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Bi-layer nano-TiO_2/FHA composite coatings on Mg–Zn–Ce alloy prepared by combined physical vapour deposition and electrochemical deposition methods

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ABSTRACT

In this study, physical vapour deposition (PVD) method was carried out to prepare nano-titania (TiO_2) as an intermediate layer on Mg–Zn–Ce alloy and subsequently electrochemical deposition (ED) method was applied to develop nano-fluorine-doped hydroxyapatite (FHA) as an outer layer. X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and transmission electron microscopy (TEM) methods were used to characterize the coatings. Corrosion behaviour of coated samples was evaluated and compared to that of uncoated substrate in SBF solution using immersion test and electrochemical measurements. The resulting TiO_2/FHA composite coating shows uniform, compact, and smooth surface morphology, with 10 μm thickness and crystallite size of around 75–85 nm. As a result, the bi-layer TiO_2/FHA composite coating specimen presents higher corrosion resistance and superior stability in SBF solution than that of mono-layer TiO_2 coated specimen. Nano-TiO_2/FHA composite coating increased corrosion resistance of Mg–Zn–Ce alloys by thirty orders of magnitude owing to low solubility, thickness and compactness of the coating. The results suggested that the nano-TiO_2/FHA composite coated Mg alloy could provide a suitable corrosion behaviour for use as biodegradable bone implant.

1. Introduction

Magnesium and its alloys as biodegradable materials can support the healing process, a decided benefit over other metallic materials as they do not have to be removed from the human body after the healing procedure is completed [1]. The presence of implants in the human body may cause problems such as sensitization and allergy or other physical problems in the long term. Several studied indicated that magnesium alloys had good biocompatibility in vitro and in vivo assessments [2]. However, the use of magnesium is hindered by its poor corrosion resistance which causes the mechanical properties of the implant to significantly decrease resulting in the inability of tissue to heal [3–5]. Furthermore, Mg corrosion process involves evolution of hydrogen gas which accumulates in vivo adjacent to the implant. The H_2 gas and subsequent formation of hydrogen bubbles can noticeably impair other clinical applications of Mg. Surface modification has been widely applied in order to reduce the initial degradation rate of Mg alloys [6]. Recently, TiO_2 coating with interconnected porosity, good adhesion with the substrate was reported to offer the ability of apatite formation and antimicrobial activity [6]. Hu et al. [7] investigated the effect of nano-TiO_2 coating by sol–gel method on the corrosion behaviour of Mg alloy and their result showed that TiO_2 coating can significantly improve corrosion resistance of the Mg alloy. Several reports also exhibit superior antibacterial performance of TiO_2 thin film [8]. Calcium phosphate (Ca–P) coating is considered to be one of the effective coating materials for decreasing the degradation rate of magnesium alloys [9]. In addition, calcium phosphate was also applied in several types of surgical treatments such as bone replacement material in orthopaedic surgery and craniofacial augmentation as well as sinus occlusion and ossicular chain reconstruction in otolaryngological surgery [10,11]. Among the Ca–P coating, fluorine-doped hydroxyapatite (FHA; $Ca_{10}(PO_4)_6\,(OH)_{2-x}F_x$, where $0 < x < 2$) was reported as promising candidate for replacement of hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) due to its lower solubility and comparable biocompatibility over HA [7,12,13]. Previous studies [12,14,15]

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showed that single layer FHA coating could effectively induce the precipitation of more Ca^{2+} and PO_4^{3-} ions and can significantly reduce the initial degradation rate of the Mg alloy. Therefore, it is reasonable to deduce that bi-layered nano-TiO_2/FHA composite coating could be beneficial for the enhancement of corrosion resistance of Mg alloys. In the present study physical vapour deposition (PVD) is conducted for TiO_2 coating as a clean environmentally friendly technique which does not produce waste or appreciable atmospheric emissions [16,17]. Previous studied showed [7,18–20] that electrodeposition (ED) received great attention as a superior technique for the coating of bioceramic, inorganic and organic composites. Hence it would be appropriate to perform ED technique for FHA coating due to its simple operation, ease of particle-size control, compact coating, low temperature process and low cost [20]. Various surface modification methods such as micro-arcoxidation (MAO), plasma electrolytic oxidation (PEO), ion implantation, dip coating, physical vapour deposition (PVD) and electrodeposition (ED) have been performed on magnesium alloys for the improvement of their corrosion resistance [18,20,21]. However, synthesis of the nano-TiO_2/FHA composite coating by a combination of PVD and ED methods has not been reported elsewhere. Thus the main aim of this study is the synthesis of a double layered nano-TiO_2/FHA composite coating on Mg–Zn–Ce alloy by PVD followed by electrochemical deposition method. In addition, the effect on in-vitro corrosion behaviour of these coating systems was evaluated.

