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The hydrothermal treated Zn-incorporated titania based microarc oxidation coating: Surface characteristics, apatite-inducing ability and antibacterial ability

Qing Du[a,b], Daqing Wei[b,c,*], Shang Liu[a,b], Su Cheng[d], Narisu Hu[e], Yaming Wang[a,b], Baoqiang Li[a,b], Dechang Jia[a,b], Yu Zhou[a,b]

[a] Institute for Advanced Ceramics, Department of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[b] Key Laboratory of Advanced Structural-Functional Integration Materials & Green Manufacturing Technology, Harbin Institute of Technology, Harbin 150001, China
[c] Center of analysis and measurement, Harbin Institute of Technology, Harbin 150001, China
[d] Department of Mechanical Engineering, School of Architecture and Civil Engineering, Harbin University of Science and Technology, Harbin 150001, China
[e] Oral Implant Center, Second Affiliated Hospital of Harbin Medical University, Harbin 150086, China

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ABSTRACT

To improve the bioactivity and antibacterial ability of Zn-incorporated microarc oxidation (MAO-Zn) coating, the MAO-Zn coating was modified by hydrothermal treatment with deionized water (MAO-Zn-HT-0) and 5 mol/L $NH_3{\cdot}H_2O$ solution (MAO-Zn-HT-5). The hydrothermal treatment had a significantly effect on the structure, element and phase compositions of MAO-Zn coating. The hydrothermal treated MAO-Zn coatings remained the rough porous structure. Meanwhile, there were some TiO_2 or $CaTiO_3$ particles formed on the MAO-Zn-HT-0 and MAO-Zn-HT-5 coatings. Moreover, due to the dissolution of Ca and P elements and the enrichment of Zn element, the content of Zn element on the hydrothermal treated MAO-Zn coating surface was greatly increased. In addition, the Zn element existed in the amorphous ZnO after hydrothermal treatment. The release behavior of Zn element in the hydrothermal treated MAO-Zn coating exhibited slow, stable and continued. Compared to MAO-Zn coating, the MAO-Zn-HT-5 coating showed excellent apatite-inducing ability due to the formation of $CaTiO_3$ and Ti-OH. Likewise, the antibacterial rates of the MAO-Zn-HT-0 coatings for *E. coli* and *S. aureus* were significantly improved due to the increase of Zn element on the MAO-Zn-HT-0 coating surfaces. Thus, the hydrothermal treatment was an effective method to improve the bioactivity and antibacterial ability of MAO-Zn coating.

1. Introduction

Titanium (Ti) and titanium alloys are used as a potential and promising hard tissue replacement and repair materials due to the excellent biocompatibility, mechanical properties and corrosion resistance. Especially, the dental implants are under the complex oral environment, and the bacterial infections easily occurred at the interface between the associated bone and implants after implant surgery. Thus, the Ti implants usually failed due to the lack of high bioactivity on the implants and high incidence of associated infections. Thus, an ideal biomaterial is required to possess to both high bioactivity and excellent antibacterial ability. On one hand, in order to obtain the high bioactivity on the pure Ti plate, most researchers have reported a variety of the modified technique, such as plasma immersion ion implants [1,2], chemical treatment [3,4], anodized oxidation [5–8] and microarc oxidation (MAO) [9–20], to modify the surface of the implants. These modified methods are effective to improve the bioactivity of the implants.

On the other hand, in order to improve the antibacterial ability of the bioactive coating, some studies reported that the antibacterial elements including silver (Ag) [21–24], copper (Cu) [25–30], zinc (Zn) [31,32] silicon (Si) [33], strontium (Sr) [7,17,34,35] and fluorine (F) [33] elements could be incorporated into the coating formed on the Ti implant surfaces to improve the antibacterial ability. Among the antibacterial elements, the studies proved that Ag and Cu possess much better antibacterial ability than the Zn, F, Si and Sr elements. However, their potential cytotoxicity must be considered when the antibacterial ability was improved with the increase of Ag or Cu elements contents.

* Corresponding author at: P.O. Box 3022#, Institute for Advanced Ceramics, Science Park, Harbin Institute of Technology, NO. 2, Yi kuang Street, Harbin 150080, China.
E-mail address: daqingwei@hit.edu.cn (D. Wei).

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Although the Zn element possessed a relatively weak antibacterial ability, it has been proved that the Zn elements are recognized as the essential element in human bone [36,37]. In addition, the Zn elements are an essential part for DNA synthesis, enzyme activity, nucleic acid metabolism, biomineralization and hormonal activity [13]. Thus, the Zn elements have been attracted great interest for biological application.

