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Surface modification of magnesium alloy via cathodic plasma electrolysis and its influence on corrosion resistance and cytocompatibility

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ABSTRACT

To improve corrosion resistance and enhance biocompatibility of magnesium alloy, cathodic plasma electrolysis (CPE), a liquid phase plasma technique, was used to fabricate zirconia (ZrO_2) coatings onto WE43 magnesium alloy substrate. Surface morphology and phase composition of the coatings on magnesium alloy substrates were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD), respectively. The potentiodynamic polarization test in simulated body fluid (SBF) indicated that corrosion resistance of magnesium alloy was significantly improved by this CPE treatment. The results of cytocompatibility including osteoblasts adhesion and viability suggested that surface modification of magnesium alloy with ZrO_2 coating fo'rmed via CPE technique is beneficial for cell proliferation and differentiation. The approach presented here should be an attractive way for surface modification of magnesium-based implants to improve anticorrosion and bone osseointegration.

1. Introduction

Magnesium (Mg) and its alloys have attracted extensive attention as potential metallic implants due to exceptionally light weight, excellent mechanical properties close to natural bone, and ability to degrade in vivo [1–3]. However, Mg and its alloys exhibit poor corrosion resistance especially in the physiological environment, which restricts their widespread use in clinical application [4,5]. In addition to poor anticorrosion, the interfacial situations of the Mg alloy implants cannot highly induce the bone-forming cells response to the implants or effectively integrate with the surrounding bone tissue, especially at the early stage of implantation. In this respect, surface modification plays an important role by providing a means to selectively enhance anticorrosion property and cellular response without affecting the desirable bulk attributes of magnesium and its alloys [6,7].

In present work, a zirconia (zirconium dioxide, ZrO_2) coating prepared by cathodic plasma electrolysis (CPE) technique was employed to enhance corrosion resistance and osteoblast response of WE43 Mg alloy. CPE is a novel liquid phase plasma process in which the plasma discharge occurs in liquid precursors at atmospheric pressure and the plasma is confined to the cathode in a superheated vapor sheath surrounded by the liquid phase [8]. The device used for CPE is quite simple comparing with that in gas phase plasma because the system does not require vacuum and gases control. Recently, cathodic plasma electrolysis has attracted much attention due to its unique properties and useful applications in depositing a wide range of films or coatings on Ti, NiTi and Mg alloy substrates [9–11]. Here, CPE technique was used to fabricate a ZrO_2 coating on WE43 Mg alloy substrate. The ZrO_2 coating has good chemical stability, offering superior corrosion and scratch resistance [12,13]. In addition, zirconia coatings have been shown to enhance osteoblasts adhesion, growth and proliferation [14–16]. The aim of this study is to investigate the microstructure, phase composition, corrosion resistance and biocompatibility of this ceramic coating. We hoped that the ZrO_2 coating via CPE method would be beneficial for improving the corrosion resistance and bioactivity of Mg alloy substrates.

2. Materials and methods

Commercial as-extruded WE43 Mg alloy rods (4.1%Y–2.3%Nd–1.0%Heavy Rare Earth–0.5%Zr with balance Mg, Shenxintai Metal

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Corporation, China), are machined into cylindrical discs with a thickness of 2 mm and a diameter of 15 mm. The discs were ground with 1000 grit paper using water as lubricating liquid. The samples were successively cleaned twice in an ultrasonic bath of acetone for 5 min each prior to undergoing the CPE process.

CPE process was performed with the instrument and the protocol previous reported [9–11]. Magnesium alloy as cathode was discharged for 60 min with graphite as the anode. The electrolyte employed in this work was the solution of $Zr(NO_3)_4$ 50 g/L and ethanol. Electrolyte temperature was controlled at 25 ± 2 °C during the treatment. A DC pulse power source was used. Pulse frequency and duty cycle were fixed at 100 Hz and 40%. Magnesium alloy samples were treated with applied voltage 400 V.

Scanning electron microscopy (SEM) (Quanta 200 Philips-FEI Corporation, Netherlands) was used to investigate the surface morphology the coatings. The phase composition of the samples was characterized by X-ray diffraction (XRD) (D/Max2550VB+/PC Rigaku Corporation, Japan) with Cu $K\alpha$ radiation, with in a 2θ range of 10–90° and a step size of 0.02°.

To assess corrosion behavior of the samples, a three-electrode electro-chemical workstation (CHI660C, China) was performed. The counter electrode was made of platinum and a reference electrode was saturated calomel electrode (SCE). The simulated body fluid (SBF) solution was prepared according to a previous study [17]. All the specimens were allowed to equilibrate to reach a stable open circuit potential, before initiating the potentiodynamic polarization tests at a scan rate of 0.5 mV/s. All the tests were carried out at 37 °C. The hydrogen evolution measurement was performed to investigate the long-term corrosion behavior of magnesium alloy sample. Each sample was placed into SBF at 37 °C. Then hydrogen was collected and measured at different times of intervals. The mean value of four replicates was used as the final result for each sample in hydrogen evolution measurement.

