Corrosion resistance of a novel SnO2-doped dicalcium phosphate coating on AZ31 magnesium alloy

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Abstract
A SnO2-doped dicalcium phosphate coating was prepared on AZ31 alloy by means of hydrothermal deposition. The results showed that the coating possessed a globular morphology with a long lamellar crystalline structure and a thickness of approximately 40 μm. The surface of the coating became smooth with an increase additive amount of the SnO2 nanoparticles. The corrosion current density and hydrogen evolution rate of the coating prepared in presence of SnO2 were reduced compared to the coating without SnO2 and the bare AZ31 substrate, indicating an improvement in the corrosion resistance of the SnO2-doped coating.

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1. Introduction
Metallic biomaterials such as stainless steels and titanium alloys play a critical role in orthopedic surgery [1]. However, the human body causes a hostile response to the traditional metallic implants. Magnesium (Mg) and its alloys hold a promise as temporary implants due to their biodegradability and good biocompatibility [1–4]. Therefore, Mg alloys draw a significant attention to scientists in the biomedical field [5–7]. While the restriction of fast corrosion rate of Mg alloys hampers their clinical applications. It is thus important to slow down the degradation rate of the alloys in order to well match the formation rate of the newly formed bone nearby the implants [8].

Calcium phosphate coatings, including tricalcium phosphate (TCP), dicalcium phosphate anhydrous (DCPA) and hydroxyapatite (HA), may be good choices for surface modification on the degradable Mg alloys [9–12]. Particularly, calcium phosphate is the main component of the bone, attributing to its excellent bioactivity and biocompatibility. There are many approaches, i.e., electrodeposition, sol-gel, biomimetic immersion, to obtain the calcium phosphate coating on Mg alloys [13–14]. Song, Zhang and Guan et al. [15–18] has successfully applied calcium phosphate coating on Mg alloys to improve the biocompatibility and corrosion resistance. Moreover, hydrothermal synthesis is often applied to improve the adhesion strength between the calcium phosphate coating and the Mg substrates, due to its low-cost and time-saving [19,20]. In addition, the morphology and crystallization of the coating can be tailored by the hydrothermal parameters [21].

Previous studies [22,23] have suggested that titanium dioxide (TiO2) can induce the formation of a calcium phosphate layer on Mg alloys. Tin oxide (SnO2) has a similar crystal structure [24,25] with TiO2, it is postulated that SnO2 can have a similar effect to TiO2 on inducing the formation of the calcium phosphate layer. In addition, nanocrystalline-doped tin dioxide has been reported to exhibit antibacterial activity [26,27]. Thus, we attempted to use SnO2 nanoparticles to induce the formation of a Ca-P coating on the surface of Mg alloys and thus achieve a novel SnO22-doped Ca-P coating with improved corrosion resistance and biocompatibility.
2. Experimental

2.1. Preparation of coatings

As-extruded AZ31 substrates were cut into squares with dimensions of 20 mm × 20 mm × 5 mm, and then ground with SiC papers up to 1500 grit, washed with alcohol and hot dried in air. A hydrothermal synthesis was conducted on the prepared AZ31 samples in a solution with 125 mM ethylenediaminetetraacetic acid disodium salt (Na-EDTA: C_{10}H_{14}N_{2}Na_{2}O_{8}.2H_{2}O), 254 mM calcium nitrate (Ca(NO_{3})_{2}.4H_{2}O) and 128 mM sodium dihydrogen phosphate (NaH_{2}PO_{4}.2H_{2}O) together with 33.2 mM (5 g L^{-1}) or 66.4 mM (10 g L^{-1}) SnO_{2} nanoparticles (50–70 nm in diameter) at a pH value of approximately 2.9. Then the solution and the samples were transferred into 100 mL Teflon-lined stainless reactors, which were kept in an electric oven (DHG-9070A, China) at a temperature of 100 °C for 20 h. Finally, the samples were taken out and washed thoroughly with distilled water for at least three times and dried with warm air. All the reagents were of analytical grade and distilled water was used in all of the experiments.

2.2. Surface analysis and corrosion testing

The phase and morphology of the samples were characterized using X-ray diffraction (XRD, Model D/max 2500PC Rigaku, Japan) and field emission scanning electron microscopy (FE-SEM, Nova Nano SEM 450, USA), respectively. The corrosion behavior was investigated in Hank’s solution without any change during the immersion (8.0 g L^{-1} NaCl, 0.4 g L^{-1} KCl, 0.14 g L^{-1} CaCl_{2}, 0.35 g L^{-1} NaHCO_{3}, 1.0 g L^{-1} glucose (C_{6}H_{12}O_{6}), 0.1 g L^{-1} MgCl_{2}.6H_{2}O, 0.06 g L^{-1} MgSO_{4}.7H_{2}O, 0.06 g L^{-1} KH_{2}PO_{4} and 0.06 g L^{-1} Na_{2}HPO_{4}.12H_{2}O). The ratio of the sample surface area to solution volume was 1: 45 cm^{2} mL^{-1}, and the temperature was controlled at 37 ± 0.2 °C by a water bath. The electrochemical corrosion behavior was obtained by an electrochemical analyser (PAR Model 2273, PAR, USA).

