Increasing the in-vitro corrosion resistance of AZ31B-Mg alloy via coating with hydroxyapatite using plasma electrolytic oxidation

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ABSTRACT
This study investigates the effect of hydroxyapatite (HA) coating by plasma electrolytic oxidation (PEO) on the corrosion resistance of AZ31B Mg alloy. The effect of the HA concentration (5, 10 and 15 g.L\textsuperscript{−1}) on the microstructure and corrosion behavior of coatings in the electrolyte was studied. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were used to study the microstructure and composition. Polarization and electrochemical impedance spectroscopy (EIS) tests were applied to the bare and coated samples in simulated body fluid (SBF) to determine the resistance behavior and the kinetics of corrosion coatings. The results showed that HA could be distributed inside the coating along with MgO and Mg\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}. Moreover, it was found that the porosity declined and the thickness of coatings increased with increases in the HA concentration. The results also indicated that the corrosion resistance of AZ31B Mg alloy was enhanced by coating with any amount of HA. The highest corrosion resistance was obtained with an electrolyte comprising 15 g.L\textsuperscript{−1} HA. The lowest corrosion current density (1.99 × 10\textsuperscript{−6} A.cm\textsuperscript{−2}) was monitored in respect to the highest corrosion resistance.

1. Introduction
Attaining suitable biocompatibility has redefined magnesium (Mg) and its alloys as biomaterials. Since Mg, as the fourth most numerous cation in the body, serves as a crucial metal for human metabolism, and since it is naturally present in bone tissue, the biocompatibility of magnesium alloys is more appropriate than that of stainless steel, titanium or cobalt alloys [1–4]. In spite of the above mentioned advantages, magnesium alloys, intrinsic corrosion resistance has considerably limited their clinical applications [5,6]. Mg is a metal that is corroded rapidly at high corrosion rates in aqueous environments. Magnesium implants, early decomposition in the body undermines the alloys’ mechanical properties and causes destruction of the implants before the patient’s tissues improve. The low corrosion resistance of magnesium and its alloys in chloride ion environments such as SBF and blood plasma release a large amount of hydrogen gas through the adjacency of magnesium implants [7,8].

Many coating methods have been developed to improve the corrosion behavior of magnesium alloys, including thermal spraying, sol-gel, physical vapor deposition, anodizing and chemical vapor deposition [9–13]. PEO is a surface modification technique that applies a thick coating on light metals such as Al, Ti and Mg [14,15]. PEO-based coatings have porous surfaces that helping bone tissues grow and bone implant joints rise, thus making Mg a suitable biomaterial [16]. Calcium phosphates have ample chemical composition similarities to the mineral contents of bone and indicate splendid biocompatibility. The most commonly consumed calcium phosphate in implant production and fabrication is HA. HA has a unique ability to bind with natural bone, and this chemical bond accelerates the interaction with the host bone and copulative tissue. It also has no toxic effects in the body and provides very good biocompatibility with hard tissues. This material is used in low-load orthopedic applications such as filler for bone defects, coating on implants and drug release materials [17–19]. Xu et al. reported that calcium phosphate coating of a magnesium alloy is an effective way to improve surface biocompatibility. Yang et al. studied the corrosion behavior of coatings in the presence of HA particles. They found that the addition of HA significantly increased the corrosion resistance of the coatings [20,21].

In the present work, PEO-based coatings containing HA NPs were applied to AZ31 magnesium alloys with different HA concentrations in alkaline electrolytes. The effects of the HA concentration (5, 10 and 15 g.L\textsuperscript{−1}) on the coating morphology and composition were studied using SEM and XRD patterns by grazing incident XRD (GIXRD), respectively. Furthermore, the corrosion resistance of the coated specimens was investigated in SBF solution.
2. Materials and methods

2.1. Synthesis of hydroxyapatite nanoparticles

The synthesis of the HA nanoparticles (HA NPs) was carried out using the wet chemical precipitation method [22]. First, 16.9 g L\(^{-1}\) of calcium acetate (C\(_2\)H\(_4\)O\(_2\)Ca, Merck, 109,325) as a source of calcium and 7.8 g L\(^{-1}\) of hydrogen phosphate di-ammonium (H\(_3\)N\(_2\)O\(_4\)P, Merck, 101,207), which is rich in phosphate, were dissolved separately in water and passed through a filter after homogenization. The calcium solution was then added slowly and dripped into a mixing phosphate solution. Ammonia was added dropwise to achieve a pH of 9 to stabilize the HA in the solution. The temperature was controlled at 45°C during the procedure. The obtained solution was stirred by the agitator for 24 h, and then washed three times and eventually dried at 80°C.

