Behaviors of Nanocomposite Mg-Alloy in Simulated Bodily Fluids and pH Fluctuations

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Article

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Abstract

Its biodegradability, non-poisonousness, and exceptional natural and machinery features make Mg and its components attractive alternatives for biomedical implantation supplies, according to the National Institute of Health. SBF is used as a standard electrolyte for in vitro corrosion research. Each SBF module's independent and synergistic corrosion effects are studied in this study. Artificial pH variations increase degradation, according to the results. This experiment examined the Mg corrosion submerged in a simulated bodily fluid (SBF) solution. The effect of pH changes on the rate of corrosion of Mg immersed in standard SBF solution was investigated. According to the previously published study, the corrosion process of Mg has been confirmed by scanning electron microscopy observations of damaged surface morphology (SEM). Because of these investigations, pH 7 was selected as the pH for bodily fluids since it is neutral.

1. Introduction

Since Mg density is just 1.74 g/cm$^3$, it has high machinability and thermal conductivity, making it a vital element for human health and well-being$^{1,2}$. By comparing magnesium alloys with other metals, it has been observed that there are many differences. The first phase is formed when magnesium is mixed with most other metals, and its stability increases with the increase in the electrical capacity of other metals$^3$. Attributable to its biodegradability, non-toxicity, low density, good mechanical characteristics, and outstanding mechanical and physical features, Mg and its composites are developing appealing options for materials of the biomedical implant. Because of their exceptional mechanical properties, low density, and specific biodegradation characteristics, biodegradable magnesium alloys have gotten a lot of interest for application in orthopedic implants. Mg alloys’ rapid corrosion and poor antibacterial properties, equally, limit their use in implant applications.

The rapid rate of magnesium corrosion and similar alloys in the humanoid body, equally, would bring about a loss of mechanical integrity before considerable bone rebuilding could occur. Based on the surface coating techniques, they have been a research emphasis on increasing the resistance of corrosion for Mg-based implantations since it is an effective, quick, and low-cost approach. Even though the actual bodily fluids may have values of pH that range from 5 to 10, the SBF's chemical composition indicates that it has a pH value of roughly 7. Both Zn and Mg corrode more quickly in acidic environments$^4$. SBF was converted into pH 5 and 10 solutions by adding small amounts of HCl or NaOH. For these reasons, rates of corrosion were also evaluated in those solutions. The rate of Mg corrosion was shown to be strongly dependent on the content of the electrolyte in various media. Nevertheless, that investigation was primarily concerned with the electrolyte's local pH near the deteriorating Mg.

Several separate electrolytes were created to clarify the specific impact of each component on the Mg corrosion rate in this study. Hydrogen evolution and immersion experiments, monitoring of local and bulk pH values, and EIS were employed to survey the consequences of various pH levels and their combinations on Mg corrosion. Approaching the human skeleton in conditions of elastic modulus and...
compressive yield strength, and so on. However, because Mg has an active chemical property (the typical electrode potential is −2.36 V), the formed oxide layer on its surface in corrosive fluids is porous and cannot provide enough protection to the environment, which is exacerbated in a physical environment rich in Cl-. Bone has the same density (1.75 g/cm³) as synthetic collagen (1.74 g/cm³). As a result, it is appropriate for use as biological implant material. Mg and its alloys are broadly suggested for improving biodegradability. Aluminum has already become the most important alloying component for increasing tensile strength by generating the intermetallic phase Mg₁₇Al₁₂. A similar effect may be achieved using the minerals zinc and manganese. Magnesium alloys established on the AZ-based Mg system are the highest popular.

These alloys, AZ91 have the best mechanical properties. Automotive parts, laptop computers, smartphones, and other things contain the substance. Despite this, many Mg and its alloys are extremely receptive to general and localized (pitting) corrosion, which severely limits their broad use. Corrosion research on Mg and its alloys is an intriguing field of study that might lead to the improvement of these materials' potential usage in a wide range of technological and artistic applications. Overall, magnesium's stability is significantly smaller than water. Therefore, Mg and its alloys are becoming attractive alternatives for biomedical implant materials because of their biodegradability and nontoxicity.

