Fabrication and Characterization of Functionally Graded Nano-Micro Porous Titanium Surface by Anodizing

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Abstract: The purpose of this study was to fabricate and characterize nanotubular structure on machined titanium (MA) and resorbable blast media (RBM) treated titanium by anodizing. The anodized MA and RBM were characterized with scanning electron microscopy, transmission electron microscopy, X-ray diffraction, energy disperse spectra, X-ray photoelectron spectra, and nano-indentation and scratch test. Highly ordered nanotubular layers of individually 100 nm in diameter and 500 nm in length approximately were formed regardless of the substrates. The nanotubular layers consisted mainly of amorphous TiO2 with trace fluorine. The nanotubular surfaces on both the substrates significantly reduced water contact angles and elastic modulus compared with those prior to anodizing. The anodizing treatment significantly increased the surface roughness of the smooth MA, but significantly decreased the surface roughness of the roughened RBM. The critical delamination forces of the nanotubular layer were not obtained due to the limitation of surface roughness. The anodized RBM consisted of a nano-micro porous graded structure, or a nanotubular amorphous fluoride containing TiO2 layer on top of micro-roughened titanium surface, which is expected to significantly improve the surface area that can be used to deliver drugs and growth factors and alleviate the interfacial elastic modulus mismatch as to enhance osseointegration when compared with conventional dental and orthopedic implant devices with smooth or acid etched surface. © 2008 Wiley Periodicals, Inc. J Biomed Mater Res Part B: Appl Biomater 88B: 427–435, 2009

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INTRODUCTION

Titanium and its alloy implants have been widely used to restore the function of missing teeth or severely degenerated hip joints. Titanium and its alloy possess high mechanical strength, biocompatibility, and low toxicity. In addition, titanium exhibits better longevity in comparison with other miscellaneous alloys such as stainless steel and cobalt chromium alloys. The clinical success of dental implants is due to the osseointegration. Osseointegration, the histological direct bone–implant contact, has been considered the pre-requisite for implant loading, and is critical for initial fixation and long-term clinical success of endosseous dental and orthopedic implants. To achieve secure osseointegration, the following factors must be recognized: biocompatibility of implant material; implant surface;...
implant design; surgical approach; condition of the patient; biomechanical status and time. In addition, osseointegration may fail to occur in the absence of primary stability and limitation of micromotion of the implant during healing. Many researchers have investigated the effect of implant surface treatment on the improvement of bone-to-implant contact without an intervening fibrous soft tissue. Various methods have been studied for creating a rough surface and enhancing the osseointegration of dental implants, such as titanium plasma spraying, grit-blasting, acid-etching, anodizing, and calcium phosphate. The roughened implants affect the rate of osseointegration and biomechanical fixation. Roughened titanium dental implants exhibit higher bone–implant contact area and greater pull out strength.

Among these methods, anodizing is an electrochemical treatment and used to modify titanium surface. In anodizing, the titanium specimen is immersed in an electrolyte and applied with electricity. As a result, a rough and porous titanium oxide (TiO₂) thin layer is then formed. The formed TiO₂ layer has been reported to efficiently improve the cellular activities on titanium in vitro and bone–implant bonding properties in vivo. Recently, a nanoscale titanium oxide texture is of great interest because of the higher surface area. The nanostructured TiO₂ films coated by metal-organic chemical vapor deposition enhanced the osseointegration. The osteoblast adhesion was increased on Ti, Ti-6Al-4V, and CoCrMo alloy with nanophasic compared with conventionally sized particles, and osteoblasts were observed to adhere specifically at nanometer particle boundaries. In the past, we have developed new Ti-10Ta-10Nb alloy, which has been proved to have excellent mechanical properties and corrosion resistance, and also evaluated its sputtered nanoscale coating for biomedical applications. In another previous study, we treated smooth machined titanium using anodizing and optimized the parameters to prepare nanotubular structure. In the present work, we fabricated the nanotubular structure on the roughened resorbable blast media (RBM) treated titanium and characterized the surface properties of the anodized RBM.

