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# Effects of Sr incorporation on surface structure and corrosion resistance of hydroxyapatite coated Mg-4Zn alloy for biomedical applications

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Abstract: Hydroxyapatite (HA) and strontium (Sr) incorporated HA coatings with different Sr contents were prepared on Mg–4Zn substrates by electrochemical deposition method. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electrochemical workstation were applied for the composition, phase constitution, morphology analyses and corrosion tests. The results reveal that the incorporation of Sr in coatings does not lead to dramatical change of functional groups and the crystal structure of the HA phase, but the crystal size and crystallinity decrease with increasing Sr content, which should be attributed to the lattice distortion and different occupancies of Sr and Ca ions. The 10SrHA@Mg–4Zn samples show the lowest corrosion current density and the highest corrosion potential, and also exhibit the lowest amount of hydrogen evolution among all coated samples.

Key words: Mg-4Zn alloy; strontium-incorporated hydroxyapatite; electrochemical polarization; corrosion resistance

### **1** Introduction

Magnesium (Mg) alloys have drawn extensive attention for the potential applications as biomedical materials, owing to the good biocompatibility, low elastic modulus and the biodegradable property [1]. However, the high reactivity of Mg and Mg alloys usually leads to rapid corrosion rate in an electrolytic aqueous environment, which may cause detrimental interactions with the surrounding tissues [2]. Therefore, a suitable degradation kinetics is critical to a Mg-based implant until the damaged tissues have been recovered or healed [3].

There are generally two main approaches: 1) the introduction of alloying elements; 2) surface treatment or deposition of a biocompatible coating [4]. The selection of alloying elements can significantly influence the corrosion rate in the biological environment, e.g., Mg–Zn alloy shows significantly lower hydrogen evolution volume than Mg, while the addition of Y and Si into Mg leads to dramatically increased corrosion

rate [5]. Owing to the high chemical and structural similarities to the mineral component of bones and teeth, hydroxyapatite (HA) is widely used as coatings on metallic biomaterials [6,7]. For instance, the deposition of HA on commercially pure Mg significantly enhances the corrosion resistance [8]. Furthermore, the incorporation of some elements (such as Mg, Ag and Zn) into HA can improve the characteristic properties of HA [9]. Strontium (Sr) is a trace element in human bones and can induce bone formation [10]. Sr can be incorporated in HA lattice without any solubility limit, but usually low dosage of Sr is preferred in order to obtain better biocompatibility [11]. The Sr-doped HA ceramics have been confirmed to show better mechanical properties and biocompatibility compared with the pure HA [12]. For example, the Sr-doped HA coatings on commercially pure Ti (CP-Ti) and Ti-6Al-4V alloy can significantly enhance the osteogenic differentiation and mineralization [13,14]. The influence of Sr and Mg incorporation on HA coatings has also been compared by ROY et al [15]. Both of the Sr-doped and Mg-doped HA coatings show better adhesive bond strengths than the

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minimum requirements for HA-coated implants, and the Sr-doped HA shows considerably improved cell proliferation compared with the Mg-doped HA and pure HA coatings. However, the influence of the Sr-doped HA on the corrosion resistance of Mg alloys is still not clear.

Since a Sr/(Ca+Sr) mole ratio ranging from 0.03:1 to 0.1:1 is usually preferred for osteoblast activity and differentiation [16,17], two Sr-doped HA coatings with Sr concentrations of 5% and 10% were prepared on Mg–4Zn substrates in the present work. The aim of this study is to investigate the influence of Sr incorporation on the composition and structure of HA coatings as well as the corrosion resistance of the Mg–4Zn substrates.

### 2 Experimental

#### 2.1 Material preparation

Mg–4Zn alloy sheets were obtained from College of Materials Science and Engineering, Hunan University, China, and the processing details are shown in the reference [18]. The as-received materials were wireelectrode cut into 10 mm  $\times$  10 mm  $\times$  2 mm plates, and then ground with 600, 1000 and 2000 grit SiC paper. The ground plates were ultrasonically cleaned in ethanol, immersed into 100 g/L NaOH solution at 90 °C for 10 min, and then washed by 180 g/L CrO<sub>3</sub> solution for 5 min to remove oil and surface oxide. Afterwards, the Mg–4Zn samples were ultrasonically cleaned in deionized water for 10 min and dried at 60 °C.