So, excessive amounts of magnesium that people consume every day, benefit from increased bone density and strength. Metallic or polymer implants cannot compare to Mg/Mg alloys for bone replacement applications. Since Mg's mechanical and physical features are like those of bone, no extra surgery is necessary after healing the bone mass. However, Mg's rapid rate of corrosion in the fluid of the human body is a disadvantage as a possible bone transplant material.

Mg's mechanical and physical characteristics deteriorate because of corrosion progression. Too rapidly degrading implants may fail in stressful situations. An assortment of procedures must be employed to verify how quickly magnesium/magnesium alloys corrode before they are implanted, including DI water, simulated body fluid, PBS, and cell culture medium. Moreover, in the case of immersion of Mg in an acidic medium, hydrogen evolution, and electrochemical tests, the corrosion behavior of the metals was assessed.

Alloys of magnesium, which may be biodegradable, have both properties of acceptable mechanical and biocompatibility. An abundant source of Mg²⁺ is observed in the body fluid of humans. It is beneficial to the bone system if Mg is present. It is established that the bone of humans has a specific density of 1.74–2 g/cm³ and based on Young's modulus of 41–45 GPa, Mg and its alloys are the closest to the specific density. Because of this, magnesium alloys outperform any other metallic or polymer implant in the mechanical and physical characteristics, as the variance in Young's modulus between an implant and natural human bone can source impacts of stress shielding, resulting in stress concentration at the argument where the bone meets the implant, lowering new bone growth rate. Recently, a huge number
of studies have been performed on the behavior of Mg alloy corrosion in artificial physiological fluids. They were considering an Al-Mg alloy, though 21.

In the human body, most of the alloying components dissolve during the degradation of magnesium alloys. Due to excessively high corrosion rates, magnesium alloys did not function well 22. Based on the excessive impurities in these magnesium alloys, the screws and plates corroded too fast, resulting in subcutaneous gas cavities in treated individuals. Magnesium alloys, require slower corrosion rates to be viable as a possible biomaterial 23. It was decided to employ Mn and Zn because of their excellent biocompatibility to produce a magnesium alloy including Mg, Zn, and Mn for biomedical purposes 24.

2. Materials And Methods

2.1. Materials

Die-cast Mg-Al-alloy (AZ91D) with the chemical composition and balance given in the following weight percentages Al, 9.0, Zn 0.67, Mn 0.33, Cu 0.03, Si 0.01, Fe 0.005, Ni 0.002, Be 0.0008 and Mg represent the balance of the total content. This alloy was used in the current experiment. Cylindrical rods made by Johnson and Malthey (England) have an alloy surface area of roughly 0.2 cm². When polishing the electrode surface to a mirror-like sheen, technicians used finer and finer emery paper grades (600–1200 grade). Following the toxicology of the calomel electrode, the Ag/AgCl reference and the rectangular platinum sheet were used in the standard three-electrode cell in this work.

As illustrated in Table 1, SBF is an aqueous solution aerated and sealed to mimic human physiological fluid. The solutions used to examine the effect of fluoride ions and albumin on the alloy under study as a biomaterial and the electrochemical activity were applied. The electrodes were carefully prepared and washed in triple-distilled water before carrying out the experimental work. This was followed by acetone degreasing, alcohol washing, and drying in the air. AZ91D alloy polarization curves were scanned at 1mVs⁻¹. We utilized a 10 mV sinusoidal potential applied 30 kHz to 100 million times per second to get OCP and impedance graphs. Zahner-elektrik GmbH, Im6e electrochemical workstation. The coupon was connected to an electrical wire in a glass tube filled with Araldite epoxy glue and stored at 37°C and pH 7.4. and the area of the electrode is 2 cm² AZ91D alloy 25.
Table 1  
Composition of simulated body fluid at pH 7.4

<table>
<thead>
<tr>
<th>SBF at pH 7.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
</tr>
<tr>
<td>NaCl</td>
</tr>
<tr>
<td>NaHCO₃</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
</tr>
<tr>
<td>NaH₂PO₄</td>
</tr>
<tr>
<td>Albumin</td>
</tr>
<tr>
<td>KF</td>
</tr>
</tbody>
</table>

The SEM micrographs were taken using a JEOL JXA-840A electron probe analyzer. Unless otherwise stated, electrochemical experiments were conducted at 37°C in an air thermostat. Immersion experiments, potentiodynamic measurements, and pH monitoring were used to investigate Mg-alloy corrosion. SEM was utilized to investigate both uncorroded and corroded metal surfaces. This work investigated Mg corrosion in an aerated (SBF) \(^{26}\). SBF is chemically neutral, while biological fluids' pH might be slightly higher or lower than 7 as in Table 2.

