



The influence of alkali pretreatments of AZ31 magnesium alloys on bonding of bioglass–ceramic coatings and corrosion resistance for biomedical applications

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Abstract

Coating defects and poor interface bonding between substrates and coatings derived through sol–gel technique are common problems, which are detrimental to protective effects of coatings. Alkali pretreatment was adopted to prepare 45S5 bioglass–ceramic coatings on AZ31 magnesium alloy. After pretreatment, the 45S5 coating was uniform, dense, crack-free and close bonding to substrates. Electrochemical tests in simulated body fluid (SBF) revealed that 45S5 coatings after pretreatment could obviously improve the pitting corrosion potential and polarization resistance of AZ31 substrate, and lessen corrosion current density, suggesting effective protection. The results showed that alkali pretreatment could be a potential process for development of other coatings on magnesium alloy.

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1. Introduction

Magnesium (Mg) and its alloys have been regarded as a promising metallic material for biodegradable bone implants due to their desirable mechanical properties, biocompatibilities and biodegradability [1,2]. As a biodegradable implant material, it is projected to present in the body and maintain its mechanical integrity over a timescale of 12–18 weeks for generation of new tissue, and eventually be replaced by natural tissue [1,3]. However, in moisture environment, especially in chloride containing environment, such as human body fluid or blood plasma, magnesium and its alloys suffer from weak

corrosion resistance, resulting in a rapid deteriorate of its mechanical strength, and a high pH value surrounding the tissues, which delays the healing of the implanted area [4,5]. Therefore, it is pivotal to improve the corrosion resistance of magnesium and its alloys without the loss of mechanical properties to guarantee their successful application as biomedical implant materials. Surface modification, especially protective coatings on Mg alloys has been become an effective way of decreasing their initial degradation rates *in vivo* and maintaining mechanical properties [6,7]. Among various surface coating methods, an appropriate coating on Mg alloys through sol–gel process is regarded as a rational way to reduce the degradation rate of Mg alloys [3,8–11]. Sol–gel method offers certain advantages, including (i) easier composition, purity and structure control of coatings, (ii) a high bioactivity and (iii) reduced heat treatment temperature, which is beneficial to maintaining the mechanical properties

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of Mg alloys [12,13]. Researchers have successfully prepared different kinds of inorganic coatings on Mg alloy through sol–gel method, such as bioglass [8], calcium phosphate [9], Si-containing calcium phosphate [14] and hybrid sol–gel coatings [15,16] etc.

Bioglass 45S5, as a commercially available inorganic material, possesses excellent bioactivity, favorable biocompatibility and controllable biodegradability, which has been prepared as protective coatings on AZ31 alloy by sol–gel method to improve corrosion resistance [17,18]. Yet we found that the wettability of clean flat magnesium surface was bad, with over 80° wetting contact angle of distilled water, and that cracks along with peeling-off were easily propagated both in preparation and *in vitro* immersion [19,20]. In general, cracks, peeling-off or even delamination are common defects of inorganic glass coatings on magnesium surface, which is closely relevant to the wettability of substrates, surface roughness and discrepancy between the expansion coefficients of magnesium alloys (Mg: $26.1 \times 10^{-6} \text{ K}^{-1}$) and coating materials (e.g. vitreous silica: $0.55 \times 10^{-6} \text{ K}^{-1}$ at 20 °C) [21]. These defects directly influence the protective effects of coatings.

What's more, a weak adhesion stress between coatings and substrates also leads to coating defects. As reported before, the adhesion strength between 45S5 coatings and AZ31 alloy is ~ 10 MPa, far below the adhesion strength between conversion coatings and magnesium alloys (normally above 20 MPa) [22]. Difference should ascribe to the bonding types at the interface. Delamination of coatings and their adhesion ability have been studied using mechanical testing methods such as T-peel testing, pull-off and tape tests and cross-hatch test.

