BIOACTIVE MICROARC OXIDIZED TIO$_2$-BASED COATINGS ON TITANIUM ALLOY FOR BIOMEDICAL IMPLICATION

Yu Zhou, Daqing Wei
Institute for Advanced Ceramics, Harbin Institute of Technology, Harbin 150001, P. R. of China
zhouyu@hit.edu.cn

1. Title
BIOACTIVE MICROARC OXIDIZED TIO$_2$-BASED COATINGS ON TITANIUM ALLOY FOR BIOMEDICAL IMPLICATION

2. Authors
Yu Zhou, Daqing Wei
zhouyu@hit.edu.cn

3. Body of Summary
INTRODUCTION
Using microarc oxidation technique to deposit bioactive ceramic coatings on titanium and its alloys has received much attention in recent years [1-10]. To prepare the bioactive coatings on Ti and its alloys, introductions of Ca and P elements into MAO films were taken into account. It has been reported that the titania-based films containing Ca and P on titanium and titanium alloys were formed by MAO technique in electrolytes containing calcium glycerophosphate (Ca-GP) or $\beta$-glycerophosphate disodium ($\beta$-GP), calcium acetate (CA), Ca-EDTA chelate complex and phosphates [1-3,6,9].

Besides TiO$_2$-based coatings containing crystalline CaP compounds, TiO$_2$-based coatings containing amorphous CaP phases have also been noticed. This MAO coating was prepared in an electrolyte containing Ca(CH$_3$COO)$_2$·H$_2$O, Ca(H$_2$PO$_4$)$_2$·H$_2$O, EDTA-2Na and NaOH [7,10]. And the effects of applied voltage on the structures (e.g., phase composition, surface morphology, micropore number and size, element distribution on the surface and cross-sectional characters, etc.) of the MAO film are investigated [10]. However the effect of the applied voltage on the apatite-forming ability is not clear up to now. Details regarding the in vitro behavior of MAO coatings are very important, which may promote a further development of these biocoatings. Thus, this study reported the effect of applied voltage on apatite-forming ability of the MAO coating containing TiO$_2$ and amorphous phase with Ca and P composition, as well as preliminary biological properties.
MATERIALS AND METHODS

In the MAO process, Ti6Al4V plates (10×10×1.5 mm³) were used as anodes, and stainless steel plates were used as cathodes in an electrolytic bath. The plates were ground with 400#, 800# and 1000# abrasive papers, ultrasonically washed with acetone and deionized water, and dried at 40°C. An electrolyte was prepared by the dissolution of reagent-grade chemicals of Ca(CH₃COO)₂·H₂O (13.2g/L), Ca(H₂PO₄)₂·H₂O (6.3g/L), EDTA-2Na (15g/L) and NaOH (15g/L) into deionized water. The applied voltages of 200, 250, 300, 350, 400 and 450V were used to prepare MAO films. The frequency, duty cycle and oxidizing time were 600 Hz, 8.0 % and 5 min, respectively. The temperature of the electrolyte was kept at 40 °C by a cooling system.

The MAO samples were soaked in 15 mL SBF [11] with ionic concentrations nearly equal to those of human blood plasma immersing for 28 and 56 days, and the SBF was refreshed every other day. The SBF was prepared by dissolving reagent-grade chemicals of NaCl, NaHCO₃, KCl, K₂HPO₄·3H₂O, MgCl₂·6H₂O, CaCl₂, and Na₂SO₄ into deionized water and buffering at pH=7.40 with tris-hydroxymethylaminomethane ((CH₂OH)₃CNH₂) and 1.0-M/l HCl at 37°C.

Surface phase compositions of the samples were analyzed by a glace-angle X-ray diffraction (XRD, Philips X’Pert, Holland) using Cu Ka radiation (40 kV, 35 mA). The angle of the incident beam was fixed at 1° against the sample surfaces and the measurements were performed with a continuous scanning mode at a rate of 2 °/min.

An X-ray photoelectron spectroscopy (XPS, PHI 5700, America physical electronics) was used to determine the chemical composition of the samples. In the XPS experiment. An MgKα (1253.6 eV) X-ray source was used to analyze chemical states of Ca, P and Ti, etc in a high-resolution mode. The XPS take-off angle was set at 45°, detecting the depth range of 5~10 nm. The region of 2 mm×0.8 mm on the surfaces of the samples was analyzed with a hemispherical analyzer.

The surface morphologies of the samples were observed by a scanning electron microscopy (SEM, CamScan MX2600, CamScan Co., England). In addition, the elemental composition of the sample surfaces were detected by an energy dispersive X-ray spectrometer (EDS, Oxford Model 7537, England) equipped on the SEM system.

