Original Article

Effect of electrolyte composition on the microstructure and bio-corrosion behavior of micro-arc oxidized coatings on biomedical Ti6Al4V alloy

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ABSTRACT

In view of the low bioactivity and the inability to form bone fusion with surrounding bones in vivo, bioactive ceramic coatings were prepared on the bio-inert Ti6Al4V (TC4) alloys by micro-arc oxidation (MAO) technology in two different electrolytes. The effects of electrolyte composition and applied positive voltage on the microstructure and corrosion resistance of the MAO coating were studied. The surface morphology, composition, and microstructure of the MAO coatings were systematically characterized. The corrosion behaviors of the MAO coatings were studied by electrochemical corrosion test and simulated body fluid (SBF) immersion test in vitro. After soaking in SBF solution, CaP apatites formed on the surface of the MAO coatings. Results showed that the MAO coatings obtained from the silicate electrolyte grew rapidly and corroded faster in SBF solution, while MAO coatings obtained from the calcium phosphate electrolyte had excellent surface and corrosion resistance properties. The formation and corrosion mechanisms of the MAO coatings obtained from the two different electrolytes were discussed.

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1. Introduction

Titanium (Ti) alloys have been considered as one of the most widely used hard-tissue implant materials due to their high strength, low density and elastic modulus, high immunity to corrosion and good biocompatibility [1–3]. However, titanium alloys cannot form osseointegration with the surrounding bones in vivo because of their bio-inert nature, and therefore the resultant implant loosening and failure remains one of the major challenges in the field of orthopaedics and dentistry [2,4]. The ideal implant for bone tissue reconstruction should resemble natural bone in structural, mechanical and biological properties. As an ideal titanium-based bone tissue implant, not only the materials chemistry but also the surface porous structure is considered as a crucial role for bone regeneration [5]. Surface modification is necessary for
the improvement of the structural and biological properties of the titanium alloys. Among a variety of surface modification methods of titanium alloys substrates for biomedical applications, micro-arc oxidation (MAO) has become a potential method to prepare biocompatible and bioactive coating [6–8]. The interface bonding strength between the coating and substrate prepared by the MAO technology is high. The formation and properties of MAO coatings can be widely controlled by adjusting process parameters such as applied voltage, frequency, processing time and electrolyte composition. In recent years, researchers are taking an extraordinary effort to focus on developing composites by mimicking the unique structure and composition of the bone tissue using MAO technology. In order to further improve the bioactivity of titanium alloys, selecting environmentally friendly electrolytes is very important. Yerokhin et al. [9] employed calcium acetate and sodium phosphate (with Ca:P ratio of 2) as electrolytes for the formation of the MAO coating on Ti, results showed that the precipitation of calcium phosphate containing compounds occurred via chemical mechanisms, and plasma discharge was responsible for the partial crystallisation and decomposition of the deposited compounds. Wang et al. [10] fabricated MAO coatings containing different zinc and phosphorus using an orthogonal experiment of four factors with three levels in an electrolyte containing EDTA-ZnNa2, KOH and phytic acid, to clarify the mechanism that zinc and phosphorus elements entering the MAO coatings developed on Ti6Al4V alloys. Their results indicated that phosphorus took part in coating formation mainly by diffusion, while zinc entered into MAO coatings with phosphorus from phytic acid. Karbownikczek et al. [11] used three different electrolytes to obtain hydroxyapatite containing oxide coating on Ti6Al7Nb alloys. Their results showed that the electrolyte composition significantly influenced thickness, roughness and chemical composition of the MAO coatings. The addition of calcium acetate hydrate (C15H14O12Ca2H2O) and disodium hydrogen phosphate (Na2HPO4) favor the formation of the crystalline hydroxyapatite. Zhang et al. [12] investigated the influences of processing factors including EDTA-Na2 concentration, Ca(CH2COO)2 concentration, current density and treating time on the amounts of calcium and phosphorus elements in MAO coatings on Ti6Al4V alloy in a solution containing 15 g/L phytic acid and 10 g/L KOH, results indicated that Ca and P elements of MAO coatings existed mainly as CaTiO3, PO43− and HPO42−. The entrance mechanism of calcium element includes diffusion and electromigration, while the phosphorus amount of the MAO coatings strongly depends on Ca(CH2COO)2 concentration. Zhang et al. selected sodium phytate [13] and phytic acid [14] as the main electrolyte of micro-arc oxidation (MAO) on Ti6Al4V alloys, respectively. They found that the organic phosphate, sodium phytate and phytic acid took part in the coating formation and phytates were developed in anodic coatings. In addition, MTT tests indicated that both Ti6Al4V and the MAO treated Ti6Al4V achieved good biocompatibility. The MAO treated Ti6Al4V alloys in phytic acid solution can be used as implants for orthopaedic applications. Li et al. [15] prepared a novel “cortex-like” micro/nano dual-scale structured TiO2 coating on a titanium surface by micro-arc oxidation with tetraborate electrolytes. Results indicated that the combination of the dual-scale structure and the hydrophilicity of the “cortex-like” TiO2 coating synergistically resulted in an outstanding cytocompatibility and osseointegration.

