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Synthesis and characterization of magnesium phytic acid/apatite composite coating on AZ31 Mg alloy by microwave assisted treatment

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ABSTRACT

To improve the corrosion resistance and bioactivity of AZ31 magnesium alloy, a crack-free magnesium phytic acid/apatite composite coating was synthesized on AZ31 substrate *via* chemical conversion deposition and followed a rapid microwave assisted treatment. The influences of pH values of the microwave solution on the morphology, composition and corrosion resistance properties of the composite coating were investigated. An apatite coating with bilayer structure was completely covered the magnesium phytic acid conversion coating after microwave radiation in the solution of pH 6.5, which reached the thickness of ~7.0 μm. During the electrochemical and immersion tests in simulated body fluid (SBF), the samples with composite coating exhibited a remarkably improved corrosion resistance, slower degradation rate and rapid inducing of Ca-P apatite deposition, suggesting that the composite coating could provide a long-time protection for substrates and promote the bioactivity of AZ31 magnesium alloys. Moreover, after 5 days of incubation, the composite coating showed non-cytotoxicity, good osteoblast adhesion and proliferation.

1. Introduction

In recent years, magnesium (Mg) and its alloys have received extensive attention as potential biodegradable implanted biomaterials due to their suitable biosecurity and biocompatibility, outstanding physical and mechanical properties which are similar to those of the human bone [1,2]. Nevertheless, electrochemical properties of Mg and its alloys are active, and they tend to erode quickly when exposed to the chloride containing environment such as human body fluid [3,4]. This defect may cause consequent loss in mechanical integrity prematurely and the release of hydrogen surrounding the implant, which preclude their clinical applications [5,6].

Up to now, various sorts of surface modification technique have been adopted to tailor the degradation rates of magnesium alloys, such as plasma electrolytic oxidation treatment [7], anodization [8], chemical conversion treatment [9], plasma spraying [10], electrochemical deposition [11], *etc*. Among these, chemical conversion coating is widely applied due to their combinations of properties such as low-cost, strong adhesion to substrate and facility for irregular surface [9]. One potential coating that has been devoted to improving the corrosion resistance of magnesium alloys is phytic acid ($C_6H_{18}O_{24}P_6$, PA), a natural macromolecule compound that has special capability to chelate with diverse metal ions such as Mg^{2+}, Cu^{2+}, Zn^{2+} to form stable metal-phytic complexes [12–14]. What's more, PA shows comparatively biodegradable and biocompatible in human physiological environment. However, the existence of microcracks in the conversion coating and the lack of bioactivity restrict the application of single PA coated magnesium alloys as biodegradable implants [15,16]. Although many attempts have been addressed to eliminate these microcracks [17–19], most of them only focused on enhancing the corrosion resistance of the coating but ignored the bioactivity of using this coating for bone implants. To solve these deficiencies, inorganic/organic composite coating [20] that unites the PA conversion coating with the apatite can be an effective choice. On the one hand, the PA conversion coating is a desirable choice of interlayer because it covalently immobilizes on the surface of magnesium alloy through the chelating reaction and the abundant residual groups, hydroxyl and phosphate anion, can interact with Ca^{2+} to improve the bond property of the following apatite coating and reduce its degradation rate [21]. On the other hand, the apatite coating, as bone mineral constituent, could remarkably promote the bioactive of the pretreatment coating. And our previous work demonstrated that the hydroxyapatite particles could *in-situ* repair the defect on PA conversion coating [22,23]. Although the composite coating enhanced the corrosion resistance of PA conversion coating, the

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study of the phytic acid and its composite as a coating mainly focused on their degradation performances of short immersion times (hours or a few days) [16,21]. The composite coating in the present work will be acted as a corrosion inhibitor to prolong the degradation period of the coated magnesium alloy and also to improve the mineralization ability *in vitro*.

Compared with these conventional methods, the microwave assisted deposition treatment [24–27] has several noticeable advantages: one is that the fast and homogeneous microwave irradiation leads to shorten processing time (only few minutes) and the other is its high efficiency for utilizing electromagnetic energy. What's more, this method can effectively coat on diverse biomaterials with special microstructures in a relatively low temperature, which cannot be obtained by traditional wet-chemical precipitation [28]. Nowadays, the microwave-assisted coating has become a hotspot issue. Ren et al. [24,28,29] used microwave-assisted technology to synthesize osseointegrable magnesium phosphate coating and calcium deficient hydroxyapatite (CDHA) coating on PEEK and AZ31 substrates, respectively. And Kaynak Bayrak et al. [26] coated the 3D chitosan scaffolds with a homogenous HA coating under the similar microwave-assisted process. In our previous efforts [30–32], we have successfully prepared uniform, crack-free hydroxyapatite (HA) and strontium doped hydroxyapatite (SrHA) coating directly on substrates, such as AZ31 and Ti6Al4V alloy *via* optimized microwave assisted treatment. Nevertheless, as far as electrochemistry is concerned, the relative reactive Mg always serves as the anodic or corroding part when it directly contacts with most inorganic phase [19,33,34]. Once the aggressive mediums penetrate the inorganic coating, the electrochemical corrosion may accelerate the degradation of coated magnesium. The PA conversion coating as an organic interlayer might cut off this contraction and release such electrochemical corrosion. Meanwhile, the PA conversion coating could firmly adhere to the matrix and supply the growth site for the apatite coating.