Among the above-mentioned modification technologies, the MAO was a promising method to prepare the antibacterial and bioactive coating at the same time owing to good bonding strength and composition controlled property. B.H. Zhao et al. [9] reported that the antibacterial ability of MAO coating can be adjusted by varying the amounts of Zn elements during the MAO treatment process. The antibacterial ability of the MAO coatings could be increased via increasing the concentration of Zn element in the electrolyte, while the antibacterial ability on the Zn-incorporated MAO coating could be further modified. Thus, other studies reported that two antibacterial elements such as Cu & Zn [38] were together introduced to MAO coating to improve the antibacterial ability, while the bioactivity on the MAO coating surface was not good. The high antibacterial ability and bioactivity cannot be together obtained on the MAO coating surface. Thus, in this work, the hydrothermal treatment was used to improve antibacterial ability and bioactivity on the MAO-Zn coating surface. The surface structure, bioactivity and antibacterial ability of MAO coating, MAO-Zn coating, and the hydrothermal treated MAO-Zn coatings are systematically studied. The relationship between the structure (such as element composition, chemical state and surface morphology) and antibacterial ability on the MAO-Zn coatings before and after hydrothermal treatment for *E. coli* and *S. aureus* are also studied.

2. Experimental procedure

2.1. Micro arc oxidation (MAO) treatment

In the MAO process, the pure Ti plates ($10 \times 10 \times 1\ mm^3$) were used as the anodes, and the stainless steel plates were used as cathodes in an electrolytic bath. The pure Ti plates were ground with abrasive papers of 200#, 400#, 600# and 800#, then ultrasonically washed with acetone and distilled water for three times, respectively. The applied voltage, pulse frequency, duty cycle and oxidized time were set as 350 V, 600 Hz, 8% and 5 min. The chemical ingredients of three electrolytes and sample labels were shown in Table 1.

2.2. Hydrothermal treatment

The MAO and MAO-Zn samples were placed in the Teflon-lined autoclaves with the volume of 100 mL, then the 40 mL deionized water and 5 mol/L $NH_3{\cdot}H_2O$ solutions were added in the autoclave, respectively. In the following, the autoclave was kept at 200 °C for 24 h. Then the hydrothermal treatment parameters including temperature, time and the concentration of solution, as well as the sample labels were shown in Table 2.

2.3. Simulated body fluid (SBF) immersion

The samples were immersed in the 30 mL simulated body fluid (SBF) [39] for 1, 3 and 7 days to evaluate the apatite-inducing ability, and the SBF were refreshed every other day. The SBF was prepared by dissolving of NaCl (8.036 g), $NaHCO_3$ (0.352 g), KCl (0.225 g), $K_2HPO_4{\cdot}3H_2O$ (0.23 g), $MgCl_2{\cdot}6H_2O$ (0.311 g), $CaCl_2$ (0.293 g), Na_2SO_4 (0.072 g) in 1 L deionized water. After that, the SBF solutions were buffered at pH 7.4 with the Tris-hydroxymethylaminomethane ($(CH_2OH)_3CNH_2$) (6.063 $g{\cdot}L^{-1}$) and 1 mol/L HCl (40 mL) at 37 °C.

Table 2
The hydrothermal treatment parameters and sample labels.

Sample labels	Hydrothermal treatment parameters			
	Temperature (°C)	Time (h)	Solution	Concentration (mol/L)
MAO-HT-0	200	24	Deionized water	0
MAO-HT-5	200	24	$NH_3{\cdot}H_2O$	5
MAO-Zn-HT-0	200	24	Deionized water	0
MAO-Zn-HT-5	200	24	$NH_3{\cdot}H_2O$	5

2.4. Structure characterization

2.4.1. X-ray diffraction (XRD)

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

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

Scanning electron microscopy (SEM, Helios Nanolab 600i, FEI Co., USA) was used to observe the surface morphologies of the samples. In addition, the element mapping distribution of MAO-Zn coatings were detected by an energy dispersive X-ray spectroscopy (EDS, EDAX, USA) equipped on the SEM system.

2.4.3. X-ray photoelectron spectroscopy (XPS)

An X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermofisher Scientific Co, USA) was used to detect the chemical compositions of MAO-Zn coating and hydrothermal treated MAO-Zn coatings. An AlKα (1486.6 eV) X-ray source was used for XPS work at 1.0×10^{-8} mbar. The current of X-ray beam was set at 6 mA and their solution for energy was set at 0.5 eV with a scanning step of 0.1 eV. The regions of 400 μm^2 on the sample surfaces were analyzed. The measured binding energies were calibrated by the C1s of 285.0 eV. The chemical states of various elements after Ar^+ etching for 60s were analyzed.

2.4.4. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM, Talos F200x, FEI Co. USA) with an accelerated voltage of 200 kV was used to analyze the microstructures of MAO-Zn-HT-0 coating. The powders collected from on the MAO-Zn-HT-0 coating were used to confirm the phase compositions. In TEM operation, the morphologies of the coating were observed. The

Table 1
The chemical ingredients of three electrolytes and the sample labels.

Sample labels	Concentration (g/L or ml/L)						
	EDTA-2Na	$Ca(CH_3COO)_2{\cdot}H_2O$	$Ca(H_2PO_4){\cdot}H_2O$	$Na_2SiO_3{\cdot}9H_2O$	NaOH	H_2O_2	$Zn(AC)_2$
MAO	15	8.8	6.3	7.1	5	6	–
MAO-Zn	15	8.8	6.3	7.1	5	6	8.8