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45S5 bioactive glass–ceramic coated AZ31 magnesium alloy with improved corrosion resistance

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ABSTRACT

To control the biodegradation rate, 45S5 glass–ceramic coatings were prepared on the commercial AZ31 magnesium alloy substrates by dip-coating method from a synthesized sol–gel. Sol concentration, calcination temperature and dip-coating cycle have been optimized to prepare the compact coatings. The results showed that homogeneous and crack-free coatings with a thickness of 0.48–1.00 μm, consisting of amorphous phase and $Na_2Ca_2Si_3O_9$, were successfully fabricated on AZ31 magnesium alloys. The effects of these coatings on the corrosion behavior of the magnesium alloy substrates have been investigated *in vitro* by soaking samples into modified simulated body fluid (m-SBF) for different periods. It was found that optimized 45S5 glass–ceramic coatings could slow down the degradation rate and decrease the mass loss of the magnesium alloy substrate from 78.04% to 2.31% in the 7th day test, showing a good anti-corrosion property in a certain period. Meanwhile, calcium-deficient hydroxyapatite deposition was observed on the surface of sample 3A500, indicating its biomineralization property in m-SBF. Nevertheless, cracking of the coating during the immersion test is the major factor for 45S5 glass–ceramic coatings to fail to protect the magnesium alloy substrates in the later immersion period.

1. Introduction

Magnesium (Mg) and its alloys have been considered as a promising metallic material for biodegradable bone implants due to their desirable mechanical properties, biocompatibilities and biodegradabilities. The density of magnesium, 1.74 $g \cdot cm^{-3}$, is close to that of natural bones (1.7–2.1 $g \cdot cm^{-3}$) [1], showing excellent biomechanical compatibility. More importantly, compared with other metallic implant materials such as stainless steels and Ti alloy, magnesium and its alloys have a moderate elastic modulus closer to that of bone. Combined with a density very close to that of bone, stress-shielding effect and the risk of inducing osteoporosis can be effectively minimized [1,2]. Magnesium has no noxiousness and largely presents in human body, and excess of magnesium can be easily excreted [3]. Moreover, magnesium plays an important role in bone metabolism and may promote the formation of new bone tissue [4]. As biodegradable orthopaedic implant materials, it is projected that magnesium and its alloys would remain to present in the body and maintain their mechanical integrity over a timescale of 12–18 weeks while the bone tissue heals, eventually being replaced by natural tissue [1,5]. However, the high corrosion rate of magnesium and its alloys in chloride containing environment, such as human body fluid or blood plasma, led to the fast loss of mechanical integrity and the release of hydrogen, which limited their biomedical applications [6,7]. Therefore, it is important to improve the corrosion resistance of magnesium and its alloys for their successful application as bone implant materials. Surface modification with appropriate coatings on Mg-based alloys, such as micro-arc oxidation [8,9], electrochemical deposition [10,11], plasma electrolytic oxidation [12] and sol–gel [13,14] etc., is regarded as an effective way to reduce the degradation rate of these Mg alloys. Among these methods, coatings formed through sol–gel method on metal surface can be more adherent, uniform [15,16] and bioactive [17]. Meanwhile, this method has several other advantages, such as ease of composition control, low processing temperature, and being efficient in producing films or coatings on complex shaped implants and porous scaffolds [18].

Bioactive glasses and glass–ceramics have been widely used in biomedical applications as their superior bioactivities. The primary characteristic of bioactive glasses and glass–ceramics is their rapid rate of surface reaction when used as human body implant materials, leading to direct and fast attachment to bone by a chemical bond [19]. Therefore, applying bioactive glasses and glass–ceramics as coating materials on magnesium and its alloys for surface modification not only combines the bioactivities of bioactive glasses and glass–ceramics with the fine mechanical properties of metallic materials but also improves the anti-corrosion performance. Researchers have applied bioactive glasses on conventional metallic biomaterials, such as stainless steels [20] and Ti-based alloys [21] for decades, and these materials have been proved to have increased corrosion resistance. Fathi et al. [20] have reported that the corrosion current density (85 nA/cm^2) of the 316 L stainless steel coated with bioactive glass coating was smaller than that of uncoated sample (265 nA/cm^2) and its corrosion potential was 26%

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higher in the normal saline solution, indicating the enhancement of corrosion resistance.

Nevertheless, little researches have focused on the bioactive glass–ceramic coatings on magnesium and its alloys, and the corrosion resistance of such coatings has not been determined. In this work, crack-free 45S5 bioactive glass–ceramic coatings have been successfully fabricated on AZ31 magnesium alloys through sol–gel dip-coating method via controlling the preparation parameters. The *in vitro* corrosion properties of 45S5 glass–ceramics coated AZ31 magnesium alloys were also investigated by immersing the samples in modified simulated body fluid (m-SBF) at 37 °C for different periods.

2. Material and methods

2.1. Preparation of 45S5 glass–ceramic coatings on AZ31 magnesium alloy substrates

Magnesium alloy pieces ($12 \times 12 \times 2$ mm^3) were cut from the commercial AZ31 magnesium alloy plate (Al 3 wt.%, Zn 1 wt.%, Mn 0.2 wt.%, Fe < 0.005 wt.%) as substrates in this study. The substrate surfaces were ground to grits of 1000, 1500 and 2000 by SiC papers progressively, followed by ultrasonically cleaning in distilled water, ethanol and acetone successively for 15 min, respectively, and then dried at room temperature.

