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Preliminary study on a bioactive Sr containing Ca–P coating on pure magnesium by a two-step procedure

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ABSTRACT

In this study, a bioactive Sr containing Ca–P (Sr–CaP MAO) coating was obtained through the combination of preceding chemical deposition and micro-arc oxidation treatments for the purpose of modifying the surface of the magnesium to promote the bioactivity and to reduce the degradation rate. The microstructure, element and phase composition of the coating were investigated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Electrochemical and immersion tests were conducted to evaluate the degradation behavior of the Sr–CaP MAO coating in a Hank's solution. The results showed that Sr was successfully incorporated into the Pre-CaP coating by the two-step procedure. The *in vitro* degradation evaluation indicated that the Sr–CaP MAO coating could significantly reduce the corrosion rate of pure magnesium and show better biomineralization property.

1. Introduction

Biodegradable magnesium and its alloys are the potential materials for orthopedic implants over other traditional metallic materials due to the similar mechanical properties to human bone, excellent biocompatibility, especially osteopromotion, and biodegradability in the physiological body environment [1]. However, the main limitation is the initial fast degradation, which could not match the bone reconstruction and afford effective biomechanical support. To overcome this drawback, several surface modification techniques, *i.e.* electrochemical deposition [2], polymer treatment [3], chemical deposition [4], and micro-arc oxidation (MAO) techniques [5,6], have been introduced to improve the degradation rate and bioactivity of magnesium and its alloys. MAO coating, also named as plasma electrolytic oxidation (PEO) coating, has been intensively researched as a class of biomedical coatings on magnesium alloys and titanium alloys in recent years due to the better corrosion resistance, abrasion resistance and bioactivity. As is well-known, the human bone is mainly composed of apatite crystals deposited on organic collagen fibers [7]. Therefore Ca–P ceramics, such as HA and β-TCP, are favorable coatings to improve the bioactivity of magnesium [8–11]. Likewise, the electrolyte solutions containing calcium and phosphate have been developed to enhance the biological compatibility and activity of MAO coatings for magnesium and its alloys in prior literatures [12–14]. Gan et al. [15] fabricated a bioactive Ca–P coating on pure magnesium in an electrolyte solution consisting of calcium hydroxide, sodium hexametaphosphate and potassium fluoride. Their results suggested that the Ca–P containing MAO coatings could significantly enhance the corrosion resistance of magnesium substrate in a Hanks' solution with a great potential for medical application. On the other hand, strontium element is also a natural bone-seeking trace element similar to calcium element, which has the ability to stimulate osteoblasts and inhibit osteoclast production and proliferation. Especially, stable strontium at low dose levels is of great benefit to bone formation. There are growing evidences that Sr containing calcium phosphate biomaterials can promote better osteo-precursor cell attachment and proliferation than pure calcium phosphate biomaterials [16,17]. Considering the beneficial effects of strontium in the bone there has been increasing researches on Sr-incorporated scaffolds and bioactive coatings for implant applications [18–21]. According to Tian et al. [22], porous strontium-doped calcium polyphosphate scaffolds for bone substitute applications were performed on a rabbit model over a period of 16 weeks. Their results showed that the scaffolds presented good biocompatibility, osteogenesis property and biodegradability. Capuccini et al. [19] reported that the Sr–HA coating was prepared on titanium substrate by the pulsed laser deposition method. Their results indicated that Sr–HA coating enhanced osteoblast activity, while it restrained osteoclast production and proliferation. It was also reported by Chen et al. [23] that strontium phosphate conversion coatings were developed on magnesium to protect magnesium from the initial degradation, which suggested that the strontium phosphate coatings were a promising option for improving the early rapid degradation rate and the surface bioactivity of magnesium implants.

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Recently, it is interesting to note that the combinations of two kinds of surface modification methods were employed to fabricate calcium phosphate composite coatings on magnesium [24,25], *i.e.* MAO and hydrothermal treatment [26,27] and PEO and electrophoretic deposition [25,28]. Liu et al. [29] prepared a calcium phosphate coating on micro-arc oxidized magnesium by chemical deposition to improve the bioactivity of the micro-arc oxidized magnesium. However, up to date, to the author's knowledge, the combined method of preceding chemical deposition and MAO process to form calcium phosphate composite coating on magnesium alloys is seldom investigated for the purpose of modifying the surface of magnesium and its alloys to promote the bioactivity and to reduce the degradation rate. In this study, an attempt was made to incorporate Sr into a Ca–P precursor coating on pure magnesium by a two-step procedure combining the preceding chemical deposition and MAO process. The surface morphology, chemistry composition and initial degradation evaluation of Sr containing Ca–P coating on pure magnesium were investigated.