2.2. PEO process

Prior to coating, the AZ31B Mg alloy specimens (20 × 15 × 3 mm\(^3\)) were provided. Numbers of 220 to 2000 T sandpapers were used to polish the surface and edges of the samples. The polished samples were washed with distilled water and, finally, dried by applying a cold air flow. The chemical composition of the magnesium alloy is given in Table 1. The coating was applied using a model PM 700/7 PRC (IPS) power supply. A one-liter stainless steel bath serving as the cathode (negative pole) of the device was used for the coating process. In order to conduct the coating process as the anode (positive pole), magnesium samples were immersed in the electrolyte. The cooling system was used to control the temperature throughout the coating process. The alkaline electrolytes used contained 3 g L\(^{-1}\) of potassium hydroxide (KOH, Merck, 105,032) and 5 g L\(^{-1}\) of sodium phosphate (Na\(_3\)PO\(_4\).12H\(_2\)O, Merck, 106,578) in addition to various concentrations of HA (5, 10 and 15 g L\(^{-1}\)). The chemical composition of the electrolyte used in the coating process is indicated in Table 2. All PEO procedures were conducted under constant current density (300 mA/dm\(^2\)).

Table 1. AZ31 magnesium alloy chemical composition.

| Element | Wt.% | Ca | Zn | Si | Ni | Fe | Mn | Al | Mg |
|---------|------|----|----|----|----|----|----|----|----|
| Sample  |      |    |    |    |    |    |    |    |    |
| AZ31    | 0.006 | 0.96 | 0.01 | 0.01 | 0.006 | 0.39 | 2.65 | Surplus |   |

Table 2. Chemical composition of the used electrolyte in the coating procedure.

| Sample | Electrolyte (g L\(^{-1}\)) | KOH Na\(_3\)PO\(_4\).12H\(_2\)O HA | pH | Conductivity (ms/cm) |
|--------|---------------------------|---------------------------------|----|----------------------|
| HA 5   | 2.5 S                     | 13.33                            | 13.33 | 18.50               |
| HA 10  | 2.5 S                     | 13.36                            | 13.36 | 18.33               |
| HA 15  | 2.5 S                     | 13.40                            | 13.40 | 18.02               |

2.3. Characterization

To study the HA NPs surface charge for various pH amounts (5, 7, 9 and 11), a qualitative survey and identification of HA powder and its functional molecular groups, a Zetasizer nano model as Zeta potential (ζ) device and BRUKER-ALPHA model infrared Fourier transform spectrometer were used, respectively. In addition, XRD patterns measured by the GIXRD method (Philips PW1730 diffuser, Cu-Kαλ=1.54 A\(^{\prime}\)) were utilized to identify the present phases in the coated samples. Diffraction patterns were analyzed using Xpert HighScore software. SEM (model: FEI ESEM QUANTA 200) was applied to study the microstructures of the coatings.

2.4. Electrochemical measurements

SBF solution was prepared based on the proposed method of Kokubo in order to conduct corrosion tests [23]. The compounds used to make this solution are shown in Table 3. All of tests were carried out using a µAutolab Type III/FRA2. Potentiodynamic polarization tests and EIS tests were carried out on AZ31B magnesium alloy samples with and without coating at ambient temperature. Three-electrode flat cells were utilized in order to conduct the corrosion tests. A platinum electrode as an auxiliary electrode and a silver/silver saturated silver reference electrode and tested sample as a working electrode were used. All specimens were subjected to an EIS test with a frequency range of 100 kHz to 10 mHz. Before starting the electrochemical tests, the samples were exposed to a corrosive solution for 30 minutes at ambient temperature in order to reach their open-circuit potential.

