Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi

Suleyman Demirel University
Journal of Natural and Applied Science

18(SI: Biomechanics), 147-151, 2014

Characterization and In Vitro Bioactivity of Calcium and Phosphorous Containing Titania Layer on Ti6Al4V Alloy

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(Received: 15 September 2014, Accepted: 27 November 2014)

Keywords
Ti6Al4V
Micro Arc Oxidation
Titania layer
Hydrothermal Treatment
Bioactivity

Abstract: Calcium and phosphorous containing titania layers on Ti6Al4V biomedical alloy were formed by micro arc oxidation (MAO) in an electrolyte containing calcium acetate and sodium phosphate, and then subjected to hydrothermal treatment (HT) in order to achieve improved biocompability with modified titania layer. Samples were hydrothermally treated in water solution whose pH was adjusted to 11.0-11.5 by adding NaOH, at 230 °C for 10 h and cooled in the autoclave. Surface morphology, microstructure, and phase composition of titania layer were investigated systematically before and after HT. Their biomimetic apatite inducing ability in a simulated body fluid (SBF) was investigated. The bioactivity tests of modified MAO surface on Ti6Al4V alloy showed a considerable improvement compared to the unmodified MAO surface.

Ti6Al4V Alaşımı Üzerinde Oluşturulan Kalsiyum ve Fosfor İçeren Titanyum oksit Tabakasının Karakterizasyonu ve In Vitro Biyoaktivite İncelemesi

Anahtar Kelimeler
Ti6Al4V
Mikro ark oksidasyon
Titanyum oksit tabaka
Hidrotermal İşlem
Biyoaktivite

Abstract: Ti6Al4V biomedikal titanyum alaşımı üzerinde kalsiyum asetat ve sodyum fosfat içeren elektrolit içinde gerçekleştirilen mikro ark oksidasyon işlemi ile kalsiyum ve fosfor içeren titanyum oksit tabakası oluşturulmuştur. Oluşturulan oksit tabakasının biyomimetik apatit oluşturma özelliğini iyileştirmek amacıyla numuneler 10 saat süreyle 230 °C'de sodyum hidroksit içeren sulu çözelti içerisinde hidrotermal işleme maruz bırakılmıştır. Numunelerin yüzey morfolojileri, oksit tabakaların mikroyapısı ve faz kompozisyonları hidrotermal işlem öncesi ve sonrasında incelenmiştir. Numunelerin biyomimetik apatit oluşum karakteristiği incelemesi yapay vücut sıvısı içinde gerçekleştirilmiştir. Mikro ark oksidasyon işlemini takiben uygulanan hidrotermal işlem sonucunda Ti6Al4V numunenin yüzeyinde biyomimetik apatit oluşumunun iyileştiği gözlemlenmiştir.

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1. Introduction

Titanium and its alloys exhibit good mechanical properties, superior corrosion resistance, low Young modulus, relatively low density and good biocompatibility (Geetha et al., 2009; Leyens and Peters, 2003). Therefore, titanium-based biomaterials are greatly preferred in biomedical applications (i.e. orthopedics and dentistry). Among the biomedical titanium alloys, Ti6Al4V alloy is widely used for orthopedics applications through its superior mechanical properties, while commercially pure titanium (Cp-Ti) is used applications not bearing high loadings such as dentistry. Their bio-inertness provided by formation of natural titanium oxide film (in nano scale) in ambient environment makes them very attractive for biomedical fields (Xue et al., 2002). However, one of the important issues of bio-inert materials is to achieve chemical bonding with the bone tissue shortly after implantation. In order to provide a bio-active surface on titanium alloys, calcium and phosphorous containing compounds are deposited on titanium-based alloys (Liu et al., 2005b). These compounds stimulate the surface to attract the osteoblast cells onto the implant surface and ensure a chemical and firm bonding between implant surface and bone tissue (Zhang et al., 2004).

Micro arc oxidation (MAO) is an effective and highly efficient method to produce porous, rough and thick titania layer on titanium-based alloys. The MAO formed Titania layer is far thicker than naturally formed oxide layer and firmly bonded onto the surface of the implant (Liu et al., 2005a). Besides the benefits of MAO formed titania layer, calcium and phosphorus species can be integrated and/or formed on the titania layer by MAO process. Moreover, biocompatible compounds containing titania layer is also improved by hydrothermal treatment (HT). The phase composition and the morphology of the surface are highly associated with applied temperature and pressure in HT process. By the aid of HT, hydroxyl groups which provide suitable sites for apatite nucleation are formed on the titania layer (Ryu et al., 2008).

