Preparation, Microstructure and Property of Zinc-substituted Hydroxyapatite/magnesium Biocomposite

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Abstract:
Zinc-substituted hydroxyapatite (Zn-HA, \(\text{Ca}_{10-x}\text{Zn}_x(\text{PO}_4)_6(\text{OH})_2\)) is used as the modified material of hydroxyapatite (HA, \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\)). In this work, Zn-HA with Zn contents of 10-30 mol% was used to produce Zn-HA/Mg composites by powder metallurgy. The calculated results showed that the crystallite size and lattice parameters of Zn-HA powders varied with the contents of 0-30 mol% Zn, confirming that the divalent Zn\(^{2+}\) ions can substitute Ca\(^{2+}\) ions in HA. Furthermore, the microstructure, mechanical property and electrochemical corrosion behavior of Zn-HA/Mg composites were investigated by SEM, compression tests, and electrochemical corrosion tests, respectively. The results indicate that the highest density and lowest porosity are obtained and the optimal mechanical property and corrosion resistance are achieved in the Zn-HA/Mg composites with 20 mol% Zn.

Keywords: Zinc-substituted hydroxyapatite; Zinc-substituted hydroxyapatite/magnesium composites; Powder metallurgy; Compressive property; Corrosion resistance.

1. Introduction

Magnesium (Mg) and its alloys are potential biodegradable implant materials due to their attractive biocompatibility and excellent bioactivity [1-2]. However, because of the rapid degradation of pure magnesium, it is likely to lose its mechanical stability before bonding with the bone tissue [3-4]. It has become a critical issue to control degradation rate and improve mechanical property of the magnesium. As a natural bone composition, HA is known to possess a low solubility and excellent biocompatibility in body environment [5]. Therefore, it seems to be appropriate as reinforcements in magnesium matrix [5-7]. Besides HA, there are also some essential constituents for human bone tissue such as CO\(^{3-}\), Na\(^+\), Mn\(^{2+}\), Mg\(^{2+}\), Si\(^{2+}\) and Zn\(^{2+}\) [8], thus these constituents are often used to introduce into the HA to improve the performance of HA. Currently, magnesium-substituted hydroxyapatite [9] and silicon-substituted hydroxyapatite [10] have been prepared and investigated. Once Ca\(^{2+}\), PO\(^{3-}\) or OH\(^-\) in the HA structure are substituted by the ions that human body needs, the properties of HA will be improved [11].

Among the different elements that can substitute Ca\(^{2+}\), PO\(^{3-}\) or OH\(^-\) in the HA, Zn is the potential candidate [12]. It is the most abundant and an essential trace metallic element found in bone, which is beneficial to the growth of bone tissue [13]. The addition of
appropriate Zn contents can refine the HA grains, improve the bioactivity of HA and maintain the crystal structure of HA. Although Zn-HA has advantages over other biological ceramic in terms of its biocompatibility and bioactivity, the toughness of Zn-HA is known to be poor, which limits its application as an implant material. As reinforcement in metal matrix composites, Zn-HA is suitable to meet the requirement of its strength. Therefore, based on the characteristics of magnesium and Zn-HA, Zn-HA/Mg biological composites can be successfully implemented.

Magnesium matrix composites are usually prepared by spray forming [14], stir casting [15] and powder metallurgy [16,17]. Among these methods, the powder metallurgy is simple, which can make the reinforced particles distribute homogeneously in the matrix and improve the plastic processing performance of the composites. Thus, this paper aims to prepare Zn-HA/Mg biological composites with good mechanical property and corrosion resistance by powder metallurgy.

2. Experimental materials and procedures

Ca(NO$_3$)$_2$·4H$_2$O, H$_3$PO$_4$, NH$_3$·H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O were used as raw materials to prepare HA and Zn-HA powder with the fractions of 10 mol%, 20 mol% and 30 mol% Zn by chemical precipitation method, which was named as HA, Zn1-HA, Zn2-HA, and Zn3-HA, respectively. These kinds of HA and Zn-HA powders were added into Mg powders at the mass ratio of 1:9, and then stirred with a magnetic stirrer for 6 h. The mixed powders were dried to a constant weight at 50°C in the constant temperature vacuum drying chamber and pressed as samples under the pressure of 500 MPa. Subsequently, the samples were sintered at 500°C for 2 h and then cooled in a furnace. This sintering was performed in an Ar atmosphere.

