



A study of degradation resistance and cytocompatibility of super-hydrophobic coating on magnesium

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ABSTRACT

Calcium stearate based super-hydrophobic coating was deposited on plasma electrolytic oxidation (PEO) pre-treated magnesium substrate. The pre-treated magnesium and super-hydrophobic coating covered sample were characterized by scanning electron microscopy, X-ray diffraction and electrochemical corrosion measurements. The cytocompatibility and degradation resistance of magnesium, pre-treated magnesium and super-hydrophobic coating were analysed in terms of cell adhesion and osteoblast differentiation. The results indicate that the calcium stearate top coating shows super-hydrophobicity and that the surface is composed of micro/nanostructure. The super-hydrophobic coating covered sample shows higher barrier properties compared with the PEO pre-treated magnesium and bare magnesium. Human osteoblast proliferation, but not differentiation is enhanced by the PEO coating. Contrary, the super-hydrophobic coating reduces proliferation, but enhances differentiation of osteoblast, observable by the formation of hydroxyapatite. The combination of corrosion protection and cell reaction indicates that this system could be interesting for biomedical applications.

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1. Introduction

Magnesium and its alloys show potential value as a class of biodegradable implant materials [1]. This is because they are biodegradable, exhibit mechanical properties similar to bone, and are physiologically compatible [1,2], as well as showing osteoinductive behavior [3,4]. In the human body, Mg^{2+} is one of the most abundant cations and is essential to all living cells [5]. The density of magnesium (1.74 g/cm^3) is similar to that of natural bone. The elastic modulus of magnesium (42 GPa) is closer to that of bone compared with conventional implant materials, which can avoid stress shielding and osteopenia [6]. The biodegradability of magnesium and its alloys in the body environment avoids the second surgery for temporary implants. Mg and its alloys show more appropriate mechanical properties compared with other degradable materials, such as polymers and ceramics [7]. However, the poor corrosion resistance of commercially pure magnesium and its alloy restricts their wide application as a biomaterial [8].

Recently, the focus of research lies on the control of the degradation of magnesium and magnesium alloys targeted for temporary applications in the biomedical field. In this regard, many magnesium alloys (for example, Mg-Ca, Mg-Zn, Mg-Mn-Zn and Mg-Sr alloys etc.) have been adapted for biomaterial applications [9–11]. These magnesium

alloys showed good biocompatibility, but the too high initial degradation rate of magnesium alloys would be a major obstacle for the clinical application [7,11]. Besides, many coatings have been employed to improve the corrosion resistance of magnesium and its alloys [2,12]. Given the premise that the coating material is non-toxic, bioactive and the coating is biodegradable, it not only restricts the degradation of the magnesium based materials, but also improves the biocompatibility of the coated system. Such coatings include phosphate chemical conversion coating [13], plasma electrolytic oxidation coating [14], sol-gel coating [15], and various other approaches.

Among these coating systems, the super-hydrophobic coating is a promising biomimetic coating. Super-hydrophobic coatings have attracted much attention because of their unique properties, including self-cleaning, anti-icing, anti-fogging, resistance to corrosion and mechanical robustness. The super-hydrophobicity of the coating is due to the combination of the rough micro/nanostructure and the low surface energy. Super-hydrophobic coatings have a wide range of application in areas such as multifunctional coatings on transmission lines, eyeglasses, self-cleaning windows, anti-fogging and antireflection optical devices, underwater structures, ships' hulls and corrosion prevention in various industrial processes [16–20]. Particularly, a super-hydrophobic coating can greatly reduce the degradation rate of magnesium and magnesium alloys because the hierarchical micro/nanostructure on the coating surface can trap air [21–23]. Furthermore, the air trapped on the coating surface can block the path of water and aggressive ions to penetrate into the coating. The higher corrosion resistance of the super-

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hydrophobic coating on magnesium alloys has been reported in many previous studies [24–32]. However, some toxic chemicals, such as fluoroalkylsilane (FAS, $(\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3)$), are employed in the fabrication process of the hydrophobic/super-hydrophobic coating to reduce the surface energy [31–33].

Many researches have studied the hydrophobic/super-hydrophobic coatings in the biomedical field [34–39]. Machado et al. [35] prepared different substrates with different properties of hydrophobicity/hydrophilicity to compare the properties of cell adhesion. It was indicated that oxygen plasma treatment and high density of vertically aligned carbon nanotube scaffolds (VACNTs) were superior to allow cell adhesion. Compared to hydrophobic surfaces, hydrophilic surface seemed to facilitate cell adhesion. Hung et al. [36] indicated that the hydrophobic rutile TiO_2 film with the nanoporous structure prepared using oxygen plasma immersion ion implantation (oxygen PIII) was good to improve the blood compatibility. In addition, some studies also investigated the hemocompatibility, cytotoxicity and bacterial adhesion of the super-hydrophobic coatings on magnesium alloys [40,41]. Wan et al. [40] studied the hemocompatibility of stearic acid based super-hydrophobic coating on AZ31, and the results showed that this coating could inhibit blood platelet adhesion, implying good hemocompatibility. Wang et al. [41] focussed on bacterial adhesion on magnesium hydroxide and stearic acid based super-hydrophobic coating on AZ91D magnesium alloy. The results showed that the coating can obviously restrict the adhesion of the bacteria on magnesium alloy.