3. Results and discussion

3.1. Characterization of nanoparticles in the electrolytes

The chemical and physical specifications of PEO process electrolytes have significant roles in determining the coating microstructure as well as the distribution of HA NPs. Hence, the products of the wet chemical precipitation method were analyzed prior to the coating process. Figure 1 shows XRD patterns of particles precipitated

Table 3. Values of SBF solution compositions in 1000 ml [22].

| Order | Reagent     | Amount |
|-------|-------------|--------|
| 1     | NaCl        | 8.035 (g) |
| 2     | NaHCO\(_3\) | 0.355 (g) |
| 3     | KCl         | 0.225 (g) |
| 4     | K\(_2\)HPO\(_4\).3H\(_2\)O | 0.231 (g) |
| 5     | MgCl\(_2\).6H\(_2\)O | 0.311 (g) |
| 6     | 1M-HCl      | 39 ml   |
| 7     | CaCl\(_2\)  | 0.292 (g) |
| 8     | Na\(_2\)SP \(_4\) | 0.072 (g) |
| 9     | Tris        | 6.118 (g) |
| 10    | 1M-HCl      | 0–5 ml  |
from the wet chemical precipitation method. It was observed that the obtained product was a single-phase HA according to the JCDPS 01-086-1199 standard card. There was also good agreement between the product diffraction peaks and the presented standard. An SEM image of HA powder is presented in Figure 2. HA particles occur mainly needle and spherical shapes. pH is a factor that plays an important role in the structure of HA NPs. Nanoparticle synthesis using a wet deposition with a pH of less than 9 causes the formation of needle-shaped structures, while an alkaline pH of above 9 leads to spherical structures [24]. It was observed based on the figure that the particles had a quasi-spherical structure. Crushing powder particles cause deformation of the particles and regular binding and breakage due to particle agglomeration. The average particle size of the HA was calculated as 165 nm using a wet chemical deposition technique.

Figure 3 illustrates the FTIR of HA. According to the individual peak wave numbers that show the presence of particular functional groups in the specimens [25], the OH and P-O bands in (PO$_4$) groups are seen in the spectrum of HA. In this spectrum, the major phosphate group peaks appear in the wave numbers 563 cm$^{-1}$, 603 cm$^{-1}$ and 1037 cm$^{-1}$. An HPO$_4^-$ related peak is observed in the regions of 470 cm$^{-1}$ and 873 cm$^{-1}$. This peak presence is due to HA formation with a calcium deficiency (CDHA). The long, flat OH$^−$ peak in the region of 3446 cm$^{-1}$ is also related to the water structure, moreover, and the presence of peaks is related to the carbonate group in the range of 1456 cm$^{-1}$ and 1568 cm$^{-1}$. The CO$_3^{−}$ ion might have been produced during the preparation of HA particles due to carbon dioxide absorption by the atmosphere. Since carbonate is formed easily, biological apatites gain an amount of carbonate equivalent to bone under laboratory conditions [26].

Figure 4 shows variations in the $\zeta$ potential at different pH values. The stability of NPs in a suspension can be prolonged at higher $\zeta$ potential values due to the stronger repulsive force between HA NPs [27]. The $\zeta$ potential value of HA NPs was 6.96 and 1.78 mV at pH levels of 5 and 7, respectively. It is favored to absorb more HA NPs during the PEO process, since the substrate serves as the positive pole. The agglomerated HA can be exchanged using the suspended HA NPs by adding more alkaline to the PEO electrolyte due to the higher negative $\zeta$ potential values. When the pH was increased to 9 and 11, the surface charges in the HA NPs were equal to $-17.8$ and $-28.3$ mV, respectively. The higher negative zeta potential results in stronger
electrophoretic forces between the particles, leading to absorption of more HA NPs as well as to proper particle stability.

