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Bond strength and corrosion resistance of bioglass coated magnesium alloy fabricated by uniaxial pressing and microwave hybrid heating

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ABSTRACT

Bioactive ceramics coated magnesium alloys with a combination of suitable mechanical strength and adjustable corrosion resistance are desired for biodegradable implants. In this study, a dense bioglass coated magnesium alloy was fabricated by uniaxial pressing and microwave hybrid heating technique. The microstructure, bond strength and corrosion behavior of the samples were evaluated by means of scanning electron microscopy, X-ray diffraction, tensile bond test, electrochemical and immersion test. It was shown that uniaxial pressing conducted at the glass transition temperature significantly densified the sol–gel derived bioglass coating, which was free of pores and micro-cracks. The compact coating structure combined with mild interfacial stress not only improved the cohesion/adhesion strength (25.8 ± 2.6 MPa) but also enhanced corrosion resistance by retarding the penetration of corrosive solution. Furthermore, the formed CaP precipitates on the surface of the coating would provide another protection for the magnesium alloy to some extent.

1. Introduction

In recent years, biodegradable magnesium alloys have attracted great concern as promising temporary implant in bone tissue engineering due to their excellent mechanical compatibility and biocompatibility [1–4]. However, these alloys suffer severe corrosion in human physiological conditions, resulting in a quick decline of mechanical integrity to support the broken bones and an evolution of hydrogen gas bubbles, influencing the cell adhesion and growth [5,6]. Therefore, it is important to improve the corrosion resistance of magnesium alloy to prolong the in vivo service period to match the self-healing process of the surrounding tissues. A promising approach is to fabricate bioactive coatings on magnesium alloys.

Bioglass®, discovered by Hench, with the best-known bioactivity and adjustable biodegradability [7], was synthesized using sol–gel technique as protective coatings on magnesium alloys to improve the corrosion resistance and biocompatibility in our previous study [8,9]. Because of the porous nature of sol–gel derived coatings due to a hydrolysis-condensation reaction involved in a liquid medium [10], conventional heat-treatment process would induce some defects within the coating matrix, such as pores and micro-cracks, which might acting as additional channels for the penetration of corrosive solution, therefore, the protection of the bioglass coating for magnesium alloys seemed unsatisfactory. In addition to corrosion resistance, the bond strength between protective coatings and magnesium alloy substrates also plays a crucial role for the success of implantation [11]. It has been confirmed that bioglass can form strong bonding with bone tissues [7], thus the cohesion strength within coating and adhesion strength of coating to substrate became the controlling factors.

In order to improve the bond strength and corrosion resistance of the conventional sol–gel derived bioglass coated magnesium alloy, uniaxial pressing conducted at the glass transition temperature of the bioglass coating seemed to be an effective way. The advantage of this idea lies in two aspects. Firstly, according to Ollagnier et al., glass based materials are very sensitive to mechanical stress during heat treatment [12], which could increase the driving force for elimination of residual pores in the prepared bioglass coatings and enhance the densification kinetics by viscous flow [13], which would benefit to the barrier effect of the coating. Secondly, amorphous bioglass may exhibit excellent flowability [14] as well as high bioactivity [15] than the crystallized ones. Bioglass tends to quickly crystallize above the glass transition temperature [14], so the heat treatment temperature must be carefully controlled. Taking into consideration of heat treatment, uniform volumetric heating is always preferred [16–18], so herein a combined microwave hybrid heating and uniaxial pressing technique was designed. This novel technique has a wide range of applications by free selection of different bioactive coatings and implant substrates.

The glass transition temperature of the sol–gel derived bioglass was found in the range from 385 °C to 420 °C in our previous study [8]. In this work, uniaxial pressing and microwave hybrid heating technique

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was conducted at 400 °C to the bioglass coated magnesium alloy. The microstructure, bond strength, and corrosion resistance in simulated body fluid (SBF) of the samples were investigated.

2. Experimental work

2.1. Material preparation

2.1.1. Basic configuration of uniaxial pressing and microwave hybrid heating apparatus

The basic configuration of uniaxial pressing and microwave hybrid heating apparatus is shown in Fig. 1. A microwave micro-zone heater was mounted on an electronic universal testing machine. Two pressure heads (nickel-based alloy; diameter, 35 mm) were surrounded by a microwave heating chamber, which consists of a mullite fiber chamber for heat insulation and a silicon carbide (SiC) coating sprayed on its inner surface as susceptor material (pre-heater). Since bioglass is low loss, a room temperature susceptor is indispensable to preheat the samples through thermal radiation. With heat treatment temperature rising, both bioglass and magnesium alloy substrate would turn into absorptive due to enhanced dielectric loss and resistance loss, respectively, thus microwave hybrid heating was achieved.