Table 2  
Composition of simulated body fluid at pH 7

<table>
<thead>
<tr>
<th>SBF at pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
</tr>
<tr>
<td>NaCl</td>
</tr>
<tr>
<td>KCl</td>
</tr>
<tr>
<td>CaCl₂</td>
</tr>
<tr>
<td>NaHCO₃</td>
</tr>
<tr>
<td>Glucose</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
</tr>
<tr>
<td>KH₂PO₄</td>
</tr>
<tr>
<td>Na₂HPO₄·12H₂O</td>
</tr>
</tbody>
</table>
For the accelerating test, we must obtain an acidic electrolyte so pH 5 was adjusted before carrying out the experimental work\textsuperscript{27}. Acidity has long been known to accelerate Zn and Mg corrosion. SBF was also tested at pH 5 and 10 using HCl and NaOH. Henceforth SBF pH 5 and SBF pH 10 shall be referred to as such. And for comparison, the SBF according to Cigada was used see Table 3.

<table>
<thead>
<tr>
<th>SBF according to Cigada</th>
<th>Materials</th>
<th>Wt. g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>8.74 g/L</td>
<td></td>
</tr>
<tr>
<td>NaHCO\textsubscript{3}</td>
<td>0.35 g/L</td>
<td></td>
</tr>
<tr>
<td>Na\textsubscript{2}HPO\textsubscript{4}</td>
<td>0.06 g/L</td>
<td></td>
</tr>
<tr>
<td>NaH\textsubscript{2}PO\textsubscript{4}</td>
<td>0.06 g/L</td>
<td></td>
</tr>
</tbody>
</table>

### 2.2. Methods

#### 2.2.1. Electrochemical Techniques

The OCP $E_{oc}$, PD, and EIS were measured using the IM6e Zahner-Electrik GmbH electrochemical workstation (Mebtechnik, Kronach, Germany). To test the open-circuit potential, $E_{oc}$, a freshly polished sample was submerged in naturally ventilated aqueous solutions for 24 hrs. After an hour in SBF, SBF-KF, and SBF + Albumin, titanium and Cu-Al-Ni alloys were potentiodynamic polarized. The polarization approach was used at a 2 mVs\textsuperscript{-1} scan rate to measure (EIS) at the open-circuit potential.

The impedance spectra were acquired with a perturbation of 10 mV. EIS plots were created after immersing the specimens in the test solution for up to 24 hrs. Otherwise, all experiments were done at 37°C. We used a Gamry PCI300/4 Potentiometer, Galvanometer, and Zra Analyzer to conduct PD and RA (EIS). A 5-mV peak-to-peak AC signal was superimposed on the impedance measurements at the (OCP). This approach directly measures EIS, Z, and phase shift. With a scan rate of 1 mV/s\textsuperscript{-1}, potentiodynamic trials were performed, and the cell was submerged in a water thermostat with a temperature range of 298–338 K. SEM was used to examine the surface. Unless otherwise specified, all tests were performed at 298K. The details of the experiment are elsewhere\textsuperscript{28}.

### 3. Results And Discussion

#### 3.1. Open-Circuit Potential and Potentiodynamic Polarization Measurements
Corrosion measurements of open circuit potential reveal electrochemical processes at the metal surface solution contact ($E_{\text{corr}}$). An electrode solution interface may be examined by varying the open-circuit voltage as the Mg alloy corrodes over time. Figure 1A shows a typical $E_{\text{corr}}$-t curve for the AZ91 Mg alloy. After roughly 50 ks, the potential stabilizes, with no large fluctuations observable during the immersion. At roughly 16.6 ks, the open-circuit voltage rapidly decreases, indicating pitting corrosion. A further drop at 19 kilometers indicates the expansion of the second pit. An increase in open circuit potential after a decrease in potential indicates self-limiting localized corrosion.