Table 1

| Spectrum | C     | O     | P     | Ca    | Mg    | Ca/P ratio |
|----------|-------|-------|-------|-------|-------|------------|
| Point A  | 13.59 | 65.51 | 11.61 | 9.1   | 0.19  | 0.78       |
| Point B  | 12.49 | 70.04 | 9.75  | 7.49  | 0.23  | 0.77       |
| Point C  | 11.89 | 64.39 | 13.21 | 10.37 | 0.15  | 0.79       |
| Point D  | 14.57 | 65.57 | 9.93  | 8.94  | 0.99  | 0.90       |
| Point E  | 9.47  | 62.79 | 14.70 | 12.86 | 0.18  | 0.87       |
| Point F  | 10.09 | 55.09 | 15.65 | 16.67 | 1.50  | 1.07       |
Princeton, USA). A three-electrode cell set-up was used in which the prepared sample was the working electrode and a platinum sheet and a saturated calomel electrode were used as the counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) studies were performed at a disturbing potential of 10 mV over a frequency range of 100 kHz to 0.01 Hz at OCP. Then, the potentiodynamic polarization was performed from approximately \(-2000\) to \(1000\) mV/SCE at a scan rate of \(1\) mV s\(^{-1}\).

The hydrogen evolution was carried out by placing the sample under an inverted funnel, which was connected to a graduated burette [28]. The detailed process was recorded in our previous study [29–31].

3. Results and discussion

Fig. 1 exhibits the surface and cross-sectional SEM morphologies of the coatings prepared by different conditions. The different elemental contents and Ca/P ratio for the samples are shown in Table 1. It is found that the coating in absence of SnO\(_2\) contains a large number of globular structures (Fig. 1a and b). In the globular structures, thin lamellas interlocks together (Fig. 1a–c). The cross-sectional image (Fig. 1d) discloses that the coating has a thickness of approximately 39.95 ± 0.42 \(\mu\)m and a three-layer structure: (I) the inner layer is very thin and connects with the substrate closely; (II) the mid-layer is much thicker than the inner layer; (III) the outer layer is composed of the globular structures with a thickness close to the mid-layer. Several pores are observed in the middle of mid-layer and along the mid-layer/substrate interface.

When the coating doped with \(5\) g L\(^{-1}\) SnO\(_2\) nano-particles, the globular morphology still exist, but the number of globular structures declines, and the gaps between thin lamellas enlarge (Fig. 1e–g). Note that the coating has a thickness of about 39.46 ± 0.57 \(\mu\)m and a three-layer structure, similar to the coating without SnO\(_2\) (Fig. 1h). However, there are many micro-cracks vertical to and along the mid-layer/substrate interface. Larger pores are discerned along the mid-layer/substrate interface. The outer layer has a rougher surface with \(5\) g L\(^{-1}\) SnO\(_2\) than that of the coating in absence of SnO\(_2\). More pores exist in the outer layer.

While doped with \(10\) g L\(^{-1}\) SnO\(_2\), the coating exhibits a flat morphology with few large globular structures randomly distributed on the coating surface (Fig. 1i). It is found that the coating with SnO\(_2\) nano-particles is similar to that in Fig. 1f and g. From the cross-sectional image of the coating (Fig. 1i), it is clear that the coating has a thickness of 43.69 ± 0.36 \(\mu\)m and a three-layer structure similar to the coating without SnO\(_2\), but micro-cracks and pores are evident, indicating the good adhesion of the coating to the substrate. The Ca/P ratio increases up to about 1.0 with the addition of the SnO\(_2\) nanoparticles. That is, the main composition of the SnO\(_2\) doped Ca-P coating may be CaHPO\(_4\) (DCPA) or CaHPO\(_4\) \(2H_2O\) (DCPD).

Fig. 2 shows the XRD patterns of the samples. Except for \(\alpha\)-Mg diffraction peaks, the major diffraction peaks are DCPA [32], indicating that the DCPA coatings are successfully deposited on the Mg alloys by hydrothermal deposition methods. Furthermore, SnO\(_2\) diffraction peaks, particularly at \(2\theta\) of 26° and 58° are observed for both Fig. 2(iv) and (v). Moreover, the relative intensity of diffraction peaks of SnO\(_2\) in Fig. 2(v) are higher than that in Fig. 2(iv), suggesting that the SnO\(_2\) are successfully deposited in the coating. The more content the SnO\(_2\) nanoparticles, the higher the peak intensity.