**MATERIALS AND METHODS**

The disks of commercially pure titanium with 15 mm diameter and 1 mm thickness were used and divided to machined (MA) and RBM-treated surfaces. Before anodizing, the specimens were ultrasonically cleaned in acetone, ethanol for 10 min successively, followed by rinsing with distilled water for 30 min and drying.

The disks were used as an anode, and platinum plate as a cathode. The distance between the anode and cathode was 10 mm. Based on our previous optimizing anodizing parameters, the anodizing procedure was carried out using a 20 direct current (DC) voltage (Fine Power F-3005, SG EMD, Korea) for 10 min in the electrolyte of 1M H₃PO₄ solution with the addition of 1.5 wt % HF at room temperature. The working current transient curve is shown in Figure 1. A high current was observed instantly when the anodizing voltage was applied to the titanium specimen and then decrease to a stable state within a few minutes. Small range of current fluctuation can be observed in the stable state (insert box in Figure 1).

![Figure 1. Current-time curve at constant voltage during the anodizing process in 1M H₃PO₄ + 1.5 wt % HF electrolyte. A high current was observed instantly when the anodizing voltage was applied to the specimen and this high current dropped to the stable state within a few minutes. Small range of current fluctuation can be observed in the stable state (insert box in Figure 1).](image)

The structure, morphology and chemical composition of the surfaces were characterized using field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan) with energy dispersive spectra (EDS). Transmission electron microscopy (TEM, JEM-2000FXII, JEOL, Japan) was used to observe the thickness and topography of the porous layer scraped from the surface of specimen with knife. The compositions of the porous layer were also investigated by X-ray photoemission spectroscopy (XPS, MultiLab 2000 System, ThermoVG Scientific, UK) with Ar⁺ sputtering at 2 kV. In the XPS spectra, all the characteristic peaks were calibrated to the binding energy of C 1s (284.6 eV). A D8 Advanced X-ray diffractometer (Bruker, Madison, WI) was used to characterize the structure of sample surfaces. Surface roughness was measured using a profilometer (Diate DH-7, Asmeto AG, Switzerland). The measured surface roughness was represented as Rₚ (arithmetical mean roughness), and 10 samples per group were used. Water contact angles were measured using an optima video contact angle measuring system (AST, Billerica, MA), and 10 samples per group were used.Nano-indentation and scratch test were performed using a Triboindentor (Hysitron, Minneapolis, MN) to evaluate elastic modulus and delaminating failure. Nano-indentation tests were carried out using continuous measurement technique. An array of 16 indents was performed on each sample with successive indents separated by 50 μm. Scratch test input parameters: scratch length: 10 μm; scratch velocity: 1 μm/s; the normal load...
Figure 2. FE-SEM images of TiO₂ nanotubes; (a) machined surface ×1000, (b) anodized machined surface ×5000, (c) anodized machined surface ×50,000, (d) RBM surface ×1000, micro-roughened surface by sandblasting, (e) anodized RBM surface ×5000, the sharp edges of micro-roughened surface was smoothed, (f) anodized RBM surface ×50,000. The morphology and diameter of nanotubes on the micro-roughened surfaces were similar to those of the machined surfaces.

Figure 3. Cross-section and top-view FE-SEM images of TiO₂ nanotubes at 20 V for 10 min in 1M H₃PO₄ + 1.5 wt % HF electrolyte. Machined (a,b) and RBM (c,d) surface. It is observed that the one-end closed individual nanotubes were connected with each other via the sidewalls of the tubes. The formed individual nanotubes were ~500 nm in length and 100 nm in diameter.
was increased from 0 μN to maximum load up to 1000 μN; the scratch tests were performed in ramp positive forward mode. Scratch critical load or critical force for delamination was determined using the program combined with analyses from penetration curve versus scratch distance, friction force along scratch versus scratch distance, friction coefficient versus scratch distance and observation of the scratch. Three samples per group were used for nanoindentation and nano-scratch test. The surface roughness, water contact angles, and elastic moduli of the samples were statistically compared using ANOVA, and difference was considered significant if $p < 0.05$.

