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ScienceDirect
Acta Biomaterialia 4 (2008) 1518–1529
Acta BIOMATERIALIA
www.elsevier.com/locate/actabiomat

# UV-enhanced bioactivity and cell response of micro-arc oxidized titania coatings

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Received 3 November 2007; received in revised form 31 January 2008; accepted 20 March 2008
Available online 8 April 2008

**Abstract**

Using ultraviolet (UV) irradiation of micro-arc oxidized (MAO) titania coating in distilled water for 0.5 and 2 h, we have achieved an enhanced bioactivity and cell response to titania surface. The MAO coating appears porous and predominantly consists of nanocrystallized anatase $TiO_2$. Compared with the MAO coating, the UV-irradiated coatings do not exhibit any obvious change in surface roughness, morphology, grain size and phase component; however, they have more abundant basic Ti–OH groups and become more hydrophilic because the water contact angle decreases significantly from $17.9 \pm 0.8°$ to 0°. In simulated body fluid (SBF), bonelike apatite-forming ability is significantly stronger on the UV-irradiated coatings than the MAO coating. SaOS-2 human osteoblast-like cell attachment, proliferation and alkaline phosphatase of the cell are greater on the UV-irradiated coatings relative to the MAO coating. UV irradiation of titania results in the conversion of $Ti^{4+}$ to $Ti^{3+}$ and the generation of oxygen vacancies, which could react with the absorbed water to form basic Ti–OH groups. The enhanced bioactivity and cell response of the UV-irradiated coatings are proven to result from abundant Ti–OH groups on the coating surfaces. After storing the UV-irradiated coatings in the dark for two weeks, the basic Ti–OH groups on the coatings slightly decrease in amount and can induce apatite formation after a short period of SBF immersion, and show relative long-term stability.


*Keywords:* UV-light; Titania coating; Bioactivity; Cell response; Micro-arc oxidation

## 1. Introduction

Titanium and its alloys are widely used for orthopedic and dental implants due to their good mechanical properties and biocompatibility. However, titanium is bio-inert and cannot directly bond to bone immediately after implantation. To overcome this drawback, hydroxyapatite (HA) coatings are used as bioactive surfaces of titanium implants, and many processing techniques for such materials have been developed [1–5]. In addition, alternative biolayers formed by ion implantation of calcium and phosphorus onto titanium surface have been explored [6–8]. All the efforts in both construction and processing are intended to endow the bioactive coatings or layers with firm adhesion and structural stability for long-term clinical use. Although such coatings and layers are to a great extent successful, it is difficult to make them porous and to apply them to implants with complex surface geometry. It is known that a micrometer-sized porous [9] and nanocrystallized [10] surface of an implant is beneficial to promoting osteoblast attachment and proliferation, and accelerating osseointergration. On the other hand, a titanium implant coated with a low elastic modulus substance can eliminate stress-shielding, promoting bone remodeling and preventing the implant from fracture failure [11,12]. Hence, bioactive, porous and nanocrystallized coatings with low elastic modulus on titanium implants are of great interest.

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doi:10.1016/j.actbio.2008.03.005

Micro-arc oxidation (MAO) is a relatively convenient technique for forming oxide ceramic coatings on Ti, Al, Mg and their alloys. An advantage of the MAO process is that the formed coatings are not only porous but also uniformly coated on metal surfaces with complex geometry. Moreover, MAO coatings usually exhibit good adhesion to substrates. Since Ishizawa et al. first applied the technique to biological modification of titanium implants [13–15], two kinds of titania-based coatings formed by a one-step approach to MAO have been developed for the purpose. One is titania-based duplex coatings composed of $TiO_2$, $CaTiO_3$, $Ca_2P_2O_7$ and $Ca_3(PO_4)_2$ [16–18] or $TiO_2$ and HA [19–21], which are bioactive and can be produced in electrolytes containing Ca and P at high applied voltage; the other is monophasic $TiO_2$ coatings, produced in electrolytes containing Ca and P at applied voltages lower than 400 V [13–15,22,23] or in electrolytes containing $H_2SO_4$, $H_3PO_4$ or HCl [24,25]. Although the MAO-formed monophasic $TiO_2$ coatings have no apatite-forming ability [14,16,23–25], it is worth noting that these coatings are porous, nanocrystallized and firmly adhered (adhesive strength more than 40 MPa) [26,27], and exhibit a low elastic modulus and significant plasticity [28,29]. These meet the aforementioned combination of requirements for biocoatings, except with respect to bioactivity. To improve the bioactivity of the MAO-formed monophasic $TiO_2$ coatings, subsequent activation methods such as hydrothermal treatment [14,15,30], heat treatment [24,25] and chemical treatment [23] have been investigated. However, hydrothermal treatment and heat treatment resulted in a significant decrease in the bond strength of the coatings [13,14], whereas the residual chloride and sulfate on the chemically treated sample causes cell safety concerns [25].