2. Experimental

Magnesium alloys were prepared by melting 99.9% pure magnesium ingots, pure zinc (99.99%), and Mg–30 wt.% Ce. The melts, with a constant concentration of Ce (3.5 wt.%) and Zn (2.2 wt.%), were then cast into a 300 °C pre-heated stainless steel mould to produce an ingot. In preparation for further experiments, several Mg–2.2Zn–3.5Ce specimens with dimensions of 15 mm × 10 mm × 10 mm were cut from the ingot. The ingots were mechanically wet ground with 320–2000 SiC grit papers until all visible scratches were removed. A hybrid ion beam deposition system consisting of a linear ion source and a magnetron sputtering source was selected to deposit the coatings on the substrates. The Mg alloys were ultrasonically washed in pure alcohol for 5 min before placement inside a vacuum chamber. An ion source with Ar gas was used to clean the surface of the Mg alloys for 40 min. This pre-treatment was performed when the base pressure of the chamber was below 4×10^{-3} Torr. Physical vapour deposition was performed at room temperature with argon gas as a sputtering gas. The PVD parameters are as follows: a working pressure of 8×10^{-3} Torr, an RF sputtering power of 200 W, a deposition time of 90 min and a bias voltage of −150 V. For coating of FHA through the electrodeposition method, a conventional cell was fitted with a graphite rod as the anode and the Mg–2.2Zn–3.5Ce sheet (15 × 10 × 10 mm) as the cathode. The electrolyte was prepared by dissolution of $Ca(NO_3)_2$ (0.042 mol/L), $NH_4H_2PO_4$ (0.025 mol/L), $NaNO_3$ (0.1 mol/L) and H_2O_2 (10 mol/L) at pH 5 in room temperature. The addition of 2 mM NaF to the electrolyte ensured a crystallized apatite structure in the FHA coating. The FHA coating was deposited at 60 °C and the current density was controlled at 4 mA/cm^2 throughout the electrodeposition for 1 h. The addition of $NaNO_3$ leads to an enhancement of the ionic strength. The pH value of the solution was adjusted to 5.0 by adding HNO_3 and $(CH_2OH)_3CNH_2$ at room temperature. An X-ray diffractometer (Siemens-D5000) was used to evaluate the phase transformation using Cu-Kα radiation ($\lambda = 1.5405$ Å) generated at 35 kV and 25 mA. The crystallite size was determined by the following Scherer equation [22]:

$$\beta = 0.89\lambda / t \cos\theta \tag{1}$$

where β is the diffraction peak width at mid-height, λ is the X-ray wavelength, t is the average crystallite size (nm) and θ is the Bragg diffraction angle. Fourier-transform infrared (FTIR) spectroscopy was used to determine the surface functional groups of the coated sample. The FTIR spectrum was recorded in a spectral range of 3950–400 cm^{-1}. The surface topography of the coated and uncoated specimens was evaluated by using atomic-force microscopy (AFM; NanoScope IV, Digital Instruments). AFM imaging was performed in the tapping mode at room temperature using a standard silicon nitride probe with a spring constant of 0.58 N/m and a typical radius of 10 nm. The scanning area selected was 10 × 10 μm. Microstructural observation was performed using a scanning electron microscope (SEM, JEOL JSM-6380LA), equipped with an EDS and a transmission electron microscope (TEM, HT7700 Hitachi). The bonding strength of the coated specimens was measured according to ASTM F1044 standard using universal testing machine (Instron 5569). Rectangular specimens with dimensions of 30 mm × 10 mm were prepared. The cross-head displacement rate was 1 mm/min with a 10 kN load cell. Three coated specimens were tested and the average value was reported. Rectangular specimens with a surface area of 1 cm^2 were mounted in epoxy resin for electrochemical tests. The test was conducted at 37 °C in an open air glass cell containing 350 ml Kokubo solution with a pH of 7.4 using PARSTAT 2263 potentiostat/galvanostat (Princeton Applied Research). A three-electrode cell was used for potentiodynamic polarization tests. The reference electrode was saturated calomel electrode (SCE), the counter electrode was made of graphite rod, and the specimen was the working electrode. All experiments were carried out at a constant scan rate of 0.5 mV/s initiated at −250 mV below the open-circuit potential. The electrochemical impedance spectra were measured over a frequency range from 0.01 Hz to 100 kHz and the data were analysed using ZsimpWin software. EIS test was also performed by using VersaSTAT 3 machine. The immersion test procedure was carried out based on ASTM: G1–03. The specimens were then immersed in a beaker containing 200 ml of Kokubo simulated body fluid (SBF) with a chemical composition as listed in Table 1 [23]. The average pH value of the SBF from three measurements was recorded during the soaking experiment after every 24 h interval. The hydrogen evolution rate of the specimens was also measured during the 168 h immersion in Kokubo solution experiment. A sample was immersed in a beaker while a funnel was located over the samples to collect evolved hydrogen in a burette above the funnel. The hydrogen evolution rate was calculated in ml/cm^2/day before renewing the solution and the volume of hydrogen was measured with a scaled burette.

3. Results and discussion

3.1. Microstructure and composition

Fig. 1 shows the XRD patterns of the as-cast Mg–2.2Zn–3.5Ce, TiO_2 coated and TiO_2/FHA composite coated specimen. XRD spectrum (Fig. 1a) shows that the main phases in Mg–2.2Zn–3.5Ce alloy

Table 1
Chemical composition of the Kokubo simulated body fluid (SBF) compared to the human blood plasma.

Solution	Ion concentration (mmol/L)							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	HPO_4^{2-}	SO_4^{2-}
Plasma	142.0	5.0	2.5	1.5	27.0	103.0	1.0	0.5
Kokubo (c–SBF)	142.0	5.0	2.5	1.5	4.2	147.8	1.0	0.5