2. Experiment

2.1. Preparation of samples

The pure magnesium with the purity of 99.99% (0.0014Fe, 0.0001Ni, 0.0002Cu, 0.0016Si, 0.0004Al, 0.0004Mn and balance Mg, wt.%) was cut into plates of 10 mm × 10 mm × 2 mm. These samples were ground with SiC papers to 1200 grit, then ultrasonically cleaned in acetone for 15 min, rinsed in distilled water and finally dried at room temperature. Sr containing Ca–P MAO coatings were prepared *via* a two-step procedure illustrated in Fig. 1. Firstly, the magnesium samples were pretreated by chemical deposition treatment in a Ca–P containing electrolyte solution that dissolved by 40 g/L $Ca(NO_3)_2 \cdot 4H_2O$ and 16 g/L $NaH_2PO_4 \cdot 2H_2O$ for 5 min at 70 °C, then the MAO treatment followed. For the MAO treatment, the preceding Ca–P coated magnesium samples and the stainless steel were used as anodes and cathodes in an electrolytic bath, respectively. A new MAO coatings were fabricated in the Ca-free electrolyte solution consisting of 4 g/L NaOH, 3 g/L $(Na_2PO_3)_6$, 2 g/L $Na_4P_2O_7 \cdot 10H_2O$ and 0.5 g/L $Sr(OH)_2$ for 5 min under the applied voltage of 450 V, a frequency of 1000 Hz and a duty cycle of 40%.

2.2. Characterization of Sr containing Ca–P coating

The surface and cross-section morphologies of the coating were studied by a scanning electron microscope (SEM, S-3400 N, Hitachi, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS). Phase composition of the Sr containing Ca–P coating was identified by X-ray diffraction (XRD, Rigaku D/MAX) with Cu Ka radiation, and the scan range was from 15° to 85° at a step of 0.04°. The XRD pattern was analyzed with MDI Jade 5.0 software.

2.3. Electrochemical corrosion measurements

Potentiodynamic polarization measurements were carried out using an Autolab system in the Hanks' solution (8.00 g NaCl, 0.40 g KCl, 0.10 g $MgCl_2 \cdot 7H_2O$, 0.35 g $NaHCO_3$, 0.10 g $MgSO_4 \cdot 6H_2O$, 0.14 g $CaCl_2$, 0.12 g $Na_2HPO_4 \cdot 12H_2O$, 0.06 g KH_2PO_4 and 1.00 g glucose) at 37 °C to evaluate the corrosion resistance of the coating on the magnesium substrate. A three-electrode cell was used for the electrochemical measurements. The counter electrode was made of platinum and a saturated calomel electrode (SCE) was used as the reference electrode. A sample with an exposed area of 1 cm^2 was taken as the working electrode. Before the test, all samples were immersed in the Hanks' solution for 30 min to establish a relatively stable potential. 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.

2.4. In vitro immersion test

The initial degradation behavior of the Sr containing Ca–P coating was studied through *in vitro* immersion test in the Hanks' solution. Each sample was soaked with the Hanks' solution kept in an airtight container at 37 °C in a carbon dioxide incubator. The ratio of sample area to solution volume was 1.25 cm^2/mL. The immersion solutions were changed every day to simulate *in vivo* circumstance. The pH values of immersion solutions were recorded every day. The mean value of three duplicates was provided in the results. The morphology and phase composition of coating after 10 days of immersion were studied by SEM and XRD, respectively.

3. Results and discussion

3.1. Microstructure and phase identification

The SEM image of the Pre-CaP coating on magnesium is shown in Fig. 2a. The magnesium surface is covered by a poor-crystallized fish scale-like structure after the chemical deposition treatment in a Ca–P containing electrolyte solution for 5 min. The EDS pattern, as shown in Fig. 2b, indicates that the main compositions of the Pre-CaP coating are O, Mg, P, and Ca. As shown in Fig. 2c, the MAO coating appears typical morphology with the dispersion of micro-pores. According to the previous study, the pores were formed by the molten oxide and gas bubbles thrown out of micro-arc discharge channels during the growing oxide layer [30]. The EDS pattern of the MAO coating in Fig. 2d displays that the peaks of O, Mg, P, Sr, and Ca were detected in the coating. Obviously, the Ca element came from the chemical deposition, while the Sr element was dropped during the MAO process, revealing that Sr element successfully incorporated into the preceding Ca–P coating during the MAO process. On the other side, this also reveals that the

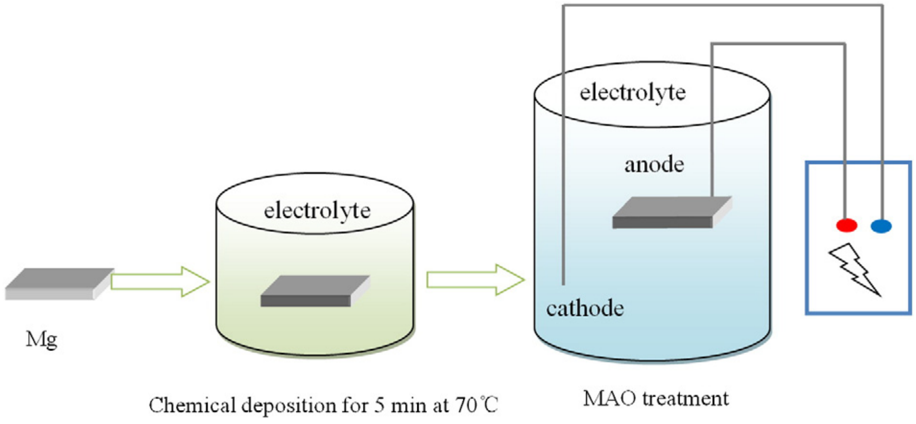

Fig. 1. Schematic diagram of the combination of chemical deposition and MAO process.