### 3.2. Voltage-time diagram

Figure 5 displays a voltage-time diagram for coatings in three electrolytes formed at different HA concentrations (5, 10 and 15 g.L\(^{-1}\)) over 7 min. Generally, the diagram is divided into three stages in accordance with the voltage alteration. In the first step, all the specimens’ voltages increased linearly with high slopes in various concentrations. The electric field created a propulsion to transfer the cations and anions in the electrolyte all across the protective layer. Under these conditions, an oxide layer was formed on the surface. Increasing the thickness, the oxide layer to act as a barrier inhibiting the flow. The dielectric failure of the oxide layer then took place in areas with less resistance, forming small sparks in the failure voltage (the beginning of the second step). At this level, a number of bright sparks appeared on the surface [28-30]. The results showed that the failure voltages of the coatings formed by 5, 10 and 15 g.L\(^{-1}\) concentrations of HA were 227, 317 and 321 V, respectively. A time voltage diagram of the specimen with a higher concentration of 15 g.L\(^{-1}\) of HA is slightly higher than those of the other samples as a result of HA particle absorption into the coating. In the third step, the voltage reaches a stable value. The sparks become gradually larger and more stable, changing color from white to orange. Increasing the HA NP concentration from 5 to 15 g.L\(^{-1}\) also caused the final voltage to rise from 506 V to 522 V. As can be seen, coated samples have the same behavior and failure voltage, and their
final potential is almost the same due to the weak effect of HA NPs on the electrolytic conductivity of the electrolyte. As the concentration of nanoparticles in the coating electrolyte augment was raised, the electrical conductivity of the solution registered moderate decline, and the ignition voltage and final voltage increased.

### 3.3. Microstructures of the coatings

An overhead view of SEM images of coatings formed by different concentrations of HA NPs (5, 10 and 15 g.L⁻¹) is presented in Figure 6(a–c). Open porosities are observed on the surface of all the samples. This formation of porosity, which is due to remaining gases, that released microcracks arising from thermal stresses created during the coating process [31,32]. The percentages of surface porosity observed for HA5, HA10 and HA15 specimens were 11.3, 8.3 and 6.7%, respectively. The HA5 sample surface showed a great deal of porosity, which declined while the percentage of nanoparticle porosity increased. It seems that the porosities on the surface of the HA 15 specimen were filled by HA NPs. The HA NPs could enter in the evacuated channels under a strong electric field that may have caused the discharge channels to be blocked at higher concentrations of nanoparticles. Cross-sections of SEM micrographs of these specimens

![Figure 5. Voltage-time diagram for coated samples at different concentrations of 5, 10 and 15 g.L⁻¹ of HA.](image)

![Figure 6. SEM images of the cross-sections and surfaces at various concentrations of HA.](image)
are shown in Figure 6(d–f). The average thickness of the HA5, HA10 and HA15 coatings was obtained as 25, 26.2 and 28.7 μm, respectively. The thickness of the coating increased by approximately 13% with increases in the concentration of HA NPs. This was because the condenser voltage of the sample containing 15 g.L−1 was higher than the others. More heat and energy in the discharge channels created proper conditions for the reaction. Consequently, more particles entered the discharge channels and formed thicker walls [33].

3.4. Composition of the coatings

Figure 7 shows GIXRD patterns of AZ31B coated with different concentrations of HA NPs. The presence of the HA peak confirms the incorporation of HA NPs into the coatings. The peak intensity of the HA phase rises with increases in the concentration of HA NPs. According to the patterns, the entrance of HA NPs into the coatings was accompanied by formation of similar compositions. The formation of Mg3(PO4)2 in the coatings occurred because of a reaction between the available anions from the phosphate salts and the dissolved cations from the Mg substrate. The detection of the MgO phase is a result of the melting the Mg substrate and post-oxidation [34]. The amount of MgO in the coatings was intensified with increases in the HA concentration. This phenomenon can be elucidated by the ignition voltage, in which the higher ignition voltage and subsequently higher heat input occurred in response to the higher electrolyte concentration [35].

Elemental distribution maps of Mg, O, Ca and P on the surface of and along the coating of HA15 are displayed in Figure 8. According to the obtained results, a uniform distribution of Ca, P and O elements throughout the coating can be seen. The matched maps of Ca and P demonstrate the formation of HA especially along the coating, in response to Ca10(PO4)6OH2. The distribution map of Mg as the main element along the coating displays the movement of a small amount of Mg away from the substrate and enrichment of the outer layer to form Mg3(PO4)2. The dissolved PO4 ions in the electrolyte rose to the surface in the final stage of processing and formed Mg3(PO4)2. On the other hand, the molten Mg substrate was oxidized during the failure voltage stage because of exposure to the highest heating input. Hence, MgO was formed at the interface of the Mg substrate and the coating. The distribution map of O confirms the formation of an oxide layer at the interface.

