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The entrance mechanism of calcium and phosphorus elements into micro arc oxidation coatings developed on Ti6Al4V alloy

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ABSTRACT

In a solution containing 15 g/L phytic acid and 10 g/L KOH, the influences of processing factors including EDTA-Na_2 concentration, $Ca(CH_3COO)_2$ concentration, current density and treating time on the amounts of calcium and phosphorus elements in anodic coatings obtained by microarc oxidation (MAO) on Ti6Al4V alloy were investigated by an orthogonal experiment of four factors with three levels. Surface morphology, chemical composition and structure of anodic coating were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier infrared spectrum (FT-IR) and X-ray photoelectron spectroscopy (XPS). Calcium and phosphorus elements of MAO coatings exist mainly as $CaTiO_3$, PO_4^{3-} and HPO_4^{2-}. The affecting sequence of factors on the calcium content in MAO coatings is $Ca(CH_3COO)_2$ concentration > current density > EDTA-Na_2 concentration > treating time, indicating that the entrance mechanism of calcium element includes diffusion and electromigration. The influencing order on the phosphorus amount is $Ca(CH_3COO)_2$ concentration > treating time > current density > EDTA-Na_2 concentration, suggesting that at a fixed concentration of phytic acid, the phosphorus amount of anodic coatings strongly depends on $Ca(CH_3COO)_2$ concentration.

1. Introduction

Owing to excellent mechanical properties, good corrosion resistance and outstanding biocompatibility, titanium and its alloys have been widely used for orthopedic implants [1–3]. However, as one of inert materials, titanium and its alloys exhibit poor osteoinductive properties [1,2]. Therefore, it is essential to develop surface modification technologies to improve the bioactivity of titanium alloys.

Microarc oxidation (MAO) is highlighted as a cost effective and convenient way to modify the surface of titanium alloys with porous structures for good bioactivity [3,4]. Calcium phosphate (CaP) coatings, especially those made with hydroxyapatite (HA), are usually deposited on implant surface to achieve an early and functional bone apposition [1,5]. The content and phase structure of Ca and P elements in anodic coatings greatly influence the bioactivity of MAO treated titanium alloys [6,7]. Inorganic phosphates such as calcium phosphate [8], sodium phosphate [3,7] and $NaH_2PO_42H_2O$ [9,10] are usually selected as phosphorus-containing MAO electrolytes, while calcium acetate is one of the widely used calcium-containing electrolytes on titanium alloys. From the perspective of biology, organic–inorganic composite coatings are bioactive due to their similarity in composition as the natural bone. Therefore, to further improve the bioactivity of titanium alloys used for biomaterials, it is meaningful to investigate the performance of MAO coatings developed in environmentally friendly organic phosphates.

Phytic acid ($C_6H_6(H_2PO_4)_6$, abbreviated as $H_{12}Phy$), generally extracted from legume seed, cereal grains and beans, is a naturally derived and nontoxic organic macromolecule [11]. Phytic acid consists of 24 oxygen atoms, 12 hydroxyl groups and 6 phosphate carboxyl groups and has powerful chelating capability with divalent and trivalent cations such as Fe^{3+}, Ca^{2+} and Mg^{2+} to form stable metal-phytic complexes [11–13]. Phytates can be used as anti-canner agent, food antistaling agent and inhibitor for renal stone development [12,13].

Besides the used electrolyte composition and concentration, the applied electric parameters such as current density [14], treating time [10,15–17] and final voltage [10,14,18,19] can also influence the coating compositions by changing the ion transferring process. Cations and anions in water solution need to firstly arrive at the anode/electrolyte interface and then enter into MAO coatings. There are three ways by which ions move to the anode, namely, diffusion, electric migration and convection [20]. During MAO, an electric field is developed between the anode and the cathode. With the increase of the applied current density or final voltage, the developed electric field becomes strong. Therefore, anions can arrive at the anode by diffusion and electromigration, but cations move to the anode by diffusion. Previous studies have demonstrated that diffusion is the entrance mechanism for calcium element [9,21,22], while phosphorus element enter into the MAO

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Table 1
Factors and levels of the orthogonal experiment.

Levels	Factors			
	EDTA-Na_2 concentration (g/L)	$Ca(CH_3COO)_2$ concentration (g/L)	Current density (mA/cm^2)	Treating time (min)
1	5	2	20	2
2	10	6	50	4
3	15	10	80	6

coatings by electromigration [9,21,23]. However, in a solution containing chelating agent such as disodium ethylenediaminetetracetate (EDTA-Na_2, $_2(NaOOCCH_2)NCH_2CH_2N(CH_2COOH)_2$, abbreviated as Na_2H_2Y, $Y = [_2(OOCCH_2)NCH_2CH_2N(CH_2COO)_2)]^{4-}$) [24–27], Ca^{2+} ions are combined with the chelating agent and become negatively charged. Under the condition, the entrance mechanism of Ca element into anodic coatings may include both diffusion and electromigration. Therefore, revealing the main factor is important but not reported at present.