Several in vitro and in vivo studies have shown that MAO-modified Ti surfaces have a higher early level of cell attachment than the untreated Ti surface. Our previous work showed that a $TiO_2$ coating formed by MAO at 300 V in aqueous electrolyte containing 0.2 M acetate monohydrate and 0.02 M β-glycerophosphate disodium salt pentahydrate exhibited higher cell adhesion and proliferation rates than did the untreated Ti surface [31]. It was also reported that an anodized Ti surface had a greater number of osteoblasts with higher cell activity than did bare Ti surface [25,32–35].

Ultraviolet (UV) irradiation has been used to investigate the photocatalysis of titania powders and films. A hydrophilic $TiO_2$ surface has been obtained by UV irradiation [36–39]. For biological application of UV irradiation, our previous study showed that $TiO_2$ coatings subjected to UV irradiation in simulated body fluid (SBF) had improved bioactivity [27]. However, the changes in microstructure, activation mechanism, bioactivity stability and cell response of the UV-irradiated $TiO_2$ coatings are still not clear. In the present work, the effect of UV irradiation on the microstructure (including morphology, phase component, grain size, element composition, chemical species and roughness), wettability, apatite-forming ability and cell response of MAO-formed $TiO_2$ coatings are investigated. The reasons for the enhanced bioactivity and cell response of the UV-irradiated $TiO_2$ coatings are also discussed.

## 2. Materials and methods

### 2.1. Sample preparation

Titanium discs 15 mm diameter × 2 mm thick were cut from commercially pure titanium rods, ground with 400# and 1000# abrasive papers to remove cutting-derived rough scratches, and ultrasonically cleaned with acetone, alcohol and distilled water. According to the MAO processing reported in our previous work [16,27,31], 149 titanium discs were treated by MAO in an aqueous electrolyte containing 0.2 M calcium acetate monohydrate and 0.02 M β-glycerophosphate disodium salt pentahydrate at the applied voltage of 300 V for 5 min.

After ultrasonically cleaning in alcohol and rinsing in distilled water, 100 samples of the MAO coating were irradiated by UV-light in distilled water for 0.5 and 2 h at room temperature, respectively. UV irradiation was provided by a 1000 W high-pressure mercury lamp, which generates light in the 300–600 nm range with a maximum intensity at 365 nm. The MAO coatings after UV irradiation for 0.5 and 2 h were labeled as UV-0.5 h and UV-2 h, respectively.

### 2.2. Structural analysis of the MAO and UV-irradiated coatings

For each structural analysis, three samples from each kind of MAO, UV-0.5 h and UV-2 h coatings were employed. The elements and chemical species on the coatings surfaces were examined by X-ray photoelectron spectroscopy (XPS; AXIS ULTRA, Kratos Analytical Ltd., UK). In XPS tests, Mg $K_\alpha$ radiation was used as an X-ray source, and the photoelectron take-off angle was set at 45°. The obtained XPS spectra were corrected to the C 1s (hydrocarbon C–C, C–H) contribution at the binding energy of 284.8 eV. The phase components of the coatings were analyzed by X-ray diffraction (XRD; D/MAX-2400, Rigaku, Japan) in $\theta$–$2\theta$ geometry using Cu $K_\alpha$ radiation at a step of 0.033°. Field emission scanning electron microscopy (FESEM; JSM-6700F, JEOL, Japan) was employed to observe the grain size of the coatings without sputtering any discharge-preventing materials such as gold and carbon, which is proven to be feasible for grain size observation as reported elsewhere [20,23]. The surface morphologies of the coatings were observed by scanning electron microscopy (SEM; S-2700, Hitachi, Japan) at a low magnification. Prior to the SEM observation, thin gold films were sputtered on the coatings. The structural analysis of the coatings is performed in the order XPS, XRD, FESEM and SEM.