



The effect of applied voltages on the structure, apatite-inducing ability and antibacterial ability of micro arc oxidation coating formed on titanium surface

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ABSTRACT

The micro arc oxidation (MAO) coatings with different concentrations of Ca, P and Zn elements are successfully formed on the titanium substrate at the different applied voltages. After MAO treatment, the MAO coating exhibits the porous surface structure and composed of anatase and rutile TiO₂ phases. Meanwhile, the average size and density of micro-pores on the MAO coatings have been modified via the adjusting the applied voltages. In addition, the contents of the incorporated elements such as Zn, Ca and P elements in the MAO coatings have been optimized. The bonding strength test results reveal that the MAO coating shows higher bonding strength, which is up to 45 ± 5 MPa. Compared to the pure Ti plate, the MAO coating formed at 350 and 400 V show good apatite-inducing ability. Meanwhile, the MAO coating containing Zn, Ca and P elements have better antibacterial ability for *E.coli* and *S.aureus*. Thus, the incorporation of Zn, Ca and P elements was an effective method to improve the antibacterial ability. Moreover, the concentrations of Zn, Ca and P elements could be adjusted with the changing of the applied voltages. As a result, the enhancement of the antibacterial ability on the MAO coating surfaces was depended on the comprehensive effect of the incorporated elements and the surface property of MAO coatings.

1. Introduction

Titanium and its alloys are widely applied to the repair and replacement of hard tissue [1,2] (bone and teeth) due to the good corrosion resistance and excellent biocompatibility [3]. However, the bacteria infection could occur after the surgery, which could affect the repairment of bone defect and the success of implant surgery [4].

In order to improve the antibacterial ability of titanium and its alloys, some modified methods including sol-gel method [5,6], electrochemical deposition method [7–10] and micro arc oxidation method [10–16] are used to fabricate the coating containing antibacterial elements such as Ag, Zn and Cu elements.

According to previous studies [4–8,17–21], it was well known that the Ag and Cu elements possess good antibacterial ability. However,

their potential cytotoxicity must be considered. Among the antibacterial elements, the Zinc element has poor cytotoxicity [14] and could improve the antibacterial activity of titanium implants [22,23]. Meanwhile, the previous studies [11,13,14] have reported that the Zn element has relatively weak antibacterial ability, which can be enhanced via increasing the amounts of Zn elements. The concentrations of Zn elements in the coatings are adjusted via increasing the concentrations of electrolyte during the sol-gel and electrochemical deposition process [24]. However, the bonding strength between the antibacterial coating and titanium substrate is poor, which restricts its application.

Owing to the high bonding strength and composition-controlled property, the micro arc oxidation (MAO) is an effective method to adjust the concentrations of Zn element [10,11,13]. Moreover, the

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properties and composition concentrations of the MAO coatings are mainly affected by some parameters including the applied voltage, duty cycle, pulse frequency and oxidize time. In this work, the Zn-incorporated MAO coatings are fabricated on the titanium at the different applied voltage, and the contents of Zn element in the MAO coatings are adjusted by changing the applied voltages. The surface and cross-section structure, apatite-inducing ability and antibacterial ability of the Zn-incorporated MAO coating formed at the different applied voltage are studied.

2. Experimental procedure

2.1. Micro arc oxidation (MAO) treatment

In the MAO process, the pure Ti plates ($10 \times 10 \times 1 \text{ mm}^3$) are used as the anodes, and the stainless steel plates are used as cathodes in an electrolytic bath. The pure Ti plates are ground with abrasive papers of 200#, 400#, 600# and 800#, then ultrasonically washed with acetone and distilled water for three times, respectively, then dried at 40°C . The electrolyte is prepared by the dissolving the EDTA-2Na (15 g), $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (8.8 g), $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (6.3 g), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (7.1 g), NaOH (5 g), H_2O_2 (6 mL) and $\text{Zn}(\text{CH}_3\text{COO})_2$ (8.5 g) in 1 L deionized water. The applied voltage was set as 350, 400, 450 and 500 V for MAO experiment. The pulse frequency, duty cycle and oxidized time are set at 600 Hz, 8% and 7 min, respectively. The labels of MAO coatings formed at the different voltages are shown in Table 1.

2.2. Simulated body fluid (SBF) immersion

To evaluate the apatite-inducing ability, the samples are immersed in the 30 mL simulated body fluid (SBF) [25] for 14 and 21 days, and the SBF are refreshed every other day. The SBF is prepared by the dissolving of NaCl (8.036 g), NaHCO_3 (0.352 g), KCl (0.225 g), $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ (0.23 g), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.311 g), CaCl_2 (0.293 g), Na_2SO_4 (0.072 g) in 1 L deionized water. In the following, the SBF solutions are buffered at pH 7.4 with the Tris-hydroxymethylaminomethane ($(\text{CH}_2\text{OH})_3\text{CNH}_2$) (6.063 g L^{-1}) and 1 mol/L HCl (40 mL) at 37°C .

