Effect of Applied Voltage on the Microstructure and Bioactivity of MAO Film on Ti Substrate

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Various MAO films were prepared on Ti-6Al-4V substrate at voltages from 300 to 550 V in an electrolyte containing 0.18 M calcium acetate and 0.1 M sodium dihydrogen phosphate using an AC mode. Microstructures and phases of the MAO films were investigated by SEM with EDS and XRD. Bioactivity was examined using an apatite formation test in a simulated body fluid. The results show that the applied voltage has a significant influence on the microstructure and composition. With the increase in the applied voltage the sizes of micropores increase, and Ca P contents and Ca/P ratio in the MAO film increase too. And the Ca P contents in this work are increased obviously compared to DC MAO mode. The MAO films contain rutile, anatase and amorphous calcium phosphate, and higher voltage is favorable to form rutile phase. The results of the apatite formation test show that the AC MAO films exhibit higher ability to form apatite than DC mode. It is suggested that the AC MAO mode is more effective to incorporate calcium and phosphorous in the oxide layer than DC mode because higher applied voltages can be applied in it, and the AC MAO film present a better performance in the formation of calcium phosphate which may be result from a more effective release of CaP from MAO film into SBF. [doi:10.2320/matertrans.M2013004]

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1. Introduction

Due to its excellent mechanical properties, biocompatibility, manufacturability, and osseointegration behavior, titanium metal and its alloys have become an excellent material for dental and orthopedic implants.^{1–3)} However, titanium is a bioinert material that neither chemically connects to bone nor actively induces bone growth. Various surface modifications on titanium implants have been carried out to improve its bioactivity.

Among the surface modification methods used to improve Ti alloys bioactivity, anodic oxidation has attracted considerable attention on account of its many advantages, which include its capability to produce porous titanium oxide films through dielectric breakdown known as microarc oxidation (MAO), improved adhesion to the substrate metal, and the ability to change the composition of the oxide film depending on the type of electrolyte used.^{4,5)} Some reports have shown that the wear resistance, chemical stability, and biocompatibility of the metals can be significantly improved after a MAO treatment. Previous researches also indicated that MAO TiO₂-based film containing Ca and P can be prepared by treating the Ti alloy in an electrolyte containing Ca and P, and the addition of Ca and P in the MAO film improved the bioactivity.^{6,7)}

Some researchers reported that the applied voltage had important influences on the microstructure and Ca and P concentration of the MAO films, and higher voltage is beneficial to obtain higher content of Ca and P film.^{8,9)} But conventional anodic oxidation treatments have been accomplished using an electric power supply in direct-current mode (DC) at lower voltages. Recently, an alternating-current (AC)-type MAO method was introduced to modify the

surface of dental or orthopedic implants owing to its high wear and corrosion resistance, porous topology and good adhesion to Ti metal. The AC mode with higher voltages supply may be a better choice for MAO treatment. It provides higher local discharge intensity than DC mode, which facilitates the formation of the large thickness film and the change of the MAO composition.¹⁰⁾ Ho-Jun Song *et al.*¹¹⁾ carried out MAO treatments to fabricate Ti oxide film containing CaP with the AC mode at 150 or 175 V, which shows that the characteristics of the oxide films fabricated using the AC-type MAO depend on the voltage and frequency.

In this study, the MAO films containing calcium and phosphorus were fabricated on titanium metal using the AC mode at higher voltages from 300 to 550 V. Micro-morphology, crystalline structure and the Ca and P content of the films were evaluated. In addition, the bioactivity of the MAO films prepared at various voltages was examined using the formation of apatite test in an SBF.

2. Experiment

Commercial medical Ti-6Al-4V plates (sample size: 15 × 30 × 1.5 mm) were used in the study. Samples were abraded using SiC sandpaper no. 800, then rinsed using a mixture of hydrofluoric and nitric acids (1 : 3 HF/HNO₃), and finally washed with acetone in an ultrasonic cleaner. MAO was performed with a rectangular pulse power supply. Electrolytes were prepared by dissolution of calcium acetate 0.18 M and sodium dihydrogen phosphate 0.1 M in deionized water. The electrolyte cell consisted of a stainless steel container. Schematic diagram and parameters representation of microarc oxidation process used in this experiment are presented in Fig. 1. The frequency of the rectangular pulse used in the MAO was 400 Hz (t_1/t was 20% and t_2/t was

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Fig. 1 Schematic diagram and parameters representation of microarc oxidation process.