Previous studies have revealed that titanium implants with calcium and phosphorus-containing MAO coatings can improve cell adhesion and proliferation [14,16,17]. Multiple inorganic phosphorus-containing electrolytes such as H3PO4 [16,18,19], Na2HPO4 [11], KH2PO4 [20], NaH2PO4 [21], Na2PO4 [9,22], (NaPO3)2 [23] and calcium phosphate [24], have been used in micro-arc oxidation for the surface modification of titanium alloys. However, the effect of electrolyte composition on the correlations between the growth, corrosion mechanisms and properties of MAO coatings on Ti6Al4V alloy are seldom clarified. In the present work, sodium silicate (Na2SiO3·9H2O) and calcium glycerophosphate (CaH2CaO3P) were used respectively as the main content of the MAO electrolytes to modify Ti6Al4V alloys. The effects of silicate and calcium phosphate on the microstructure and corrosion behavior of micro-arc oxidized coatings on biomedical Ti6Al4V alloys were investigated.

2. Experimental methods

2.1. MAO treatment

Ti6Al4V alloys were machined into samples with cuboidal shape of 10 × 10 × 8 mm3. All samples were progressively ground with SiC paper from 80 to 1000 grit, washed with distilled water and dried with a blow drier. Two electrolytes were prepared from a solution containing (NaPO3)2 (2.5 g·L−1), NaF (2.0 g·L−1), KOH (2.0 g·L−1) and C2H6O3 (5 mL·L−1) in deionized water. Sodium silicate (Na2SiO3·9H2O, (7.5 g·L−1)) and calcium glycerophosphate (CaH2CaO3P, (2.1 g·L−1)) were added to the above two electrolytes respectively. All drugs used were of analytical grade. Corresponding to the Na2SiO3·9H2O and C2H6O3CaO3P containing electrolyte solutions, the samples were referred to as A and B, respectively. The applied positive voltages for these three samples treated in electrolyte A and B were 400, 425 and 450V, and the samples were referred to as A1/B1, A2/B2 and A3/B3 respectively in the following sections. The pulse frequency, positive duty ratio, negative duty ratio, ratio of positive and negative pulses and oxidizing time were set to be 600 Hz, 35%, 20%, 1:1 and 10 min, respectively. The MAO device consists of a pulse power supply unit, a stirring and a cooling circulating system and a stainless steel container which served as cathode. The samples were served as anode. The electrolyte temperature was kept at about 30 °C. The MAO-coated samples were flushed with distilled water after the treatment, and dried with a blower.

2.2. Microstructural characterization

Before and after immersion in the simulated body fluid (SBF), the phase compositions of the samples were analyzed by X-ray diffraction (XRD, Shimadzu XRD-6100, Japan) using a Cu-Kα radiation with a continuous scanning mode at a rate of 4°·min−1. The accelerating voltage and current were set at 40 kV and 40 mA. Field emission scanning electron micro-
scope (SEM, FEI Sirion200, FEI Co., USA) was used to observe the surface and cross-sectional morphologies. In addition, the elemental concentrations of the samples were detected by an energy dispersive X-ray spectrometer (EDS, EDAX, USA) equipped on the SEM system.

2.3. Simulated body fluid immersion

The Ti6Al4V alloy and MAO coating covered Ti6Al4V samples were soaked in simulated body fluid (SBF) for 2, 4 and 6 days to evaluate their degradability, and soaked in SBF for 50 days to evaluate their apatite-inducing ability. The SBF solution has similar composition and concentration to those of the inorganic part of human plasma [25,26]. 1 L SBF solution was prepared by dissolving the reagents in the following contents and order: 7.996 g NaCl, 0.350 g NaHCO3, 0.224 g KCl, 0.228 g K2HPO4, 3H2O, 0.305 g MgCl2·6H2O, 40 mL HCl (1 mol/L), 0.278 g CaCl2 and 0.071 g Na2SO3. At last, it was buffered at pH 7.30 with triis-hydroxymethylaminomethane ((CH2OH)3CNH2) and 1.0 mol·L−1 HCl at 36.5 °C. Triplicate samples were used during the soaking test. And the ratio of surface plane area to solution volume was 0.08 cm²/mL. The SBF was refreshed every other day. At the end of each period of soaking time, samples were collected from solution, washed in distilled water, cleaned in 200 g/L CrO3+10 g/L AgNO3 solution, dried to constant weight and measured on an electronic balance.