This phenomenon is connected to the cathodic reaction. The presence of OH indicates a cathodic process, which increases the development and stability of the oxide layer and reduces localized corrosion. As previously stated, when an Mg alloy is exposed to corrosive fluids, chemical dissolution coupled with electrolyte penetration induces spontaneous corrosion throughout the whole surface, resulting in Mg(OH)$_2$ and Mg$_3$(PO$_4$)$_2$. Due to OH diffusion, corrosion products concentrate around the micro anode. Therefore, the active zone diminishes, and the corrosion products create a protective layer.

The inhomogeneous crystal phenomena cause localized corrosion in Mg-alloys. With a greater standard voltage 7 than the surrounding matrix, Mg$_{17}$Al$_{12}$ forms an electrolysis junction. The selective attack usually generates pits with Mg$_{12}$Al$_{17}$ networks. After prolonged immersion, the corrosion process moves from broad to localized corrosion pitting start. The critical concentration of Cl$^-$ anions required to initiate localized corrosion on Mg is roughly 30 mmol/L, compared to 142 mmol/l in SBF. Therefore, pitting propagation is common in Mg-alloys treated to SBF.

The corrosion potential ($E_{\text{corr}}$), corrosion current ($j_{\text{corr}}$), polarization resistance ($R_P$), and rate of corrosion of Mg were all tested ($K_{\text{corr}}$). Electron expenditure on Mg occurs through hydrogen ion unloading in SBF (acidic corrosion).

\[
2H^+ + 2e^- = H_2 \quad (1)
\]
\[
H_2O = H^+ + OH^- \quad (2)
\]
\[
2\text{Mg} = 2\text{Mg}^{2+} + 4e^- \quad (3)
\]
\[
\text{Mg} + \text{O} = \text{MgO} \quad (4)
\]
\[
\text{Mg}^{2+} + 2\text{OH}^- = \text{Mg(OH)}_2 \quad (5)
\]

However, Eq. 2 shows that dissociated water is the source of H$^+$ ions (specifically, the hydronium ion H$_3$O). Eq. 3 depicts Mg's condition since it meets the test electrolyte, and experiences an anodic process.
that dissolves it, forming MgO as part of the anodic process\textsuperscript{33}. Finally, the Mg ion from Eq. 4 reacts with the OH\textsuperscript{−} from Eq. 2 to form Mg(OH)\textsubscript{2}, as shown in Eq. 5. cathodic (c) and anodic (a) Tafel slope values, corrosion potentials (E\textsubscript{corr}), corrosion currents (i\textsubscript{corr}), pitting potentials (E\textsubscript{pit}), polarization resistance (R\textsubscript{P}), and corrosion rate (K\textsubscript{corr}) are shown in Table 4.

As seen in Fig. 1\textsubscript{b}, the vigorous SBF solution caused the alloy to aggressively disintegrate. HAp is shown to exist and increase in concentration with Mg in Fig. 1\textsubscript{b}. Low Mg dissolution, cathodic, j\textsubscript{corr} and anodic currents, including K\textsubscript{corr}, decreased, whereas E\textsubscript{corr} increased, and R\textsubscript{P} decreased. This effect was amplified when E\textsubscript{pit} decreased to negative levels. E\textsubscript{corr} and j\textsubscript{corr} values were obtained via extrapolating anodic and cathodic lopes from Tafel lines next to linearized current areas\textsuperscript{34}.

However, polarization data was used to calculate R\textsubscript{P} and K\textsubscript{corr}. It improves Mg’s resistance to homogenous corrosion while increasing the risk of localized corrosion. Caused by HAp particles having greater noble potential than Mg-particles as mentioned in Fig. 2.

Table 4: Polarization parameters extracted from Figs. 2\textsubscript{A,B,C}.