In this study, MAO and HT processes were applied successively to modify the surface of Ti6Al4V alloy. The surface morphology, phase composition and roughness of the MAO coatings were examined before and after HT process. In order to evaluate bioactivity of HT modified surfaces, SBF immersion test was utilized.

2. Materials and Methods

2.1. Micro Arc Oxidation

Ti6Al4V discs were used as the substrates for MAO process. The samples (Ø10 mm and 4 mm in thickness) were ground with SiC abrasive paper up to #1200 and then ultrasonically cleaned 15 min in acetone, 15 min in ethanol and 15 min in distilled water, respectively. The oxidation process was performed at 400 V for 5 min. Samples were oxidized in an electrolytic solution containing calcium acetate and sodium phosphate and coded as MAO.

2.2. Hydrothermal Treatment

After the MAO process, the samples were placed vertically at the bottom of an autoclave with 500 mL of water solution whose pH was adjusted to 11.0-11.5 by adding NaOH. The samples were hydrothermally treated at 230 °C for 10 h and cooled in the autoclave (Ernst Haage). At hydrothermal treatment conditions, both temperature and pressure of the solution were maintained at constant levels by using a stirred batch reactor equipped with a digital temperature control unit. The samples were gently washed with distilled water and finally dried overnight at room temperature. The samples were coded as MAO+HT.

2.3. Characterization

The surface morphology of the oxide layers were analyzed by a scanning electron microscope (SEM, Hitachi TM-1000). The phase composition of the coatings was identified by X-ray diffractometer (XRD, GBC MMA 027) using Cu-Kα radiation (λ = 0.154 nm) at 35 kV and 28.5 mA with a scan range between 20-80° at a step of 0.02° and a scanning speed of 2°/min. The average surface roughness (Ra) of the samples was examined by using surface profilometer (Veeco Dectac 6M) under 5 mg load, with a scan distance of 2000 μm. Ten examinations were done for each sample to calculate an average roughness value.

2.4. Bioactivity Test

For apatite induction, MAO and MAO+HT samples were investigated by simulated body fluid (SBF) soaking test. To produce biomimetic apatite coatings, the samples were soaked in 120 mL of 1.5X SBF in closed screw-capped polypropylene bottles for 1, 3 and 7 days while being kept in a vertical position. The SBF was prepared by dissolving reagent-grade chemicals of NaCl, $NaHCO_3$, KCl, Na_2HPO_4, $MgCl_2.6H_2O$, $CaCl_2.2H_2O$ and Na_2SO_4 into deionized water and buffering at pH 7.40 with tris–hydroxymethyl–aminomethane ($(CH_2OH)_3CNH_2$) and 1.0 mol/l HCl at 36.5 °C. The SBF was refreshed every two days to maintain the ion concentrations. After 1, 3, and 7 days, the samples was removed from SBF and gently rinsed with distilled water. The surface of the samples was dried in air at room temperature.

3. Results

The XRD patterns of the oxide layers obtained by MAO only and after HT process at 230 °C are given in Figure1. On the XRD patterns, the peaks of rutile, calcium titanate, anatase, hydroxyapatite (HA) and titanium were appeared. Titanium peaks were detected due to penetration of X-rays beyond the oxide layer. It is suggested that HA was the dominant phase on the outer surface which was formed by the calcium and phosphorous species in the electrolyte. After MAO process, the oxide layers were treated hydrothermally in an autoclave for 10 h at 230 °C. It should be noted that the peak intensities and the crystallinity of HA and anatase phase were significantly increased after HT process. Due to high cooling rate of molten oxides during MAO process, HA and titania phases were deposited in both amorphous and crystalline state. According to the XRD patterns of MAO and MAO+HT samples, it is concluded that HT induces crystallization of HA and transforms amorphous titania to anatase (semi-stable phase of titania) on the oxide surface.