2.4. Electrochemical corrosion tests

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) experiments were performed on electrochemical workstation (CHI 660E, Shanghai Chenhua Co., China). All measurements were carried out in a 300 ml beaker using typical three-electrode cell at 36.5 ± 0.5 °C. Saturated calomel electrode (SCE) was used as reference electrode, a platinum wire was used as counter electrode and the sample (1.0 cm² exposed surface area) was used as working electrode. SBF solution was used as the corrosion media. Potentiodynamic polarization experiments were carried out in SBF solution at a scan rate of 1 mV/s.

2.5. X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS, PHI-5300versaprobe) was used to characterize calcium and phosphorus elements in corrosion products of MAO coatings obtained from the silicate electrolytes. The XPS measurements were performed using an Al Kα (1486.6 eV) as the excitation source for photoelectron emission with the resolution of 0.80 eV. The power was 250 W. The sensitivity was 80000 CPS. The vacuum of the analyzer was 2.9 × 10⁻⁷ Pa. The Xpspeak 4.1 software was used for data acquisition and data analysis. The measured binding energies were corrected by referring the binding energy of C1s of methylene groups of the hydrocarbon (284.8 eV) absorbed on the surface of substrate.

Fig. 1 – Macroscopic morphology of the MAO coated samples obtained in different electrolyte systems: (a): sample A1, (a1): sample A2, (a2): sample A3, and (b): sample B1, (b1): sample B2, (b2): sample B3.

3. Results

3.1. Microstructure

Fig. 1 shows the macroscopic morphology of the MAO coated samples obtained in different electrolyte systems. As seen in Fig. 1, the surface morphology of the sample A3 is roughest. Compared with the (b), the macromorphology of the coatings obtained from the silicate electrolyte system changed obviously with the increase of the voltage, and the surface of the coatings became rougher. Fig. 2 shows the SEM microstructure of the MAO coated samples obtained from different positive voltage and different electrolytes systems. From Fig. 2, it can be seen that the surface of the MAO coatings is porous. Meanwhile there are also some micro-cracks. It’s difficult to form homogeneous and porous morphology on the surface of the samples obtained from the silicate electrolyte system. With the increase of the applied positive voltage, the morphology erosion phenomenon occurred, resulting in the disappearance of the porous microstructure. On the contrary, the surface of the coating obtained from the calcium phosphate electrolyte system is smooth, and with micropores relatively well separated and homogeneously distributed. Compared with the samples A1, A2 and A3, the MAO coatings obtained from the different positive voltages in silicate electrolyte system have different micropores shapes and sizes. The amount of micropores reduces with the increase of the voltage. Compared with the samples B1, B2 and B3, the MAO coatings obtained from calcium phosphate electrolyte system show a volcano-like surface morphology with homogeneously distributed micropores in spite of different positive voltages. As can be seen from Fig. 2, with the increase of positive voltage in the silicate electrolyte system, the pore size and depth of the micropores become larger and deeper, micro-cracks and erosion
Fig. 2 – SEM microstructure images of the MAO coated samples: (a1): sample A1, (a2): sample A2, (a3): sample A3, and (b1): sample B1, (b2): sample B2, (b3): sample B3.

Fig. 3 – Surface elemental composition of the MAO coated samples: (a) sample A2, and (b) sample B2.
morphologies appeared. However, the change of the surface microstructure is not noticeable with the increase of positive voltage in the calcium phosphate electrolyte system. The surface elemental compositions of the MAO coatings before the SBF soaking are shown in Fig. 3. It is observed that the elements of MAO coatings in different electrolyte systems are mainly Ti, Al and O. In the silicate electrolyte, Si and P entered the MAO coating through the MAO reaction, while in the calcium phosphate electrolyte, Ca and P entered the MAO coating through MAO reaction.

The cross-section image and linear composition of the MAO coatings in Fig. 4 show that there is no apparent discontinuity to the substrate in the bond zone. While the outer layer of the coating allows some micropores to exit, the inner layer does not due to its compactness. Fig. 4 shows that the elemental compositions of the MAO coatings obtained from the silicate electrolyte system mainly include Ti, Si and O elements. The MAO coatings obtained from the calcium phosphate electrolyte system mainly contain Ti, P, Ca and O elements.