The microstructure of the powders and sintered samples were observed by JEM-2100F transmission electron microscope (TEM) and EVO-18 scanning electron microscope (SEM) combined with energy dispersive spectrometer (EDS), respectively. NEXUS fourier translation infrared spectroscopy (FT-IR) was used to analyze the chemical composition of sintered samples. D/Max-2500PC X-ray diffraction (XRD) was used to analyze the crystallite size and lattice parameters of starting powders and identify the phases present in the sintered samples. The density and open porosity in the sintered samples were measured by the Archimedes method. The mechanical behavior of the sintered body in compressive loading was determined by a MTS testing machine. The potentiodynamic polarization was measured in the simulated body fluid (SBF) at 37±0.5°C by an electrochemical workstation (CHI660D).

3. Results and Discussion

3.1. TEM, XRD and FT-IR analysis of powder

Fig. 1 shows the TEM micrographs of the HA and Zn-HA powders with various contents of Zn. As seen in the pictures, the particle sizes do not exceed 50 nm and slightly vary with the addition of Zn.

Fig. 2 shows the XRD patterns of the HA and Zn-HA powders with various contents of Zn. It can be found that Zn1-HA, Zn2-HA, and HA have the similar diffraction peaks, indicating that the HA crystal structure maintained with the addition of Zn. However, when the content of Zn is 30 mol%, as shown in Fig. 2d, some new peaks assigned to the phases of β-TCP and Ca$_{19}$Zn$_3$(PO$_4$)$_4$ were detected. According to XRD patterns, the crystallite dimensions (D) and the lattice parameters of the samples calculated by Rietveld refinement are given in Tab. I [18].
Fig. 1. TEM images: (a) HA, (b) Zn1-HA, (c) Zn2-HA and (d) Zn3-HA.

Fig. 2. XRD patterns: (a) HA, (b) Zn1-HA, (c) Zn2-HA and (d) Zn3-HA.

Tab. I The calculated values of crystallite sizes and lattice parameters from XRD peaks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D (nm)</th>
<th>a (nm)</th>
<th>c (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>31.0</td>
<td>0.9427</td>
<td>0.6896</td>
</tr>
<tr>
<td>Zn1-HA</td>
<td>29.5</td>
<td>0.9407</td>
<td>0.6927</td>
</tr>
<tr>
<td>Zn2-HA</td>
<td>21.9</td>
<td>0.9405</td>
<td>0.6765</td>
</tr>
<tr>
<td>Zn3-HA</td>
<td>49.8</td>
<td>0.9397</td>
<td>0.6748</td>
</tr>
</tbody>
</table>

It is clearly seen that the crystallite size of Zn-HA decrease at first, and then increase with increasing of Zn content. The decrease in crystallite size can be explained by disagreement between Ca and Zn in terms of ionic radius. The ionic radius of Zn$^{2+}$ ions (0.074nm) is slightly smaller than that of Ca$^{2+}$ ions (0.099nm). Due to that difference, the presence of Zn$^{2+}$ ions can result in a deformation of the crystal structure of HA and inhibit the
crystal growth [19]. The increase in crystallite size of Zn3-HA can be explained by some new phases of β-TCP and Ca$_{10}$Zn$_5$(PO$_4$)$_4$ that were formed. Additionally, it can be seen that the parameter a monotonously decreases with increasing Zn content. The lattice parameter c of Zn2-HA and Zn3-HA is smaller than that of HA. Such contraction in a and c may be caused by the smaller ionic radius in Zn$^{2+}$ (0.074 nm) than in Ca$^{2+}$ (0.099 nm). The same effect has been noticed by G. D. Venkatasubbu et.al. for Zn substitution [20]. In general, the XRD data pointed out the incorporation of small amounts of Zn$^{2+}$ into the structure of HA by replacing the Ca$^{2+}$ and the crystallite size of Zn2-HA reaches a minimum.

