 °C and 5% CO2. The aim of the study is to evaluate the effect of the buffer layer of Mg(OH)2 on the corrosion performance of MgF2 coating on the surface of Mg alloy ZK60.

2. Materials and methods

2.1. Sample preparation

ZK60 (Mg-6.9Zn-0.8Zr) discs of diameter 25.4 mm and a thickness of 5 mm were cut from the commercially available ZK60 rod (Source One Metals * , MI, USA). The surface of the discs was grit-blasted subsequently with 180, 320, 400, 600, 800 and 1200 grit size SiC emery papers to get a smooth surface. To avoid any surface contaminations, the samples were cleaned ultrasonically in acetone and deionized water for 2 min. Finally, the discs were air-dried. The untreated samples are called as ZK60-UT in the following discussion.

2.2. Coating procedure

The grinded discs were boiled in NaOH solution having a concentration of 200 g/L [43–45] for 4 h. After the NaOH treatment, the samples were removed from the solution, ultrasonically cleaned in deionized water for 2 min and dried in air. These samples are termed as ZK60-NT in the following discussion.

The ZK60-NT samples were finally immersed in HF acid (48%) contained in a polypropylene beaker for 96 h. The concentrated acid was used to ensure uniform and dense coatings [46]. Afterwards, the samples were removed and washed ultrasonically in deionized water for 2 min and air dried. These samples are labeled as ZK60-DT (Dual Treatment).

For comparative analysis, ZK60 samples were also treated with HF acid for 96 h but without any buffer layer of Mg(OH)2. Afterwards, samples were ultrasonically washed and air dried. The MgF2 coated samples without buffer layer are named as ZK60-HT.

2.3. Surface characterization

The surface morphology of the formed films was characterized using scanning electron microscopy (SEM, Hitachi 3400). The film thickness and elemental content mapping were also measured using SEM. The film thickness was measured at 5 different points to find an average thickness value. The elemental composition at the surface of samples was evaluated by the energy dispersive spectroscopy (EDS) coupled with SEM. All the EDS measurements were repeated at least 3 times to ensure repeatability. The average values are presented in the discussion. The phase composition of the coating was identified using X-ray diffraction with the Cu-Kα radiation having a wavelength of 0.15406 nm. The samples were scanned from 10°–90° at a scan rate of 0.5°/min. FTIR-ATR spectrometer ( NicoletTMISTM 50) was used to obtain the Infra-red (IR) spectra of the samples under study in the attenuated total reflection (ATR) mode.

Wettability of the surfaces was evaluated by measuring the contact angle using a contact angle goniometer (Attension Theta- DSC Q 2000) with the monochromatic light source by pouring a drop of deionized water on the surface of samples. The contact angles at 3 different spots of the sample surface were measured and the average value of all the readings was used. A still camera was used to capture the image of the water droplet.

2.4. Electrochemical testing

The electrochemical behavior of the samples was studied using a three-electrode cell setup with Mg samples as working electrodes, saturated calomel electrode (SCE) as a reference, and graphite rod as a counter electrode. The Gamry-Potentiotstat (Ref-3000) was used for the electrochemical studies. The electrolyte for the electrochemical tests was phosphate buffer saline (PBS) with a pH value of 7.4. PBS tablets (Sigma-Aldrich®) were dissolved in deionized water to prepare an electrolyte. The concentration of the PBS was 1 tablet/200 mL of deionized water. The composition of the PBS is given in Table 1 [5]. All
the electrochemical tests were performed inside a humidified incubator maintained at 37 °C and 5% CO2. The exposed surface area was 1 cm². Before each test, the open circuit potential was stabilized for 10 h. The potentiodynamic scans were conducted by polarizing the surface over the potential range of −1.5 to 1.5 V vs. OCP at the scan rate 5 mV/s.