Osteoblasts were isolated from neonatal rat calvaria via a sequential collagenase digestion method. Then, osteoblasts at the 3rd passage were seeded onto native magnesium alloy and CPE treated magnesium alloy at a density of 10^4 cells per disk. After 3 days, the cells were stained with rhodamine phalloidin (Invitrogen, USA) at room temperature for 1 h and then stained with Hoechst fluorescent dyes (Sigma, USA) for 5 min. Cells were stained with actin filaments (red) and cell nuclei (blue), observed and captured with confocal laser scanning microscopy (CLSM, Leica DMI 6000, Germany). Cells densities on samples were measured by analyzing all cell nuclei in 6 individual fields of 3 samples per sample type.

Cell viability assay was measured by an indirect evaluation method according to a previous study [18]. The extraction media were prepared using DMEM serum free medium with the surface area/extraction medium ratio 0.5 cm^2/ml and placed at 37 °C for 72 h in a humidified atmosphere with 5% CO_2. The control groups involved the use of DMEM medium as negative control and 10% DMSO DMEM medium as positive control. Cells were incubated in 96-well cell culture plates at 5×10^3 cells/100 μl medium in each well and incubated for 24 h to allow attachment. The medium was then replaced with 100 μl of extraction medium. After 1, 4 and 7 days, the cell monolayer was washed twice with PBS and incubated with trypsin-EDTA solution (0.25% trypsin, 1 mM EDTA, Gibco) for 5 min at 37 °C to detach the cells. Then, 24 h later, normal incubation could allow the cells to fully attach for MTT assays. The absorbance of the solution was measured by using a microplate reader (BIO-RAD 680) at wavelength 490 nm.

3. Result and discussion

Fabrication and characterizations of ZrO_2 coating: SEM images of native and CPE modified magnesium alloys were shown in Fig. 1. It can be seen that the as-polished magnesium alloy surface display visible scratches, which was attributed to polishing abrasion (Fig. 1a). After CPE treatment, large distribution of molten particle with different sizes and a few small pores are observed on coating surface (Fig. 1b). The cross-sectional microstructure of CPE coating was displayed in Fig. 1c. The thickness of the resulting coating was about 70 μm.

XRD patterns of untreated WE43 magnesium alloy and magnesium alloy treated by CPE are shown in Fig. 2. In the pattern of native magnesium alloy, no additional peaks were found except for Mg peaks (Fig. 2a). In the pattern of CPE coating, it can be found that the coatings exhibit complex composition, which is composed of *t*-ZrO_2, *m*-ZrO_2 and Mg (Fig. 2b).

The potentiodynamic polarization curves of native and CPE treated magnesium alloys were shown in Fig. 3a. By use of the method of Tafel least square fitting, the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were derived. As shown in

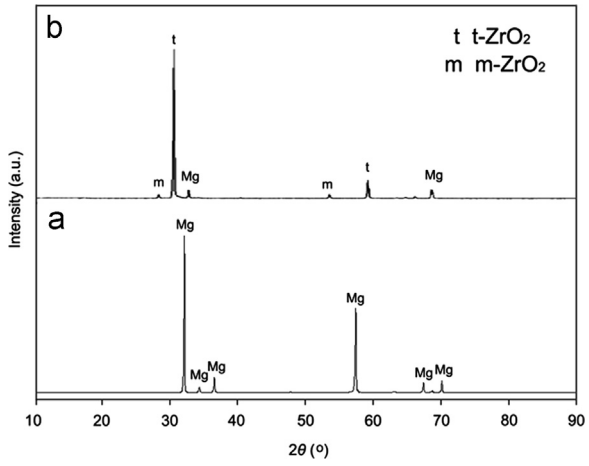

Fig. 2. XRD patterns of (a) native and (b) CPE-treated WE43 Mg alloy substrates.

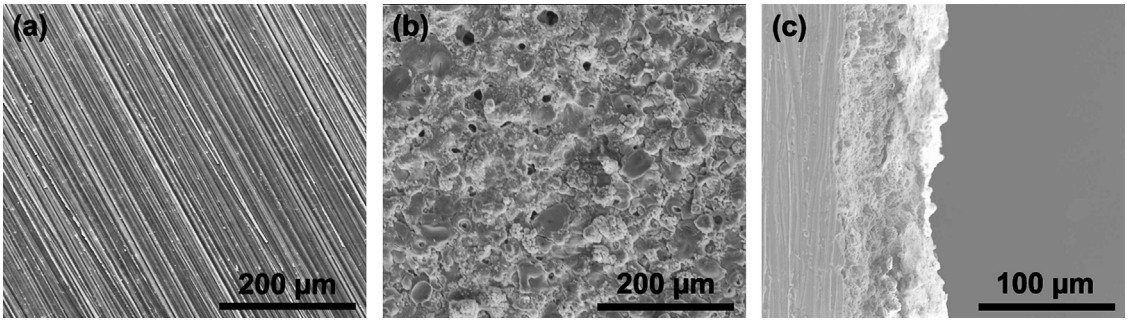

Fig. 1. SEM images of (a) native, and (b) and (c) CPE-treated WE43 Mg alloy substrates.