3.5. Corrosion behavior

Figure 9 shows the Nyquist and Bode curves of the EIS measurements for coated samples of HA NPs at various concentrations. These diagrams consist of a real impedance section on the imaginary part of it after 30 minutes immersion in an SBF solution. The Nyquist diagram (Figure 9(a)) shows that the uncoated specimen has inductive behavior, since magnesium alloys are formed as being exposed to the atmosphere, a porous oxide layer is formed on them, and when they are immersed in a corrosive solution, the oxide layer of the corrosive solution passes through them and reaches the substrate, causing an induction behavior due to their low corrosion resistance [36]. The Nyquist diagram shows that the coatings produced at different concentrations of HA have the same behavior. The coatings consist of two capacitive loops and an inductive behavior that the presence of these three loops show the presence of three processes. The created loop at high frequencies is related to the external porous layer and shows the inner dense layer at medium frequencies and also reveals the corrosion process at low frequencies having an inductive behavior [37]. The inductive behavior indicates that pitting corrosion has occurred in the samples. With increases in the percentage of HA NPs from 5 to 15 g.L−1, the Nyquist loop
diameter increases which shows that the corrosion resistance of the coatings has been augmented. Figure 9(b) shows the Bode curve in this condition. As can be seen, the curve at high frequencies shows linear behavior in which the impedance value indicates the solution strength. A steep slope was created by the capacitive behavior occurring in the circuit at median frequencies. There is a new slope in the curve after it is linearized at low frequencies that is much less steep than the slope at intermediate frequencies. This slope is as a result of the inductive behavior at low frequencies that confirms the behavior of the Nyquist curve. Based on the Bode curve in the low frequency range, the impedance value indicates the corrosion resistance due to the presence of a higher percentage of nanoparticles filling the cavities, reducing the porosity, and thus diminishing the defects. Thus, the HA 15 specimen has the highest impedance and the best corrosion behavior.

To consider the electrochemical behavior of the uncoated and coated samples, a proposed equivalent circuit is shown in Figure 10. In this equivalent circuit, $R_s$ is dissolved strength, $R_0$ and CPE$_O$ are related to the resistance and the phase element of the outer porous layer, respectively, $R_i$ and CPE$_i$ stand for the resistance and the phase element of the inner compressed layer, respectively, and $R_1$ and $L$ are related to the inductor and inductor resistance at low frequencies, respectively [38–41].

Table 4 shows the results of modeling of the coatings electrochemical behavior. As is clear, all the coated samples have higher corrosion resistance than the uncoated samples that are exposed to
Increasing the percentage of HA NPs from 5 to 15 g.L\(^{-1}\) causes the resistance of the inner and outer layers to increase. The sample containing 15 g.L\(^{-1}\) of HA has the highest outer larger resistance (5.8 MΩ.cm\(^2\)) and inner layer resistance (0.63 MΩ.cm\(^2\)), and thus it has the best corrosion resistance behavior.

Figure 11 illustrates the potentiodynamic polarization curves of coated and uncoated specimens at various HA concentrations after 30 minutes immersion in SBF solution. When ceramic coatings were applied to the AZ31B alloy, all the potentiodynamic polarization curves of the coatings have transferred to a greater negative potential and lower corrosion current density than that of the substrate. This shows that a thermodynamic tendency for corrosion phenomena occurs with application of a ceramic coating, whereas the kinetics of corrosion are diminished. The results of the potentiodynamic polymerization test include the corrosion current density (\(i_{\text{corr}}\)), corrosion potential (\(E_{\text{corr}}\)), slope of the anode and cathode branches (\(\beta_a, \beta_c\)), polarization resistance (\(R_p\)) and porosity percentage. Table 5 shows results extracted from these diagrams. The polarization resistance can be calculated by the Stern-Geary equation [42]:

\[
R_p = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)i_{\text{corr}}} \tag{1}
\]