2.5. Hydrogen evolution

The hydrogen evolution experiments were performed in the PBS at the temperature of 37 °C. The temperature was maintained by setting the evolution setup in an incubator. Three samples of each type were used in the study. The samples were immersed in a beaker containing the PBS solution. An inverted funnel was placed in each beaker to collect the hydrogen gas. Graduated cylinders filled with PBS were placed above the funnel to observe the amount of released hydrogen. The released hydrogen gas lowers the level of PBS in the tube by displacing the PBS. The difference in the initial level and level at observation time gives the value of evolved hydrogen gas. The values were measured at every 24 h for 7 days. The pH was measured at the end of day 7 to calculate the effect of degradation on the pH of PBS. The initial pH of the PBS was 7.4.

3. Results and discussion

3.1. Characterization of coatings

The surface morphologies and elemental composition at the surface of Mg samples are presented in the Fig. 1, and Table 2, respectively. The change in the surface morphologies in all samples is evident from the SEM images in Fig. 1. Fig. 1a represents the surface image of untreated Mg alloy ZK60-UT and a smooth grinded surface with few grinding marks are visible indicating the formation of very thin layer in the HF acid is governed by the following reaction [43].

\[
\text{Mg(OH)}_2 + 2\text{HF} \rightarrow \text{MgF}_2 + 2\text{H}_2\text{O}
\]

The film thickness of all the coated surfaces is presented in Fig. 2. A very thin film with a thickness of 0.62 ± 0.19 μm was identified at the surface of ZK60-HT as shown in Fig. 2b. Given the thin nature of the film, few grinding marks in Fig. 1c were clearly visible even after the coating. The boiling of samples in NaOH resulted in the formation of a relatively thick layer of Mg(OH)2 with a thickness of 25.35 ± 0.80 μm. The reaction of Mg(OH)2 intermediate surface with the HF acid led to a new layer of MgF2 with a thickness of 6.32 ± 1.22 μm and can be seen in Fig. 2c. The two-step conversion process formed a MgF2 layer with a greater thickness than formed by one step conversion procedure.

The elemental distribution mapping of samples is presented in Fig. 3. The elemental distribution of ZK60-HT in Fig. 3b confirms the high content of oxygen on the surface. The Mg and O are homogeneously distributed on the surface. The elemental mapping of ZK60-HT in Fig. 3c represents the uniformly distributed fluorine on the surface of the sample. The mapping confirms the uniform nature of MgF2 film in case of ZK60-HT. Fig. 3d represents the elemental distribution on the surface of ZK60-DT. The fluorine is distributed all over the surface solidifying the idea the uniform layer. Although the MgF2 coating in two-step conversion is not as uniform as in ZK60-HT, it is almost 10 times thicker than the MgF2 in ZK60-HT. The uniformity of MgF2 protective coating in two-step conversion procedure highly depends on the intermediate Mg(OH)2 surface. The NaOH solution should be stirred continuously in coating procedure to ensure uniform Mg(OH)2 layer. The uniform Mg(OH)2 will assist in the more uniform conversion of MgF2.

The chemical composition of the surface was further evaluated by employing the IR spectroscopy. Fig. 4 presents the IR spectra of the samples. The peaks in the range 1800–2250 cm⁻¹ appeared because of the diamond crystal used in the ATR mode [49]. Furthermore, no obvious peaks are observed in case of ZK60-UT while after treatment with hydroxide enrich solution (ZK60-HT) a sharp peak of Mg(OH)2 was appeared around 3688 cm⁻¹ [50,51] because of the OH bond stretch. For ZK60-DT (Fig. 4d), the peak around 440 and 1650 cm⁻¹ was observed owing to the stretching vibrations between Mg and F in MgF2 bond [52,53]. Additionally, a broad peak centering around 3250 cm⁻¹ appeared which could be referred to the residual Mg(OH)2 content. A strong peak of MgF2 around 575 cm⁻¹ appeared in case of ZK60-HT (Fig. 4e) [52]. It is evident from the fig. 4e and d that MgF2 is formed on the surface as a result of the chemical conversion process.

