



Synthesis and properties of a bio-composite coating formed on magnesium alloy by one-step method of micro-arc oxidation



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ARTICLE INFO

Article history:

Received 26 September 2013
Received in revised form 15 December 2013
Accepted 16 December 2013
Available online 21 December 2013

Keywords:

Magnesium alloy
Hydroxyapatite
Bio-composite coating
Micro-arc oxidation
Bonding strength
Biodegradability

ABSTRACT

Magnesium alloys have been used as biodegradable implants in load bearing applications due to their biodegradability and excellent mechanical properties. However, the rapid corrosion rate still needs to be improved by surface modification, and so does the biocompatibility according to clinical demands for bone implants. This study demonstrated the effectiveness of applying a bio-composite coating on magnesium alloy by adding HA particles in electrolyte during MAO process (MAO–HA). The results suggested that HA particles took part in MAO process, getting decomposed into $\text{Ca}_3(\text{PO}_4)_2$ under a high temperature caused by the intense micro-arc discharge generated at high applied voltage. In the meantime, synthesis of $\text{Mg}_3(\text{PO}_4)_2$ was promoted under the high temperature. The sintering-caused phases $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$ combined with HA composed the bioactive coating. Testified by scratch test, electrochemical test and short-term immersion test, the composite coating showed high bonding strength and improved corrosion resistance owing to the sintering-caused products sealed partial pores of the MAO coating. Therefore, this study indicated that the bio-composite coating obtained by MAO–HA process may be suitable for synthesizing promising bone implant materials in clinical application.

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1. Introduction

Enormous patients with bone defects inducing traumas, inflammations and tumors all over the world have led to huge demand for bone replacements and rapid development of bone repair materials [1,2]. Among all the artificially synthesized materials, including polymers, metals and ceramics, magnesium alloys have drew extensive attention as biodegradable implants in load bearing applications due to their biodegradability in the physiological environment and their excellent mechanical properties such as high tensile strength and possessing an elastic modulus close to that of bone [1–6]. Nevertheless, magnesium and its alloys are chemically active to degrade rapidly in aqueous environments via an electrochemical reaction (corrosion) which produces pH changes and hydrogen gas [3], so when implanted in human body, they may lead to damage of surrounding tissues and an early loss of mechanical stability of the Mg alloy implants before the end of the healing process [6,7]. An effective way to solve this problem is surface modification [8].

Micro-arc oxidation (MAO) coating is being widely used for surface modification of Ti, Mg alloys for biomedical application due to

its good adhesion with the substrate and bioactive feature [8–11]. However, the MAO coating consists of not only the compact diffusion layer in contact with the substrate but also the external porous region containing discharge channels [12]. The external porous region declines the bonding strength between the coatings and hence may be adverse for mechanical strength and corrosion resistance. Furthermore, the bioactivity, a very important requirement of clinical indication for bone implants [13], is still needed to be improved.

Owing to the structural and chemical similarities between HA and mineral components of natural bones [14], and the bioactivity of HA to enhance bone bonding with implants surface directly [15], further modifications by HA such as chemical deposition [16], solution treatment [17], electrochemical deposition technique [18,19] were performed onto the MAO coating in order to enhance the corrosion resistance and improve the bioactivity of the MAO coatings. However, the two-step methods are time-consuming. Meanwhile, some authors obtained Ca-containing MAO coating just through changing the composition of electrolyte. Such as, Pan [20] fabricated bioactive CaP coatings by MAO in electrolytes containing calcium acetate monohydrate and different phosphates, and Wang [21] prepared biocompatible metasilicate-based ceramic coatings by MAO in sodium silicate solution with $\text{Ca}(\text{H}_2\text{PO}_4)_2$ additive. But the structures of the Ca-containing MAO coatings are still porous.

In this paper, we improved the properties of magnesium alloy via one-step method of MAO–HA, which was just by adding HA

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particles in alkaline electrolyte in order to make HA particles negatively charged to migrate towards magnesium alloy under electric field and get involved in the synthesis of coating during MAO process. This paper aims at investigating the feasibility of the one-step method in fabricating calcium apatite containing coating and evaluating the relationship between the structures and the properties of the coating.