20%). Because the MAO film on Ti substrate was formed only when Ti was applied a positive voltage, positive voltage play a more important role during MAO process than negative voltage. The applied voltage (V_1) in this work was 300, 350, 400, 450, 500 and 550 V, respectively, and V_2 was fixed at 20 V. The temperature of the electrolyte was kept at 40 to 60°C by a cooling system. The MAO processes were performed for 10 min. After MAO treated, the samples were washed with deionized water (dipping into deionized water 5 times).

The oxide film microstructures were observed by scanning electron microscopy (SEM: FEI Quatan 450, Japan) equipped with EDS, which was used to also analyze the composition of the samples. The surface phases of the films were analyzed by X-ray diffraction (XRD: D8-Advanced; Bruker, Germany) using Cu K α radiation at a scanning speed of 4.0°/min and using a scanning range (2θ) of 20 to 65°. The bioactivity of the films was examined using the formation of apatite in simulated body fluid (SBF). The SBF was prepared by dissolving reagent-grade NaCl, NaHCO₃, KCl, K₂HPO₄·3H₂O, MgCl₂, CaCl₂ and Na₂SO₄ into deionized water and buffering at pH 7.40 with tris (hydroxymethyl) amino-methane ((CH₂OH)₃CNH₂) and 1.0 M HCl. In this test, the MAO samples were soaked in 50 ml of SBF at 37°C for 7 days, then were gently washed with deionized water and dried at 25°C. Ca and P concentrations of the SBF immersion of the MAO coatings for 12, 24, 48, 72, 96 h were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 5300DV, Perkin-Elmer, America). The micrograph of the apatite formed on the MAO films was observed by scanning electron microscopy.

3. Results and Discussion

3.1 Phases identification and MAO film thickness

Figure 2 shows the XRD patterns of the MAO film performed at 350, 450 and 550 V. As shown in Fig. 2, the film consists of rutile TiO₂ and anatase TiO₂ besides Ti phase, and no additional crystal phases formed by Ca or P can be identified in this work. This result is in accordance with previous reports which show that Ca and P in the MAO film is an amorphous phase.^{12,13} It also can be seen from Fig. 2 that the peak of rutile become stronger in the patterns when the applied voltage is increased from 350 to 550 V, which can be seen from the peak of rutile at 26.2° compared to that of anatase at 27.5°. This result indicates that high voltage applied in MAO is favorable to form rutile phase. On the other hand, the peaks of rutile are more obvious in the

Fig. 2 X-ray diffraction patterns of the MAO films.

patterns of AC MAO film presented in Fig. 2 than those of DC MAO film,¹⁴ which may be resulted from a higher voltage used in AC mode than DC mode.

The thicknesses of the oxide films in this work were examined by SEM. The thickness of the prepared MAO films is about 5 μ m (300 V), 9 μ m (350 V), 12 μ m (400 V), 15 μ m (450 V), 17 μ m (500 V), 19 μ m (550 V), respectively. These results show that with the increase in the applied voltage the thickness of the oxide film increases. In general, the growth rate and maximum thickness of the oxide film are dependent on the applied voltage, and they increase with the applied voltage.

3.2 Effects of applied voltage on morphology and composition of the MAO films

3.2.1 Surface morphology

The surface morphologies of the MAO films formed at various voltages (300–550 V) are shown in Fig. 3. The MAO films show a porous structure, which is formed during microarc discharge process. The MAO films are distributed at regular intervals at low applied voltages (350 V). Above 450 V, the surfaces of the MAO films become rough and irregular. The average size of micro-pores on the MAO film increases with increasing the applied voltage. Moreover, the uniformity extent of the micro-pore size increases. The results indicate that the applied voltage has a significant effect on the surface morphology of the MAO film, especially for the size of micro-pores used the present electrolyte.