The porosity percentage plays an important role in determining the corrosion behavior of the coatings, because the penetration of corrosive ions into the substrate occurs through these porosities. The equation shows 2% porosity with electrochemical parameters [43]:

![Figure 9. (a) Nyquist and (b) Bode plots of samples coated with various concentrations of HA.](image)
In this equation, \( P \) is the porosity percentage of the coating, \( R_{ps} \) and \( R_p \) represent the corrosion resistance of the substrates and the coatings, respectively, \( \beta_a \) is the anode branch of the substrate and \( \Delta E_{corr} \) shows the differences between the corrosion potential of the substrates and the coatings. All the coatings have more negative potential and less corrosion current density than those of the substrates, which decrease with the application of a corrosion kinetics coating. With increases in the percentage of nanoparticles from 5 to 15 g.L\(^{-1}\), the polarization resistance increased by 62 percent in comparison to the magnesium substrate. The HA 15 sample has the greatest positive corrosion potential (−1.54 V) and the lowest corrosion current density (1.99 × 10\(^{-6}\) A/cm\(^2\)) and it therefore presents the best corrosion behavior. The HA 5 specimen with corrosion potential of (−1.58 V) and a highest corrosion current density of (1.99 × 10\(^{-6}\) A/cm\(^2\)) has weak corrosion resistance. The results indicate that increasing the nanoparticle concentration augments corrosion resistance owing to the denser coating formation with a lower porosity percentage.

4. Conclusions

This study focuses on the corrosion behavior of HA content coating on an AZ31B Mg alloy prepared by the PEO method. The findings showed that high-purity spherical HA NPs were synthesized via the wet chemical precipitation method adapted for use in the PEO process. It was found that HA with stable phosphate electrolyte content can be achieved under alkaline conditions due to the −28.3 mV of HA \( \zeta \) potential. The results showed that an appropriate morphology in view of lower porosity (6.7%) and greater thickness (28.7 \( \mu \)m) was achieved when the concentration of HA in the phosphate electrolyte was 15 g.L\(^{-1}\). The corresponding corrosion resistance revealed that the highest resistance was also obtained under the aforementioned process conditions. Under these conditions, the polarization resistance of the sample increased by about 62% as compared with that of the uncoated sample. The corrosion current density and polarization resistance were 1.99 × 10\(^{-6}\) A.cm\(^{-2}\) and 11.27 MΩ.cm\(^2\), respectively.
Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Vormann J. Magnesium: nutrition and metabolism. Mol Aspects Med. 2003;24:27–37.
[2] Song G, Song S. A possible biodegradable magnesium implant material. Adv Eng Mater. 2007;4:298–302.
[3] Staiger MP, Pietak AM, Huadmai J, et al. Magnesium and its alloys as orthopedic biomaterials: a review. Biomaterials. 2006;27:1728–1734.
[4] Farraro F, KwangK E, Savio L, et al. Revolutionizing orthopaedic biomaterials: the potential of biodegradable and bioresorbable magnesium-based materials for functional tissue engineering. J Biomech. 2014;47:1979–1986.
[5] Xu L, Yu G, Zhang E, et al. In vivo corrosion behavior of Mg-Mn-Zn alloy for bone implant application. J Biomed Mater Res A. 2007;83:703–711.
[6] Song G. Recent progress in corrosion and protection of magnesium alloys. Adv Eng Mater. 2005;7:563–586.
[7] Zeng R, Dietzel W, Witte F, et al. Progress and challenge for magnesium alloys as biomaterials. Adv Eng Mater. 2008;10:3–14.
[8] Witte F, Kaese V, Haferkamp H, et al. In vivo corrosion of four magnesium alloys and the associated bone response. Biomaterials. 2005;26:3557–3563.
[9] Keyvani A, Zamani M, Fattah-Alhosseini A, et al. Microstructure and corrosion resistance of MAO coatings on AZ31 magnesium. Mater Res Express. 2018;5:086510.
[10] Harada Y, Kumai S. Effect of ceramics coating using sol–gel processing on corrosion resistance and mechanical properties of AZ80 magnesium alloy substrate. Surf Coat Technol. 2013;228:59–67.
[11] Fattah-alhosseini A, Sabaghi Joni M. Effect of KOH concentration on the microstructure and electrochemical properties of MAO-coated Mg alloy AZ31B. J Mater Eng Perform. 2015;24:3444–3452.
[12] Hiromoto S, Shishido T, Yamamoto A, et al. Precipitation control of calcium phosphate on pure magnesium by anodization. Corros Sci. 2008;50:2906–2913.
[13] Kuo YL, Chang KH. Atmospheric pressure plasma enhanced chemical vapor deposition of SiOx films for improved corrosion resistant properties of AZ31 magnesium alloys. Surf Coat Technol. 2015;283:194–200.
[14] Molae M, Fattah-alhosseini A, Keshavarz MK. Investigation of microstructure and corrosion behavior of plasma electrolytic oxidation coatings on commercial pure Ti prepared in aluminate-based electrolytes with different sodium-based additives. J Asian Ceram Soc. 2019;7:247–255.
[15] Fattah-alhosseini A, Vakili-Azghandi M, Keshavarz MK. Influence of concentrations of KOH and Na2SiO3 electrolytes on the electrochemical behavior of ceramic coatings on 6061 Al alloy processed by plasma electrolytic oxidation (PEO). Acta Metall Sin. 2016;29:274–281.
[16] Sabaghi-Joni M, Fattah-alhosseini A. Effect of KOH concentration on the electrochemical behavior of coatings formed by pulsed DC micro-arc oxidation (MAO) on AZ31B Mg alloy. J Alloys Compd. 2016;661:237–244.
[17] Jarcho M, Bolen CH, Thomas MB, et al. Hydroxylapatite synthesis and characterization in dense polycrystalline form. J Mater Sci. 1976;11:2027–2035.
[18] Webster T, Siegel R. Enhanced functions of osteoblasts on nanophase ceramics. Biomaterials. 2000;21:10–1803.