<table>
<thead>
<tr>
<th>pH</th>
<th>Temp (°C)</th>
<th>E\textsubscript{cor} (V)</th>
<th>i\textsubscript{cor} (µA/cm\textsuperscript{2})</th>
<th>C.R (mpy)</th>
<th>β\textsubscript{c} (V/dec)</th>
<th>β\textsubscript{a} (V/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>25</td>
<td>-1.279</td>
<td>92</td>
<td>30.1</td>
<td>0.451</td>
<td>0.310</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-1.477</td>
<td>101</td>
<td>46.2</td>
<td>0.492</td>
<td>0.379</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-1.521</td>
<td>139</td>
<td>63.3</td>
<td>0.411</td>
<td>0.339</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>-1.538</td>
<td>261</td>
<td>116.9</td>
<td>0.349</td>
<td>0.713</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>-1.047</td>
<td>15.1</td>
<td>6.4</td>
<td>0.471</td>
<td>0.341</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-1.132</td>
<td>22.4</td>
<td>9.92</td>
<td>0.509</td>
<td>0.288</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-1.165</td>
<td>34.3</td>
<td>14.98</td>
<td>0.529</td>
<td>0.289</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>-1.158</td>
<td>41.2</td>
<td>18.91</td>
<td>0.959</td>
<td>0.260</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>-0.661</td>
<td>0.749</td>
<td>0.29</td>
<td>0.278</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-0.799</td>
<td>1.101</td>
<td>0.49</td>
<td>0.371</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-0.899</td>
<td>4.46</td>
<td>1.98</td>
<td>0.398</td>
<td>0.068</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>-0.979</td>
<td>9.32</td>
<td>3.97</td>
<td>0.375</td>
<td>0.541</td>
</tr>
</tbody>
</table>

3.3. EIS Measurements
The kinetic parameters were verified by studying electron transport at electrode/electrolyte interfaces. This method has been used to characterize metal and alloy corrosion and passivation [28–34]. Mg/0.0 wt.% HAp, Mg/1.0 wt.% HAp, Mg/2.0 wt.% HAp, Mg/4.0 wt.% HAp, Mg/5.0% HAp after 15 minutes of engagement in the SBF solution. The equivalent circuit model for the case of two-time constants was fitted to the Nyquist plots to assess their EIS as seen in Fig. 5. Table 5 shows the characteristics of a similar circuit see Fig. 5D. These parameters are defined as follows: Cdl1 and RP1 relate to solution resistance, Q and RP2 to constant phase elements (CPEs), and RP3 to extra polarization resistance. In this circuit, a double-layer capacitance (Cdl2) is linked to RP3's variation. The resulting Nyquist curves showed two semicircles of discouraged capacitive see Fig. 5A,B,C. The experimental findings linked Mg\(^+\), an intermediate species, to Mg corrosion at coat defects or on a free coat surface. Electrochemical oxidation of Mg yields Mg\(^+\), which reacts with H\(_2\)O to form hydrogen and Mg\(^{2+}\). Low-frequency RC circuit parallelism is visible. In Eq. 6, RP3 reflects the variance of the reaction's transfer resistance. 

\[
Mg^+ = Mg^{2+} + e^- \quad (6)
\]

As seen in Fig. 3 and Table 4, adding HAp to the medium increases the resistances of Rs, RP1, RP2, and RP3. Resistivity rises when HAp is incorporated into a surface layer, especially at low ionic resistance defects. Because HAp particles reduced Cdl1 and CPE values, they enhanced Mg-corrosion resistance in SBF solution. It is possible to measure the interface impedance (|Z|) of (1) Mg/0.0 wt.% HAp, (2) Mg/1.0 wt.% HAp, (3) Mg/2.0 wt.% HAp, (4) Mg/3.0 wt.% HAp, and (5) Mg/4.0 wt.% HAp after 15 min in SBF solution. The corrosion resistance of the Mg surface rises with |Z|, especially in the low-frequency zone. The EIS measurements and polarization findings match with the previous research Figs. 3,4.