**RESULTS**

Figure 2 shows the representative surface morphology of the treated surfaces. At low magnification, the MA surface was smooth and scratched [Figure 2(a)]. The RBM surface was rough [Figure 2(b)]. At higher magnification, the MA surface is smooth and dense [Figure 2(c)]. The sharp edge of micro-roughened surface of the RBM was smoothed by anodizing but the micro-roughness was maintained [Figure 2(d)]. At even higher magnification, highly ordered nanotubular textures were observed on both the anodized smooth MA and rough RBM [Figure 2(e,f)]. The newly formed nanotubular structures were similar in morphology and size regardless of the substrates. On the contrary, at very high magnification, both the MA and RBM in the absence of anodizing are very dense (data not shown).

Figure 3 shows the high resolution cross-section and top-view morphology of the nanotubular layer prepared by anodizing. A one-end closed nanotubular layer was observed. The formed individual nanotubes were ~500 nm in length and 100 nm in diameter (Figure 3). The individ-
tubular structures were connected with each other via the sidewalls of the tubes, which was similar to other studies. The one-end closed nanotubular structure was clearly confirmed by the TEM images (Figure 4). The closed end was in contact with the titanium substrate and the open end with the electrolyte. The sizes of the nanotubes are consistent with the data in Figure 3. The selected area diffraction pattern (SADP) clearly exhibits that the nanotubular layer has an amorphous structure (Figure 4). The amorphous structure of the nanotubes was also verified by the XRD patterns because only z-phase titanium peaks instead of TiO2 peaks were observed (Figure 5).

In addition to surface morphology and crystal structure, the chemical composition of the nanotubular layer was characterized using EDX and XPS. The presence of titanium, oxygen and trace of fluorine were detected from the EDX spectra. The peak of copper was arisen from the grid used for the sample preparation (Figure 6). In the XPS spectra, the binding energy of O 1s was 530.6 eV, which is similar to that of oxygen in TiO2. The Ti 2p3 peak was at 458.7 eV (TiO2 reference 458.5 eV). It suggested that the nanotubes are consisted of TiO2. Carbon, oxygen, titanium, and trace of fluorine were also detected on the anodized nanotubular surfaces (Figure 7).

After anodizing, the surface roughness of the MA was significantly increased, but the surface roughness of RBM was significantly decreased (Table I). The decrease in roughness of the anodized RBM is probably due to the smoothing of the sharp edge shown in Figure 1. Table II lists water contact angles on the MA and RBM in the absence and presence of anodizing. The water contact angles on the anodized nanotubular MA and RBM were significantly decreased compared with those in the absence of anodizing. In addition, the rough RBM exhibited significantly lower water contact angles compared to the smooth MA.

Nano-indentation results revealed that the elastic moduli of the MA and RBM are 128.4 ± 13.3 and 110.3 ± 30.7 GPa, respectively. The elastic moduli of the anodized nanotubular MA and RBM are 78.8 ± 29.4 and 59.1 ± 29.2 GPa, respectively. The anodized nanotubular layer on the MA and RBM significantly reduced their elastic moduli compared with the substrates without anodizing. However, the critical delamination force was not obtained in this experiment because of the limitation of surface roughness of the samples.