In the previous study a calcium stearate based hydrophobic coating on AZ21 magnesium alloy by electrodeposition method was fabricated [42]. The results show that the deposition time and the working voltage have a significant effect on the formation and corrosion resistance of the coating. After parameter optimization the highest corrosion resistance was obtained on the coating fabricated at 50 V for 60 min [42]. The formation mechanism and corrosion mechanism of the coating have been investigated in detail [42]. In addition, influence of surface pre-treatment on the deposition and corrosion properties of this hydrophobic coating has been studied [43]. The results indicate that hydrophobic coating with pre-treatment based on plasma electrolytic oxidation shows the best corrosion resistance in a simulated body fluid [43]. Unfortunately, there are few studies about the influence of this calcium stearate based coating on bone formation. The influence of surface wettability and/or structure on osteoblast adhesion and differentiation is controversially discussed [44]. Moreover, the studied Mg-based alloys contain aluminum (Al) because the addition significantly enhances the mechanical properties by precipitation strengthening effect. However, the Al ions may induce neurotoxicity in the human body [45]. The association of Al with Alzheimer's disease is still under discussion [11].

In this study, pure magnesium was selected as a substrate in order to avoid the negative effects of the Al element. A super-hydrophobic coating was prepared on the pure magnesium with a plasma electrolytic oxidation (PEO) pre-treatment. The cytocompatibility and degradation resistance of all states were analysed in terms of cell adhesion and osteoblast differentiation.

2. Experimental

2.1. Materials and specimen preparation

Commercial pure magnesium (chemical composition of the received material determined by a spark emission spectrometer (Spectrolab 9, Spectro) is shown in Table 1) of 3 mm thickness was cut into samples with dimensions of 15×15 mm. The specimens were abraded with SiC emery paper up to 1500 grade, and cleaned with deionized water and pure ethanol separately. Finally, they were dried in air. All chemicals used in the present work were from analytical grade.

Table 1
Chemical composition of the as received material.

Element	Ag	Al	Ca	Ce	Cu
wt%	<0.00005	0.01400	<0.00010	<0.00040	0.00030
Element	Fe	La	Mn	Ni	Pb
wt%	0.00620	<0.00050	0.01110	<0.00020	0.00164
Element	Si	Sn	Zn	Zr	Mg
wt%	0.05910	0.00174	0.00690	<0.00050	99.90000

2.2. Plasma electrolytic oxidation

The plasma electrolytic oxidation (PEO) process was carried out by using a self-made pulsed direct current (DC) power source ($T_{\text{on}}:T_{\text{off}} = 0.4 \text{ ms}:3.6 \text{ ms}$) under constant voltage regime (400 V) for 10 min and a current density limit of 0.25 A/cm^2 . During the PEO process, the specimen and a stainless steel tube were used as the anode and cathode, respectively. The electrolyte for the PEO process was composed of sodium phosphate (10 g/L) and potassium hydroxide (1 g/L). Clay particles [46], 5 g/L (Nanofil 116, Rockwood, natural montmorillonite, about 100% bentonite) with an average size of $12 \mu\text{m}$ were dispersed into the electrolyte. The temperature of the PEO electrolyte was kept at $10 \pm 2 \text{ }^\circ\text{C}$ by a water cooling system. After PEO process, the specimen was etched in diluted phosphoric acid ($60 \text{ g/L H}_3\text{PO}_4$) for 15 s at room temperature.

2.3. Fabrication of the super-hydrophobic coating

The coating was cathodic electrodeposited on the PEO pre-treated magnesium using a two-electrode cell, in which the PEO pre-treated specimen was used as the cathode and a graphite sheet was used as the anode. The electrolyte contained $0.05 \text{ mol/L Ca}(\text{NO}_3)_2$ and 0.05 mol/L stearic acid in ethanol ($\geq 99.5\%$) as solvent. The deposition process was performed at 50 V for 60 min using a DC power supply (EA-PS 8720-15, Elektro-Automatik GmbH) in voltage control mode at room temperature. After electrodeposition, the coated specimens were cleaned with ethanol and dried in air. The current density vs. time (J - t) curve was recorded within the first 900 s of the coating preparation.

The specimen coated with the super-hydrophobic coating was named PEO-SHC and the plasma electrolytic oxidation pre-treated specimen was named PEO.

2.4. Characterization of the super-hydrophobic coating

The surface morphology of the PEO pre-treated layer and the coating along with the cross-sectional morphology of the coating were

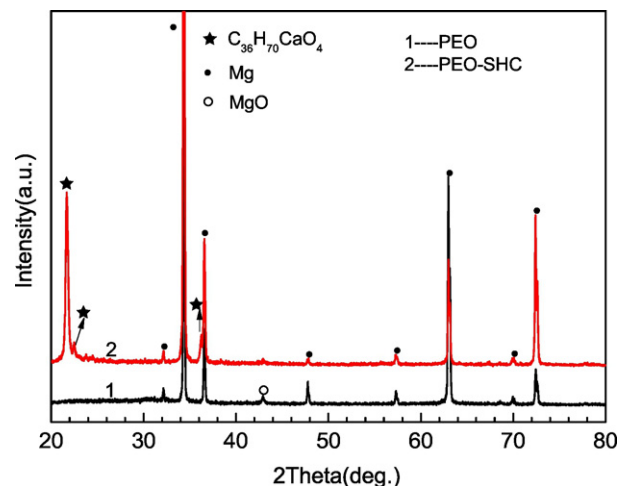


Fig. 1. XRD patterns of the PEO and the PEO-SHC. The main peaks are magnesium (Mg), magnesium oxide (MgO) and calcium stearate ($\text{C}_{36}\text{H}_{70}\text{CaO}_4$).

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