



In-vitro corrosion inhibition mechanism of fluorine-doped hydroxyapatite and brushite coated Mg–Ca alloys for biomedical applications

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Abstract

Magnesium alloys have received great attention as a new kind of biodegradable metallic biomaterials. However, they suffer from poor corrosion resistance. In this study, Mg–Ca alloy was coated with nano-fluorine-doped hydroxyapatite (FHA), and brushite (DCPD); via electrochemical deposition (ED). Coatings were characterized by X-ray diffraction (XRD), Fourier-transformed infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The results revealed that nano-fluorine-doped hydroxyapatite coating produced more dense and uniform coating layer, compared to the brushite coating. The compression tests of the ED-coated Mg alloy samples immersed in simulated body fluid for different time periods showed higher yield strength (YS) and ultimate tensile strength (UTS), compared to those of the uncoated samples. The degradation behavior and corrosion properties of the ED-coated Mg alloy samples were examined via electrochemical measurements and immersion tests. The results showed that FHA coating could effectively induce the precipitation of more Ca^{2+} and PO_4^{3-} ions than DCPD coating, because the nanophase can provide higher specific surface area. It was also found that FHA and DCPD coatings can significantly decline the initial degradation rate of the alloy. A corrosion mechanism of the ED-coated alloy is proposed and discussed in this paper.

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1. Introduction

Biodegradable implants are receiving huge attention in medical applications [1]. They are dissolved and absorbed in the human body after the healing process is complete [1,2]. In that regard, they are superior to permanent implants, since their presence in the human body may cause problems such as sensitization, physical irritation, allergy and/or other physical problems in the long term. Equally, the patient's morbidity and overall cost can be reduced, significantly, by using degradable implants; since there is no need for extra surgery for their removal [2,3]. Recently, accessible degradable implants are mainly made of polymers or ceramics, such as poly-L-lactic acid, polyglycolic acid (PGA), polyglyconate and calcium phosphate ceramics [4,5]. However,

polymeric materials possess lower mechanical strength, compared to metallic materials. Hence, these materials are mainly employed for low load-bearing applications [2]. Compared to the commonly used biodegradable materials, magnesium alloys show great potential for implant applications as a result of their outstanding mechanical properties, biocompatibility and non-toxicity [3,6].

Magnesium is a lightweight metal with a density of 1.74 g/cm^3 , similar to that of natural bones ($1.8\text{--}2.1 \text{ g/cm}^3$), and an elastic modulus of 44 GPa. The density of Mg is 1.6 and 4.5 times lower than that of aluminum and steel, respectively. Its elastic modulus is close to that of cortical bone (17 GPa), which results stress shielding effect [3,7,8]. In the human body, large amount of Mg^{2+} ions exist; taking part in several metabolic reactions [1]. However, the application of these materials has been limited due to their high corrosion rate and fast biodegradation before the adequate healing of the new tissue [9,10]. Several types of corrosion, such as galvanic and pitting corrosions, are observed in magnesium alloys [11].

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The simplest way to reduce the corrosion rate of magnesium and its alloys is by coating, which acts as a protective layer against a corrosive environment [1,12]. To modify the surface of metal implants; bioactive coatings, such as various ceramic calcium phosphate (Ca–P) compounds, are promising candidates [13]. Brushite (DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), and hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) are two kinds of Ca–P coatings, which form a protective layer on Mg alloys to improve their biocompatibility and corrosion resistance [14]. Brushite crystals are composed of CaPO_4 chains, arranged parallel to each other, while lattice water molecules are interlayered among them [15]. Brushite also has biocompatibility with different cell lines such as murine fibroblast cells [16]. In medical field, it is used as calcium orthophosphate cements and for tooth remineralization [15]. Addition of brushite to toothpaste for caries prevention and as gentle polishing agent has also been reported [16]. However, brushite encounters higher solubility than other types of calcium phosphate phases. Thus, it is mainly applied as a precursor to synthesize the more stable HA phase. This is attributed to the modification of brushite crystal size via homogeneous precipitation, which can be easily converted to HA through alkaline treatment [16]. Similar approach was used by other researchers to convert brushite to calcium deficient hydroxyapatite (CDHA) using NaOH [15,16]. Hydroxyapatite is widely used as a bone implant material owing to its excellent biocompatibility and it can also form strong chemical bond with the bone [17,18]. HA can also be used as a coating material on biodegradable and permanent metallic implants due to its chemical and biological similarity to the natural bone [19,20]. The deposit of HA on the surface of magnesium alloys enhances bioactivity and improves both bone-bonding ability and corrosion resistance of these alloys [1]. However, HA coating suffers from relatively high dissolution rate in the biological environment of human body, which is unfavorable for long-term stability of the implants [17,19,21,22]. Therefore, recently, hydroxyapatite is doped with different quantities of cations and anions such as Na^+ , Mg^{2+} , CO_3^{2-} and F^- [23]. Among these, F^- ion plays a crucial role owing to its effect on the physical and biological properties of hydroxyapatite. F^- ion also prevents dental cavities in a bacteria containing and acidic environment. It equally acts as a good nucleation agent for apatite, which promotes bone forming process [24]. Therefore, FHA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{F}_x$, where $0 < x < 2$) was developed as a promising candidate for the replacement of HA in orthopedic applications [25]. FHA also shows high phase stability at higher temperatures due to the replacement of OH^- by F^- which leads to contraction in the *a*-axis without changing the *c*-axis. This causes an enhancement of the crystallinity and stability [17]. Different surface treatments, such as polymer coating, hydrothermal, chemical, sol–gel, electrochemical deposition, dip coating, anodizing and micro-arc oxidation (MAO) have been carried out on magnesium alloys for the enhancement of their corrosion resistance [11]. Among these, electrodeposition (ED) is a promising method for coating calcium phosphate on magnesium and its alloys owing to its simple set up, cost-effectiveness, ability to form a uniform