To analyze the chemical composition of sintered samples FT-IR of the samples was detected and shown in Fig. 3. The different vibrational modes of the orthophosphate groups were observed at 1102, 1014, 962, 608 and 561 cm$^{-1}$. The characteristic vibrational modes of the hydroxyl group were detected at 3571 and 631 cm$^{-1}$ [21]. Since the FT-IR technique is sensitive to study the covalent bonds only, it is unable to provide direct evidence on a possible incorporation of Zn$^{2+}$ ions into the crystal structure of HA. Nevertheless, since FT-IR spectra of Zn1-HA and Zn2-HA were similar, the anions of Zn1-HA and Zn2-HA were also similar and were equal to those of HA, which is in favor of Zn$^{2+}$ ions incorporation into the crystal lattice by replacing the Ca$^{2+}$. With increasing of Zn fraction, the separation of phosphate peaks at 1102, 1014, 962 cm$^{-1}$ becomes less pronounced and intensity of hydroxyl peak at 631 cm$^{-1}$ slightly decreases. These changes have also been observed by some other authors and they have been interpreted via decreasing of crystallinity of hydroxyapatite with an increase of Zn fraction [8, 20]. The change in FT-IR spectra of Zn3-HA can be explained by some new phases of β-TCP and Ca$_{10}$Zn$_5$(PO$_4$)$_4$ that were formed.

![Fig. 3. FT-IR patterns: (a) HA, (b) Zn1-HA, (c) Zn2-HA and (d) Zn3-HA.](image)

3.2. XRD analysis of composites

Fig. 4 shows XRD patterns of the Zn2-HA powders and Zn2-HA/Mg composite after sintering at 500°C for 2 h. Fig. 4b shows that the Mg and Zn2-HA phases of Zn2-HA/Mg composite prepared by powder metallurgy are still visible. The results of the XRD analysis revealed that there is no reaction between Zn2-HA and magnesium matrix, which is beneficial to keep the original bioactivity of Zn2-HA and magnesium. A small amount of MgO may be caused by the oxidation of Mg during the preparation of composites.
3.3. Effect of Zn content on the microstructure of composites

Fig. 5 shows the microstructure of composites with various contents of Zn after sintering at 500°C for 2 h and EDS analysis results of the Zn2-HA/Mg composite are illustrated in Fig. 6. It can be seen that HA and Zn-HA are distributed in the magnesium matrix. And the size of sintered Zn-HA particles decreases at first and then increase with increasing of Zn content. In particular, the Zn2-HA particles are very small and the distribution of Zn2-HA particles in the magnesium matrix is homogenous. Concerning the quantitative data, the Ca/P molar ratio of the Zn2-HA/Mg composite was found to be 1.72, which is very close to the theoretical value for the stoichiometric HA (1.67). The deviation can result from the fact Zn substitution can lead to a crystal defect. However, when the content of Zn is 30 mol%, the particles start to agglomerate. It can be seen that a large number of pores and voids are visible in the Zn-HA/Mg interface, but the pores are fewer in Fig. 5c.

Fig. 4. XRD patterns: (a) Zn2-HA powders and (b) Zn2-HA/Mg composite.

Fig. 5. SEM images: (a) HA/Mg composite, (b) Zn1-HA/Mg composite, (c) Zn2-HA/Mg.
Fig. 6. EDS analysis results of the Zn2-HA/Mg composite.

The density and porosity of HA/Mg and Zn-HA/Mg composites are presented in Tab. II. Combined with Tab. II, it can be also found that the addition of Zn can affect the density and porosity of the composites and the Zn2-HA/Mg composite with 20 mol% Zn have the lowest porosity.

**Tab. II** The density and porosity of HA/Mg and Zn-HA/Mg composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density of sintered body ρs (g/cm³)</th>
<th>Theoretical density ρt (g/cm³)</th>
<th>Relative density ρr (%)</th>
<th>Porosity P (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA/Mg</td>
<td>1.5793±0.0008</td>
<td>1.8096</td>
<td>87.27±0.04</td>
<td>12.73</td>
</tr>
<tr>
<td>Zn1-HA/Mg</td>
<td>1.6563±0.0005</td>
<td>1.8232</td>
<td>90.84±0.03</td>
<td>9.16</td>
</tr>
<tr>
<td>Zn2-HA/Mg</td>
<td>1.6691±0.0002</td>
<td>1.8237</td>
<td>91.52±0.01</td>
<td>8.48</td>
</tr>
<tr>
<td>Zn3-HA/Mg</td>
<td>1.6328±0.0001</td>
<td>1.8220</td>
<td>89.61±0.01</td>
<td>10.39</td>
</tr>
</tbody>
</table>

3.4. Effect of Zn content on the compressive property

The representative compressive stress-strain curves of the HA/Mg and Zn-HA/Mg composites are illustrated in Fig. 7.

