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Influence of albumin and inorganic ions on electrochemical corrosion behavior of plasma electrolytic oxidation coated magnesium for surgical implants

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ABSTRACT

Magnesium and its alloys are of great interest for biodegradable metallic devices. However, the degradation behavior and mechanisms of magnesium treated with coating in physiological environment in the presence of organic compound such as albumin have not been elucidated. In this study, the plasma electrolytic oxidation coated magnesium immersed in four different simulated body fluids: NaCl, PBS and with the addition of albumin to investigate the influence of protein and inorganic ions on degradation behavior by electrochemical methods. The results of electrochemical tests showed that aggressive corrosion took place in 0.9 wt.% NaCl solution; whereas albumin can act as an inhibitor, its adsorption impeded further dissolution of the coating. The mechanism was attributed to the synergistic effect of protein adsorption and precipitation of insoluble salts.

1. Introduction

Magnesium and its alloys have been considered as the revolutionary biodegradable implant material. They can provide several advantages including eliminating the effects of stress shielding, improving biocompatibility concerns *in vivo* and degradation properties removing the requirement of a second surgery for implant removal. However, the rapid degradation *in vivo* environment leads to implant failure by losing the mechanical integrity before complete restoration [1]. It is necessary to control the corrosion rates of materials to match the rates of bone healing.

Many attempts are being adopted for enhancing the corrosion resistance properties, including addition of alloy elements, substrate texture control, surface modification by suitable treatments and so on [2]. Among these techniques surface treatments are paid more attention, such as alkali-heat treatment, electrodepositing, conversion coatings, anodizing, ion implantation, laser surface alloying and polymer coatings [3–7]. Plasma electrolytic oxidation (PEO) treatment, also known as microarc oxidation, is a common technique for corrosion protection of magnesium alloys in the industrial sector. In plasma electrolytic oxidation, higher potentials are applied which locally exceeds the dielectric breakdown potential of the growing oxide film and discharges occur. These discharges result in localized plasma reactions, with conditions of high temperature and pressure which modify the growing oxide. Processes include melting, melt-flow, re-solidification, sintering and densification of the growing oxide [8]. By the PEO process, a relatively thick, dense and hard oxide coating can be produced on the surface of magnesium alloys [9]. The coating is a chemical conversion of the substrate metal into its oxide, and grows both inwards and outwards from the original metal surface, which has excellent adhesion to the substrate and offers protection against wear and corrosion. Recently the PEO coating, mainly composed of calcium/magnesium, silicate/phosphate based bioactive ceramics, has attempted to magnesium implant for improving its corrosion resistance and biocompatibility. Gu et al. [10] reported PEO coating exhibited beneficial effects on the corrosion resistance of, and thus improved the cell adhesion to, the Mg–Ca alloy. Yao et al. [11] introduced Ca and P into a ceramic coating on PEO-treated AZ91D alloy and found the coating reduced the corrosion current density by two orders of magnitude.

Overall, the PEO coating is very stable, hard, biocompatible and corrosion resistant [12]. For orthopedic implants PEO treatment could be supposed to slow down the corrosion rate. Hence, PEO treatment should be used to protect the substrate in combination with a subsequent coating process. Corrosion of PEO-treated Mg-alloy samples in Hanks' solution was studied first by Zhang et al. [13], then by Xu et al. [14] and later in SBF by Jo et al. [15]. In all

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studies, PEO showed a lower corrosion current density in polarization studies than the uncoated sample. Besides, the effect of various electrolytes on the electrochemical corrosion behavior of PEO coating has previously been studied [16]. Liang et al. [17] also reported the influence of pH on the deterioration of PEO coated AM50 alloy in NaCl solutions. However, many of the *in vitro* studies employed simulated body fluids such as Hanks' solution, PBS, or NaCl solution and so the implants only encountered inorganic matter.

Organic molecules, such as serums and proteins, have been found to affect the corrosion of metallic implants [18]. The influence of albumin or serum proteins on the corrosion rates of magnesium alloys has been studied. Yamamoto et al. [19] have investigated the corrosion rate of pure magnesium in NaCl, E-MEM and E-MEM with fetal bovine serum (FBS). It is found that protein adsorption and precipitation of insoluble salts decreased the corrosion rate. Liu [20] has found that the corrosion resistance in SBF + 1 g/L albumin is approximately twice that in SBF. Rettig [21,22] have investigated the time-dependent electrochemical behavior of WE43 alloy in SBF with and without 40 g/L albumin. The results showed the inhibitive effect of protein resulted from a blocking layer on the surface during the initial hours of exposure.

In this work, a PEO coating was obtained from silicate based electrolyte. In order to fully understand the corrosion mechanism of PEO coated magnesium in the presence of albumin, four kinds of solutions (NaCl, NaCl + albumin, PBS and PBS + albumin) were adopted. The electrochemical corrosion behavior was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The morphologies of coating surface after 14 days immersion were characterized by SEM equipped with EDS. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemistries after the exposure in albumin solutions. The interactive effects of albumin and inorganic ions (Cl^-, phosphate) were elucidated and a mechanism explaining the reduced corrosion rate was proposed.