45S5 bioactive glass–ceramic coatings were dip-coated from a synthesized sol based on previous investigation [22]. Briefly, the molar ratios of tetraethyl orthosilicate (TEOS), sodium nitrate ($NaNO_3$), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and triethyl phosphate (TEP) were designed according to the molar ratios of SiO_2, Na_2O, CaO and P_2O_5 in 45S5 (46.14 %, 24.35 %, 26.91 %, and 2.60%, respectively). The sol for fabrication of 45S5 bioactive glass–ceramic coatings was prepared by mixing two separate solutions. Solution I was prepared by dissolving TEOS into the HNO_3 (0.1 M) aqueous solution at room temperature and stirring for 30 min to hydrolysis. Thereupon, TEP was added into the solution to hydrolyze for 20 min. Solution II was prepared by dissolving $NaNO_3$ and $Ca(NO_3)_2 \cdot 4H_2O$ in distilled water. Then the two solutions were mixed together and stirred for 3 h to obtain a homogeneous, clear and transparent sol. Two sols with different concentrations were synthesized by adjusting the molar ratio of TEOS/H_2O to 0.007 or 0.014, and were labeled as A and B, respectively. Then coatings were deposited on AZ31 magnesium alloy for 1–5 cycles via dip-coating technique with a withdrawal speed of 0.5 mm/s, aged at room temperature for 24 h, dried at 60 °C for 1 h and calcinated at temperature of 400 and 500 °C for 90 min, respectively. Each layer in the multilayered coatings was performed after the drying of the previous one. The processing condition used in the experiment and the different samples studied are listed in Table 1.

2.2. Coating characterization

The surface morphologies of the coatings were observed by field emission scanning electron microscope (FE-SEM, JOEL6700F, Japan), and the chemical composition of the coating and deposition on the coating after being immersed for different period was analyzed by energy dispersive spectrum (EDS, 7401 Oxford). Low-angle (1°) X-ray diffraction (XRD, Rigaku D, Japan) was used to examine the phase composition of the coating. Datas were collected for 2θ ranging between 10° and 80° using Cu Kα radiation.

2.3. Immersion experiment

In this study, *in vitro* immersion tests were carried out at 37 °C in m-SBF (pH = 7.40) prepared by Oyane et al. [23] for intervals from 1 to 7 days to investigate the corrosion properties of the uncoated and coated samples. The volume of solution was calculated based on a volume-to-sample area of 20 mL/cm^2, according to ASTM G31-72 [24]. After predetermined periods of time, the samples were removed from the m-SBF, washed gently with distilled water and dried in air at room temperature for the use of surface observation by FE-SEM. The residual solutions were used to determine the pH values by a pH meter (PB-10, China). To evaluate the mass loss of AZ31 magnesium alloy substrates, samples immersed for different periods were cleaned in a chromic acid solution ($K_2Cr_2O_7 + H_2SO_4$) to remove the coatings and corrosion products formed on the samples, and then rinsed with distilled water, cleaned ultrasonically in ethanol and dried in air. The mass loss was calculated as follows:

$$\text{Mass Loss} = \frac{m_0 - m_l}{m_0} \times 100 \quad (1)$$

where m_0 is the substrate mass before immersing, and m_l is the mass of immersed sample after being cleaned by chromic acid. An average of three measurements was used for evaluating the sample mass variation. The surface observation of the immersed samples through FE-SEM technology has been taken without washing by chromic acid solution.

3. Results and discussion

3.1. Surface morphologies and phase composition of 45S5 glass–ceramic coatings

The corrosion resistance of magnesium alloy substrates coated with sol–gel coatings is ascribed to the coating physical barrier properties and coating solubility related to the chemical composition, so forming a homogenous and crack-free coating is important to improve the anti-corrosion performance of such a coated sample. To prepare an intact coating without cracks, the sol concentrations, calcinated temperatures and coating thickness (dip-coating cycles) were optimized in this work.

Surface morphologies of different coated samples prepared by using different molar ratio of TEOS/H_2O and followed drying at 60 °C and calcinating at different temperatures (400 and 500 °C) are shown in Fig. 1. FE-SEM images display that samples obtained from both sol B cracked when calcinated at 400 °C and 500 °C (Fig. 1a and b). On the surface of sample B500 (Fig. 1b), reticular cracks sized among 1–3 μm can be observed, larger than those of sample B400. For coatings derived from sol A, small size of cracks also was found on the sample surfaces after calcinated at 400 °C (Fig. 1c), while a relative smooth and uniform sol–gel coating can be obtained when the calcinate temperature is 500 °C, as shown in Fig. 1d. It is considered that the surface morphology of the sol–gel coating is affected by the properties of the precursory sols, such as the viscosity, surface tension, stability and etc. In this case, the concentration of the 45S5 glass–ceramic precursor sols increases with the enhancement of the molar radio of TEOS/H_2O, which simultaneously leads to the increase of viscosity of the precursor sols. The surface tension is high for the coating prepared from sol with high viscosity [25] and the tension would deteriorate the surface quality and integrality of the sol–gel coating [26], thus it can be deduced that the obvious cracks formed on the

Table 1
Processing conditions used for preparing different 45S5 bioactive glass–ceramic coatings.

Sample name	TEOS/H_2O	Calcination temperature/°C	Dip-coating cycle
A400	0.007	400	1
A500	0.007	500	1
2A500	0.007	500	2
3A500	0.007	500	3
4A500	0.007	500	4
5A500	0.007	500	5
B400	0.014	400	1
B500	0.014	500	1