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Surface characterization and corrosion behavior of micro-arc oxidized Ti surface modified with hydrothermal treatment and chitosan coating

Madhav Prasad Neupane, Il Song Park *, Min Ho Lee *

Department of Dental Biomaterials and Institute of Oral Bioscience, School of Dentistry, Chonbuk National University, Jeonju 561-756, South Korea

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ABSTRACT

In the present work, we describe the surface modification of commercially pure titanium (CP-Ti) by a composite/multilayer coating approach for biomedical applications. CP-Ti samples were treated by micro-arc oxidation (MAO) and subsequently some of the samples were coated with chitosan (Chi) by dip coating method, while others were subjected to hydrothermal treatment (HT) followed by chitosan coating. The MAO, MAO/Chi, and MAO/HT/Chi coated Ti were characterized and their characteristics were compared with CP-Ti. X-ray diffraction and scanning electron microscopy were used to assess the structural and morphological characteristics. The average surface roughness was determined using a surface profilometer. The corrosion resistance of untreated and surface modified Ti in commercial saline at 298 K was evaluated by potentiodynamic polarization test. The results indicated that the chitosan coating is very well integrated with the MAO and MAO/HT coating by physically interlocking itself with the coated layer and almost sealed all the pores. The surface roughness of hydrothermally treated and chitosan coated MAO film was superior evidently to that with other sample groups. The corrosion studies demonstrated that the MAO, hydrothermally treated and chitosan coated sample enhanced the corrosion resistance of titanium. The result indicates that fabrication of hydrothermally treated MAO surface coatings with chitosan is a significant approach to protect the titanium from corrosion, hence enhancing the potential use of titanium as bio-implants.

1. Introduction

Titanium and its alloy implants have been increasingly used in orthopedic, dental and craniofacial surgery since the pioneering work of Brånemark in 1969 [1]. The clinical acceptance of titanium implants is accredited to their ability of osseointegration which is a direct and stable anchorage of the implant by the formation of bony tissue at the bone implant interface. There are still challenges in implementing these implants because titanium is a bioinert material, so that it passively integrates with the bone when implanted and the process of osseointegration between the bone and the titanium implant surface needs a longer time [2]. Prevention of acute inflammation around the implant and its susceptibility to biocorrosion in physiological conditions are also major issues when designing such implants. In the presence of chloride ions of simulated body fluid, localized corrosion such as pitting and formation of crevices is observed on titanium [3,4]. Therefore, considerable research has been carried out to address these problems and to improve the performance of titanium implants. Previous studies have shown that surface treatment of titanium with chitosan coatings [5], calcium and phosphorus ion implantation [6,7], (Ti, Zr) N layer deposition [8], carbon nanotubes hydroxyapatite composite coatings [9], and chitosan–hydroxyapatite-multiwalled carbon nanotube composite coatings [10] could effectively reduce the limitations of implants. Micro-arc oxidation (MAO) is a simple and promising electrochemical approach which can produce porous, relatively rough, and firmly adherent titanium oxide coatings on the surface that alters the surface characteristics of titanium [11]. After MAO, hydrothermal treatments (HT) have been used to transform the Ca–P compounds incorporated in the MAO-treated oxide layer to hydroxyapatite which alters the surface characteristics of the MAO-treated surfaces. A variety of surface modification techniques have also been used to reduce the period of osseointegration and increase their applicability to poor bone quality [12,13]. Also, the topographic features of implants on the nanoscale are thought to determine the biological response of the host [14,15].

Chitosan (Chi) is a linear polyamine that possesses unique physicochemical properties like biocompatibility, non-toxicity, biodegradability, excellent film forming ability and antibacterial activity [16]. Further, byproducts of degraded chitosan are also non-toxic, since they are simple sugars and are processed as part of normal cellular metabolism [17]. It has been reported that chitosan and its derivatives are environment friendly and they can be deposited as protective coatings on metallic implants aiming to control the rate of corrosion and to increase the biocompatibility [18–20]. Considerable research has been devoted towards modification of titanium surfaces by composite coatings in order to obtain different types of coatings that are more biocompatible, bioactive and corrosion resistant. Martin et al. [5] have reported that chitosan coating enhanced the integration of dental and orthopedic implants in

* Corresponding authors. Tel.: +82 63 270 4042; fax: +82 63 270 4040.
E-mail addresses: ilsong@jbnu.ac.kr (I.S. Park), mh@jbnu.ac.kr (M.H. Lee).