In general, proper compactness and thickness endow protective coatings with favorable corrosion resistance for Mg alloys [33]. In order to evaluate the protective effects of the obtained Ca-P coatings, potentiodynamic polarization and EIS tests are conducted in Hank’s solutions and the results are shown in Fig. 3. Theoretically, the lower current density (\(i_{corr}\)) and higher corrosion potential (\(E_{corr}\)) indicate the better corrosion resistance [34]. The \(i_{corr}\) of the DCPA coating without SnO\(_2\) is 7.04 × 10\(^{-6}\) A cm\(^{-2}\), which is about

![Fig. 2. XRD patterns of the (i) AZ31 substrate, (ii) SnO\(_2\), (iii) coating in absence of SnO\(_2\), coating in presence of (iv) 5 g L\(^{-1}\) and (v) 10 g L\(^{-1}\) SnO\(_2\).](image2)

![Fig. 3. The (a) polarization curves and (b) Nyquist plots of the (i) AZ31 Mg alloy, (ii) coating in absence of SnO\(_2\), coating in presence of (iii) 5 g L\(^{-1}\) and (iv) 10 g L\(^{-1}\) SnO\(_2\).](image3)
4.8 times lower than that (3.37 × 10⁻⁵ A cm⁻²) of the AZ31 substrate. The \( \sigma_{corr} \) of the DCPA coating prepared with 5 g L⁻¹ SnO₂ is 2.43 × 10⁻⁵ A cm⁻², which is approximately 2.9 times lower than that of the DCPA coating prepared without SnO₂. Although the \( \sigma_{corr} \) of the DCPA coating with 10 g L⁻¹ SnO₂ (2.13 × 10⁻⁶ A cm⁻²) is close to that in presence of 5 g L⁻¹ SnO₂, the anodic polarization curve of the former is shifted toward the left and has a higher breakdown potential (−1.16 V) than the latter (−1.24 V). The scenario implies that 10 g L⁻¹ SnO₂ changes the anodic behavior and improves the corrosion resistance of the coating due to its perfect compactness and higher thickness.

To more accurately explain our results in detail, the appropriate equivalent circuit of samples are shown in Fig. 3b. The fitting data are listed in Table 2. In the equivalent circuit, \( R_f \) shows the resistance of the coating. \( Q_1 \) and \( Q_2 \) represent constant phase elements (CPEs), \( R_1 \) and \( R_2 \) are the solution resistance and the charge transfer resistance, respectively. A higher \( R_2 \) means a better corrosion resistance of the alloy. The \( R_4 \) of the samples can be ranked in: 1153 \( \Omega \) cm² (AZ31 substrate) < 2046 \( \Omega \) cm² (coating with 5 g L⁻¹ SnO₂) < 2254 \( \Omega \) cm² (coating without SnO₂) < 4298 \( \Omega \) cm² (coatings with 10 g L⁻¹ SnO₂) (Fig. 3b). The consequence is in pronounced agreement with the result of the polarization curves (Fig. 3a) and the cross-sectional images (Fig. 1). The DCPA coating, doped with 10 g L⁻¹ SnO₂, has the best corrosion resistance. Note that, the subtle difference in \( R_2 \) between coating with 5 g L⁻¹ SnO₂ and coating without SnO₂ may be ascribed to the presence of the micro-pores and micro-cracks in the coating prepared with 5 g L⁻¹ SnO₂.

Fig. 4 exhibits the curves of hydrogen evolution rates (HER) and SEM images for the samples during and after an immersion of 204 h, respectively. The HERs of the AZ31 Mg alloy, the coating without and with 5 g L⁻¹ SnO₂ are very high and decreases significantly in the first 36 h of immersion (Fig. 4i, ii and iii), due to the existence of defects (Fig. 1d and h) in the coatings. After 36 h of immersion, the HER of the samples maintain a stable value and last for about 108 h, indicating the formation of Mg(OH)₂ film and Ca-P precipitate on the AZ31 substrate, so that the coatings was self-healed in Hank’s solution [2,35]. After 108 h of immersion, the HERs of the AZ31 Mg alloy increases firstly, follows by the coating without SnO₂, and then the coating in presence of 5 g L⁻¹ SnO₂. This result can be attributed to the dissolution of Mg(OH)₂ film into soluble MgCl₂ for the substrate, and the delaminating and peeling-off of the coatings. Note that, the HER of the coating prepared in presence of 10 g L⁻¹ SnO₂ maintains a lower value during the immersion time. After 10 days of immersion, the HERs of the AZ31 substrate, the coating without SnO₂, the coatings in presence of 5 g L⁻¹ and 10 g L⁻¹ SnO₂ can be ranked in: 218.1 × 10⁻² > 1.04 × 10⁻² > 2.3 × 10⁻³ > 4.72 × 10⁻⁴ mL cm⁻² h⁻¹. In Fig. 4b, all of samples keep a relatively intact morphology in comparison with Fig. 1, which ascribed to the corrosion protection of the DCPA coating and the formation of Mg(OH)₂ film and Ca-P precipitate. The finding demonstrates that the coating doped by 10 g L⁻¹ SnO₂ has the best corrosion resistance. This result agrees well with that of the above electrochemical tests.