Fourier transform infrared spectroscopy (FT-IR, Bruker Vector 22, Germany) was used to analyze the phase and structure of the samples after SBF immersion. In FT-IR experiment, the scanning range and resolution were 4000~400 cm⁻¹ and 4 cm⁻¹, respectively.

RESULTS

The XPS surveys of the surfaces of the MAO coatings formed at various applied voltages indicated that the major surface constituents of the MAO coating are Ti, Ca, P, O and C, etc.. (Fig. 1). On all surfaces, no N and V were detected. The values of the binding energies (BE) of Ti2p₃/2 and Ti2p₁/2 are 458.4 eV and 464.3 eV corresponding to a chemical state of Ti⁴⁺, which are typical BE for TiO₂ according to the reported results [7]. The Ca2p spectra of the MAO coatings reveals a doublet with Ca2p₃/2 (BE of 347.3 eV) and Ca2p₁/2 (BE of 351.1 eV), corresponding to the presence of Ca²⁺ [7,9]. The P2p spectra of the MAO coatings reveal a single peak at BE position of 133.2 eV (P2p₃/2), indicating the presence of P⁵⁺ according to published data [7,9]. The XPS results indicated that the applied voltage has no effect on the chemical states of Ti, Ca and P elements.
The MAO coatings after SBF immersion for 28 days were shown in Fig. 2. No obvious modification was found on the surfaces of the MAO coatings formed at 200, 250, 400 and 450 V, except of 300 and 350 V. However, some initial microarc oxidized pores were also observed on the surface formed at 350 V. In the case of 300 V, entire surface was covered by a new layer. EDS results further indicated that the new layer mainly contain Ca, P and O, as well as a few Na elements (not shown here). After SBF immersion for 56 days, all the surfaces were covered by the new layers (not shown here).

According to the XRD patterns of the MAO coatings formed at various applied voltages after SBF immersion for 28 days (not shown here), no diffraction peaks of apatite were found on the surfaces expect of that formed at 300 V. And the diffraction peaks of titanium were detected on the surfaces formed at 200 and 250 V. On the surfaces formed at 350-450 V, only TiO₂ peaks were found, consisting with the SEM results. Though apatite was deposited on the surface formed at 350 V, no apatite peaks were observed. This is due to small content of apatite and its poor crystallinity. According to the XRD and SEM results, it was indicated that the applied
voltage has obvious influence on the apatite-forming ability of the MAO coatings. And the MAO coatings formed at low and high applied voltages are not suitable for apatite formation; while moderate applied voltage is recommended.

According to the FT-IR spectra of the MAO coatings formed at various applied voltages after SBF immersion for 56 days (not shown here), all the curves seem to be analogical regarding to the function groups of PO$_4$, CO$_3$ and HPO$_4$. The spectra shows the presence of bonded water according to a broad absorption band at 3443 cm$^{-1}$ and a bending mode at 1650 cm$^{-1}$. The FT-IR spectra shows absorption bands of PO$_4$ groups including the triply degenerated asymmetric stretching mode of $v_3$PO$_4$ band at 1031 cm$^{-1}$, triply degenerated bending mode of $v_4$PO$_4$ band at 600 and 562 cm$^{-1}$ and double degenerated bending mode of $v_2$PO$_4$ band at 472 cm$^{-1}$. In addition, CO$_3^{2-}$ absorption bands were observed including bending mode of $v_4$CO$_3^{2-}$ group in A-type carbonated HA (CHA) at 1550 cm$^{-1}$, characteristic stretching mode of $v_3$CO$_3^{2-}$ group in CHA at 1506 cm$^{-1}$, characteristic stretching mode of $v_1$CO$_3^{2-}$ group in A-type CHA at 1461 cm$^{-1}$, stretching mode of $v_1$CO$_3^{2-}$ group in B-type CHA at 1427 cm$^{-1}$ and bending mode of ($v_3$ or $v_4$) CO$_3^{2-}$ group in CHA at 873 cm$^{-1}$. The FT-IR results confirm that the apatite formed on the all coatings has a carbonated structure. Also, the characteristic shoulders at 1096, 962 and 871 cm$^{-1}$ suggest the presence of HPO$_4^{2-}$ in the apatite.

**CONCLUSIONS**

In this work, MAO coatings were prepared in an electrolyte containing Ca and P at different voltages. The applied voltage has no effect on the chemical states of Ca, P and Ti elements. In the case of the MAO coatings formed at low applied voltage, the contents of the Ca and P released from these coatings were little and then the SBF supersaturation decreased relatively, which could further lower the apatite-forming ability of these coatings. High applied voltages would lead to the formation of rutile in the MAO coatings, which does not facilitate the apatite formation. the MAO coating formed at moderate applied voltage shows good apatite-forming ability. The apatite formed on the all coatings has a carbonated structure.

**REFERENCES**