![Figure 5. X-ray diffraction patterns of machined and RBM surfaces; (a) before anodizing, (b) after anodizing. Only z-phase titanium peaks were observed.](image)

![Figure 6. EDX data of TiO2 nanotubes; (a) machined surface, (b) RBM surface. The presence of titanium, oxygen, and trace of fluorine were detected from the EDX spectra. The peak of copper was arisen from the grid used for the sample preparation.](image)
Surface topography, wettability and mechanical properties of implant devices are of great importance for dental and orthopedic applications. In our previous study, functionally macro–micro porous graded titanium coatings have been prepared using plasma spraying. The macro-pore size was more than $150 \mu m$ that allows bone ingrowth and the micro-pore size was less than $10 \mu m$ that allows increasing surface area. Their biological evaluation exhibited improved cell response \textit{in vitro} and osseointegration \textit{in vivo}. In general, the morphology and dimension of nanotubular layer on titanium are determined by applied voltage, electrolyte concentration, and anodizing time. The hydrofluoric acid has been used as electrolyte to dissolve the titanium oxide, and nanotubes can be formed in fluoride containing electrolytes or in a mixture of fluoride and other acids such as sulfuric acid and acetic acid. A highly ordered TiO$_2$ nanotubular layer up to about 500 nm thickness were formed in electrolyte with hydrofluoric acid and at low potential of 5–20 V. Anodic oxidation of titanium in an aqueous solution containing 0.5–3.5 wt % hydrofluoric acid were reported to prepare well-aligned and high-density arrays of titanium oxide. In this study, the sharp drop in current transient curve within a few seconds in Figure 1 indicates the formation of an oxide layer. The relatively uniform nanotubular layer, individually 100 nm in diameter and 500 nm in length approximately, were fabricated in the 1M H$_3$PO$_4$ and 20 V in voltage regardless of the smooth MA and rough RBM substrates. This has suggested that surface roughness of titanium substrate did not affect morphology and dimension of the nanotubular layer prepared by the anodizing.

In addition to morphology, the SADP and XRD patterns clearly revealed that the as-anodized nanotubular layer has an amorphous structure, which was consistent with other study. It is worth noting that titanium dioxide can be both amorphous and crystalline structures depending on anodizing parameters. The structure of the nanotubes has been reported to be amorphous at low voltages, and crystallization takes place at higher voltages. The amorphous structure also can be changed to crystalline structure with heat treatment. The crystalline structure of TiO$_2$ layer affects the formation of apatite and biocompatibility. A mixed anatase and rutile nanotubular structure appears to be more efficient to promote the formation of apatite compared with a plain anatase structure.

In terms of chemistry, in addition to majority titanium and oxygen, the trace of fluorine (F) was detected from the micro-roughened surface as a nano-micro porous graded structure on titanium substrate.

The formation of nanotubular structure on titanium depends on the equilibrium between chemical oxide dissolution and electrochemical oxide formation in electrolyte. In brief, the formation mechanism of nanotubular layer on titanium is probably related to selectively and orientationally localized dissolution with electrolyte and electrical field assistance. In general, the morphology and dimension of nanotubular layer on titanium are determined by applied voltage, electrolyte concentration, and anodizing time. The hydrofluoric acid has been used as electrolyte to dissolve the titanium oxide, and nanotubes can be formed in fluoride containing electrolytes or in a mixture of fluoride and other acids such as sulfuric acid and acetic acid. A highly ordered TiO$_2$ nanotubular layer up to about 500 nm thickness were formed in electrolyte with hydrofluoric acid and at low potential of 5–20 V. Anodic oxidation of titanium in an aqueous solution containing 0.5–3.5 wt % hydrofluoric acid were reported to prepare well-aligned and high-density arrays of titanium oxide. In this study, the sharp drop in current transient curve within a few seconds in Figure 1 indicates the formation of an oxide layer. The relatively uniform nanotubular layer, individually 100 nm in diameter and 500 nm in length approximately, were fabricated in the 1M H$_3$PO$_4$ and 20 V in voltage regardless of the smooth MA and rough RBM substrates. This has suggested that surface roughness of titanium substrate did not affect morphology and dimension of the nanotubular layer prepared by the anodizing.

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**Figure 7.** XPS profiles of the anodized specimens; (a) anodized machined surface, (b) anodized RBM surface. Carbon, oxygen, titanium, and trace of fluorine were detected on both smooth and rough surfaces.