3.2.2 Ca and P contents and Ca/P of MAO film

The CaP contents and Ca/P ratios of the MAO films formed at various voltages (300–550 V) are shown in Fig. 4. The results reveal that the Ca content and Ca/P ratio of the MAO films increases with increasing the applied voltage, which indicates that the Ca, P contents and Ca/P ratios of the MAO films can be controlled by the voltage applied in MAO process. Above 400 V, a slow increase in P content was observed, but the Ca content and Ca/P ratio increase continuously, which shows that high voltage is favorable to increase the content of Ca and P in MAO film, especially to increase the content of Ca. The highest CaP and Ca content is about 27 at%, 18 at%, respectively. L. Fu *et al.*¹⁴ show that the CaP and Ca content of the MAO film prepared by DC mode are not more than 15 and 10 at%. In this work, the

Fig. 3 SEM of the MAO films surface prepared at various applied voltages; (a) 300 V, (b) 350 V, (c) 450 V, (d) 550 V.

Fig. 4 Changes in the Ca, P content and Ca/P ratio of the MAO film as a function of the applied voltage during MAO process.

Ca/P ratio of the MAO film prepared at 500 V is 1.63, which is the nearest one to that of human bone (1.67). Because higher voltage can be applied in AC mode MAO, AC mode is more helpful to prepare the MAO films with high Ca/P contents than DC mode.

On the other hand, the increase of the Ca and P contents could lead to the formation of a large quantity of amorphous Ca and P phase. T. Nakamura *et al.*¹⁵⁾ has believed that amorphous Ca and P phase facilitates the initial fixation of porous materials due to their excellent osteoconductive property. Thus, the present results may provide a variety of choices due to all the MAO films containing amorphous Ca and P phase. Furthermore, the Ca and P content could

Table 1 Ion concentrations of the SBF used in this work and those in human blood plasma.

Ion	Concentration (c/mM)	
	SBF	Blood plasma
Na ⁺	142.0	142.0
K ⁺	5.0	5.0
Mg ²⁺	1.5	1.5
Ca ⁺	2.5	2.5
Cl ⁻	147.8	103.8
HCO ₃ ²⁻	4.2	27
HPO ₄ ²⁻	1.0	1.0
SO ₄ ²⁻	0.5	0.5

influence biological performance of the MAO film, which is presented in the following.

3.3 Ca and P release and apatite formation of the MAO films in SBF

The bioactivity of the films was examined using the apatite formation test in the SBF. The ionic concentrations of the SBF and that of the human blood plasma are presented in Table 1. The Ca and P concentrations of the SBF after immersed for various time are presented in Fig. 5. As presented in Fig. 5, the concentrations of Ca and P increase obviously in the first 72 h during immersion process. After 72 h, the concentration of Ca and P in the SBF does not increase any more. The increase of Ca and P concentration

indicates that Ca and P are released from the MAO film into the SBF during the immersion process. Many micropores in the MAO film supply faster channels for the release of Ca and P. Furthermore, D. Q. Wei *et al.*¹⁶⁾ reported that the release rate of Ca and P was decreased by heat treatment applied on the MAO film. This phenomenon may result from the recrystallization of Ca and P. Generally, the Ca and P in amorphous state are easier to release into SBF than that in crystal phase.

Fig. 5 Ca and P concentration in the SBF as a function of MAO coating immersion time.

SEMs of the apatite formed on the MAO coatings prepared at various voltages are presented in Fig. 6. Figure 6 shows that many apatite particles have formed on the MAO films during immersion process. With the increase in voltages applied in the MAO process, the amount of formed apatite increase, even the film prepare at 550 V is covered by a complete layer of apatite (as presented in Fig. 6(d)). L. Fu *et al.*¹⁴⁾ reported the apatite formation results of the DC MAO film, and these results presented in Fig. 6 show that the apatite formation performance of the AC MAO film superior to the DC mode, and more apatite was formed by the AC MAO film in the same conditions. As presented in 3.2.2, with the increase in voltage the Ca P contents increase, which indicates that the effect of voltage on the apatite formation of MAO film may be result from a higher Ca P content and release capacity of the MAO film.

