

Coatings of Bioactive TiO₂ Films on Ti6Al4V Alloy by Micro Arc Oxidation

A. AYDAY*

Sakarya University, Faculty of Engineering, Department of Metallurgical and Materials Engineering, Sakarya, 54187, Turkey

Micro arc oxidized TiO₂ coatings were prepared in different concentrations of (CH₃COO)₂Ca·H₂O and different coating times on biomedical Ti6Al4V alloy. The surface topography, phase, and element composition of the coatings were characterized by scanning electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectrometry, respectively. The micro arc oxidation treated Ti6Al4V alloy was immersed in a simulated body fluid to study the bioactive deposition properties on the surface of TiO₂ coating. Immersion tests indicate that the specimens coated in the high rate Ca-containing electrolyte are most effective when compared with the specimen containing less Ca-content.

DOI: [10.12693/APhysPolA.134.412](https://doi.org/10.12693/APhysPolA.134.412)

PACS/topics: TiO₂, bioactivity, micro arc oxidation, corrosion resistance

1. Introduction

Titanium and its alloys are widely used in metallic implants materials due to their high strength, low density, high corrosion resistance, and excellent biocompatibility. TiO₂ coating such as sol-gel, CVD/PVD and anodizing on Ti and its alloys was studied for many years because of its stability, nontoxicity, and bioactivity. Recently, micro arc oxidation (MAO) process was used for titanium based implants [1–3]. MAO produces rough, micro-porous, thick, titanium oxide (TiO₂) coatings containing bioactive compounds (such as hydroxyapatite, calcium phosphate, or calcium titanate). Electrochemical oxidation in the electrolyte formed TiO₂, biocompatible compound formations are caused by the Ca and P containing electrolytes. Therefore, the composition of electrolyte has a important effect on the characteristics and structural properties and morphology of the MAO coatings [3–6]. In these study Ti6Al4V alloy was coated by MAO process in different electrolyte and two different coating times. The time and electrolyte compositions were tested. The surface morphology and composition of coating layers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), respectively. The corrosion properties of the Ti6Al4V alloy before and after MAO treatment were investigated in a simulated body fluid (SBF).

2. Experimental details

Ti6Al4V alloy was cut into rectangular samples with the size of 30 mm×15 mm×5 mm. The samples were successively polished with SiC sandpaper down to 600 grid. A direct current power supply was used for preparation of MAO coatings on Ti alloy (anode) substrate.

The MAO process was operated in a stainless steel container (cathode). The MAO coating parameters were given in Table I. During the experiment process, the electrolyte solution was continuously stirred and cooled below 28 °C using ice bath. After the treatment, the samples were rinsed with distilled water and dried in warm air. The surface microstructure of coating was detected under SEM (JEOL 6060). The chemical composition and the elements in the coatings were detected by XRD (Rigaku) with an Cu K_α X-ray source, and EDS analysis. Untreated and MAO treated samples were immersed in a Kokubo SBF solution to evaluate the TiO₂ forming ability. SBF solution was refreshed every 24 h and the weight loss was calculated.

3. Results and discussion

Figure 1 shows the surface morphology of the MAO coatings that were generated in the electrolytes with different concentrations of (CH₃COO)₂Ca·H₂O and different coating times. It was observed that the amount of calcium and phosphate salt formed on the titanium surface increased with the oxidation time, resulting in a change in the surface morphology, as shown in Fig. 1. At an oxidation time of 3 min, a porous TiO₂ layer formed on the surface of the titanium substrate. Only a few Ca–P precipitates mixed with the TiO₂ and solidified together; these were primarily located around the discharge channel (Fig. 1a). Increase of Ca content did not change the surface morphology (Fig. 1c). With increase of time, the surface roughness value decreased linear, shown in Fig. 1b and Fig. 1d. Figure 2 shows the elemental analysis of Ca and P amount of Ti-2Ca-5 (Fig. 2a) and Ti-4Ca-5 samples (Fig. 2b) Ca and P amount. With increase of the oxidation time and solution concentration of 5 min and 4 g/l calcium acetate, there was an obvious increase in the amount of Ca–P precipitate (Fig. 2b). Ca and P peaks were detected with relatively higher intensity compared to other coatings.