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the surrounding bone tissue. Bumgardner et al. [17] have demonstrated that the chitosan coatings were chemically bonded to titanium and improved the biological response of osteoblastic cells. Hydroxyapatite/chitosan (HA/Chi) is of special interest for biomedical applications. Many reports have focused on the fabrication of HA/Chi coatings [21,22]. However, not many reports have explored the characteristics of hydrothermally-treated, MAO-coated Ti surfaces which have been subsequently coated with chitosan polyelectrolyte. The present paper aims to address surface modification of commercially pure titanium (CP-Ti) substrate by MAO and in situ hydrothermal crystallization of HA. Chitosan is also coated on MAO treated Ti and MAO/HT titanium, in order to modify the surface properties with the ultimate goal of developing composite/multilayer coatings with better anticorrosion and bioactive properties. Besides its biocompatibility, the choice of chitosan is made on the basis that the reactive amine and hydroxyl groups of chitosan could be exploited to impart a better corrosion resistance with self-healing properties and good adhesion.

2. Experimental details

2.1. Surface preparation and surface treatment by microarc oxidation, hydrothermal treatment and chitosan coating

Commercially pure titanium (CP-Ti) (grade 2) plates (dimensions: 20 mm × 10 mm × 2 mm) were used as the substrate material. They were abraded using successive grades of SiC coated abrasive paper (220 to 800 grits) and chemically pickled using a mixture of HNO_3, HF and water in the volume ratio of 1:3:6. The Ti samples prepared according to the above procedure are referred as pure Ti. The pure Ti samples were subjected to different surface treatments. One set of samples was treated by MAO in 0.15 M calcium acetate and 0.02 M calcium glycerophosphate as the electrolyte solution at 350 V and 50 mA/cm^2 for 10 min [11]. During MAO treatment, the Ti plates served as the anode while a Pt plate served as the cathode. These samples are referred to as MAO. One set of MAO treated Ti samples were subjected to hydrothermal treatment in 200 ml deionized water at 250 °C for 3 h in an autoclave (ILSHIN, Korea). After hydrothermal treatment, the samples were washed with deionized water and dried in oven at 40 °C for 24 h. These samples are referred as MAO/HT. One set of MAO and MAO/HT samples were subjected to chitosan coating. Chitosan powder (Mw = 200 kDa, ≥93% deacetylated) from Sigma-Aldrich Chemicals was used. The chitosan solution was prepared using 1 wt.% acetic acid as the solvent in which 1 g of chitosan was dissolved per 100 mL to give 1% solution. The chitosan coating was deposited by dip coating method which involves immersion of the MAO and MAO/HT samples in the petri dishes for 5 min at room temperature followed by its slow withdrawal at the rate of 1.5 mm/s and drying at 37 °C. These samples will be referred to as MAO/Chi and MAO/HT/Chi, respectively.