**Table 5:** EIS parameters extracted from Figs. 3,4,5.
### pH Parameters

<table>
<thead>
<tr>
<th>pH</th>
<th>Parameters</th>
<th>30 min</th>
<th>60 min</th>
<th>90 min</th>
<th>120 min</th>
<th>150 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>$R_{po}$ ohms</td>
<td>67.0</td>
<td>76.8</td>
<td>86.7</td>
<td>96.8</td>
<td>106.5</td>
</tr>
<tr>
<td></td>
<td>$C_c$ F</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$1.7 \times 10^{-5}$</td>
<td>$1.75 \times 10^{-5}$</td>
<td>$1.8 \times 10^{-5}$</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$R_f$ ohms</td>
<td>38.9</td>
<td>32.8</td>
<td>33.9</td>
<td>37.9</td>
<td>39.5</td>
</tr>
<tr>
<td></td>
<td>$C_f$ F</td>
<td>$2.9 \times 10^{-3}$</td>
<td>$3.09 \times 10^{-3}$</td>
<td>$3.2 \times 10^{-3}$</td>
<td>$4.2 \times 10^{-3}$</td>
<td>$4.6 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$R_u$ ohms</td>
<td>22.0</td>
<td>22.26</td>
<td>22.37</td>
<td>22.42</td>
<td>22.49</td>
</tr>
<tr>
<td>7</td>
<td>$R_{po}$ ohms</td>
<td>79.0</td>
<td>438.0</td>
<td>486.0</td>
<td>537</td>
<td>568</td>
</tr>
<tr>
<td></td>
<td>$C_c$ F</td>
<td>$2.0 \times 10^{-5}$</td>
<td>$3.9 \times 10^{-6}$</td>
<td>$5 \times 10^{-6}$</td>
<td>$1.1 \times 10^{-5}$</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$R_f$ ohms</td>
<td>55.0</td>
<td>458.0</td>
<td>540.0</td>
<td>550.0</td>
<td>568.5</td>
</tr>
<tr>
<td></td>
<td>$C_f$ F</td>
<td>$3.0 \times 10^{-3}$</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$2.4 \times 10^{-4}$</td>
<td>$3.5 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$R_u$ ohms</td>
<td>16.0</td>
<td>32.46</td>
<td>33.0</td>
<td>34.5</td>
<td>36.0</td>
</tr>
<tr>
<td>10</td>
<td>$R_{po}$ ohms</td>
<td>589.0</td>
<td>798.5</td>
<td>948.5</td>
<td>1098.5</td>
<td>1188</td>
</tr>
<tr>
<td></td>
<td>$C_c$ F</td>
<td>$7.0 \times 10^{-6}$</td>
<td>$1.2 \times 10^{-5}$</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$1.1 \times 10^{-5}$</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$R_f$ ohms</td>
<td>658.0</td>
<td>1198.0</td>
<td>1548.5</td>
<td>1900</td>
<td>1938</td>
</tr>
<tr>
<td></td>
<td>$C_f$ F</td>
<td>$6.9 \times 10^{-4}$</td>
<td>$8.9 \times 10^{-4}$</td>
<td>$9.0 \times 10^{-4}$</td>
<td>$1.1 \times 10^{-3}$</td>
<td>$1.2 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$R_u$ ohms</td>
<td>29.0</td>
<td>29.6</td>
<td>29.97</td>
<td>30.2</td>
<td>31.7</td>
</tr>
</tbody>
</table>

#### 3.4. Morphology

Figure 6 shows SEM images of milled powder and as shown, every Mg particle, big or little, is covered with HAp particles. The results showed that the HAp includes Ca, P, and O. High magnification revealed an Mg-rich secondary phase. No HAp phase structure was found in our investigation, but we think its existence improves the mechanical and physical properties of Mg-HAp complexes over pure Mg. Mg and/or Mg-alloys are possible biodegradable biomaterials due to their comparable density and Young’s modulus to human bone, non-toxicity, and strong biocompatibility. Because of its low bioactivity and low mechanical strength, Mg and/or Mg alloys are not presently employed in clinics. An Mg/HAp nanocomposite with different concentrations of HAp (0–5 wt.%) was swiftly solidified with HFIHS to create a biodegradable hard tissue component.