*e-mail: aayday@sakarya.edu.tr

Coating parameters of micro arc oxidation process

TABLE I

Sample codes	(CH ₃ COO) ₂ Ca·H ₂ O [g/l]	Na ₃ PO ₄ [g/l]	Breaking voltage [V]	Final voltage [V]	Time [min]	pH
Ti6Al4V	-	-	-	-	-	-
Ti-2Ca-3	2	4	170	550	3	11.4
Ti-2Ca-5	2	4	170	565	5	11.4
Ti-4Ca-3	4	4	150	441	3	11.7
Ti-4Ca-5	4	4	150	470	5	11.7

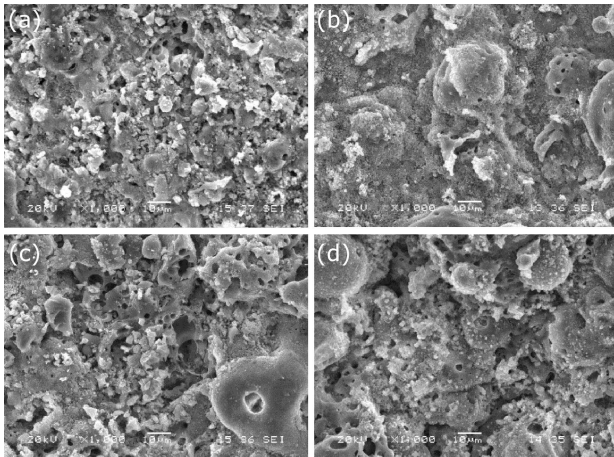


Fig. 1. Surface morphologies of (a) Ti-2Ca-3, (b) Ti-2Ca-5, (c) Ti-4Ca-3, (d) Ti-4Ca-5.

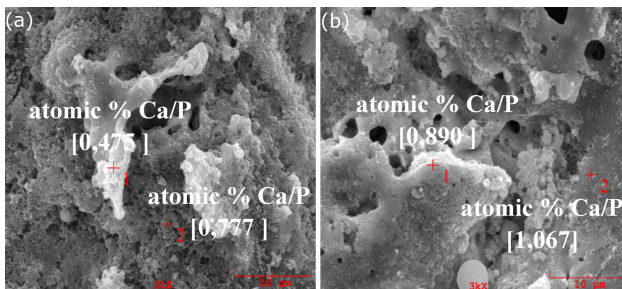


Fig. 2. SEM micrographs and EDS analysis of points 1 and 2: (a) Ti-2Ca-5, (b) Ti-4Ca-5.

The XRD patterns of uncoated Ti6Al4V, Ti-2Ca-5, Ti-4Ca-5 are shown in Fig. 3. The uncoated samples main phase is α -Ti. After MAO treatment Ti-2Ca-5 Ti-4Ca-5 samples were composed of anatase-TiO₂ and rutile-TiO₂. The Ti-4Ca-5 samples phase intensity of anatase-TiO₂ and rutile-TiO₂ is higher than Ti-2Ca-5. TiO₂ is the main oxide existing in the coatings, increase of the Ca did not change the coating composition

Figure 4 shows the relationship between weight loss and immersion time for uncoated Ti6Al4V and MAO coated alloys in SBF. It can be observed from Fig. 4 that the weight loss of all specimens has increased in 1 h. Then uncoated samples weight increases in 8 h and all of the coated samples weight growth nearly in 16 h, because of the samples can produce oxide film in SBF solution.

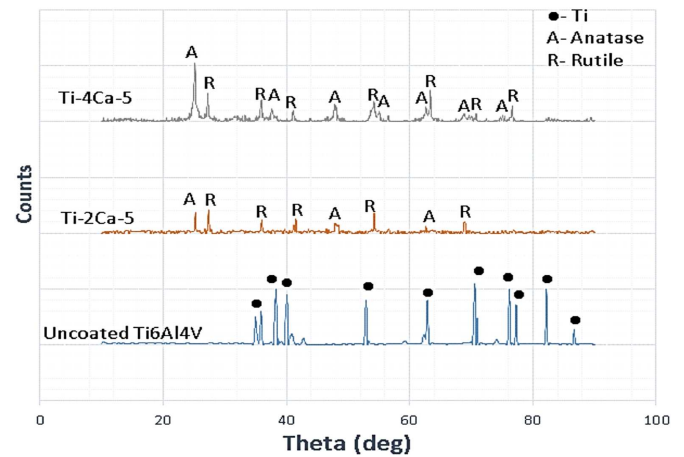


Fig. 3. XRD patterns of (a) uncoated Ti6Al4V, (b) Ti-2Ca-5, (c) Ti-4Ca-5 coatings.