2.2. Surface characterization

The surface morphology of the treated samples was characterized by scanning electron microscopy (SEM) (JEOL JSM-5900, Japan) with an accelerating voltage of 15.0 kV. ImageJ software (NIH, USA) was used to measure individual diameters of the pores in each micrographs. The structural characteristics of the coatings were determined by X-ray diffraction (XRD) (Dmax III-A type, Rigaku Co., Japan) using Cu Kα incident radiation, a tube voltage of 40 kV and a current of 30 mA. The scanning angle ranged from 10° to 70° 2θ with a scanning rate of 4°/min. The surface roughness was determined using a Surftest Formtracer (Surftest SV-402, Mitutoyo Instruments, Tokyo, Japan). A 2-μm diamond stylus was used to determine the center line average roughness (R_a) along a length of 10 mm. Among the various roughness parameters, the average surface roughness (R_a) was used as the parameter for comparing the influence of different surface treatments. The corrosion resistance of treated and untreated Ti samples was evaluated using potentiodynamic polarization studies using commercial saline at 298 K as the corrosive medium. A standard three-electrode electrochemical cell (PAR STAT 2273) with an electrolyte volume of 200 ml was used for the electrochemical measurements. Treated and untreated Ti samples having an exposed area of 0.78 cm^2 were served as the working electrode, whereas Ag/AgCl/satd KCl electrode and a Pt gauze electrode served as the reference and counter electrodes, respectively. The polarization scan was performed within the range of −0.6 to +0.6 V potential (vs. Ag/AgCl, KCl satd) at a scan rate of 2 mV/s.

2.3. Statistical analysis

Statistical analysis was performed using one-way analysis of variance to evaluate differences between the groups. Data were presented as the mean ± SD (n = 3). $p < 0.05$ was considered statistically significant.

3. Results and discussion

Fig. 1 shows the surface morphologies of MAO, MAO/Chi, MAO/HT, and MAO/HT/Chi coated titanium over an area 1 cm^2 assessed by SEM. The surfaces of MAO treated samples (Fig. 1(a)) revealed the presence of dispersively distributed pores with the pore diameter ranging from 1 to 2 μm and some microcracks. The size of the pores depends on the nature of the electrolyte used and applied voltage. The morphological features of MAO/Chi coated titanium (Fig. 1(b)) revealed sealing of the porous structure of the MAO treated surface by the chitosan coating. The chitosan coating was well integrated with MAO coating by physical interlocking. The chitosan coating not only covered the surface but also penetrated through the pores and micro-cracks, originally present on the MAO treated surface. The surface of MAO/HT treated Ti exhibited the formation of HA crystals, which were precipitated around or inside the pores and throughout the surface (Fig. 1(c)). The Ti–OH groups formed on the surface of MAO treated Ti during hydrothermal treatment induced nucleation of HA [23]. Fig. 1(d) shows the morphological features of MAO/HT/Chi coated titanium. It is evident that the chitosan coating is tightly entrapped within hydroxyapatite crystals. The porous structure of MAO coating was sealed by the HA crystals and chitosan coating. The sealing of pores in MAO coating by HA and chitosan is likely to diminish the direct contact of the Ti substrate with the simulated body fluid and would offer a better corrosion protection. In addition, both HA and chitosan are biocompatible, the MAO/HT/Chi coated titanium is expected to serve as a biocompatible surface with corrosion protective ability for the development of bio-implants. Although, the degradation of chitosan in later phase is inevitable, the layers of HA and titanium oxide protect the properties of the implants. On initial implantation stage chitosan shows bactericidal effect, hemostatic activities and promotes wound healing [24,25].

Fig. 2 shows the XRD patterns of both untreated and surface modified samples obtained using different treatments. CP-Ti revealed the presence of the α-titanium peaks only, (Fig. 2(a)) because it is a material with α-titanium structure. MAO treated Ti indicated the presence of anatase and small amount of rutile TiO_2 crystalline phases (Fig. 2(b)). During anodic oxidation of titanium, TiO_2 film formation takes place due to the migration of oxygen ions towards the anode and titanium ions from anode towards the metal-electrolyte interface when current is passed through an electrolyte [26]. The appearance of rutile phase in the oxide layer signifies that MAO coating has a stable structure. The XRD patterns of the MAO/Chi coated Ti showed no notable change in the peak intensities (Fig. 2(c)) when compared with MAO treated Ti (Fig. 2(b)). This inference indicates that the thin chitosan coating remained attached to the TiO_2 film but did not cause any significant change in the peak intensity of the TiO_2 coating after the deposition of the chitosan. The XRD pattern of MAO/HT titanium revealed the presence of several peaks corresponding to HA in addition to the peaks associated with anatase TiO_2 phase (Fig. 2(d)). Moreover, the hydrothermal treatment promoted the crystallization of anatase TiO_2 as