2.3. Structure characterization

2.3.1. X-ray diffraction (XRD)

The phase compositions of the samples were analyzed by X-ray diffraction (XRD, D/max- γB , Japan) using a $\text{CuK}\alpha$ radiation with a continuous scanning mode at a rate of 4°min^{-1} . And the scanning range is from 10° to 90° . The accelerating voltage and current are set at 40 kV and 50 mV.

2.3.2. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

Scanning electron microscopy (SEM, Helios Nanolab 600i, FEI Co., USA) is used to observe the surface and cross-sectional morphologies of the samples. In addition, the element concentration on the coatings surface are detected by an energy dispersive X-ray spectroscopy (EDS, EDAX, USA) equipped on the SEM system.

Table 1
The labels of MAO coatings formed at different voltages.

Applied voltage (V)	Pulse frequency (Hz)	Duty cycle (%)	Oxidized time (min)	Labels
300	600	8	7	MAO-300
350				MAO-350
400				MAO-400
450				MAO-450
500				MAO-500

2.3.3. Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 5300DV, Perkin-Elmer, USA) was used to measure the Zn^{2+} release amounts of MAO coatings after immersion in phosphate buffered solution (PBS) solution (pH 7.4) for different time. In the ICP-OES measurement, the Zn ion concentrations of 10 mL PBS solution after immersion of every sample with $10 \times 10 \text{ mm}^2$ were measured, and two independent analyses were carried out for each solution.

2.4. Bonding strength test

The bonding strength between coating and titanium substrate was investigated by the direct pull-off method. In the pull-off tests, the samples ($\Phi 30 \times 1 \text{ mm}^3$) were bonded to the untreated steel using epoxy resin. The pull-off test was carrying out on an electronic tensile testing machine (Instron 1195, Instron Co., USA). A load to the coating was continually applied on the steel cylinder at a rate of 0.5 mm min^{-1} until the sample was broken. The maximum instant load was recorded. The bonding strength was determined by Eqn (1).

$$P = F_{\max}/S \quad (1)$$

Where F_{\max} was the maximum load, S is the area of the coating, and P is the bonding strength.

2.5. Zn^{2+} release test

The MAO coatings formed at different applied voltages were immersed into 10 mL PBS solution for 1, 3, 5, 7, 11, 13 and 15 days. In the following, the Zn^{2+} release amounts in the PBS solution were measured by ICP-OES. And each group was measured for three times.

2.6. In vitro antibacterial test

The antibacterial ability of the samples is accessed using *E. coli* (ATCC 25922) and *S. aureus* (ATCC 25923). The *E. coli* are placed in the Luria-Bertani (LB) agar plates, and the *S. aureus* was cultured in tryptic soy agar (TSA) plates, and then cultured in the incubator at 37°C for 24 h. Then the *E. coli* is transferred to the fresh LB plates every 24 h. After cultured in the LB plates for twice times, some active bacterium are transferred into the liquid bacterial medium and cultured in the incubator for 24 h. Then the active bacterial concentrations of *E. coli* are determined by measuring the absorbance at 620 nm (EZ Read 800 Plus Microplate reader, Biochrom). And the bacterial concentrations are adjusted to the final $1.0 \times 10^7 \text{ cfu/ml}$ by adding the phosphate buffer saline (PBS) solutions.

Before the bacteria are seeded on all the samples, the samples are placed inside the 24-cell cultural plate and all samples are sterilized by the autoclave at 121°C for 30 min. Then the $30 \mu\text{L}$ of *E. coli* and *S. aureus* with a concentration of $1.0 \times 10^7 \text{ cfu ml}^{-1}$ are seeded on the samples. Then the samples are placed inside the 24-cell culture plate and cultured in the incubator at 37°C for 24 h. In the following, the samples are washed by the sterilized PBS solution for twice times, and the $100 \mu\text{L}$ PBS solution are withdrawn from the 10 mL washed PBS solution with the pipette. Finally, the $100 \mu\text{L}$ solution containing bacteria are transferred to the LB and TSA plates and placed in the incubator at 37°C for 24 h. The bacterium numbers are measured at optical microscopy, the bacteria number of blank groups are set as A, and the bacteria number of sample groups are set as B. the bacterial rate(R) is calibrated by Eqn. (2) to evaluate the bacterial ability of the samples.

$$R = (A-B)/A \times 100\% \quad (2)$$

The morphology of *E. coli* and *S. aureus* seeded on the MAO coating was observed by the SEM. In the SEM experiment, the *E. coli* and *S. aureus* were seeded on the MAO coating formed at different applied voltage, cultured in the incubation at 37°C for 24 h, then fixed with 3%

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