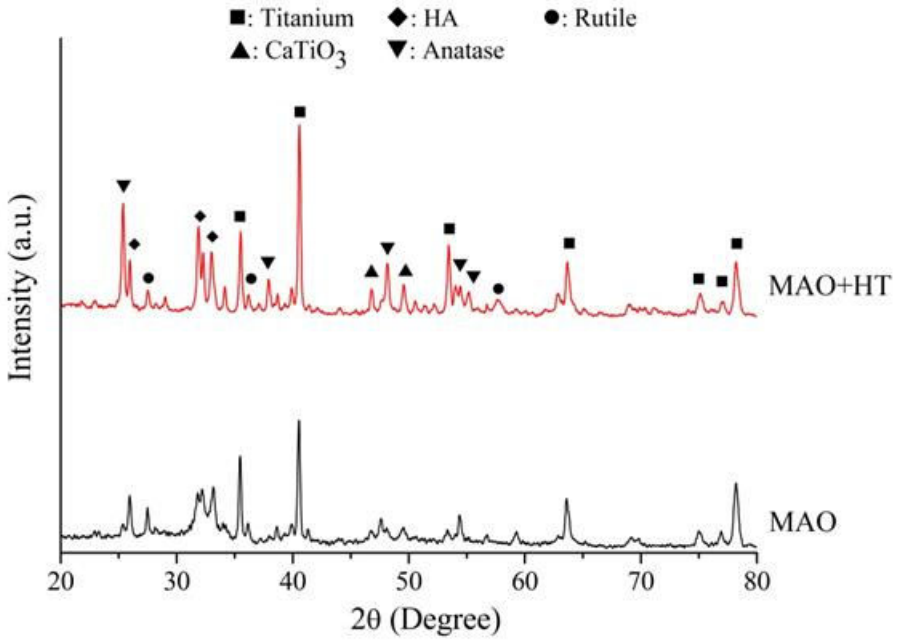

Figure 1. XRD patterns of oxide layers formed on Ti6Al4V before and after HT process.

HT has been applied to the MAO sample at 230 °C for 10 h. Figure2 shows the SEM images of the coating on the surface before and after MAO process. After the MAO process, it can be clearly observed that the whole surface is covered with spherical hydroxyapatite clusters with different sizes between 2 and 30 μm. The characteristic porous TiO_2 layer that is formed during the MAO cannot be seen on the surface due to thick HA layer. Figure2(b) shows the SEM image for the sample that has gone through hydrothermal process at 230 °C for 10 h. After hydrothermal treatment, it was observed that the surface morphology drastically altered.

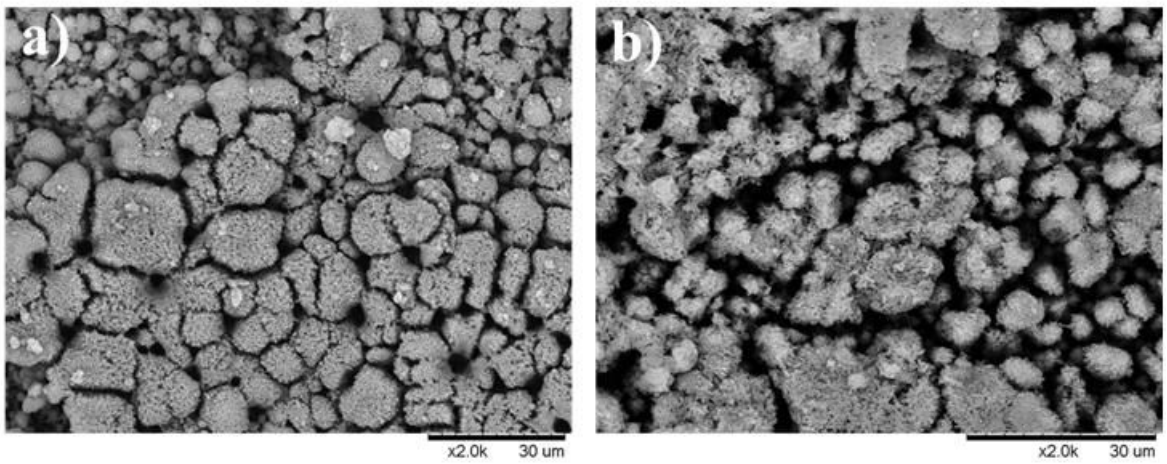

Figure 2. SEM micrographs of oxide layers formed on Ti6Al4V before (a) and after HT process (b).