The XRD pattern of ZK60-UT, ZK60-HT, ZK60-DT, and ZK60-DT are presented in the Fig. 5. The Mg planes of (100), (002), (101), (110), (200) and (004) were identified at 2θ = 33°, 35°, 37°, 57°, 68° and 72° respectively in case of ZK60-UT. The peaks of Mg were in accordance with the literature [54,55]. The XRD pattern of ZK60-HT surface confirmed the presence of a hexagonal structure of Mg(OH)2. The Mg(OH)2 peaks at 2θ = 19° and 52° for (001) and (102) planes, respectively, were well aligned with the literature [56–58]. The XRD pattern of ZK60-HT affirms the presence of monoclinic MgF2 on the surface of ZK60 after HF treatment. The MgF2 peaks at 2θ = 37° and 41° for the (111) and (120) planes were observed. Apart from the above mentioned two MgF2 peaks, an additional MgF2 peak at 2θ = 28° was identified in case of ZK60-DT. The presence of an additional MgF2 peak in ZK60-DT confirms that the MgF2 layer in ZK60-UT is more identifiable and well defined as compared to that of ZK60-HT. The peaks of MgF2 were validated from the literature [54,59] for both the cases (ZK60-HT (Fig. 5c) and ZK60-DT (Fig. 5d)).

The contact angles were measured at 3 different spots on the surfaces of samples to evaluate the wettability of formed layers and the effect of coatings on the hydrophilicity of the ZK60-UT surface. The results presented in the Fig. 6 are the averages of the three readings for each individual sample. The ZK60-UT exhibited the lowest contact angle of 82.49 ± 1.66° among the four samples. The treatment of NaOH had a negligible impact on the contact angle of untreated surface and its value only increased 1.95° with the new value was 84.44 ± 1.22°. The treatment of sample without a buffer layer demonstrated an increase in the contact angle with a value of 91.21 ± 2.01°. The ZK60-DT has exhibited the highest contact angle of

| Table 1: Chemical composition of PBS solution (g/L). |
|---------------------------------|-------|-------|-------|-------|-------|-------|
| NaCl                           | 0.08  | NaH2PO4 | 0.06  | NaHCO3 | 0.35  | KCl    | 0.40  |
|                               |       |         |       |         |       | KH2PO4 | 0.06  | MgSiO4 | 0.20  | CaCl2  | 0.14  |

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all four with a value of $91.83 \pm 0.69^\circ$ indicating the increase in the hydrophobicity with the formation of the MgF$_2$ layer. The summary of contact angle values is presented in Table 3.

3.2. Electrochemical results

The effect of NaOH, HF and NaOH-HF treatment on the degradation behavior of ZK60 alloy was studied by potentiodynamic polarization. Fig. 7 presents the polarization curves of the samples. The cathodic portion of the curve demonstrates the hydrogen evolution while that of the anodic presents the active dissolution reactions [60]. The anodic region of polarization curve of ZK60-UT demonstrating a rapid increase in corrosion current density with a slight increase in the corrosion potential. At the potential $-1.10 \text{ V vs. SCE}$, the activity slowed down as afterward there was a minor increase in the current densities indicating the passivation. The treatment of ZK60-UT samples with NaOH exhibited a minor increase in corrosion potential. The value of potential increased from $-1.52 \text{ V vs. SCE}$ to $-1.50 \text{ V vs. SCE}$. Moreover, the current densities shifted from $3.32 \times 10^{-5} \text{ A/cm}^2$ to a slightly higher value of $3.44 \times 10^{-5} \text{ A/cm}^2$. The anodic region of the ZK60-NT exhibited a small passivation patch from potential of $-1.37 \text{ V vs. SCE}$ to $-1.30 \text{ V vs. SCE}$. After this potential the sample again showed rapid activity and finally stabilized at a potential of $0.90 \text{ V vs. SCE}$. This phenomenon indicates the formation of a passive layer that didn’t last long making sample again susceptible to corrosion. The treatment of ZK60-UT with HF witnessed an increase in the corrosion potential and reduction in corrosion current density. The corrosion potential was shifted from $-1.52 \text{ V vs. SCE}$ to $-1.42 \text{ V vs. SCE}$ and a corrosion current density of $4.52 \times 10^{-6} \text{ A/cm}^2$ was achieved with HF treatment. The anodic polarization region of the curve indicated the passivation at a potential of $-0.51 \text{ V vs. SCE}$. Moreover, initially the corrosion current density of ZK60-HT is much lower than ZK60-UT. The rapid increase in the corrosion current density indicates a non-stable film on the surface that draws more current once the degradation starts. The extremely thin layer of ZK60-HT along with insufficient adherence are the main reasons for this instability. The rationale behind using the intermediate Mg(OH)$_2$ is to coat MgF$_2$ layer with higher thickness to ensure stability of the surface. The potentiodynamic curve of ZK60-DT exhibited the effectiveness of buffer layer of Mg(OH)$_2$ in achieving lowest corrosion current density. The anodic region of the potentiodynamic curve of ZK60-DT suggests a formation of passive film at a potential of $-1.42 \text{ V vs. SCE}$. This passive film diminishes at $-1.32 \text{ V vs. SCE}$ and degradation activity started again. The shift in the anodic curve towards the left indicates the activity of the ZK60-DT samples at lower current