In this work, it is suggested that the presence of Ti-OH groups on surface is responsible for the MAO coating to form apatite which result in the increase in the degree of supersaturation of the solution with respect to apatite on the surface, and this triggers the apatite nucleation. Additionally, Ca and P released from the MAO film also increase the degree of supersaturation, promoting the nucleation and growth of apatite. Moreover, numerous Ca ions on the surface of the MAO coating may provide good sites for the epitaxial absorption process with respect to apatite ions.

Fig. 6 SEM of the apatite formed on the MAO films prepared at various applied voltages; (a) 300 V, (b) 350 V, (c) 450 V, (d) 550 V.

4. Summary

In this work, MAO was performed on Ti-6Al-4V in an electrolyte containing calcium and phosphate. Various MAO films were prepared on Ti-6Al-4V substrate at the applied voltages from 300 to 550 V by an AC power supply. The results show that the MAO films contain amorphous calcium phosphate. The applied voltage has a significant influence on the structure and composition of the MAO film. The MAO film consists of rutile TiO₂ and anatase TiO₂, and higher voltage is favorable to form rutile phase. With the increase in the applied voltage, the maximum size of micropores tends to increase, and calcium phosphate content and Ca/P ratio in the MAO film increase too. The MAO film with the maximum CaP content and Ca/P ratio was prepared 550 V, and 500 V at ICP-OES results indicate that Ca and P are released from the MAO film. The AC MAO mode is more effective to incorporate calcium and phosphorous in the oxide layer than DC mode because higher applied voltages can be applied in it, and the AC MAO films present a better performance in the formation of calcium phosphate which may be result the release of CaP from MAO film into SBF.

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REFERENCES

- 1) T. Albrektsson, P. I. Brånemark, H.-A. Hasson and J. Lindström: *Acta Orthop. Scand.* **52** (1981) 155–170.
- 2) M. Wang: *Biomaterials* **24** (2003) 2133–2151.
- 3) I. J. Hwang, K. R. Shin and J. S. Lee: *Mater. Trans.* **53** (2012) 559–564.
- 4) D. Q. Wei, Y. Zhou, D. C. Jia and Y. M. Wang: *Mater. Chem. Phys.* **104** (2007) 177–182.
- 5) P. Huang, K. W. Xu and Y. Han: *J. Porous Mater.* **11** (2004) 41–45.
- 6) J. Takebe, S. Itoh, J. Okada and K. Ishibashi: *J. Biomed. Mater. Res.* **51** (2000) 398–407.
- 7) X. L. Zhu, J. L. Ong, S. Y. Kim and K. H. Kim: *J. Biomed. Mater. Res.* **60** (2002) 333–338.
- 8) M. Iwasaki, K. Shimada, K. Kudo, Y. Tamagawa and H. Horikawa: *Mater. Trans.* **52** (2011) 1410–1417.
- 9) M. Fini, A. Cigada and G. Rondelli: *Biomaterials* **20** (1999) 1587–1594.
- 10) F. C. Ma, P. Liu, W. Li, X. K. Liu and X. H. Chen: *Rare Metal Mater. Eng.* **41** (2012) 478–480.
- 11) H. J. Song, K. H. Shin, M. Kook and H. K. Oh: *Surf. Coat. Tech.* **204** (2010) 2273–2278.
- 12) Y. Han, S. H. Hong and K. W. Xu: *Surf. Coat. Tech.* **168** (2003) 249–258.
- 13) X. L. Zhu, K. H. Kim and Y. S. Jeong: *Biomaterials* **22** (2001) 2199–2206.
- 14) L. Fu, Y. Song, F. P. Wang, T. Shimizu, K. Igarashi and L. Zhao: *J. Biosci. Bioeng.* **100** (2005) 100–104.
- 15) H. M. Kim, F. Miyaji, T. Kokubo and T. Nakamura: *J. Biomed. Mater. Res.* **32** (1996) 409–417.
- 16) D. Q. Wei, Y. Zhou, D. C. Jia and Y. M. Wang: *Surf. Coat. Technol.* **201** (2007) 8723–8729.