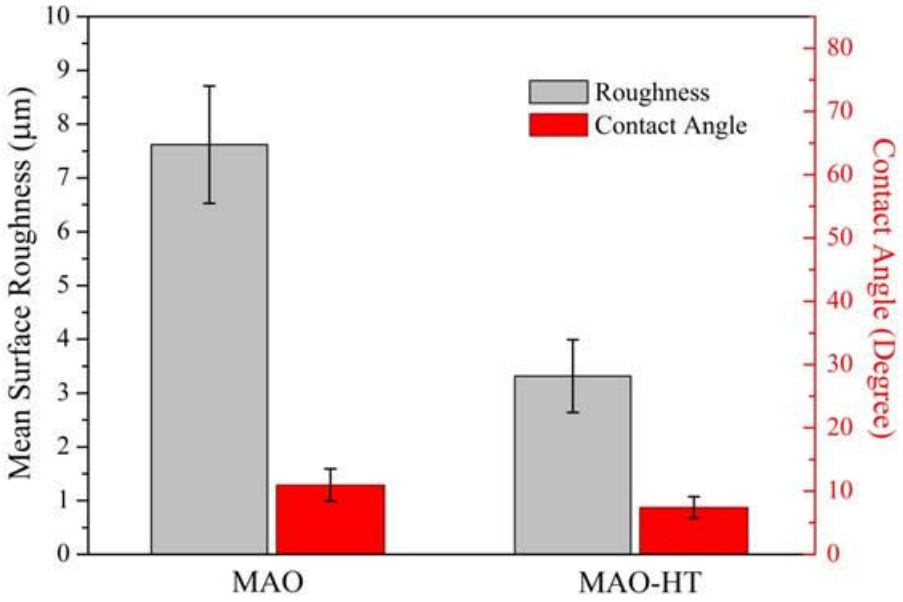

Figure 3. Mean surface roughness and contact angle of MAO and MAO-HT samples.

It is suggested that the spherical HA clusters dissolved under the high temperature and pressure during the hydrothermal process and formed a more sponge like structure. Roughness and wettability of the oxide surfaces before and after HT process (Figure 3) demonstrated that HT process smoothened the HA layer but improved the wettability which is an important indicator of good biocompatibility. The MAO and MAO+HT samples were soaked in a SBF solution at 36.5 °C to evaluate the apatite-forming ability of the samples. SBF is a metastable calcium phosphate solution supersaturated with respect to the apatite. For mimicking the ion concentrations of human blood plasma, SBF solutions have relatively low Ca^{2+} and HPO_4^{2-} concentrations of 2.5 mM and 1.0 mM, respectively. An increased concentration of calcium ions is also required to accelerate the nucleation rate of the hydroxyapatite crystals. SEM images after bioactivity test are shown in Figure4. SEM images for the sample treated for 10 h at 230 °C in HT showed a more intensive bioactive deposition than the MAO sample. Some micro-cracks have been observed on the surfaces. The formation of micro-cracks was attributed to the thickness of the apatite layer and the capillary stresses arising from evaporation of entrapped water in this layer during drying of the samples after removal from the SBF. According to these results it can be stated that the MAO+HT process increases bioactivity.

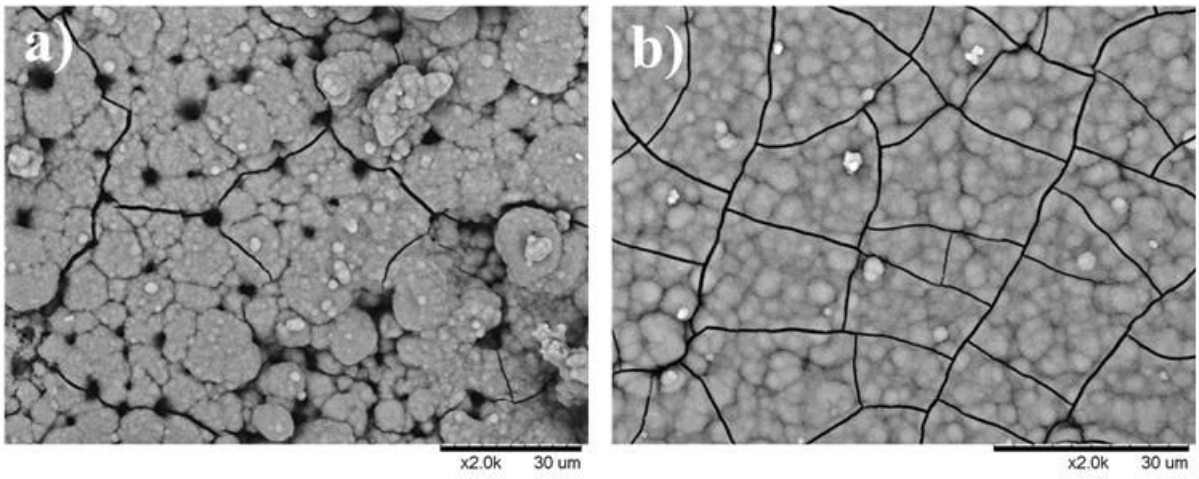

Figure 4. SEM micrographs of surfaces of MAO (a) and MAO-HT (b) samples after immersion in SBF for 72 h.

4. Discussion and Conclusion

HA incorporated titania coatings were formed by MAO process on Ti6Al4V substrate. The coating was mainly composed of rutile, anatase, HA and calcium titanate. After hydrothermal treatment, HA was precipitated on the surface of the titania layer uniformly and decreased the surface roughness. The bioactivity tests demonstrated that the biomimetic apatite deposition enhanced as an indicator of a more favorable surface for biomedical applications.

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