2. Experimental

2.1. Preparation and characterization of PEO coating

Test coupons (Φ 15 mm × 4 mm) of pure magnesium (EONTEC Co., Ltd, Dong Guan) were used as the substrate for PEO coatings. The specimens were ground and polished successively with 600, 800, 1200, 2000 grit emery sheets before the PEO treatment. The based electrolyte of alkaline silicate was prepared from the solution of $Na_2SiO_3{\cdot}9H_2O$ (10 g/L), $KF{\cdot}2H_2O$ (8 g/L) and KOH (1 g/L) in distilled water. The PEO process was implemented with a constant working voltage of 370 V for 5 min. All coated samples were rinsed thoroughly in distilled water and dried in ambient air immediately after the PEO treatment.

The PEO coated specimens were examined in a scanning electron microscope (SEM, Hitachi S-3400N) for understanding the morphological features. X-ray diffraction (XRD) was performed using an X-ray diffractometer (Rigaku D/max 2500) with Cu-K_α radiation to determine the phase composition of the oxide coatings. The XRD pattern was made with MDI Jade 5.0 software.

2.2. Electrochemical experiments

The experiments were carried out using four different simulated body solutions: 0.9 wt.% NaCl, phosphate buffered saline (0.14 M NaCl, 1 mM KH_2PO_4, 3 mM KCl, 10 mM Na_2HPO_4, pH = 7.4), with 1 g/L of albumin containing 0.9 wt.% NaCl and PBS respectively, in order to analyze the influence of protein adsorption on the electrochemical behavior of the samples. Temperature of the solution was kept at 37 °C.

The electrochemical corrosion behavior was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) using a PAR Verserstat3 potentiostat controlled by VersaStudio software. A three-electrode cell featuring a Pt counter electrode and a saturated calomel reference electrode (SCE) was employed. The samples were allowed to stabilize at their open circuit potential (OCP) for 30 min before the measurements were started. Potentiodynamic polarization tests were conducted at a sweep rate of 0.5 mV/s within a scan range of ±0.25 V with reference to OCP. Impedance experiments were carried out using a 10 mV root-mean-square perturbation from 100 kHz to 10 mHz. Fitting was performed with ZSimpwin software. All electrochemical tests were conducted in triplicate in order to ensure the reproducibility of results.

2.3. Immersion test

To evaluate the corrosion of PEO coating in four different simulated body solutions mentioned above, the *in vitro* immersion test was employed. The PEO coated specimens were soaked in 50 mL solutions for 14 days under a condition of 37 °C and 5 vol.% CO_2 in the humidified air. After the immersion, each specimen was collected, rinsed with distilled water quickly and dried to observe the surface by an optical microscope. The surface morphology was analyzed by the scanning electron microscope (SEM, Hitachi S-3400N) and equipped energy dispersive X-ray spectroscopy (EDX).

2.4. X-ray photoelectron spectroscopy

After immersion in different simulated solutions with 1 g/L albumin for 1 h, the surface chemistries of the samples were characterized by an ESCALAB250 X-ray photoelectron spectrometric with a monochromatic Al-K_α (1486.6 eV) radiation source. Survey spectra were collected over the range from 0 to 1100 eV using an analyzer pass energy of 50 eV while high resolution XPS measurements were performed with a pass energy of ~30 eV. All measurements were made at a 45° take-off angle. The base pressure of the system is about 3×10^{-1} bar. Peak identification was performed by reference to a database of XPS.

3. 3 Results

3.1. Structures and morphologies of PEO coating

Fig. 1 shows the surface morphology of plasma electrolytic oxidation coating on pure magnesium. It is rather obvious that there exist many micropores and microcracks on the surface of the coating, which is the typical feature of PEO coating. It is well known that the large discharge sparks and "melt discharging channel" during the PEO process is inevitable to induce the micropores and microcracks. XRD measurement reveals that the PEO coating prepared from silicate electrolyte is composed predominantly of MgO and a small amount of $MgSiO_3$ and Mg_2SiO_4.

3.2. Potentiodynamic polarization measurements

The potentiodynamic polarization curves of PEO coating on pure magnesium obtained after open-circuit exposure to different test electrolytes for about 30 min are exhibited in Fig. 2. Generally, the cathodic polarization curves are assumed to represent the hydrogen evolution through water reduction, while the anodic polarization curves represent the dissolution of magnesium [23]. It can be seen that the various solutions give rise to different cathodic polarization currents. Comparing the electrolyte PBS and NaCl solution, the cathodic polarization current in the former was slightly lower than that in the latter, indicating that the cathodic reaction