It can be seen that the compressive strength of composites increase at first, and then decrease with increasing of Zn content. The compressive strength of Zn-HA/Mg composites is higher than that of the HA/Mg composites. It can be found that among the Zn-HA/Mg composites with various contents of Zn, the Zn2-HA/Mg composite has the greatest deformation and the highest compressive strength before fracture. The reason for the above results is that the Zn-HA particles restrain the movement of dislocations after the gradual disappearance of pores in the compression process. The shear stress can be calculated according to the following formula:

\[ \tau = \frac{Gb}{\lambda} \]
where \( \tau \) is the shear stress; \( G \) is the shear modulus; \( b \) is Burgers Vector; \( \lambda \) is the distance between particles [22]. When the external stress is larger than \( \tau \) value, the dislocation line can pass through the particles. The reinforcement of the second phase particles is inversely proportional to the particle distance. Due to the fact that proper contents of Zn can decrease the crystallinity of Zn-HA, the particles become smaller and then the particle distance also becomes smaller, which improve the plastic deformation resistance of composites. However, when the content of Zn is 30 mol\%, the sizes of particles increase obviously, and then the compressive strength decrease.

Fig. 7. Compressive stress-strain curves for the HA/Mg and Zn-HA/Mg composites.

3.5. Effect of Zn content on the corrosion behaviors

Fig. 8 shows the potentiodynamic polarization curves of the HA/Mg and Zn-HA/Mg composites at 37±0.5°C in SBF and the parameters are listed in Tab. III. Although the corrosion potentials (\( E_{\text{corr}} \)) of the Zn-HA/Mg composites are close to each other, the polarization curves show a clear difference between the HA/Mg and Zn-HA/Mg composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Corrosion potential ( E_{\text{corr}} ) (V)</th>
<th>Corrosion density ( I_{\text{corr}} ) (A/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA/Mg</td>
<td>-1.596</td>
<td>3.38E-4</td>
</tr>
<tr>
<td>Zn1-HA/Mg</td>
<td>-1.556</td>
<td>3.26E-4</td>
</tr>
<tr>
<td>Zn2-HA/Mg</td>
<td>-1.549</td>
<td>3.23E-4</td>
</tr>
<tr>
<td>Zn3-HA/Mg</td>
<td>-1.571</td>
<td>3.43E-4</td>
</tr>
</tbody>
</table>

Compared to HA/Mg composite, the corrosion potentials (\( E_{\text{corr}} \)) of Zn-HA/Mg composites are shifted by 25-47mV toward more positive potentials, indicating the higher corrosion resistance of Zn-HA/Mg. Furthermore, it is observed that the corrosion current density (\( I_{\text{corr}} \)) of the Zn1-HA/Mg and Zn2-HA/Mg composites is lower than that of the HA/Mg composite,
confirming that the addition of 10 mol% and 20 mol% Zn can promote the corrosion resistance of composites. But when the Zn content is 30 mol%, the corrosion current density increases and the corrosion potential decreases. The above result is caused by the decomposition of Zn3-HA into some amount of \( \beta \)-TCP and Ca_{19}Zn_{2}(PO_{4})_{14}, which accelerated the corrosion rate of the composite. Thus, when the content of Zn is 20 mol%, the corrosion resistance of composite can be better improved.

Fig. 8. Potentiodynamic polarization curves of the HA/Mg and Zn-HA/Mg composites.

4. Conclusion

Zn-HA/Mg composites were successfully fabricated by powder metallurgy. Our research indicates that the crystallite size and lattice parameters of Zn-HA powders are varied with the contents of 0-30 mol% Zn, which confirms that the divalent Zn\(^{2+}\) ions can substitute Ca\(^{2+}\) ions in HA. The Zn2-HA/Mg (the content of Zn is 20 mol%) composite prepared by powder metallurgy has high density, low porosity, and high compressive strength. In the meantime, the corrosion resistance of Zn2-HA/Mg composite is the best, and the corrosion potential and the corrosion current density are -1.549V and 3.23E-4 A/cm\(^2\), respectively. Therefore, compared with other Zn content, the Zn2-HA/Mg composite can be used as a good potential biomaterial.

5. References


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