Moreover, Sn is generally considered as a relatively non-toxic metal. The reason is that Sn and its compounds are poorly absorbed and accumulated in human tissues and that Sn is rapidly excreted mainly by kidneys [36]. Note that, Kubíšek et al. [37] demonstrated that a relatively high concentration (2520 ng mL⁻¹) of Sn caused a severe toxic effect on the cells. After twofold dilution of the concentration of Sn, the cell activity was also very low. But when the Sn amount decreased to 163 ng mL⁻¹, the cells remained viable even after 5 days culture. Pan et al. [38] showed that the MG63 cells exhibited good growth in both Mg-1Sn and Mg-3Sn alloy extracts and these alloys met the requirement of cell toxicity according to ISO 10993-5: 1999. Although the degradation rate of the DCPA coating is slow, the security of the released SnO₂ nanoparticles in the coating is an another problem, which should be confirmed further.

In principle, the formation of the DCPA coatings on Mg alloys from the aqueous solution consists of two processes: nucleation and crystal growth [39]. The driving force for the above two processes involve the relative supersaturation [40], which increases

**Table 2**

| Samples                | \( R_1 \) (Ω cm²) | \( Q_1 \) (Ω⁻¹·s⁰·cm⁻²) | \( n_1 \) | \( R_2 \) (Ω cm²) | \( Q_2 \) (Ω⁻¹·s⁰·cm⁻²) | \( n_2 \) | \( R_f \) (Ω cm²) |
|------------------------|------------------|------------------------|----------|------------------|------------------------|----------|------------------|
| AZ31 substrate         | 78.07            | 1.86 × 10⁻⁵            | 0.87     | 1153             | 1.42 × 10⁻³            | 0.90     | 465              |
| DCPA coating           | 71.07            | 6.21 × 10⁻⁷            | 0.62     | 2254             | 5.92 × 10⁻⁵            | 0.70     | 5464             |
| 5 g L⁻¹ DCPA coating   | 93.78            | 1.23 × 10⁻⁶            | 0.56     | 2046             | 5.65 × 10⁻⁵            | 0.50     | 5648             |
| 10 g L⁻¹ DCPA coating  | 99.71            | 5.25 × 10⁻⁷            | 0.61     | 4298             | 4.21 × 10⁻⁵            | 0.61     | 4793             |

**Fig. 4.** (a) HERs and (b) SEM images of the (i) AZ31 Mg alloy, (ii) coating in absence of SnO₂, coating in presence of (iii) 5 g L⁻¹ and (iv) 10 g L⁻¹ SnO₂ with and after an immersion of 204 h in Hank’s solutions.
with increasing temperature and pH of the solution [41]. The formation mechanism of the coatings is attributed to the self-assembly of EDTA molecular, surface molecular recognition and biomineralization [42].

In the hydrothermal deposition, the driving force was considered not high enough, thus lamellar DCPA crystals precipitated, then continuously wrapped and agglomerated into large globules to reduce the overall surface energy [39]. Once the SnO2 nanoparticles were added into the solution, the SnO2 nanoparticles as a foreign material provided heterogeneous nucleation sites for the deposition of CaF\(^{2-}\) and HP0\(_4\)\(^{3-}\), and thus promoted the formation of the nuclei, then the surface became flat. Thereby, the deposition process accelerated and the thickness increased due to the heterogeneous nucleation resulted from the SnO2 nanoparticles. In addition, the nano-sized SnO2 particles, filled in the micro-cracks or pores of the coating, thus led to the formation of a denser film.

4. Conclusions

In summary, SnO2 nanoparticles were successfully doped to the DCPA coating on the AZ31 alloys via hydrothermal deposition, resulting in the formation of a thick and dense DCPA coating. The DCPA coating doped with 10 g L\(^{-1}\) SnO2 exhibits an improved corrosion resistance as compared to that of the DCPA coating prepared in absence of SnO2.

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