Archives of Materials Science and Engineering

Volume 68
Issue 1
July 2014
Pages 5-9

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

# Preparation and characterization of hydrothermally treated hydroxyapatite containing titania layer on commercially pure titanium

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Received 05.04.2014; published in revised form 01.07.2014

## ABSTRACT

**Purpose:** To investigate the effect of hydrothermal treatment (HT) on bioactivity of micro arc oxidized (MAO) and MAO/) commercially pure titanium (Cp-Ti).

**Design/methodology/approach:** Cp-Ti (Grade IV) samples were oxidized in order to generate titania layer via micro arc oxidation (MAO) process. The samples were treated at 400 V for 5 minutes in a calcium acetate hydrate and disodium hydrogen phosphate anhydrous containing electrolyte. Subsequently, hydrothermal treatment (HT) was applied on oxidized surface in an autoclave with a water solution whose pH adjusted to 11.0-11.5 by adding NaOH, at 200 and 230°C for 2.5, 5 and 10 h and cooled in the autoclave to achieve improved bioactivity behaviour. The bioactivity tests were employed by soaking the samples in a 1.5X simulated body fluid (SBF) to characterize biological response of treated surfaces. The mean elemental composition, surface and cross-sectional morphology, phase composition and surface roughness were examined by energy dispersive spectrometer (EDS) equipped scanning electron microscopy (SEM), X-ray diffractometer (XRD) and profilometer, respectively.

**Findings:** It is found that after MAO+HT process, the surface roughness of the samples was reduced due to the homogeneous distribution of HA agglomerates. The improved surface properties of CP-Ti modified with micro arc oxidation and hydrothermal treatment showed that it can be a good potential candidate for biomedical applications instead of bare CP-Ti.

**Originality/value:** Different HT conditions parameters and the hydroxyapatite crystallization mechanism on oxidized surfaces of the Cp-Ti samples was examined.

**Keywords:** Titanium; Micro arc oxidation; Titania layer; Hydrothermal treatment; Bioactivity

**Reference to this paper should be given in the following way:**

D. Teker, F. Muhaffel, H. Cimenoglu, Preparation and characterization of hydrothermally treated hydroxyapatite containing titania layer on commercially pure titanium, Archives of Materials Science and Engineering 68/1 (2014) 5-9.

## MATERIALS

## 1. Introduction

Titanium and its alloys are widely used in biomedical applications such as orthopaedics and dentistry fields due to their superior mechanical properties, resistance to corrosion and good biocompatibility [1,2]. Formation of native oxide layer on the surface of titanium and its alloys makes them very attractive for implant applications and hence its biocompatibility [3]. However, host responsibility of naturally grown nanometre thick titanium oxide layer is not favourable for chemical bonding with bone tissue.

For the long-term biomedical applications, surface topography of the implants plays an important role for biological interactions within biological environment [4]. Surface roughness and porosity are important factors for osseointegration. After implantation, cell adhesion onto the titanium implant would take place in several months. Therefore, biomedical surfaces should sustain successful growth of osteoblasts on and into the rough surfaces of the implant and rapid formation a structural and functional connection to the hard tissue. It has been reported that higher osseoconductive properties promoting faster attachment of osteoblast cells which play a significant role in early stages of implantations and provide better proliferation of osteoblast cells [5]. In addition, the surface roughness enhances the mechanical stability and improves the bonding strength of the implant-tissue interface [6].

In order to develop rough and porous surface, advanced surface modification techniques such as plasma spraying, anodization and micro arc oxidation (MAO) have been established [7-10]. Recently, MAO technique has received much attention to produce a relatively rough, porous and firmly adherent oxide film containing bioactive calcium and phosphorous integrated biocompatible compounds on titanium and its alloys. The phase composition and microstructure of surface layer can be controlled with adjusting the composition of the electrolyte and process parameter during MAO process. In this study, MAO and hydrothermal treatment (HT) processes were applied successively to modify the titanium surface. 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, simulated body fluid (SBF) immersion test was utilized.

## 2. Experimental procedure

Commercially available pure titanium (Cp-Ti) discs were used as the substrates for MAO process. The samples (Grade IV, Ø10 mm × 4 mm in size) 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. 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 200 and 230°C for 2.5, 5 and 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 (2.5, 5 and 10 h).