A series of SrHA coatings with Sr/(Ca+Sr) mole ratios of 0:1, 0.05:1 and 0.1:1 (0SrHA, 5SrHA and 10SrHA) were deposited on the Mg–4Zn by electrochemical deposition. Briefly, analytical grade (AR) CaCl<sub>2</sub>, SrCl<sub>2</sub>·6H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> were dissolved into deionized water with magnetic stirring at 85 °C. The coated plates with Sr/(Ca+Sr) mole ratios of 0:1, 0.05:1 and 0.1:1 are referred to as 0SrHA@Mg–4Zn, 5SrHA@Mg–4Zn and 10SrHA@Mg–4Zn, respectively.

#### 2.2 Structural characterization

Functional group analysis was performed by Fourier transform infrared (FTIR) spectroscopy (Infinity-1, Thermo Fisher Scientific, USA) in the mid-infrared range (400–4000 nm<sup>-1</sup>) using the KBr pellet method at room temperature. A X-ray diffraction (XRD, D/Max–2500/PC, Rigaku Corporation, Japan) was applied for the crystal structure and phase analyses of different samples by using Cu K<sub> $\alpha$ </sub> radiation at 40 kV and 40 mA. The surface morphology and composition of the samples were investigated by using a scanning electron microscopy (SEM, JSM–6700F, JEOL, Japan) and energy-dispersive spectroscopy (EDS, Inca, OXFORD, UK) in the SEM.

### 2.3 Electrochemical polarization and dynamic immersion tests

Electrochemical measurements were carried out on a electrochemical workstation (ChI400C, CH Instruments, USA) with the three-electrode configuration in simulated body fluid (SBF, Jisskang, China). A saturated calomel electrode (SCE) was used as the reference electrode. The counter electrode was a platinum sheet, and the sample mounted in epoxy resin constituted the working electrode. Prior to testing, the samples with an exposed surface of 1 cm<sup>2</sup> were stabilized into SBF for 5 min, and the following tests were conducted in the water bath at 37 °C.

The dynamic immersion tests were performed in simulated body fluid (SBF) solution (pH=7.4). Each sample was attached to a funnel covered by an inverted graduated cylinder full of SBF. All hydrogen (H<sub>2</sub>) bubbles released from the samples were collected in the graduated cylinder, and the H<sub>2</sub> volume was measured from the change of the SBF level before and after the corrosion test. The H<sub>2</sub> evolution rate was also calculated. Besides, the pH value of SBF was measured before and after the immersion by using a pH meter (PHS–10A, Shanghai Precision Instruments, China).

### **3** Results and discussion

## 3.1 Chemical composition and microstructure of coatings

Figure 1 shows the FTIR spectra of the three coatings on the Mg–4Zn substrates, i.e., 0SrHA, 5SrHA and 10SrHA. The absorption bands at 962 cm<sup>-1</sup> ( $v_1$ ), 462 cm<sup>-1</sup>, 475 cm<sup>-1</sup> ( $v_2$ ), 1032 cm<sup>-1</sup>, 1046 cm<sup>-1</sup>, 1087 cm<sup>-1</sup> ( $v_3$ ) and 574 cm<sup>-1</sup>, 602 cm<sup>-1</sup> ( $v_4$ ) are observed in all spectra for the coatings. These bands should be attributed to the phosphate (PO<sub>4</sub><sup>3-</sup>) characteristic absorption. The bands at 3000–3500 cm<sup>-1</sup> and 632 cm<sup>-1</sup> are due to O—H stretching and O—H librational bands,



**Fig. 1** FTIR spectra of 0SrHA, 5SrHA and 10SrHA coatings prepared on Mg–4Zn substrates

respectively. The peak observed at 1430 cm<sup>-1</sup> is indicative of the carbonate ( $CO_3^{2-}$ ) substitution at OH<sup>-</sup> (*A*-site) position, which is in accordance with a previous report [19]. One possible reason is that the Sr substitution for Ca increases lattice strain and induces an increase of  $CO_3^{2-}$  in the lattice. In addition to these spectral modes, the weak absorption band at 1640 cm<sup>-1</sup> is attributed to hydrogen phosphate (HPO<sub>4</sub><sup>2-</sup>). No significant differences in the absorption bands are observed for any of the coatings, suggesting that the introduction of Sr does not significantly change the coating composition.