Therefore, in this work, the combination of chemical conversion coating and microwave assisted deposition treatment was proposed for the first time to improve the corrosion resistance of the either single coating on magnesium alloys. And a magnesium phytic acid/apatite composite coating was synthesized on AZ31. The effects of the pH values of the microwave solution on the microstructure and composition of the composite coating were investigated. To evaluate the possible biomedical applications of the coated magnesium alloy, the *in vitro* bioactivity and cytotoxicity were also investigated.

2. Experiment

2.1. Coating preparation

Commercial AZ31 magnesium alloy plate (Al 3%, Zn 1%, Mn 0.2%, Fe < 0.005%, Mg in balance, all in wt%) with the size of 10 mm × 10 mm × 2 mm was used as the substrate material for this study. The plates were wet ground with successive grades of silicon carbide abrasive papers from P400 to P2000 and cleaned ultrasonically in acetone and distilled water respectively and dried at room temperature. Then the naked plates were immersed in 1.5 M NaOH solution at 80 °C for 1 h. After alkaline treatment, the samples were cleaned in distilled water and dried at 37 °C for use.

Based on relevant researches [17,22], 0.70 wt% phytic acid solution was chosen to prepare single PA conversion coating, and the processing parameters had been optimized by controlling the pH value, reacting time and temperature of phytic acid solution. In this study, only the optimal processing parameters were referred. The alkaline treated samples were dipped into 100 mL solution containing 0.70 wt% phytic acid at 60 °C for 40 min, meanwhile the pH value of the solution was adjusted to 5.0 by triethylamine. The samples here were referred to as PA coating. After the immersion, the samples were cleaned in distilled water and then soaked into 100 mL microwave solution in a 250-mL beaker which was covered by a Teflon lid to microwave assisted coating. As microwave solution, 0.153 g $Ca(NO_3)_2 \cdot 4H_2O$ and 0.050 g $Na_2HPO_4 \cdot 12H_2O$ were consecutively added to 100 mL distilled water under continuously magnetic stirring at room temperature for 2 h, and the pH values of the solution were adjusted to 6.0–7.0 using 1 M HNO_3 at the same time. The sample that only underwent alkaline pretreatment was also immersed in the microwave solution for comparison. The pH value of this sample was adjusted to 6.5. As reported in our previous work [31], after 10 min microwave radiation, a dense HA coating had completely covered the surface of AZ31 alloy. Thus, the samples assembled were placed into a microwave chemical reactor with 2.45 GHz microwave frequency (Tangshan nano source microwave thermal instrument, China) and radiated for 10 min when the solution boiled. After microwave heating, the samples were cleaned with distilled water and then dried in air. These samples after microwave assisted treatment with different pH values of microwave solutions were referred to as pH 6.0, pH 6.5 and pH 7.0, respectively. And the sample after microwave assisted treatment but without PA as the interlayer was referred as apatite coating.

2.2. Coating characterization

Surface morphologies of the samples before and after immersion test were investigated by Field-emission scanning electron microscope (FE-SEM, Hitachi S4800, Japan). The element compositions of the coatings were analyzed by energy dispersive spectrum (EDS, 7401 Oxford) attached to SEM mentioned above. The phase compositions were characterized by low-angle (1°) X-ray diffraction (XRD, Rigaku, Japan) with Cu K_α radiation over an angle range of 10–70° (2θ values).

2.3. Electrochemical measurement

The electrochemical corrosion behaviors of the samples before and after immersion test were examined by potentiodynamic polarization tests and electrochemical impedance spectra (EIS) measurements *via* an electrochemical workstation (CHI600C, China) in SBF (t-SBF, pH = 7.40) at 37 °C. Besides, the concentration of ions in the SBF was shown in Table 1 [35]. A conventional three-electrode cell with saturated calomel electrode as the reference electrode, platinum electrode as the counter electrode and the sample with surface area of 1.0 cm^2 as the working electrode was employed. The volume of SBF was based on a volume-to-sample area ratio of 50 mL/cm^2. The samples were allowed to equilibrate for 10 min in SBF to reach a suitably stable open circuit potential (OCP) before the tests. The potentiodynamic polarization curves were scanned with a rate of 1 mV/s, and the EIS tests were conducted over a frequency range from 100 kHz to 0.01 Hz. At least 5 parallel samples were tested to ensure repeatability.

2.4. Immersion test

Among the immersion test, all of the samples containing naked and coated substrates were immersed in SBF (pH = 7.40) at 37 ± 0.5 °C by using a WE-3 immersion oscillator, and the volume of SBF was calculated based on a volume-to sample area of 20 mL/cm^2,according to ASTM G31-72. During the whole immersion test, the SBF was refreshed every 2 days and the pH values of the solution were recorded everyday *via* a pH meter (PHS-25, Leici, Shanghai) to approximately reflect the corrosive degree of the samples. After different immersion times, the samples were taken out from SBF and then washed gently with distilled water and dried in air at room temperature. The surface microstructure

Table 1
The concentration (mM) of ions in SBF formulation.

Ions	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Concentration	142.0	5.0	1.5	2.5	125.0	27.0	1.0	0.5