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 12 hours 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 [11]. After 12 hours, the samples was removed from SBF and gently rinsed with distilled water. The surface of the samples was dried in air at room temperature.

The surface morphology of the oxide layers were analysed 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 ($R_a$) of the samples was examined by using surface profilometer (Veeco Dektak 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.

## 3. Results and discussion

XRD spectra of the oxide layers obtained by MAO and HT processes at 200 and 230°C are given in Fig. 1 and Fig. 2. The MAO coating is mainly composed of anatase, rutile, calcium titanate and HA. Titanium peaks were detected from the substrate due to penetration of X-rays beyond the coating. The oxide layers were treated

hydrothermally in an autoclave at 200 and 230°C for different durations. It can be seen that the peak intensities of HA increases with the increase of the hydrothermal treatment time. Therefore, it is concluded that HT induced the crystallization of HA phase on the oxide surface.

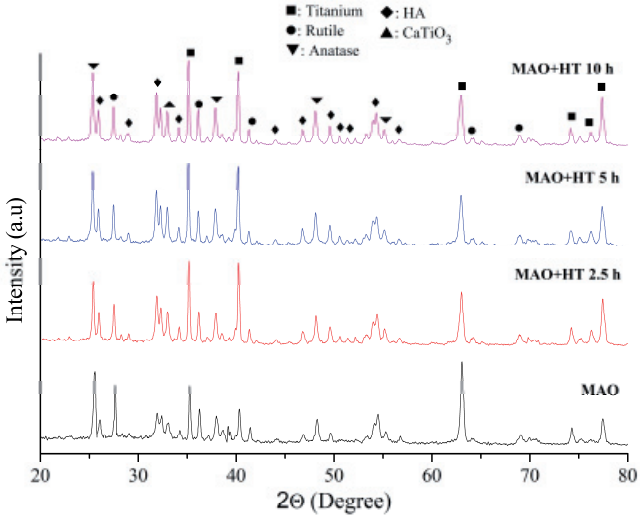


Fig. 1. XRD spectra of MAO and MAO-HT coatings hydrothermally treated at 200°C

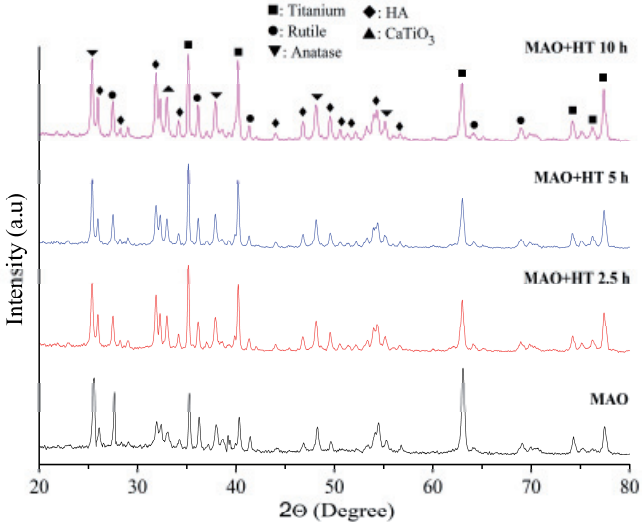


Fig. 2. XRD spectra of MAO and MAO-HT coatings hydrothermally treated at 230°C

HT process has been applied to the samples for different temperature and durations, which have previously treated with MAO process in order to obtain an oxide layer as well as hydroxyapatite phase. Figure 3 shows the SEM micrographs for the oxide samples that were treated HT process at 200°C. Figure 3a shows the SEM micrograph of the coating on the surface after MAO process. After the MAO process, it can be seen that almost the whole surface is covered with a spherical and rough hydroxyapatite layer.