The XRD spectra of the 0SrHA, 5SrHA and 10SrHA coatings are displayed in Fig. 2. It is evident that the main component of all coatings is HA phase. The diffraction peaks show blue shift with increasing Sr content in the coatings, indicating the increase of lattice parameters. The ionic radius of Sr is 1.13 Å, which is much larger than that of Ca ion (0.99 Å) [20], so the change of lattice parameters clearly demonstrates the successful incorporation of Sr into the HA phase. Besides, slight line broadening is observed in the patterns of the coatings with higher Sr content, which may due to the decrease of crystal size. For quantitative purposes, since the peaks show no interferences for all samples, the (002) reflection is used to evaluate the average crystallite size (D) and the crystallinity degree  $(X_c)$  of the three coatings. The D and  $X_{\rm c}$  are calculated according to the following equations [9]:

$$D = \frac{0.9\lambda}{B_{1/2}\cos\theta} \tag{1}$$

$$X_{\rm c} = \left(\frac{0.24}{B_{\rm 1/2}}\right)^3 \times 100\%$$
 (2)

where  $\lambda$  is the wavelength of the X-ray (0.154 nm for Cu K<sub>a</sub> radiation),  $B_{1/2}$  is the full width at half maximum (FWHM) and  $\theta$  is the diffraction angle. The calculated results are listed in Table 1. The *D* values gradually increase with higher Sr content, but the 5SrHA and



Fig. 2 XRD patterns of 0SrHA, 5SrHA and 10SrHA coatings

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 Table 1 Crystal size and crystallinity degree of 0SrHA, 5SrHA

 and 10SrHA coatings reflected by XRD patterns

	0	F	-
Coating	FWHM (002)/(°)	D/nm	Xc/%
0SrHA	0.266	32.9	73.4
5SrHA	0.356	27.8	30.6
10SrHA	0.371	24.2	27.1

10SrHA show significantly lower  $X_c$  than the 0SrHA coatings.

The change in the mean crystal size as well as the crystallinity after introducing Sr should be attributed to the Sr<sup>2+</sup> substitution style of Ca<sup>2+</sup>. Site I and Site II are inequivalent cation sites in HA phase as shown in Fig. 3. BOANINI et al [16] claimed that the change of HA crystal structures after Sr incorporation highly depends on the occupancy style of Sr<sup>2+</sup>, and Sr usually induces significantly higher lattice distortion at Site II than Site I. TERRA et al [21] investigated the influence of Sr concentration on the occupancy style, and found that Site I is preferred for  $Sr^{2+}$  when the mole ratio of Sr/(Sr+Ca)is below 0.01:1, while, Site II is progressively preferred at Sr concentration higher than 5%. In this work, the Sr/(Sr+Ca) ratios in the 5SrHA and 10SrHA coatings were designed to be 0.05:1 and 0.1:1, respectively. Therefore, the Sr<sup>2+</sup> may tend to occupy Site II instead of Site I in both coatings. The higher Sr content indicates more substitution at Site II, and thus inevitably leads to enhanced destabilization of crystal structure. Severe distortion of lattice can restrain crystal growth, resulting in a decrease of average crystal size with increasing Sr content. Besides, the lattice distortion may have a destabilizing influence on the apatite structure, because of the destroyed symmetry [20]. Consequently, the crystallinity degrees of the 5SrHA and 10SrHA were only less than half of that of the 0SrHA.

Figure 4 presents the surface morphologies and EDS results of the surface of Mg-4Zn, 0SrHA@Mg-4Zn,



Fig. 3 Schematic diagram of crystal structure of HA phase (Both Site I and Site II are cation (e.g.,  $Ca^{2+}$ ,  $Sr^{2+}$ ) sites)



Fig. 4 SEM micrographs of surface morphology (a, b, c, d) and corresponding EDS analyses (a', b', c', d'): (a, a') Mg–4Zn; (b, b') 0SrHA@Mg–4Zn; (c, c') 5SrHA@Mg–4Zn; (d, d') 10SrHA@Mg–4Zn

5SrHA@Mg-4Zn and 10SrHA@Mg-4Zn samples. The Mg-4Zn alloy exhibits typical as-ground surface with some scratches as shown in Fig. 4(a). The coatings on the 0SrHA@Mg-4Zn, 5SrHA@Mg-4Zn and 10SrHA@Mg-4Zn samples show similar structures with small HA crystal lamellar embedded among large flakes (see Figs. 4(b-d)). After adding Sr into the coatings, the size of the large crystal flakes significantly decreases from 2–4.5  $\mu$ m for the 0SrHA to 1.5–3  $\mu$ m and 1–2.5  $\mu$ m for the 5SrHA and 10SrHA coatings, respectively. The dependence of the flake size of the coatings on Sr content is in accordance with the XRD results shown in Table 1.

According to the EDS spectra of the surfaces of 0SrHA@Mg-4Zn, 5SrHA@Mg-4Zn and 10SrHA@ Mg-4Zn samples, the mole ratios of Sr/(Ca+Sr) and (Ca+Sr)/P are shown in Table 2. The Sr/(Ca+Sr) mole ratios in 5SrHA and 10SrHA coatings are 0.042:1 and 0.091:1, respectively, which are slightly lower than the designed composition, i.e., 0.05:1 for 5SrHA and 0.1:1 for 10SrHA. The (Ca+Sr)/P mole ratios for the three coatings are around 1.3:1, which are much lower than that in stoichiometric HA. Such a result indicates that the coatings are probably calcium deficient hydroxyapatite materials, which agrees with the results reported by LINDAHL et al [13].

