



Effects of sintering temperature on the corrosion behavior of AZ31 alloy with Ca–P sol–gel coating



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ABSTRACT

To slow down the initial biodegradation rate of magnesium alloy, calcium phosphate (Ca–P) coatings were prepared on AZ31 magnesium alloy by a sol–gel technique. To study the effects of sintering temperature on microstructure, bonding strength and corrosion behavior of the coatings, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and an adhesive strength test were used to characterize the coatings. The corrosion resistance of the coatings was investigated by immersion test and electrochemical corrosion techniques in simulated body fluid (SBF) solution. It shows that the sol–gel coatings consist of $\text{Ca}_2\text{P}_2\text{O}_7$, mixture of $\text{Ca}_2\text{P}_2\text{O}_7$, $\text{Ca}_3(\text{PO}_4)_2$ and hydroxyapatite, and hydroxyapatite, by sintering respectively at 300 °C, 400 °C and 500 °C. There are major cracks on the coatings. The crack area portion on the coating and the bonding strength at the interface between the calcium phosphate coating and the bare AZ31 increases, and the corrosion resistance of the coated AZ31 in SBF decreases with increasing sintering temperatures from 300 °C to 500 °C. Based on our investigations, the corrosion resistance of the coated AZ31 in SBF depends mainly on the crack area portion on the coatings, rather than on the coating phase stability.

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1. Introduction

Magnesium alloys are of growing interest for biomedical applications due to their biocompatibility, biodegradability in bio-environment and mechanical properties that are extremely similar to natural bones [1,2]. However, the rapid corrosion rate and the resulting in quick release of hydrogen bubbles limit their clinical application [3]. In addition, the fast degradation rate in physiological environment, especially at the early stage of implantation, usually induces a rapid reduction of mechanical support for the broken bone before the damaged bone healing [4]. Therefore, it is very necessary for Mg alloy implants to improve their initial corrosion resistance and make their degradation rate meet the clinical requirement.

Surface modification on Mg alloys has been widely recognized as an effective way of controlling the initial degradation and maintaining desired mechanical properties [5,6]. Recently, coatings with calcium phosphate (Ca–P) compounds attracted more attentions [7,8]. Biologically relevant Ca–P belongs to the

orthophosphate group and naturally occurs in several biological structures, including teeth and bone. Among the Ca–P compounds, the hydroxyapatite (HA), which consists of the nearly same chemical compositions and phase structure as that of human bone, can form a chemical bond with bone tissue and enhance new bone healing [9]. It is a good candidate to be applied as an implant coating to improve corrosion resistance and increase biocompatibility in orthopedic devices [8]. Therefore, many surface modifications such as biomimetic method [10], electrodeposition [11,12], hydrothermal treatment [13,14] and sol–gel techniques [15–17] have been adopted to prepare calcium phosphate on magnesium alloys to slow down the biodegradation rate and improve the bioactivity. Among all the above coating approaches, the sol–gel method has attracted much attention because of its many advantages, including high product purity, homogeneous composition, and low synthesis temperature [18,19]. Rojaee et al. [15] successfully fabricated a sol–gel nanostructure HA coating on AZ91 magnesium alloy for the first time. They found that the HA coating could improve the corrosion resistance of Mg alloy. The reported bonding strength between the HA coating and the substrate was only 4.2 MPa. Tang et al. [16] prepared sol–gel HA coating on AZ31 Mg alloy with the bonding strength being 20.5 MPa by sintering at

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400 °C. The corrosion resistance increased with increasing the sintering temperature, but no HA crystallized phase formed even at 400 °C. Ren et al. [17] synthesized calcium phosphate coatings on AZ31 Mg alloy by a sol–gel method. The obtained phase constituents of the coatings were mainly $\text{Ca}_2\text{P}_2\text{O}_7$, and $\text{Ca}_4\text{P}_6\text{O}_{19}$ by sintering at 400–500 °C. However, the corrosion resistance decreased with increasing the sintering temperature. In addition, the microstructure and the mechanical properties of the Mg alloy will be affected by sintering temperature. It was reported that the grain size increase and the hardness decrease for AZ31 Mg alloy sintered at 400–500 °C [20]. Therefore, the mechanical properties of the Mg substrate after sintering should be considered for application of the Mg alloy implants. Although the sol–gel synthesized HA coating has been proved to improve the biocompatibility and corrosion resistance of Mg alloys, the effect of sintering temperature on the corrosion resistance of HA coating still needs to be further clarified. Moreover, the degradation process of sol–gel derived HA coating in SBF needs to be investigated systematically. To meet the bonding strength requirement of implants, sol–gel preparation technique on Mg alloy needs to be further explored.

In the present work, calcium phosphate coatings were prepared on AZ31 magnesium alloy with a combination of sol–gel and dip coating method. The effects of sintering temperature on the phase morphology, the bonding strength and the corrosion resistance of the samples were systematically investigated. The tensile strength of the AZ31 alloy after sintering was examined. The degradation process of the HA coated sample in SBF solution were also discussed.