Figure 7 exhibits Mg-X wt.% HAp compact density and microhardness. First, adding HAp raised relative densities. Despite the short dwell period, the sintered samples' comparative density reached 99.7%. As shown in Fig. 7, Mg and Mg/HAp nanocomposites had microhardness testing. Microhardness values...
increased as the wt.% of nano-sized HAp reinforcement in the Mg matrix increased. 1–3% HAp-reinforced Mg. Among the nanocomposite formulations, nanopowder increased relative density and hardness the most. HV 99.7% comparative density and 1–3 wt.% durometer HAp 70 HV reinforced Mg. It was 1–3 wt.% hard. In terms of density, HAp 70 HV varied from 1 to 3 wt.% HAp 70. The presence of HAp fragmented nanoparticles at grain boundaries presumably pre-empted the increase in comparative density. These nano-sized inclusions may improve Mg's mechanical properties.

Surprisingly, relative density and microhardness reduced when HAp concentration increased over 3%. For two reasons, increasing HAp content reduces the relative density and microhardness of nanocomposites. First, HAp nanoparticles cluster to some degree. However, when the HAp concentration grows, 550 °F is no longer sufficient. The low melting temperature of the matrix surrounding Mg prevents raising the sintering temperature. In all Mg/HAp nanocomposite samples, there is a narrow distribution of hardness values.

3.5. Composite Bone Formation Test

After testing the compressive properties and density of AZ91 magnesium alloy as well as AZ91 nanocomposites, in addition to their stress curves, it was observed that the strength of compressive properties of AZ91 nanocomposites increased by increasing the added nanoparticles, reaching the maximum values by adding nearly 20% of nanoparticles. It assumed the homogeneity of nanoparticles on the surface of AZ91 magnesium during the mixing process, and this led to a significant improvement in the compressive properties of AZ91 magnesium alloy, which in turn led to an enhancement of the modulus of elasticity, making the distribution highly uniform, as well as increasing the cohesion of nanoparticles in the matrix of AZ91 magnesium alloy.

This increase in the elastic modulus of the matrix is due to the uniform distribution of reinforcement and inter-integration and a significant increase in the internal tension between the reinforcement and the matrix. It was also observed that the matrix ductility of AZ91 magnesium alloys decreased with a higher concentration of nanoparticles in the reinforcements in all AZ91 nanocomposites see Fig. 8A. Despite the use of higher concentrations of the reinforced particles, it was observed that the agglomeration of the reinforced particles reduces the ductility and also creates small gaps between them, which led to an increase in the weight percentage of the nanoparticles used as a hardness enhancer due to the presence of calcium atoms inside the matrix particles, which made them relatively more rigid which improved the mechanical evaluation of AZ91 magnesium alloy, significantly increasing the overall bulk density as shown in Fig. 8B.

For more explanation, the reinforcements worked to fill the interfacial gaps in the matrix, as the samples with porosity, which did not affect mechanical properties or erosion rates, might have better fillers in terms of tissue healing and bone production, as this was proven using the given results from EDS, as it is observed from the Fig. 9A that there is no trace or evidence of the presence of calcium in the magnesium alloy before it was introduced into the body fluid as seen in Table 6. In addition, it was observed in
the case of immersion of the magnesium alloy nanocomposite in the body fluid, the presence of a large amount of calcium as shown in Fig. 9B. These results prove that this alloy in this composition gave great compatibility with body fluids, meaning that the body can accept them, and this became more evident through the spread of calcium around the compound, which makes this alloy and the support with nanoparticles suitable to serve as good support for treating bone fractures as shown of high calcium content as in Table 7 46–50.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg K</td>
<td>21.33</td>
<td>29.12</td>
<td>25.89</td>
<td>1.55</td>
</tr>
<tr>
<td>O K</td>
<td>44.88</td>
<td>49.33</td>
<td>210.75</td>
<td>9.6</td>
</tr>
<tr>
<td>AlK</td>
<td>33.79</td>
<td>21.55</td>
<td>659.42</td>
<td>4.42</td>
</tr>
</tbody>
</table>

Table 7
EDS elemental results of nanocomposite AZ91 after bone formation

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>28.34</td>
<td>43.55</td>
<td>60.83</td>
<td>1.91</td>
</tr>
<tr>
<td>O K</td>
<td>12.53</td>
<td>7.48</td>
<td>276.77</td>
<td>3.66</td>
</tr>
<tr>
<td>P K</td>
<td>12.53</td>
<td>7.48</td>
<td>276.77</td>
<td>3.66</td>
</tr>
<tr>
<td>CaK</td>
<td>26.99</td>
<td>12.44</td>
<td>401.48</td>
<td>2.42</td>
</tr>
<tr>
<td>MgK</td>
<td>0.46</td>
<td>0.35</td>
<td>7.45</td>
<td>7.11</td>
</tr>
<tr>
<td>AlK</td>
<td>0.95</td>
<td>0.62</td>
<td>5.65</td>
<td>2.35</td>
</tr>
</tbody>
</table>