After soaking in SBF for 6 days, the surface morphologies of the MAO coatings are shown in Fig. 5. It can be seen that there is no obvious corrosion on the MAO coatings after soaking in SBF for 6 days. In order to better explore the corrosion morphology of the MAO coatings after SBF immersion, the immersion time was extended to 50 days. The surface morphologies of the MAO coatings after 50 days of SBF immersion are shown in Fig. 6. As is shown in Fig. 6, the corroded surface morphologies are rough and microcracks can be observed. Compared with the Fig. 2, it can be seen that some corrosion products were presented on the surface of the MAO coatings after SBF soaking. Fig. 7 shows the SEM image of corrosion products of the MAO coated samples after 50 days SBF soaking. From Fig. 7, it can be seen that the morphologies of the corrosion products are spherical, granular and flocculent. The surface elemental compositions of the MAO coatings after 50 days SBF immersion are shown in Fig. 8. It shows that the Ca element presents on the surface of the samples obtained from the silicate electrolyte system. Fig. 9 shows the SEM image and the chemical composition of corrosion products of the MAO coatings after 50 days of SBF soaking. From Fig. 9, it can be seen that the corrosion products of the MAO coatings are mainly composed of the elements Ca, P and O. It can be inferred that the depositions are actually Ca- and P-containing apatites. It can be seen that apatites are the corrosion deposits with spherical (Point 1) and flocculent (Point 2) shapes in Fig. 9. For further determination of the apatites composition, the results of the X-ray photoelectron spectroscopy of the corrosion products are shown in Fig. 10. High resolution photoelectron spectroscopy information of Ca 2p and P 2p is given in the spectrum. It can be seen from the spectra that Ca 2p and P 2p peaks are wide, indicating that the corrosion products may contain a variety of phases containing calcium and phosphorus elements. Fig. 10(a) shows that the high-resolution spectrum of P 2p was divided into two peaks (133.4 eV and 134.5 eV). Fig. 10(b) shows that the high resolution spectrum of Ca 2p was divided into two peaks (Ca 2p3/2 and Ca 2p1/2) as a result of the spin orbit splitting. Ca 2p3/2 is the energy peak while Ca 2p1/2 is the satellite peak.

3.2. Phase composition

The X-ray diffraction patterns of the MAO coating obtained from the different electrolyte systems are shown in Fig. 11. From Fig. 11(a), it can be seen that the coatings obtained from the silicate electrolyte are mainly composed of TiO2, SiO2, Ti3(PO4)4, TiP2O7. Also, the characteristic peaks corresponding to the anatase and rutile TiO2 appears in the X-ray diffraction pattern. From Fig. 11(b), it can be seen that the coatings obtained from the calcium phosphate electrolyte are mainly composed of TiO2, CaO, CaTiO3, Ti3(PO4)4, TiP2O7 and...
**Fig. 6** – Surface corrosion morphologies of the MAO coated samples after soaking in SBF solution for 50 days: (a₁): sample A₁, (a₂): sample A₂, (a₃): sample A₃, and (b₁): sample B₁, (b₂): sample B₂, (b₃): sample B₃.

**Fig. 7** – SEM image of corrosion products of the MAO coated samples: (a₁): sample A₁, (a₂): sample A₂, (a₃): sample A₃, and (b₁): sample B₁, (b₂): sample B₂, (b₃): sample B₃.

Ca₂P₂O₇ (calcium pyrophosphate, CPP). Similarly, the characteristic peaks of anatase and rutile TiO₂ also appear in the X-ray diffraction patterns. By comparing the X-ray diffraction patterns, it can be found that the applied positive voltages do not change the position and strength of the phase peak of the MAO coatings obtained from the same electrolyte. More derivative phases can be detected for the coating obtained from the calcium phosphate electrolyte. Fig. 12 shows the XRD results of the corrosion products of the samples A₁ and B₁ after 50 days immersion in SBF solution. It is found that the calcium phosphate, such as HA (hydroxyapatite), Ca₃(PO₄)₂ (tricalcium phosphate, TCP), and Ca₂P₂O₇ (calcium pyrophosphate, CPP), are detected after SBF immersion.

3.3. **Electrochemical corrosion behaviors**

The corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), the anode Tafel slope ($b_a$), cathode Tafel slope ($b_c$) and polarization impedance value ($R_p$) obtained from these curves are summarized in Table 1. The polarization impedance value ($R_p$) is calculated by Stern-Geary formula [27]. By comparing the parameter values in Table 1, it can be found that the $E_{corr}$ values of the samples obtained from the calcium phosphate electrolyte are higher than that from the silicate electrolyte. Meanwhile, the $I_{corr}$ values of the samples obtained from calcium phosphate electrolyte is about one order of magnitude lower than that from the silicate electrolyte. The $E_{corr}$ values of
potentiodynamic polarization curves of MAO coatings under the different electrolyte show that the MAO coatings obtained from the different electrolyte systems have a certain degree of similarity. The MAO coatings $E_{\text{corr}}$ values shift in the positive direction slightly. It can be seen from the Table 1 that the $R_p$ value of MAO coatings obtained from the calcium phosphate electrolyte is higher than that obtained from the silicate electrolyte. Meanwhile, the samples $A_2$, $B_2$ has the maximum $R_p$ value, respectively.