2. Materials and methods

2.1. Coating fabrication

As-cast Mg–2 Zn–0.24 Ca alloy (wt.%) prepared in our own lab, was used as substrate in this study. Samples which were cut into dimensions of 35 mm × 10 mm × 3 mm were ground progressively to 800 grits by using SiC papers, and then ultrasonically cleaned with ethanol for 20 min before conducting the MAO process.

The electrolyte was firstly prepared by dissolving 54 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 5 g/L $\text{KF} \cdot 2\text{H}_2\text{O}$, 0.56 g/L KOH into distilled water, and then mixed with 2 g/L HA particles (Sinopharm Chemical Reagent Co., Ltd. And the average size is 5 μm) through magnetic stirring for 0.5 h. All the reagents mentioned above were analytic grade. Afterwards, the coating was prepared under a direct voltage mode while the samples working as the anode and the stainless steel plate as the cathode. The cell potential was increased gradually to 160 V in 10 min and remained stable for 20–30 min to complete the procedure.

2.2. Characterization of the coating

The morphologies of the coating samples were studied by Quanta-2000 scanning electron microscope (SEM). And the thickness of the coating was measured by the cross-sectional SEM micrographs of the samples. X-ray diffraction (XRD, X'Pert PRO) and X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM) were used to characterize the structure and composition of the coatings. The XRD data were collected from 10° to 80° (2θ) using $\text{Cu K}\alpha$ radiation at a scanning speed of 4°/min. The XPS data were obtained through XPS spectrometer with a monochromatic $\text{AlK}\alpha$ radiation and the binding energies were calibrated with $\text{C 1s} = 284.8$ eV to reduce the influence of charging especially on insulating materials.

2.3. Scanning scratch test

The bonding strength between the coating and the substrate was analyzed utilizing a scanning scratch tester (NanoTest Vantage) with a sphero-conical indenter whose serial number is SD-A62. The indenter scanned the coating at a speed of 20 $\mu\text{N}/\text{min}$ while increased the progressive load gradually from 3 to 200 mN. Indicated by the micromorphology of the scratch which was obtained from the optical microscope of the tester, the load at where the coating is removed from the substrate is considered as the "critical load (W_c)", which could be used as an indication of the bonding strength to evaluate the coating-substrate adhesion. Three samples were involved, and each sample was tested twice to confirm the repeatability, and the average value was regarded as their critical load.

2.4. Electrochemical corrosion analysis

The electrochemical test was conducted to evaluate the corrosion resistance of the samples using a conventional three-electrode electrochemical cell with the sample as the working electrode, a platinum rod as the auxiliary electrode and a saturated calomel electrode as the reference electrode. Before polarization, the samples were stabilized in 300 mL SBF for 10 min. SBF was prepared according to Ref. [22]. The experiments were carried out in SBF solution with a scan rate of 0.5 mV s^{-1} at a temperature of 36.5 ± 0.5 °C in water bath. And the polarization curves of bare magnesium alloy and MAO without HA coating sample were obtained to be compared with the MAO–HA samples.

2.5. Immersion test

The immersion tests were carried out to monitor the degradation and the corrosion resistance of the MAO–HA samples group in SBF solution at 36.5 ± 0.5 °C. And bare Mg–Zn–Ca alloys group were immersed under the same condition to be compared with the coated ones. Before immersion, all the samples were carefully embedded into the epoxy resin with only one side exposed. Then samples were immersed into sealable capsules containing SBF solution and the ratio of SBF solution volume to specimen area was 20 mL/cm^2 . After that, the capsules were placed in a water bath at 37 °C. The SBF solution was renewed every 2 days. Five samples of every group were taken out to be tested every 3 days, and the longest immersion time was 15 days. After the pre-selected immersion periods, the samples were rinsed with distilled water and dried by a hair-drier. Microstructural and compositional changes of the samples after immersion tests were characterized

by Quanta-2000 SEM equipping with energy dispersion spectroscopy (EDS) facility. Compression testing was used to analyze and compare the bulk mechanical properties of the coated samples and bare Mg alloy samples during degradation in SBF. An electronic universal testing machine (SHIMADZU/50KN AG-1C) was employed to conduct the test, and the testing speed was set as 1 mm/min.