<table>
<thead>
<tr>
<th></th>
<th>Mg (wt%)</th>
<th>O (wt%)</th>
<th>Zn (wt%)</th>
<th>Zr (wt%)</th>
<th>F (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZK60-UT</td>
<td>90.23 ± 0.63</td>
<td>2.66 ± 0.85</td>
<td>6.53 ± 0.72</td>
<td>0.60 ± 0.20</td>
<td>–</td>
</tr>
<tr>
<td>ZK60-NT</td>
<td>43.75 ± 0.55</td>
<td>55.80 ± 0.72</td>
<td>0.30 ± 0.17</td>
<td>0.70 ± 0.11</td>
<td>–</td>
</tr>
<tr>
<td>ZK60-HT</td>
<td>64.80 ± 1.65</td>
<td>3.43 ± 0.60</td>
<td>3.46 ± 0.68</td>
<td>0.30 ± 0.00</td>
<td>27.69 ± 1.65</td>
</tr>
<tr>
<td>ZK60-DT</td>
<td>33.70 ± 0.34</td>
<td>8.56 ± 0.05</td>
<td>2.13 ± 0.51</td>
<td>0.06 ± 0.05</td>
<td>55.56 ± 0.28</td>
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Fig. 1. SEM Images of (a) ZK60-UT, (b) ZK60-NT, (c) ZK60-HT & (d) ZK60-DT.
densities. The corrosion potential of ZK60-DT improved from $-1.52 \text{ V vs. SCE}$ to $-1.49 \text{ V vs. SCE}$. The corrosion current density of ZK60-DT is $3.71 \times 10^{-6} \text{ A/cm}^2$, suggesting a reduction in the value as compared to ZK60-UT after the NaOH-HF treatment. The formation of this MgF$_2$ would act as a barrier layer to the corrosion attacks, significantly reducing the degradation. The summary of $E_{\text{corr}}$ and $I_{\text{corr}}$ values is presented in Table 4.

The conversion method is frequently used to coat Mg alloys with phosphate coatings [22,61–65]. The results of MgF$_2$ coatings in our work exhibited improvements in terms of potential increase and reduction in corrosion current density when compared to calcium phosphate, barium phosphate and magnesium phosphate coatings on Mg-Al alloys [63–65].

The electrochemical results indicated the formation of a MgF$_2$ layer with the lowest corrosion current density when pre-treated with NaOH. The formation of Mg(OH)$_2$ buffer layer lead to more corrosion resistant MgF$_2$ final layer. Although the ZK60-UT and ZK60-NT samples were treated in exactly same conditions to get ZK60-HT and ZK60-DT respectively, the effectiveness of pre-treatment with NaOH is evident from the results.
3.3. Hydrogen evolution

Fig. 8 presents the cumulative hydrogen evolved from the surfaces of samples vs. the number of days. The evolution of hydrogen gas is governed by the following reaction [66–68].

\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{OH}^- + \text{H}_2 \]

At the initial stage, the hydrogen gas evolved was maximum from the surface of ZK60-NT. The ZK60-HT and ZK60-DT samples showed the small volume of evolved hydrogen suggesting a barrier coating of MgF₂. The evolution of H₂ from the surface of ZK60-NT is associated to the Mg(OH)₂, generating the higher H₂ gas. The H₂ generation on the


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