3.4. In vitro degradation in SBF

Fig. 14 shows the weight loss percentage of the samples obtained from the different electrolytes as a function of SBF soaking time. It can be observed that the weight losses of all samples increase with the prolonged SBF soaking, however, the weight loss percentage is very low. The maximum weight loss percentage (0.3039%) is found for the sample $A_2$ after 6 days of SBF soaking. At the same soaking time, the weight loss of the samples obtained from the silicate electrolyte is slightly higher than that from calcium phosphate salt electrolyte. From Fig. 14(b), it can be found that, after 50 days of SBF soaking, the weight loss percentage of sample $A_1$ is about 1.4603%, which is slightly higher than that of sample $B_1$ (1.1739%). By combining the SEM images of Figs. 6 and 7, it also can be seen that the MAO coatings obtained from the silicate electrolyte system show more serious corrosion than that from the calcium phosphate electrolyte system. The weight loss percentage results are consistent with the electrochemical corrosion test results.

4. Discussion

The macroscopic morphology of the MAO coatings obtained from the different electrolyte systems results in Fig. 1 indicate that with the increase of positive voltage, the MAO coatings obtained from the calcium phosphate electrolyte have good
surface stability, and the macro-morphology of the coatings is smoother than that obtained from the silicate electrolyte. The results show that the surface roughness of the samples is significantly influenced by the positive voltage. This is mainly due to the different intensity of micro-arc oxidation reaction caused by the different positive voltages. The positive voltage influences the composition and structure of the coating, and thus the coatings show different color and roughness [28].

The porous and volcano-like structures of the MAO coatings in Fig. 2 are owing to the spark discharge. The micropores are the discharge channels. Sparks preferentially occurred in the weakest areas of the discharge interface, where produced oxygen and other gases. The gas bubbled out from the discharge channel and subsequently molten electrolyte-borne compounds solidified quickly around it [29]. The formation of microcracks is due to the rapid condensation of molten compounds when they were exposed to the cold electrolyte. The diameters of the micropores are small. The surfaces are relatively flat when the positive voltage is low. The diameter of the micropores increases with the increase of the voltage. The surface micropores of the MAO coatings obtained from the silicate electrolyte increases significantly with the increase of positive voltage. When the positive voltage is 450 V, the volcanic rock-like erosion appeared. However, the surface
micropores of MAO coatings obtained from the calcium phosphate electrolyte do not change significantly with the increase of positive voltage. This may be due to the fact that the growth rate and released energy of the MAO coatings obtained from the silicate electrolyte is higher than that from the calcium phosphate electrolyte, which makes it difficult for the MAO coatings obtained from the silicate electrolyte to form regular porous morphology when the applied voltage is high, and thus leads to the erosion.

The time-dependent curves of the positive voltage and current of the MAO processes carried in different electrolytes are shown in Fig. 15. It is obvious that the current for the MAO processes in different electrolytes increased sharply in the early stages, and then slowed down with the processing time. The turning points for the variation of current correspond to the breakdown voltages of the coatings [30]. By comparing Fig. 15(a) and 15(b), it can be seen that the instantaneous current changes of MAO processing in two different electrolytes are quite different. In the silicate electrolyte, when the processing time was 35 seconds, the current rose to the maximum value (10.5 A), and then began to decrease. This is due to the breakdown of the thin oxide film performed on the surface of the sample, and then resulted in better surface conductivity and higher current. However, the current decreased when the MAO coating formed on the sample surface. With the increasing time, the current reached to a stable value (about 3 A). In the calcium phosphate electrolyte, when the processing time was 35 seconds, the current rose to the maximum value (9 A), and then began to decrease. The conductivity decreases with the increase of the coating thickness and compactness, and therefore the sample electric resistance increases. It indicates that the thickness and compactness of the MAO coating obtained from the calcium phosphate electrolyte are greater than that from the silicate electrolyte when the working voltage is the same. The reason for this phenomenon is that the higher conductivity of the silicate electrolyte, the larger current generated from the same positive voltage, the greater energy released. The preformed coatings are broken down repeatedly before they can keep stable. Finally, the regular morphology of micropores disappeared and erosion occurred. However, the coating formed in this case is relatively thick because of the high energy released through the MAO reaction. The results of coating thickness are consistent with that described in Fig. 4.