2. Experimental details

2.1. Sample preparation

Commercial AZ31 magnesium alloy sheet (Al 3%, Zn 1%, Mn 0.2%, Fe < 0.005%, all in wt %) of thickness 6.5 mm was cut into rectangular samples with dimensions of $12 \times 30 \text{ mm}^2$. The samples were ground and dry polished with SiC papers up to 1200 grit, and then ultrasonically cleaned in acetone, absolute ethanol and deionized water.

9.85 g calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and 1.78 g phosphorous pentoxide (P_2O_5) were selected as Ca and P precursors and dissolved separately in 25 ml anhydrous ethanol. Ca precursor was added drop wise to P precursor and then additionally stirred for 30 min. Ammonia was used to adjust the pH of the solution to 6. Then, the mixed solution was aged for 24 h at room temperature to obtain a transparent solution.

The AZ31 substrate was dipped into the prepared solution and pulled off at the speed of 2 cm/min. The dip coated specimens were dried at 80 °C for 2 h and then heated to 300 °C, 400 °C and 500 °C, respectively (designated as Samples AZ31-H300, AZ31-H400, AZ31-H500, respectively), for 1 h at a rate of 5 °C/min.

To evaluate the crystallization process of the sol–gel, the prepared solution was also dried at 80 °C, followed by the same sintering temperature as the coatings at 300 °C, 400 °C and 500 °C for 1 h to obtain powders for the X-ray diffraction (XRD) study.

2.2. Characterization

The surface and the cross-section morphologies of the samples were obtained by a scanning electron microscope (SEM, S-3000N, Hitachi, Japan). The chemical compositions of the surface were measured by energy dispersive spectroscopy (EDS, Quet I2, Hitachi, Japan). The phase constituents of the powder (coatings) sintered at different temperatures were examined by X-ray diffraction (XRD, Dmax 2500, Japan) using Cu K_α line generated at 40 KV and 100 mA.

2.3. Tensile test

The adhesive strength at the interface between the coatings and the bare AZ31 were measured according to ISO 14916 [21]. A bare AZ31 alloy sample pre-coated with epoxy resin (3 M glue, Japan) was adhered to the coated sample and the epoxy resin was cured at room temperature for 24 h. The adhesive test was performed on a universal tensile tester with loading rate of 0.2 mm/min until the coating layer failed, and the adhesive strength was determined from the recorded maximum load being divided by the contact area.

To evaluate the effect of sintering temperatures on the mechanical property of the AZ31 substrate, the tensile tests were performed on the AZ31 substrate sintered at different temperatures using a CMT-5305 material test machine with loading rate of 1 mm/min.

2.4. Electrochemical evaluation

The electrochemical corrosion tests were performed on an electrochemical workstation (Ivium, Netherlands). All electrochemical measurements were conducted using a three electrode cell with the coated samples as working electrode, the platinum mesh as counter electrode, and the saturated calomel electrode (SCE) as reference electrode. The electrolyte was the simulated body fluid (SBF) (NaCl 8.035 g/L, NaHCO_3 0.355 g/L, KCl 0.225 g/L, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ 0.231 g/L, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 0.311 g/L, CaCl_2 0.292 g/L, Na_2SO_4 0.072 g/L) buffered at pH 7.4 using tris-hydroxymethyl aminomethane ($(\text{HOCH}_2)_3\text{CNH}_2$) and hydrochloric acid (HCl), kept at 37 °C [22]. The exposed area of the working electrode (substrate and coated samples) in SBF was 1.0 cm^2 . The open circuit potential (OCP) was continuously monitored for 2 h until the potential was stabilized less than $\pm 5 \text{ mV}$. Potentiodynamic polarization tests were carried out from -250 mV vs. OCP to $+1000 \text{ mV}$ vs. OCP at a sweep rate of 0.5 mV/s. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated with the CorrView 2 software according to Tafel extrapolation. Electrochemical impedance spectroscopy (EIS) was measured in a frequency varied from 100 kHz to 0.01 Hz with signal amplitude of 10 mV. Zsimwin 3.10 software was used for the date fitting of impedance spectra [23].

2.5. Immersion test

The immersion test was carried out in the SBF solution at 37 °C for 12 days. The ratio of the SBF volume to the surface area of the samples was 100 ml/cm^2 . The evolved hydrogen was collected by an upside down funnel above the samples and determined as the hydrogen-replaced test solution in an upper burette during immersion. The amount of hydrogen collected in the burette over time reveals the degradation rate of the samples.

3. Results and discussions

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the powders (coatings) sintered at different temperatures. The XRD peaks of the sample treated at 300 °C are mainly attributed to $\text{Ca}_2\text{P}_2\text{O}_7$. As the temperature increased to 400 °C, the peaks corresponding to $\text{Ca}_3(\text{PO}_4)_2$ and a few crystalline HA are observed in the XRD pattern. When the temperature increased to 500 °C, the single phase HA is completely formed. Similarly, Liu et al. [24] reported that the $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_2\text{P}_2\text{O}_7$ appeared while the gels being sintered at 200 °C and 300 °C, respectively. And the HA phase can be formed at temperature as low as 350 °C [25].

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