Table 5. Extracted electrochemical results from the potentiodynamic polarization curve in different percentages of HA.

| Sample | βa (mV/dec) | βc (mV/dec) | icorr (A cm−2) | Ecorr (mV) | Rp (kΩ cm2) | P (%) |
|--------|-------------|-------------|-----------------|------------|-------------|-------|
| HA 5   | 95.04       | 135.73      | 4.36 × 10−6     | −1.58      | 5.7         | 80.5  |
| HA 10  | 128.08      | 173.89      | 3.4 × 10−6      | −1.54      | 8.24        | 54.64 |
| HA 15  | 76.98       | 93.92       | 1.99 × 10−6     | −1.54      | 11.27       | 36.64 |
| AZ31   | 96.37       | 75.21       | 8.54 × 10−6     | −1.35      | 4.24        | –     |

Figure 11. Polarization curves at distinct concentrations of 5, 10 and 15 g.L−1 of HA in SBF solution for 30 minutes.
[19] Seyfoori A, Mirdamadi S, Seyedraoufi ZS, et al. Synthesis of biphasic calcium phosphate containing nanostructured films by micro-arc oxidation on magnesium alloy. Mater Chem Phys. 2013;142:87–94.

[20] Xu LP, Pan F, Yu GN, et al. In vitro and in vivo evaluation of the surface bioactivity of a calcium phosphate coated magnesium alloy. Biomaterials. 2009;30:1512–1523.

[21] Yang J, Lu X, Blawert C, et al. Microstructure and corrosion behavior of Ca/P coatings prepared on magnesium by plasma electrolytic oxidation. Surf Coat Technol. 2017;319:359–369.

[22] Esfahani H, Darvishghanbar M, Farshid B. Enhanced bone regeneration of zirconia-toughened alumina nanocomposites using PA6/HA nanofiber coating via electrospinning. J Mater Res. 2018;33(24):1–9.

[23] Kokubo T, Takadama H. How useful is SBF in predicting in vivo bone bioactivity? Biomaterials. 2006;27:2907–2915.

[24] Yubao L, Groot K, Wijn J, et al. Morphology and composition of nanograde calcium phosphate needle-like crystals formed by simple hydrothermal treatment. J Mater Sci. 1994;5:326–331.

[25] Derelisa G, Petibois C. Applications of FT-IR spectrometry to plasma contents analysis and monitoring. Vib Spectrosc. 2003;32:129–136.