The XRD results in Fig. 11(a) indicates that the MAO coating obtained from the silicate electrolyte consists of TiO$_2$, SiO$_2$, Ti$_3$(PO$_4$)$_4$ and TiP$_2$O$_7$ phases. Because of the porous structure and thin thickness of the MAO coatings, X-ray can penetrate the coating to the substrate, so the intensity of the diffraction peak corresponding to Ti phase in the XRD patterns is still very strong. Combined with the ions in the silicate electrolyte, the compounds shown in the XRD pattern may be obtained by the following reactions in the MAO process [31,32]:

$$
\text{Ti}^{4+} + 4\text{e}^- \rightarrow \text{Ti}^{4+}
$$

$$
2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-
$$
Table 1 – Electrochemical parameters of the MAO coatings obtained from the silicate electrolyte and calcium phosphate electrolyte extracted from polarization test in SBF.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$b_1$ (V)</th>
<th>$b_2$ (V)</th>
<th>$E_{corr}$ (V)</th>
<th>$I_{corr}$ (A/cm$^2$)</th>
<th>$R_p$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>3.3977</td>
<td>2.3607</td>
<td>−0.737</td>
<td>1.638 × 10$^{-5}$</td>
<td>3.6973 × 10$^4$</td>
</tr>
<tr>
<td>B₁</td>
<td>2.4626</td>
<td>4.7574</td>
<td>−0.652</td>
<td>8.211 × 10$^{-6}$</td>
<td>8.5921 × 10$^4$</td>
</tr>
<tr>
<td>A₂</td>
<td>3.5983</td>
<td>2.2659</td>
<td>−0.720</td>
<td>1.129 × 10$^{-5}$</td>
<td>5.3543 × 10$^4$</td>
</tr>
<tr>
<td>B₂</td>
<td>2.9633</td>
<td>3.2065</td>
<td>−0.668</td>
<td>6.184 × 10$^{-6}$</td>
<td>1.0828 × 10$^4$</td>
</tr>
<tr>
<td>A₃</td>
<td>3.6654</td>
<td>2.8425</td>
<td>−0.721</td>
<td>2.623 × 10$^{-5}$</td>
<td>2.6537 × 10$^4$</td>
</tr>
<tr>
<td>B₃</td>
<td>4.4559</td>
<td>3.6176</td>
<td>−0.657</td>
<td>1.889 × 10$^{-5}$</td>
<td>4.5956 × 10$^4$</td>
</tr>
</tbody>
</table>

Fig. 13 – Potentiodynamic polarization curves of different electrolyte: a₁: sample A₁; a₂: sample A₂; a₃: sample A₃; b₁: sample B₁; b₂: sample B₂; b₃: sample B₃, and the positive voltage: (a) 400 V; (b) 425 V; (c) 450 V.

Fig. 14 – Weight loss percentage variation of the MAO coated samples after soaking in SBF solution. Error bars in Fig. 14(a and b) represent standard error of mean, N = 3.

$\text{Ti}^{4+} + 4\text{OH}^- \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O}$

$2\text{SiO}_3^{2-} - 4e^- \rightarrow 2\text{SiO}_2 + O_2\uparrow$

$\text{HPO}_4^{2-} + \text{OH}^- \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$

$\text{PO}_4^{3-} + 3\text{H}^+ \rightarrow \text{H}_3\text{PO}_4$

$2\text{H}_2\text{PO}_4 \rightarrow \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O} (490 \sim 520 \text{ K})$

$\text{P}_2\text{O}_7^{4-} + \text{Ti}^{4+} \rightarrow \text{TiP}_2\text{O}_7$

$3\text{Ti}^{4+} + 4\text{PO}_4^{3-} \rightarrow \text{Ti}_3(\text{PO}_4)_4$

$\text{O}_2 + 4e^- \rightarrow 2\text{O}^{2-}$

The XRD results in Fig. 11(b) indicates that the MAO coating obtained from the calcium phosphate electrolyte consists of $\text{TiO}_2$, $\text{CaO}$, $\text{CaTiO}_3$, $\text{Ti}_2(\text{PO}_4)_4$, $\text{TiP}_2\text{O}_7$ and $\text{Ca}_2\text{P}_2\text{O}_7$ phases. These phases may be obtained by the following reactions [32]:

$3\text{Ti}^{4+} + 4\text{PO}_4^{3-} \rightarrow \text{Ti}_3(\text{PO}_4)_4$

$\text{Ti} - 4e^- \rightarrow \text{Ti}^{4+}$

$\text{TiP}_2\text{O}_7$
Ca^{2+} + O^{2-} \rightarrow \text{CaO}

\text{Tl}^{4+} + 4\text{OH}^- \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O}