Table 2 Mole ratios of Sr/(Ca+Sr) and (Ca+Sr)/P in coatings of 0SrHA@Mg-4Zn, 5SrHA@Mg-4Zn and 10SrHA@Mg-4Zn samples

Coating	Sr/(Ca+Sr) mole ratio	(Ca+Sr)/P mole ratio
0SrHA	0:1	1.34:1
5SrHA	0.042:1	1.32:1
10SrHA	0.091:1	1.29:1

### 3.2 Electrochemical polarization and dynamic degradation

The electrochemical polarization curves of four samples are shown in Fig. 5. The cathodic branch of the Tafel plot shows the H<sub>2</sub> evolution through a reduction process, whereas the anodic branch represents Mg dissolution by oxidation [22]. All the four configurations showed non-symmetrical polarization curves between the anodic and cathodic branches, so it is necessary to choose proper Tafel methods for data analyses. As stated by JIN et al [23] and SONG [24], the polarization curves of Mg and Mg alloys do not follow the traditional Tafel equation and the cathodic curve usually produces a better Tafel region. Therefore, the corrosion potential ( $\varphi_{corr}$ ) and corrosion current density  $(J_{corr})$  are determined from the cathodic region of the polarization curves as presented in Table 3. A lower  $J_{corr}$  and a positive  $\varphi_{corr}$  indicate better corrosion resistance [25]. Compared with the bare Mg–4Zn alloy, the three coated configurations show one-order magnitude lower  $J_{corr}$  and more noble  $\varphi_{corr}$ . The significantly decreased  $J_{corr}$  of the samples with HA and Sr-containing HA coatings than that of the Mg–4Zn corresponds to a much lower corrosion rate and demonstrates that the coatings act as insulative barriers between the substrates and surrounding environment. The  $\varphi_{corr}$  of Mg–4Zn alloy shifts toward the positive direction from –1.441 to –1.403, –1.382 and –1.290 V after being coated with 0SrHA, 5SrHA and 10SrHA, respectively, also indicating that the samples experience less corrosion than the bare Mg–4Zn alloy in SBF. It is important to note that as for the three coated configurations, the  $J_{corr}$  decreases and  $\varphi_{corr}$  increases with higher Sr content.



Fig. 5 Electrochemical polarization curves of four groups in SBF

 Table 3 Parameters of electrochemical polarization curves of four samples

Sample	$\varphi_{ m corr}/ m V$	$J_{\rm corr}/(\mu {\rm A}\cdot {\rm cm}^{-2})$
Mg-4Zn	-1.441	124
0SrHA@Mg-4Zn	-1.403	37.2
5SrHA@Mg-4Zn	-1.382	35.5
10SrHA@Mg-4Zn	-1.290	9.42

The contact of Mg and Mg alloys with SBF can lead to Mg degradation to release  $H_2$  and  $Mg^{2+}$ , and thus alkalization of SBF [26]. The  $H_2$  release trends and pH values of SBF immersing the four configurations as a function of immersion time were measured as shown in Fig. 6. Generally speaking, for the same duration of immersion, the  $H_2$  release (see Fig. 6(a)) and alkalization (see Fig. 6(c)) of the SBF media are lightened in order of Mg-4Zn > 0SrHA@Mg-4Zn > 5SrHA@Mg-4Zn > 10SrHA@Mg-4Zn samples.

At the beginning of immersion (the first 48 h), the accumulative amount of  $H_2$  release from the bare



**Fig. 6** H<sub>2</sub> evolution vs time (a), H<sub>2</sub> evolution rate vs time (b) and pH vs time (c) of bare Mg-4Zn alloy, 0SrHA@Mg-4Zn, 5SrHA@Mg-4Zn and 10SrHA@Mg-4Zn