**Conclusion**

Sintering at higher frequencies and temperatures quickly densified 0.5-5 % of the Mg/HAp nanocomposite in an incredibly short amount of time. The corrosion potential ($E_{corr}$), corrosion current ($i_{corr}$), and polarization resistance ($R_p$) of Mg in the test solutions were all measured during a corrosion test on the nanocomposite ($K_{corr}$). In the anodic side of the system, the high anodic potential was exacerbated by the SBF solution's abrasiveness. Even while a localized assault is less likely when HAp is present or concentrated, it is still a possibility. The most corrosion-resistant Mg/5.0 wt.% HAp solution is used in SBF applications. Because of this, Mg in the SBF medium was used in the EIS investigation to
investigate kinetic limits on electron allocation. HAp was found in 1% to 5% of patients, which was attributed to rising levels of resistance and a rise in the amount of HAp present. The more HAp there is in the solution, the more resistant Mg is to corrosion. As HAp concentration grew, Mg's interface impedance (|Z|) also increased. We can confirm the results of earlier investigations using electrochemical instruments such as PD and EIS measurements. All the composites examined in this study have exceptional mechanical and corrosion resistance.

It was noted that there is no trace or evidence of the presence of calcium in the magnesium alloy before it is introduced into the body fluid. In addition, it was observed in the case of immersion of the nanocomposite of the magnesium alloy in the body fluid, the presence of a large amount of calcium, so it can be said that these results proved that this alloy in this composition gave high compatibility with body fluids, which means that the body can accept it, and this became more evident by the diffusion of calcium around the compound, which makes this alloy suitable to serve as good support for the treatment of bone fractures as shown in the high calcium content.

**Declarations**

**Competing Interests**

The authors declare that there is no conflict of interest

**Author Contribution:**

Rabab M. El-Sherif, Khaled M. Zohdy, and Ashraf M. El-Shamy analyzed the data and wrote the manuscript, Rabab M. El-Sherif act as a consultant for the scientific information, Khaled M. Zohdy designed and supported the experiment, and Ashraf M. El-Shamy helped perform the analysis with constructive discussions.

**Funding:**

This work was supported by own

**Data availability**

Data of this study will be made available from the corresponding author on reasonable request.

**References**


**Figures**
Figure 1

Monitoring of the corrosion behavior of MG91 in SBF at different pH and at 25 °C (A) Potential time curves and (B) Potentiodynamic polarization curves
Figure 2

Effect of temperature variations on the potentiodynamic polarization curves for the corrosion behavior of MG91 in SBF at (A) pH 5, (B) pH 7, and (C) pH 10.
Figure 3

Nyquist curves results from EIS plots for the corrosion behavior of MG91 in SBF at different pH at 25°C.
Figure 4

Bode and phase angle curves result from the EIS plots for the corrosion of MG91 in SBF in several pHs at 25°C.
Figure 5

Effect of time intervals on the repeated Nyquist curves for the corrosion behavior of MG91 in SBF in (A) pH 5 (B) pH 7 (C) pH 10 at 25 °C and (D) Equivalent circuit.
Figure 6

Effect of pH on the surface characterization using SEM micrograph (A) pH = 5, (B) pH = 7 and (C) at pH = 10 for the Mg/5wt.% HAp composites
Figure 7

Effect of pH variations on the (A) the relative density and (B) the microhardness of nanocomposites of Mg-alloy.
Figure 8

Surface morphology of (A) nanocomposite AZ91 before bone formation (B) nanocomposite AZ91 after bone formation using SEM photomicrographs.
Figure 9

Detection of calcium in (A) nanocomposite AZ91 before bone formation (B) nanocomposite AZ91 after bone formation using SEM-EDS graphs.