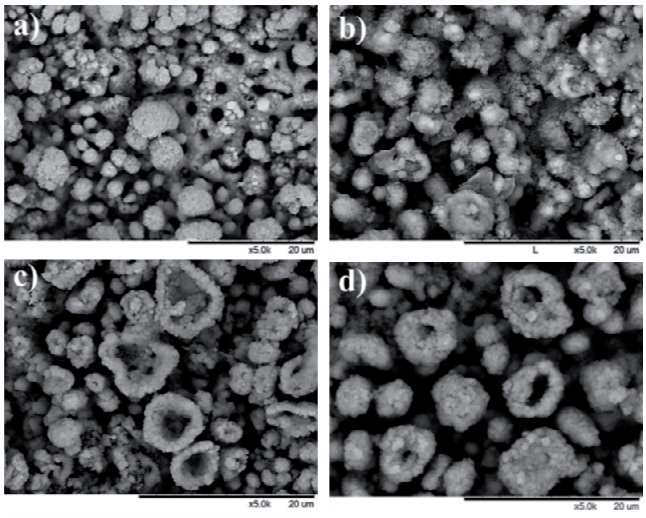


Fig. 3. Surface SEM micrographs of (a) MAO, (b) MAO-HT-2.5 h, (c) MAO-HT-5 h and (d) MAO-HT-10 h samples hydrothermally treated at 200°C

In some regions, the porous $TiO_2$ layer that is formed during the MAO process can be observed. The HT process was applied for 2.5, 5 and 10 h to the previously oxidized surfaces. After HT process, it was observed that the whole surface, as well as the porous structure of $TiO_2$ after MAO, was covered with HA. In addition, some degradations were observed on the spherical structure of the HA layer. The HA layer, which dissolves under the temperature and pressure during the hydrothermal process, formed a more needle like structure when it precipitated again.

Figure 4 shows the SEM micrographs for the samples that were treated by HT at 230°C. The HT process was applied for 2.5, 5 and 10 h, same as 200°C samples. A similar degradation of the HA layer can also be seen on the surfaces. With the increasing temperature, the needle like structure that is formed on the surface can be seen more clearly. Nevertheless, after 10 h of HT process, a different structure appeared on the surface. The HA layer on the surface of the samples at 230°C showed a crater-like structure, along with the needle like formations, after 10 hours of hydrothermal process after MAO. This crater-

like formation can be observed, though in lesser amounts, in all the samples that treated with HT process. However, the sample treated at 230°C for 10 hours is almost completely surrounded by this morphology. It is thought that this new morphology is formed by the HA layer that was coated by MAO, dissolving and re-crystallizing on the surface during the HT process. Moreover, a significant decrease of roughness was observed on the surface of the samples after HT as seen in Fig. 5.

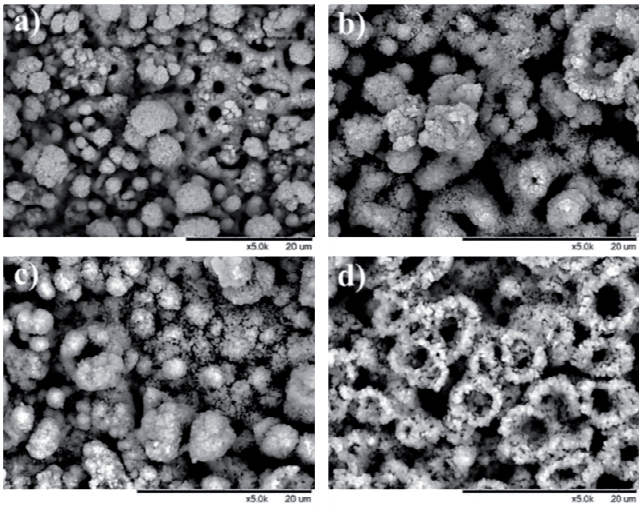


Fig. 4. Surface SEM micrographs of (a) MAO, (b) MAO-HT-2.5 h, (c) MAO-HT-5 h and (d) MAO-HT-10 h samples hydrothermally treated at 230°C

It is suggested that the crystallized apatite structure which is formed with the combination of MAO and HT processes may increase bioactivity of the treated surfaces. In order to confirm this phenomenon and evaluate the apatite-forming ability of the samples; the MAO sample and the sample which was treated with HT for 10 h at 230°C were immersed into the SBF for 12 h. 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 micrographs of MAO and MAO-HT-10 h after bioactivity test are shown in Fig. 6.