coating, low temperature requirement and ability to coat complex shapes [26]. Other studies have also reported HA coating on Mg alloys via electrodeposition method [27]. However, the degradation mechanism of fluorine-doped hydroxyapatite coating on Mg alloys in simulated body fluid (SBF) is not yet understood. Therefore, in this study, the corrosion behavior of Mg–Ca alloy with FHA, and DCPD coatings in SBF was systematically evaluated. Mechanical properties dependence on the degradation behavior of the uncoated and DCPD, and FHA specimens were also investigated.

2. Experimental

Pure magnesium (99.98% Mg), pure zinc (99.99%) and Mg–32% Ca master alloy were used to prepare magnesium alloys. Melting was conducted in an electric resistance furnace under argon gas in a mild steel crucible coated with boron nitride. The melting temperature was set at 760 °C and the melt was kept for 45 min, at this temperature. The melt, with a constant concentration of Ca (3 wt%), was then cast into a stainless steel mold pre-heated to 300 °C to produce an ingot. In preparation for further experiments, several Mg–3% Ca specimens, with composition of 0.059% Si, 0.038% Mn, 3.271% Ca, 0.021% Al, 0.013% Fe and 96.598% Mg and dimensions of 20 mm × 15 mm × 10 mm, were cut from the ingot. Then, they were mechanically wet ground with 320–2000 SiC grit papers until all visible scratches were removed. Prior to a deposition, the polished specimens were washed thoroughly with distilled water, rinsed and ultrasonically degreased with ethanol and dried in a warm stream of air. Brushite coating was produced via electrodeposition, at 70 °C, for 1 h. A conventional cell was fitted with a graphite rod as the anode and an Mg–Ca sheet (15 × 15 × 10 mm³) as the cathode. Saturated calomel electrode (SCE) served as the reference electrode, along with a potentiostat/galvanostat instrument (VersaSTAT 3-VersaStudio software) for electrochemical measurements. A current density of 0.4 mA/cm² was used for the coating process. The solution concentration was kept uniform using a magnetic stirrer, controlled at 120 rpm. The electrolyte was prepared from the mixture of $\text{Ca}(\text{NO}_3)_2$ (0.042 mol/L), $\text{NH}_4\text{H}_2\text{PO}_4$ (0.025 mol/L), NaNO_3 (0.1 mol/L) and H_2O_2 (10 mol/L). The addition of NaNO_3 enhances the ionic strength. All of the aforementioned reagents were analytically graded. The pH value of the solution was adjusted to 5.0 by adding HNO_3 and $(\text{CH}_2\text{OH})_3\text{CNH}_2$, at room temperature. The FHA coating was directly electrodeposited after adding NaF (2 mmol/L), at 60 ± 1 °C, into the electrolyte. The addition of 2 mmol/L of NaF into the electrolyte ensured a crystallized apatite structure in the FHA coating. An X-ray diffractometer (Siemens-D5000) was used to evaluate the phase transformation and crystallite size, using Cu-K α radiation ($\lambda = 1.5405$ Å) generated at 35 kV and 25 mA. The crystallite size was determined by the following Scherer equation [25]:

$$t = 0.89k\lambda/\beta \cos \theta \quad (1)$$

where *k* is a form coefficient (assuming that in our case *k* = 1), β is the diffraction peak width at mid-height, λ is the X-ray wave length, *t* is the average crystallite size (nm) and θ is the Bragg

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