2.1.2. Materials

In this study, commercial AZ31 magnesium alloy strips (3Al–1Zn–0.2Mn–Fe < 0.005, all in wt%) of 10 mm × 10 mm × 2 mm were used as the substrates. Bioglass coatings were prepared via a sol–gel dip-coating process, which was described in detail in our previous study [8]. After gelation and drying of the xerogel coatings, the green samples were degreased at 400 °C for 2 h in a muffle furnace to remove the organics and nitrates.

2.1.3. Processing

Firstly, the degreased samples were put on the top of the lower pressure head. The initial heating rate was 30 °C/min. Just before reaching the desired temperature (400 °C), the heating rate was reduced to 5 °C/min to avoid overheating. Then uniaxial pressure was applied to the samples at a speed of 10 Pa/s to the maximum value (0, 2, 4, 6 MPa) and hold for 30 min. The samples were denoted as Sample0MPa, Sample2MPa, Sample4MPa and Sample6MPa, sequentially. Finally, the samples were removed from microwave heating chamber after unloading and cooling down. The uniaxial pressing process was shown in Fig. 2.

2.2. Microstructure characterization

The phase composition of bioglass coating was determined by X-ray diffraction (XRD, D/Max-2500 Rigaku, Japan). The surface, cross-section and fracture surface morphologies of bioglass coatings were observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) equipped with an Energy Dispersive Spectrometer (EDS) (7401 Oxford).

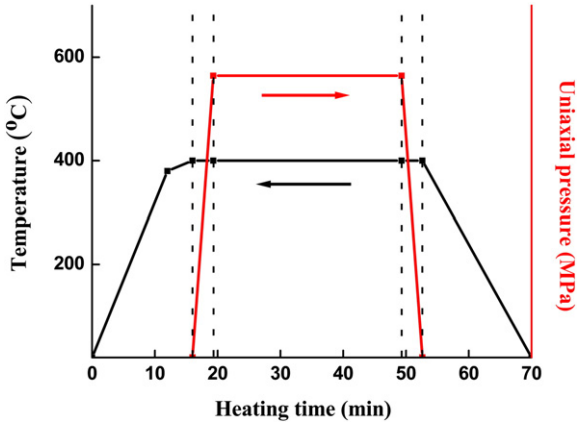

Fig. 2. Uniaxial pressing process.

2.3. Tensile bond test

Bond strength (MPa) of coatings was measured by tensile bond test, which was conducted at the speed of 1 mm/min, according to the modified ASTM C-633 method [19]. Bond strength was calculated by formula (1) [20]:

$$P = \frac{F}{S_{sub}}. \quad (1)$$

Where P is the bond strength of coatings (MPa), F is the tensile load at failure (N) and S_{sub} is the area of substrate (mm^2). In addition, area fraction of adhesive failure of coatings was estimated by formula (2) [21]:

$$x = \frac{S_{ad}}{S_{sub}}\ 100\ \% \quad (2)$$

where x is the area fraction of adhesive failure (%) and S_{ad} is the area of adhesive failure of coatings (mm^2). Statistical analysis was performed using SPSS software to evaluate the significant difference of the bond strength of samples prepared under varied uniaxial pressures. Each data point was presented as mean ± deviation from five parallel experiments. Differences were considered as significant at $p < 0.05$.

2.4. Electrochemical test

The electrochemical corrosion of bioglass coated magnesium alloy was investigated by potentiodynamic polarization in simulated body fluid (SBF) at 37 °C using an electrochemistry workstation. A typical three-electrode cell with saturated calomel electrode (SCE) as the reference electrode, platinum electrode as the counter electrode, and bioglass coated magnesium alloy with exposed area of 1.0 cm^2 as the

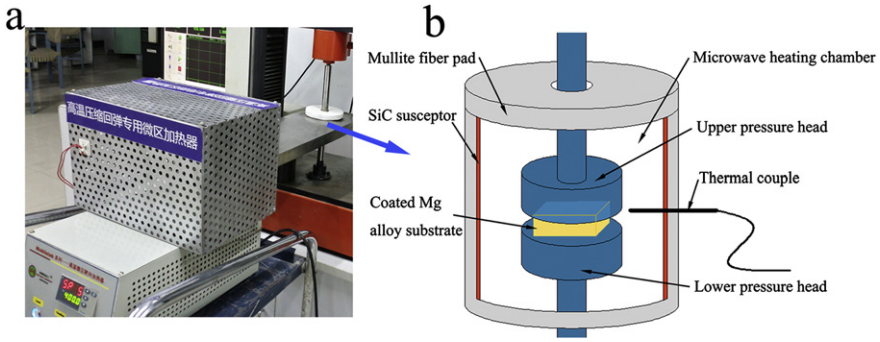

Fig. 1. (a) Photograph of uniaxial pressing and microwave hybrid heating apparatus. (b) Schematic of microwave heating chamber.