After the MAO process, the HA clusters have started to be covered by a newly formed hydroxyapatite layer at the end of the 12 h immersion in the SBF. SEM micrographs for the sample treated for 10 h at 230°C by HT showed that this sample had a more intensive bioactive coating than the sample which treated with only MAO process. The biomimetic coating which was formed in the MAO sample had larger cavities between the apatite clusters, while the MAO-HT sample exhibited relatively far less cavities on the surface. On the MAO+HT sample, some micro-cracks have been even observed after 12 h. 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 increased bioactivity as compared to MAO surface.

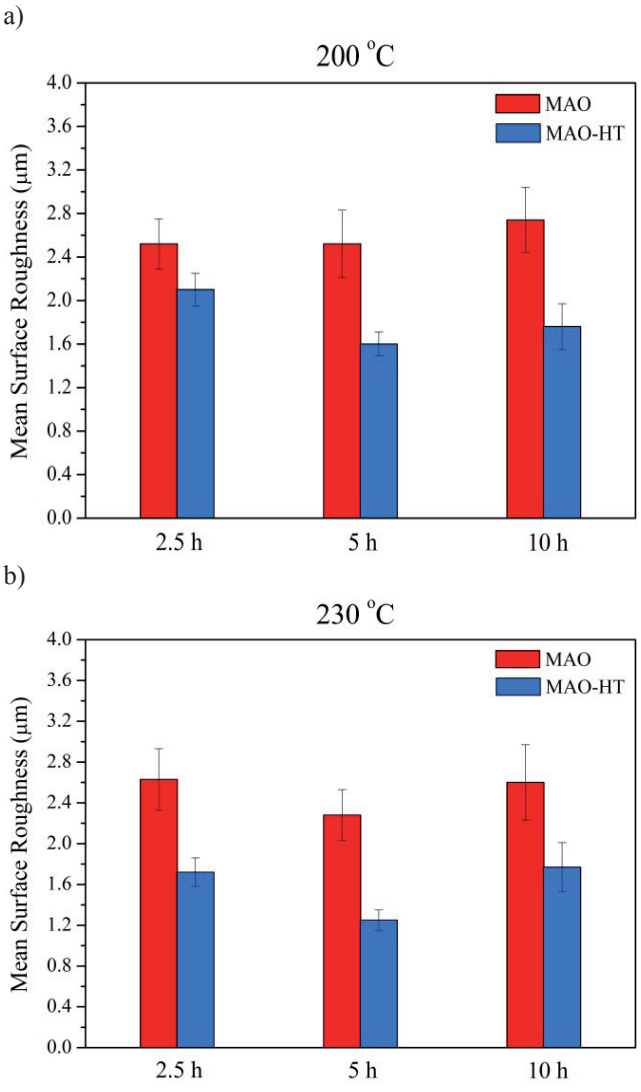


Fig. 5. Mean surface roughness of (a) MAO samples treated at 200°C and (b) MAO samples treated at 230°C before and after HT

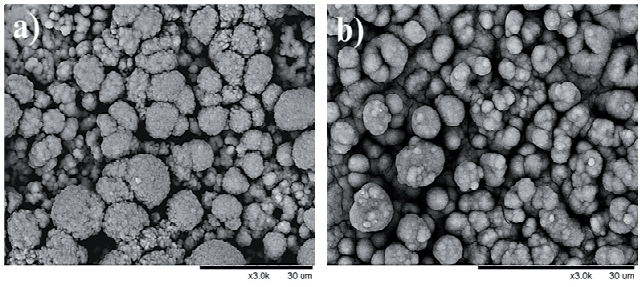


Fig. 6. Surface SEM micrographs of (a) MAO sample and (b) MAO-HT-10 h sample hydrothermally treated at 230°C after immersion in SBF for 12 h

## 4. Conclusions

HA incorporated titania coatings were formed by MAO process on Cp-Ti substrate. The coating was mainly composed of rutile, anatase, HA and calcium titanate. During HT process, 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 was enhanced as an indicator of a more favourable surface for biomedical applications.

## Acknowledgements

The authors wish to thank to the Scientific and Technological Research Council of Turkish for supporting this project (Project No: 111M517).

## Additional information

The presentation connected with the subject matter of the paper will be presented by the authors during the 15th International Materials Symposium (IMSP'2014) in Denizli, Turkey on 15th-17th October 2014.

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