\text{HPO}_4^{2-} + \text{OH}^- \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}

\text{PO}_4^{3-} + 3\text{H}^+ \rightarrow \text{H}_3\text{PO}_4

2\text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}(490\sim 520 \text{K})

\text{P}_2\text{O}_5^{4-} + \text{Tl}^{4+} \rightarrow \text{TiP}_2\text{O}_7

3\text{Tl}^{4+} + 4\text{PO}_4^{3-} \rightarrow \text{Ti}_3(\text{PO}_4)_4

\text{Ca}^{2+} + \text{O}^{2-} + \text{TiO}_2 \rightarrow \text{CaTiO}_3

\text{P}_2\text{O}_5^{4-} + 2\text{Ca}^{2+} \rightarrow \text{Ca}_2\text{P}_2\text{O}_7

According to the possible reaction in the above MAO process, it can be inferred that there are two possible growth modes of the MAO coating. One is growing outward by the migration of the ions from the substrate/coating interface to the electrolyte, and the other is growing inward by the migration of the ions from the electrolyte to the substrate/coating interface. The MAO coatings have higher growth rate in silicate electrolyte than that in calcium phosphate electrolyte due to the faster migration rate of ions in silicate electrolyte.

As to the electrochemical corrosion, the higher corrosion potential means smaller corrosion tendencies. However, corrosion potential cannot reflect the speed of corrosion. The corrosion current density is an important index reflecting the corrosion rate. In a typical polarization curve, lower corrosion current density and high polarization impedance value represents lower corrosion rate. As is shown in Fig. 13 and Table 1, the corrosion potential of the samples obtained from the calcium phosphate electrolyte is higher than that from the silicate electrolyte in spite of variation of the positive voltage. The \( I_{\text{corr}} \) value of the MAO coatings obtained from the calcium phosphate electrolyte is one order of magnitude lower than that from the silicate electrolyte. The \( R_p \) value of MAO coatings obtained from the calcium phosphate electrolyte is higher than that obtained from the silicate electrolyte. By combining the aforementioned results, it can be deduced that the MAO coatings obtained from the calcium phosphate electrolyte have lower corrosion rate and better corrosion resistance. The electrochemical corrosion results are consistent with the regularities of the sample weight loss percentage shown in Fig. 14. The degradation data indicate that the prepared MAO coatings are biodegradable. Meanwhile, the degradation rate is related to the coating composition and microstructure.

As can be seen from the Fig. 4, there is no Ca element signal in MAO coatings obtained from the silicate electrolyte. But Ca element signal appears in the Fig. 8. It can be inferred that Ca element entered the MAO coating and existed in the form of Ca-containing compounds after SBF immersion. According to the information in Figs. 6 and 7, it can be indicated that the ions in SBF solution deposited on the surface of the MAO coating form compounds with spherical and flocculent derived structures. Based on the analysis of the XPS results, the high resolution spectrum of P 2p was divided into two peaks, 133.4 eV and 134.8 eV, which corresponded to \( \text{PO}_4^{3-} \) and \( \text{HPO}_4^{2-} \), respectively. This result proved that the corrosion products consist of the compounds of \( \text{Na}_3\text{PO}_4, \text{Ca}_3(\text{PO}_4)_2 \) and CaHPO_4, etc. [33,34]. Meanwhile, the high resolution spectrum of Ca 2p was divided into four peaks, 347.5 eV (Ca 2p3/2), 347.9 eV (Ca 2p3/2), 350.9 eV (Ca 2p1/2) and 351.5 eV (Ca 2p1/2). All these peaks correspond to the dioxide state of Ca in inorganic calcium compounds. The peak at 347.5 eV indicates the possibility of one or more calcium-containing compounds, such as \( \text{Ca}_3(\text{PO}_4)_2, \text{CaO, CaHPO}_4 \), HA [32]. The binding energy peaks at 347.9 eV and 351.5 eV correspond to the energy peaks of Ca in CaF_2 [35], and the binding energy peaks at 350.9 eV correspond to the energy peaks of Ca in CaCO_3 [30]. The results show that the particles on the surface of MAO coatings soaked in SBF are calcium and phosphorus phases. Combining the XRD results in Fig. 12, it can be concluded that the depositions are actually Ca- and P-containing apatites, such as HA, TCP.
Fig. 16 – Schematic diagrams of the corrosion mechanism of MAO coatings in SBF solution: (a) the silicate electrolyte; and (b) the calcium phosphate electrolyte. The MAO coatings obtained in different electrolytes show different surface morphologies. (i) The MAO coatings obtained in silicate electrolyte show larger porosity and pore size; (ii) The MAO coatings obtained in calcium phosphate electrolyte show homogeneous micropore distribution, smaller porosity and pore size. The coatings (b) have excellent surface microstructure and corrosion resistance.