3. Results and discussion

3.1. Microstructure and composition of MAO–HA coating

The XRD pattern of the MAO–HA coating was shown in Fig. 1. The analysis result indicated that, besides the diffraction peaks from the magnesium alloy substrate, the diffraction peaks of $(\text{Mg,Ca})_3(\text{PO}_4)_2$ and HA were detected, demonstrating that $(\text{Mg,Ca})_3(\text{PO}_4)_2$ and HA were produced as the main components of the coating on Mg–Zn–Ca alloy after MAO–HA.

Fig. 2 shows the survey, Ca 2p and P 2p of XPS spectra obtained from the coating. The signals of Mg, Ca, C, P, O, Na, K, Zn, F were observed from the survey XPS spectrum in Fig. 2a, whereas not all these elements were the major constituents of the coating. The porous structure of the coating can absorb gases from the atmosphere, such as carbon and oxygen, so the organic contaminants can lead to carbon and oxygen signals appeared on the surface [23]. Therefore, the primary components of the coating were Mg, Ca, P, F, O. Calculating through the relative sensitivity factors, the ratio of Ca and P was 1.5:1. According to the analysis result of Ca 2p XPS spectra in Fig. 2b, one sub-peak featured at 347.4 eV corresponded to HA which was one constituent of the starting materials, while the other one featured at 351.8 eV corresponded to compound of calcium phosphate with magnesium ions. And the ratio of the two sub-peaks was 3.8, meaning that the amount of compound was 3.8 times more than that of HA. The P 2p XPS spectra in Fig. 2c was detected as a single peak, and its binding energy was 133.4, corresponding to PO_4^{3-} . Combined with the result of XRD, it was concluded that the coating was composed of HA, $\text{Mg}_3(\text{PO}_4)_2$ and $\text{Ca}_3(\text{PO}_4)_2$ (TCP). The MAO–HA coating was supposed to be bio-composite because of the bioactive feature of both HA and TCP phases [24,25].

Surface morphologies of the MAO and MAO–HA coating samples were observed by SEM in Fig. 3. The average pore size of both the coatings showed no significant difference. The MAO coating surface showed a glossy microgram and higher void ratio, whereas the MAO–HA coating revealed a rougher surface with white specks and relatively lower void ratio. It could be seen that some small pores on the MAO–HA surface were covered, resulting the lower

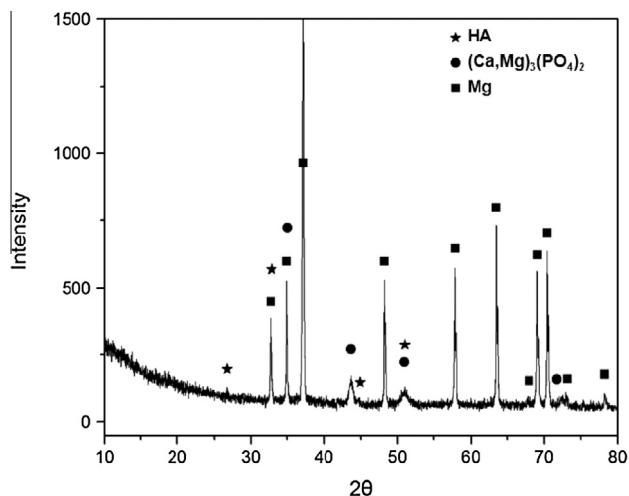


Fig. 1. XRD diffraction patterns of the MAO–HA coating synthesized on the substrate of Mg–Zn–Ca alloy.

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