[26] Zhu B, Wang S, Wang L, et al. Preparation of hydroxyapatite/tannic acid coating to enhance the corrosion resistance and cytocompatibility of AZ31 magnesium alloys. Coatings. 2017;7:105.

[27] Xu R. Progress in nanoparticles characterization: sizing and zeta potential measurement. Particuology. 2008;6:112–115.

[28] Guan Y, Xia Y. Correlation between discharging property and coatings microstructure during plasma electrolytic oxidation. Trans Nonferrous Met Soc China. 2006;16:1097–1102.

[29] Guo H, An M, Hsu H, et al. Microstructure characteristic of ceramic coatings fabricated on magnesium alloys by micro-arc oxidation in alkaline silicate solutions. Appl Surf Sci. 2006;252:7911–7916.

[30] Khaselev O, Yahalom J. The anodic behavior of binary mg-al alloys in koh-aluminate solutions. Corros Sci. 1998;40:1149–1160.

[31] Duan H, Du K, Yan C, et al. Electrochemical corrosion behavior of composite coatings of sealed MAO film on magnesium alloy AZ91D. Electrochim Acta. 2006;51:2898–2908.

[32] Lin X, Wang X, Tan L, et al. Effect of preparation parameters on the properties of hydroxyapatite containing micro-arc oxidation coating on biodegradable ZK60 magnesium alloy. Ceram Int. 2014;40:10043–10051.

[33] Xi LC, Kainer BK, Zheludkevich M. Investigation of the formation mechanisms of plasma electrolytic oxidation coatings on Mg alloy AM50 using particles. Electrochim Acta. 2016;196:680–691.

[34] Asoh H, Ono S. Enhanced uniformity of apatite coating on a PEO film formed on AZ31 Mg alloy by an alkali pretreatment. Surf Coat Technol. 2015;272:182–189.

[35] Tanga H, Hana Y, Wua T, et al. Synthesis and properties of hydroxyapatite-containing coating on AZ31 magnesium alloy by micro-arc oxidation. Appl Surf Sci. 2017;400:391–404.

[36] King AD, Birbilis N, Scully JR. Accurate electrochemical measurement of magnesium corrosion rates: a combined impedance, mass-loss and hydrogen collection study. Electrochim Acta. 2014;121:394–406.

[37] Wen C, Zhan X, Huang X, et al. Characterization and corrosion properties of hydroxyapatite/graphene oxide bio-composite coating on magnesium alloy by one-step micro-arc oxidation method. Surf Coat Technol. 2017;317:125–133.

[38] Chaharmahali R, Shadabi M, Babaei K, et al. Effect of sodium phosphate concentration on corrosion behavior of the coatings produced by plasma electrolytic oxidation (PEO) on AZ31B Mg alloy in body simulative fluid. Anal Bioanal Electrochem. 2019;11:38–48.

[39] Vakili-Azghandi M, Fattah-alhosseini A, Keshavarz MK. Effects of Al2O3 nano-particles on corrosion performance of plasma electrolytic oxidation coatings formed on 6061 aluminum alloy. J Mater Eng Perform. 2016;25:5302–5313.

[40] Chaharmahali R, Babaei K, Fattah-alhosseini A. Corrosion behavior of calcium-phosphorus coatings on AZ31B Mg alloy by plasma electrolytic oxidation in Hank’s balanced salt solution. Anal Bioanal Electrochem. 2019;11:703–714.

[41] Vakili-Azghandi M, Fattah-alhosseini A. Effects of duty cycle, current frequency, and current density on corrosion behavior of the plasma electrolytic oxidation coatings on 6061 Al alloy in artificial seawater. Metall Mater Trans A. 2017;48:4681–4692.

[42] Stern M, Geary AL. Electrochemical polarization: a theoretical analysis of the shape of polarization curves. Electrochem Soc. 1957;104:56–63.

[43] Shokouhfar M, Allahkaram SR. Effect of incorporation of nanoparticles with different composition on wear and corrosion behavior of ceramic coatings developed on pure titanium by micro arc oxidation. Surf Coat Technol. 2017;309:767–778.