Mg-4Zn samples is almost twice as high as that from the other three samples (see Fig. 6(a)), and the H<sub>2</sub> release rate from the former is also significantly higher than those from the latter as shown in Fig. 6(b). While, the three coated samples show similar H<sub>2</sub> evolution behavior. Figure 6(c) presents that the pH change of the SBF immersed with the bare Mg-4Zn samples is from 7.4 to about 10.4 after 48 h, whereas, the pH values of the SBF immersed with the coated groups for 48 h are only about 9. At the second stage of immersion (from 48 to 96 h),

the Mg-4Zn samples still show the highest H<sub>2</sub> release amount but the release rate significantly decreases from 0.04 mL/(cm<sup>2</sup>·h) to around 0.02 mL/(cm<sup>2</sup>·h). In addition, the difference in the amount of the H<sub>2</sub> evolution among the three coated groups becomes apparent, and the 10SrHA@Mg-4Zn exhibits the lowest release rate. At this stage, the pH values of the SBF immersed with the three coated groups increase from 9 to around 10.2, whereas, that of the Mg-4Zn group shows slightly increase from 10.4 to 10.6 as shown in Fig. 6(c). After immersion for 96 h, all the four groups show comparably low H<sub>2</sub> release rates, and the pH values of all groups keep stable.

The corrosion behavior of HA-coated Mg alloys is not only determined by the physical and chemical properties of the coatings, but also influenced by the distribution of the HA crystals [27]. In this study, the increase of Sr incorporation in HA phase leads to lowered crystallinity significantly degree. The amorphous phase is usually considered to be more soluble than the crystalline HA, and thus may weaken the corrosion resistance of the coatings [28]. However, the corrosion is restricted on the 5SrHA@Mg-4Zn and 10SrHA@Mg-4Zn samples as presented in Figs. 5 and 6, indicating that the crystallinity is probably not an important factor in determining the corrosion behavior in this case. It was reported that the introduction of Sr into HA phase can lead to better apatite formation ability as well as the formation of more stable inner barrier layer, which can significantly decrease the corrosion rate of the Mg-based substrates [29], so the lower  $J_{corr}$  and more positive  $\varphi_{corr}$  of the 10SrHA@Mg-4Zn samples are not unexpected. The different dynamic degradation behaviors of the four groups as shown in Fig. 6 should be due to the dissolution/recrystallization behavior of the coatings. At the beginning stage of immersion, the fast dissolution of the coatings occurs on the surfaces [8]. The densely distributed fine Sr-incorporated HA crystal flakes (see Fig. 4) might somehow lessen the contact between SBF and the substrates, and thus lead to lower corrosion rate. Afterwards, when the recrystallization of HA phase around the material surfaces becomes apparent, the better apatite formation ability of Sr<sup>2+</sup> compared with  $Ca^{2+}$  results in a lower H<sub>2</sub> evolution rate as shown in Fig. 6(b). At the last stage, since the dissolution and recrystallization processes have met a balance, the three coated groups do not show significant difference in corrosion rate. To sum up, the electrochemical deposition of Sr-incorporated HA coatings is probably a useful approach for improving the corrosion resistance of Mg alloys, and can be recommended for the development of absorbable Mg alloys for biomedical applications. The in vitro and in vivo investigations will be performed in the future, in order to better understand the influence of Sr-incorporated HA coatings on the biocompatibility of Mg-based biomaterials.

### **4** Conclusions

1) The incorporation of Sr ion does not significantly change the functional groups and the hexagonal crystal structure of HA phase. However, the crystal size and crystallinity significantly decrease from 32.9 to 24.2 nm and 73.4% to 27.1%, respectively, after coating 10SrHA on the Mg-4Zn substrates, because the occupancy of Sr ion in Site I and Site II might have led to lattice distortion and thus influenced the crystal growth mechanism.

2) Compared with the HA-coated and the bare Mg–4Zn alloy, the Sr-incorporated HA coated substrates show more noble corrosion potential and significantly lower corrosion currency. Besides, the 10SrHA-coated Mg–4Zn samples show lower hydrogen evolution rate than other samples, probably owing to the better apatite formation ability of Sr ion.

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### 引入 Sr 对生物医用羟基磷灰石涂覆 Mg-4Zn 合金表面结构和耐腐蚀性能的影响

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摘 要:采用电化学沉积法在 Mg-4Zn 合金表面制备羟基磷灰石(HA)及不同 Sr 含量的 HA 涂层。采用傅里叶红 外光谱仪、X 射线衍射仪、扫描电子显微镜、能谱和电化学工作站分析不同材料的化学成分、相组成、表面形貌 及腐蚀性能。结果表明,涂层中的 Sr 并未显著影响 HA 涂层的官能团和晶体结构,但晶体尺寸和结晶度随 Sr 含 量增加而显著下降。这主要是由于存在晶格畸变及 Sr 与 Ca 离子的不同占位。10SrHA@Mg-4Zn 样品的腐蚀电流 密度最低,腐蚀电位最高,且氢气释放量最少。

关键词: Mg-4Zn 合金; 含 Sr 羟基磷灰石; 电化学极化; 耐腐蚀性

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