In order to reveal the influencing regularity of processing factors on the amounts of calcium and phosphorus in the obtained MAO coatings, the conventional method is to separately investigate each factor but at the same time, all the other factors are fixed. Therefore, many experiments will be carried out by this method [28]. In addition, because the processing parameters are interrelated [8], the results achieved by the conventional method may be correct [29]. In this work, the orthogonal experiment was used to investigate the influences of EDTA-Na_2 concentration, $Ca(CH_3COO)_2$ concentration, current density and treating time on the amounts of calcium and phosphorus. The entrance mechanism of calcium and phosphorus elements into the MAO coatings was discussed according to the results obtained by the orthogonal experiment and the coating property characterized by SEM, XRD, FT-IR and XPS.

2. Experimental

2.1. Materials and MAO treatment

Ti6Al4V plates with the dimensions of 10 mm × 50 mm × 2 mm were used as the samples for MAO treatment. Samples were successively ground with SiC paper from 60 to 1000 grit, washed with distilled water and dried in a hot wind stream. The base solution was composed of 15 g/L phytic acid and 10 g/L KOH. In order to reveal the influence of processing factors such as EDTA-Na_2 concentration, $Ca(CH_3COO)_2$ concentration, current density and treating time on chemical compositions of MAO coatings, they were selected as four factors of the orthogonal experiment. The levels of each factor are selected according to the reported results and our previous experiments. The factors and levels of the orthogonal experiment are listed in Table 1.

A homemade MAO-50C powder supply was used under a constant current control mode. For the used power supply, pulse frequency and duty cycle can be regulated in the range of 100–3000 Hz and 5–40%, respectively. The Ti6Al4V plate was used as anode, while the stainless steel barrel containing the anodizing solution was used as the cathode. During MAO treatment, pulse frequency and duty cycle were kept constant and they were separately 2000 Hz and 35%.

2.2. Measurement

Surface morphologies of the MAO treated titanium samples were observed by a field emission scanning electron microscope (SEM, ΣIGMA, Germany). Chemical compositions of anodic coatings on the surfaces of the samples were measured by energy dispersive X-ray spectrometer (EDS) attached to SEM. The phase structure of the samples was analyzed by X-ray diffraction (XRD, Shimadzu XRD-6100, Japan). An X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VG) was used to detect the chemical states on the surface of anodic coatings. In the XPS experiment, an Al Kα anode ($\lambda = 1486.6$ eV) was used to determine the chemical states of anodic coatings after the coating surfaces were etched for 60 s by argon-ion-beam to reduce the contamination. Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 460) was used to analyze the chemical functional groups of phytic acid and the MAO coatings in the range of 400–4000 cm^{-1}.

3. Results

3.1. The results of the orthogonal experiment

The orthogonal experiment of four factors with three levels including EDTA-Na_2 concentration, $Ca(CH_3COO)_2$ concentration, current density and treatment time was used to comprehensively investigate the effects of processing factors on the contents of calcium and phosphorus elements in MAO coatings. The orthogonal experimental results are listed in Table 2.

The experimental data were treated by the method of the intuitionistic analysis. As listed in Table 2, K_1, K_2 and K_3 are the sum of calcium content of Level 1, Level 2 and Level 3 of four factors, respectively. The maximum difference between the total Ca content at two levels of each factor shows the general influence of that factor. The greater the difference, the more important the factor. Based on the values of the differences, the influencing sequence of factors on Ca content of MAO coating is $Ca(CH_3COO)_2$ concentration > current density > EDTA-Na_2 concentration > treating time.

Table 2 also shows that among nine samples, the phosphorus content of anodic coatings developed on No. 9 is the highest. The data about the P content (listed in brackets) are dealt with the same method as calcium content. The rank of influencing factors on P content of

Table 2
The orthogonal experimental array and experimental results by the intuitionistic analysis.

Experiment no.	EDTA-Na_2 concentration (g/L)	$Ca(CH_3COO)_2$ concentration (g/L)	Current density (mA/cm^2)	Treating time (min)	Ca (at.%)	P (at.%)
No. 1	5	2	20	2.0	0.69	6.00
No. 2	5	6	50	4.0	6.18	7.78
No. 3	5	10	80	6.0	7.43	7.23
No. 4	10	2	50	6.0	1.73	5.42
No. 5	10	6	80	2.0	4.98	7.94
No. 6	10	10	20	4.0	2.39	6.44
No. 7	15	2	80	4.0	1.55	4.54
No. 8	15	6	20	6.0	3.29	7.69
No. 9	15	10	50	2.0	5.16	8.19
K_1	14.3 (21.01)	3.97 (15.96)	6.37 (20.13)	10.83 (22.13)		
K_2	9.10 (19.8)	14.45 (23.41)	13.07 (21.39)	10.12 (18.76)		
K_3	10.0 (20.42)	14.98 (21.86)	13.96 (19.71)	12.45 (20.34)		
Difference	5.2 (1.21)	11.01 (7.45)	7.59 (1.68)	2.33(3.37)		
Rank	3 (4)	1 (1)	2 (3)	4 (2)		