CPP, etc. The apatites formation is well interpreted in terms of the electrostatic interaction of the functional groups with the ions in SBF solution. The ions produced by hydrolysis of TCP, CPP and the other phases in MAO coatings can interact with the HPO₄²⁻ and Ca²⁺ ions in SBF solution to form HA. The phases of HA, TCP and CPP have already been proved to be biocompatible and bioactive materials which have achieved wide-spread use for clinical application [35,36]. The anatase
and rutile phases can decrease the contact angle for apatite nucleation, and thus favor apatite formation on their specific planes [37]. Once the apatite nuclei are formed, they can grow spontaneously by consuming the Ca and P ions in SBF solution, because the SBF solution is highly supersaturated with respect to apatites [38]. The corrosion rates of MAO coatings obtained from the silicate electrolyte are faster than that from the calcium phosphate electrolyte. So the apatites-induced ability of the coatings obtained from the silicate electrolyte is stronger than that from the calcium phosphate electrolyte during the initial 6 days soaking in SBF solution. The results indicate that the apatites formation and coating corrosion are inseparable. The growth rate of apatites is related to the corrosion rate of the MAO coatings. This is also consistent with the weight loss results of the SBF immersion and electrochemical corrosion test.

The schematic diagrams of the corrosion mechanism of the MAO coatings in SBF solution are shown in Fig. 16. The corrosion process of the MAO coatings immersed in SBF includes ions penetration in SBF solution, dissolution of the MAO coatings and Ti6Al4V alloys matrix and the formation of corrosion products and CaP apatites. As shown in Fig. 16, at the beginning of the SBF soaking, the micropores of the MAO coatings were filled with the SBF solution. The Cl− and H+ ions in the solution contacted and reacted with the phases in the MAO coatings. Following, the ions, such as Ti4+, SiO32−, Ca2+, OH− and PO43−, were released into the interface region between the dissolving coatings and the SBF solution. With the consumption of H+, the pH value increased. As is shown in Fig. 16(a), the Ca2+, OH− and HPO42− ions in the SBF solution and the Ti4+, SiO32− and PO43− ions originated from the MAO coatings phase formed in the silicate electrolyte dissolution were concentrated in the dissolving coating/solution interface. In fact, apatites formation is essentially a process of heterogeneous nucleation, the micropores and rough corrosion morphology of the MAO coatings provide favorable nucleation sites for the HA and other CaP apatites. Once apatite nuclei are formed, they grow spontaneously by consuming the Ca2+, HPO42− and OH− ions in SBF solution, because the SBF solution is highly supersaturated with respect to apatites. The schematic diagram of the corrosion mechanism of MAO coatings obtained from the calcium phosphate electrolyte is the same as that of the above process. However, the surface micropores size of the MAO coatings is small. The distribution of micropores is homogeneous and the porous surface morphology has not been destroyed. The contents of Ca and the Ca/P ratio in MAO coatings obtained from the calcium phosphate electrolyte are higher than that from the silicate electrolyte after SBF soaking test.

5. Conclusion

Bioactive ceramic coatings have been successfully fabricated on the Ti6Al4V substrate by the micro-arc oxidation. The MAO coatings obtained from the calcium phosphate electrolyte have smooth surface, homogeneous micropores and stable roughness in spite of positive voltage variation. The roughness of the coatings obtained from the silicate electrolyte varies greatly, and the erosion morphology of the microstructure is found for the coatings formed at 450 V positive voltage. The potentiodynamic polarization results confirmed that the MAO coatings obtained from the calcium phosphate electrolyte have a lower corrosion rate and better corrosion resistance. The bioceramic layer induced by SBF soaking can effectively improve the corrosion resistance of the substrate. Moreover, the functional groups in MAO coatings can interact with the ions in SBF solution by electrostatic binding, which results in the formation of CaP apatites. The CaP apatites can integrate with human bone tissue and promote bone growth. It can be concluded that the composition of electrolyte has an important influence on the formation of the MAO coatings and its subsequent corrosion. The MAO coatings obtained from the silicate electrolyte grew and corroded faster, while MAO coatings obtained from the calcium phosphate electrolyte have excellent surface microstructures and corrosion properties. After 50 days of in vitro SBF immersion, the MAO coated samples obtained from calcium phosphate electrolyte still maintain excellent mechanical integrity. They have great potential as a kind of substitute material for dental and bone implants in clinic.

Conflicts of interest

The authors declare no conflicts of interest.

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