**Table I.** Surface Roughness of MA and RBM Substrates Before and After Anodizing

<table>
<thead>
<tr>
<th>Material</th>
<th>Roughness ($\mu m$)</th>
<th>Before</th>
<th>After</th>
</tr>
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<tbody>
<tr>
<td>MA</td>
<td>0.35 ± 0.05</td>
<td>0.52 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>RBM</td>
<td>1.95 ± 0.10</td>
<td>1.57 ± 0.10</td>
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Selection of length of traverse, $L_t = 4.5$ mm; Selection of cutoff, $L_c = 0.5$ mm. The data are listed as mean values ± standard deviations ($N = 10$).

**Table II.** Water Contact Angles of MA and RBM Substrates Before and After Anodizing

<table>
<thead>
<tr>
<th>Material</th>
<th>Before Anodizing</th>
<th>After Anodizing</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>65.3 ± 6.2</td>
<td>27.2 ± 5.4</td>
</tr>
<tr>
<td>RBM</td>
<td>33.6 ± 5.9</td>
<td>18.9 ± 6.1</td>
</tr>
</tbody>
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The data are listed as mean values ± standard deviations ($N = 10$).
nanotubular layer in XPS with the total sputter depth of ~10 nm. Fluorine was also detected in other studies. It originated from electrolyte but other significant anion from the electrolyte was not detected. The presence of fluorine with titanium and oxygen also was detected in the results of EDS. Therefore, the nanotubular layer is an amorphous fluoride containing titanium dioxide. The fluoride presence in the TiO$_2$ nanotubular layer will potentially affect osteoblast differentiation in vitro and interfacial bone formation in vivo.

As we discussed above, micro-scale surface roughness of titanium substrate appeared not to affect morphology and dimension of the nanotubular layer prepared by the anodizing. However, the anodizing does change the micro-scale surface roughness of the two substrates, MA, and RBM. At the micro-scale level, the anodized MA exhibited significantly greater surface roughness compared with the MA, but the anodized RBM exhibited significantly decreased surface roughness compared with the RBM. Regardless of the changes in the micro-scale surface roughness, the water contact angles on the anodized nanotubular layers were significantly reduced, which is consistent with the so-called super-hydrophilic wetting behavior of the TiO$_2$ nanotubes. The super-hydrophilicity of the nanotubular layer regardless of the microscale surface roughness is probably a result of its increased surface area. The surface area of the nanotubular layer will be further investigated.

It is interesting that the nanotubular layer on anodized titanium substrates exhibited significantly lower elastic modulus compared with the smooth MA and rough RBM, which was approaching the modulus of bones. Similar result of reduced elastic modulus of titanium nanotubes was also reported by Crawford et al. The lower elastic modulus is a result of porous structure of nanotubes and their density. Critical force for delamination using a nano-scratch test was originally attempted to evaluate the failure strength of the nanotubular layer. However, the rough surfaces, including the relatively smooth MA limited the collection of valid data. The evaluation of the failure strength of the nanotubular layer will be further studied. However, the design of nano-micro graded porous structure probably to some extent helps prevent the delamination failure of the nanotubular layer embedded in micro-scale rough surface compared with the micro-scale smooth surface.

CONCLUSION

In the present study, the functionally graded nano-micro porous titanium surface has been fabricated using anodizing. The anodized RBM is an amorphous fluoride containing titanium dioxide nanotubular layer embedded in micro-scale roughened titanium. The amorphous titanium dioxide nanotubular layer significantly improves the hydrophilicity. The increased surface area of the nanotubular layer is expected to deliver drugs to prevent infection and growth factors to enhance bone formation. The reduced elastic modulus of the nanotubular layer is expected to alleviate the severe elastic modulus mismatch between bone and implant devices, thereby possibly reducing bone resorption caused by stress shielding and enhancing osseointegration.

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REFERENCES