Recently, several attempts about Mg alloy surface modification have been reported to mitigate the discrepancy between alloy substrate and coatings, researches about Mg alloy surface modification, like alkali treatment, acid treatment and conversion treatment, have been carried out. Specially, when the pH of alkali solution is above 11, a stable layer of $\text{Mg}(\text{OH})_2$ could form on alloy surface [23]. In this work, an alkaline pretreatment was applied in preparation of 45S5 bioglass–ceramic coatings on AZ31 magnesium alloy using the dip-coating technique. A comprehensive study of influences of alkali pretreatment on the structure of coated AZ31 alloy, interface bonding and corrosion resistance was further conducted.

2. Experimental

2.1. Sample pretreatment and preparation

Commercial AZ31 Mg alloy sheets (Al 3%, Zn 1%, Mn 0.2%, Fe < 0.005%, all in wt%) were used as the substrate material for its low content of Al in this study. The substrates with a size of 12 mm \times 12 mm \times 2 mm were ground with silicon carbide paper from 800, 1000, 1500 and finally to 2000 grit, rinsed ultrasonically in ethanol for 10 minutes (min). The AZ31 substrates were noted as As-polished. Then prepared specimens were immediately boiled in hot sodium hydroxide solutions whose concentrations were separately 5 g/L, 10 g/L and 15 g/L, at the temperature of 80 °C as pretreatment. The pretreatment time varied from

30 min to 90 min with an increment of 15 min. For example, the substrate which was boiled in 5 g/L sodium hydroxide solution for 60 min was noted as L60, and the substrate which was pretreated in 10 g/L alkali solution for 60 min was labeled as M60, etc. 15 different pretreatment conditions and corresponding illustrations were listed in Table 1. After pretreatment, all substrates were ultrasonically cleaned in distill water and dried in warm air. In order to characterize the change of pretreated surface after heat treatment, some alkali pretreated samples were also heat treated according to the procedure in fabrication of coatings (noted as Heat H60, Heat H90, etc).

45S5 bioactive glass–ceramic coatings were dip-coated from a sol, which was synthesized based on previous investigation [24]. Briefly, the molar ratios of tetraethyl orthosilicate (TEOS), triethyl phosphate (TEP), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and sodium nitrate (NaNO_3) were designed according to the mole ratios of SiO_2 , CaO, Na_2O and P_2O_5 in 45S5 (46.14%, 26.91%, 24.35%, and 2.60%, respectively). By consecutively dissolving TEOS and TEP into the HNO_3 (0.1 M) aqueous solution and magnetic stirring for 60 min to hydrolysis at room temperature, the precursor was prepared. The solution was prepared by dissolving $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and NaNO_3 in deionized water. Then the precursor and the solution were mixed together and stirred for 3 h to obtain a transparent and homogeneous sol. By adjusting the molar ratio of TEOS/ H_2O to 0.007 or 0.014, two sols with different concentrations were prepared and marked as A or B. Subsequently coatings were deposited on pretreated AZ31 alloy substrates for 3 cycles *via* dip-coating technique with a withdrawal speed of 0.5 mm/s and a retention time of 1 min in sol, aged at room temperature for 24 h, and heat treated at 500 °C in a furnace for 120 min under air atmosphere. The coated samples were illustrated as A500 and B500, respectively.

2.2. Characterization of alloy substrate and coated samples

The surface topographies of the pretreated Mg substrates namely, M60, H60 and H90 was studied using atomic-force microscopy (AFM, Agilent 5500) in the tapping mode. Also the surface morphologies of the L60, H60 and H90 substrates and the coated samples A500, and B500 were obtained by field emission scanning electron microscope (FE-SEM, JOEL6700F, Japan) with an accelerating voltage of 5.0 kV, and elemental

Table 1
Pretreatment conditions used for preparing different substrates.

Sample name	Solution concentration (g/L)	Pretreatment time (min)
L30	5	30
L45	5	45
L60	5	60
L75	5	75
L90	5	90
M30	10	30
M45	10	45
...
H90	15	90

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