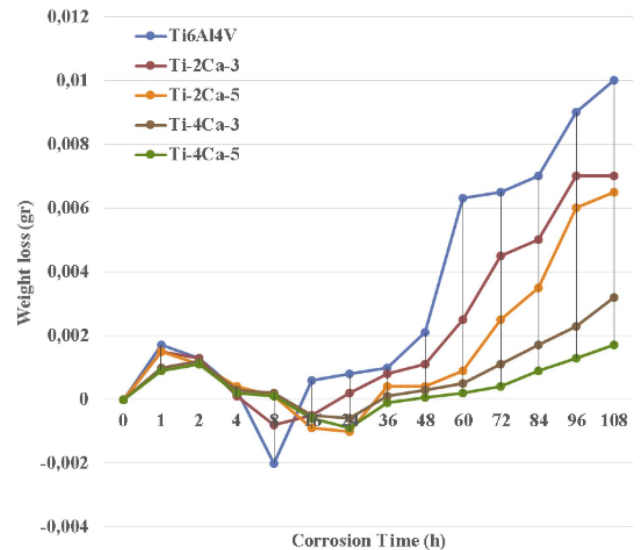


Fig. 4. Weight losses of Ti6Al4V and MAO coated alloys after immersion in SBF solution for 108 h.

When the (CH₃COO)₂Ca·H₂O concentration increased from 2 to 4 g/l, the corrosion rate of the samples decreased. Also the coating time improved the corrosion resistance. Two main factors influence the corrosion resistance: thickness and porosity of the coating [7, 8].

4. Conclusions

MAO coatings on Ti6Al4V alloy were prepared in different concentrations of $(\text{CH}_3\text{COO})_2\text{Ca}\cdot\text{H}_2\text{O}$ and different coating times. The properties (chemical composition) of the coatings are closely related to the growth mechanism and significantly influenced by electrolytes. Anatase-TiO₂ and rutile-TiO₂ phases occurred on coated layer. It implied that the MAO coating provided a good protection of titanium alloy in the SBF solution. Ti-4Ca-5 was characterized by a good adhesion to the substrate. The corrosion test support the result because of minimum weight loss shown on this sample.

Acknowledgments

The author are grateful to the Sakarya University, Department of Metallurgy and Material, Turkey for Education and Research for financial support through project 2016-01-08-018 (BAP-SAU).

References

- [1] Q. Li, W. Yang, C. Liu, D. Wang, J. Liang, *Surf. Coat. Technol.* **316**, 162 (2017).
- [2] Y. Sharkeev, E. Komarova, M. Sedelnikova, Z. Sun, Q. Zhu, J. Zhang, T. Tolкачева, P. Uvarkin, *Trans. Nonferrous Met. Soc. China* **27**, 125 (2017).
- [3] T. Wanxia, Y. Jikang, Y. Gang, G. Guoyou, D. Jinghong, Z. Jiamin, L. Yichun, S. Zhe, Y. Jianhong, *Rare Met. Mater. Eng.* **43**, 2883 (2014).
- [4] J. Karbowiczek, F. Muhaffel, G. Cempura, H. Cimenoglu, A. Czyska-Filemonowicz, *Surf. Coat. Technol.* **321**, 97 (2017).
- [5] J. Han, P. Wan, Y. Sun, Z. Liu, X. Fan, L. Tan, K. Yang, *J. Mater. Sci. Technol.* **32**, 233 (2016).
- [6] R.F. Zhang, L.P. Qiao, B. Qu, S.F. Zhang, W.H. Chang, J.H. Xiang, *Mater. Lett.* **153**, 77 (2015).
- [7] Q.-P. Tran, J.-K. Sun, Y.-C. Kuo, C.-Y. Tseng, J.-L. He, T.-S. Chin, *J. Alloys Comp.* **697**, 326 (2017).
- [8] K.-C. Kung, T.-M. Lee, T.-S. Lui, *J. Alloys Comp.* **508**, 384 (2010).