



Effect of duty cycle on the crystallinity, pore size, surface roughness and corrosion resistance of the anodized surface on titanium



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ABSTRACT

Titanium is one of the most commonly utilized metals for the manufacture of orthopedic and dental implants. The purpose of the present research was to investigate the effect of anodization duty cycle (2%–100%) using a pulsed potentiostatic waveform on the formation of crystalline titanium dioxide (anatase and rutile), surface features, and corrosion resistance while maintaining a homogenous oxide color. Based on the results of a previous study, specimens with gold and dark green colors were chosen as evaluation points in the present study. While both the gold and dark green anodized surfaces produced with the pulsed potentiostatic waveform contained anatase, significantly greater anatase levels were shown to be present on the dark green colored oxide specimens. Furthermore, rutile formation was shown only for the dark green specimens. Both the gold and dark green specimens were found to have nano-rough surfaces. The results of this study suggest that the dark green specimens produced with a lower duty cycle exhibited a thicker oxide, a higher degree of crystallinity, a homogenous nano-pore size and distribution, and a more corrosion resistant passive oxide layer.

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1. Introduction

The mechanical strength, ductility, biocompatibility, and corrosion resistance under physiological conditions make titanium one of the most commonly used metals for orthopedic and dental implants. Titanium spontaneously forms an amorphous oxide layer typically 2 to 5 nm thick when exposed to air or other oxygenated environments [1–3]. This naturally forming oxide is not bioactive enough to form a strong bond with bone cells, and therefore many attempts have been made to improve the properties of surface oxides on titanium based implants [4]. At atmospheric pressure, titanium dioxide may also exist in one or a combination of three crystalline polymorphs: brookite, rutile, and/or anatase. Brookite is seldom utilized due to lack of economical synthesis methods of nanosized particles, but it has been reported to form in mixed sulfuric and phosphoric acid electrolyte anodization techniques [5,6]. Rutile is the most thermodynamically stable form of titanium dioxide and is commonly used as a white pigment in paints, inks, cosmetics and fillers [5]. Anatase has been the most studied crystalline phase of TiO₂ and is considered the most photocatalytically active due to having a high adsorptive capacity and rate of electron hole trapping [7,8]. There is a discrepancy as to whether anatase or rutile alone, or a specific anatase/rutile phase ratio, promotes the highest levels of the antimicrobial effect or bioactivity [7]. Both the anatase and rutile phases of

titanium oxide have been shown to act as antimicrobial surfaces, increase osteoblast attachment, and not adversely affect the biocompatibility of the titanium-based substrate material [9–20]. Furthermore, recent studies have reported that a combination of anatase and rutile is more bioactive than either pure anatase or pure rutile [8,21].

Anodization is an electrochemical method that is well established for the surface modifications of orthopedic and dental implants [1,2, 22–28]. The naturally forming amorphous oxide can be converted into crystalline anatase and rutile phases through heat treatments or anodization using potentiostatic (constant voltage) or galvanostatic (constant current) techniques. These anodization methods are commonly known as either micro-arc oxidation (MAO), anodic spark deposition (ASD), or plasma electrolytic oxidation (PEO), which are different names for similar techniques [1,29]. The crystalline oxide layer produced through anodization is thicker and denser than the amorphous oxide, and the processing parameters by which the oxide is formed determine the degree of crystallinity, thickness, morphology, porosity, and color [30].

Color coding of titanium implants is a standard industry practice which aims at increasing the efficiency and accuracy of inserting devices during surgery. Anodization of titanium can result in a range of interference colors based primarily on oxide thickness [1,3,29]. The colors of the oxide are generated in a thin transparent film grown on the metal surface [29]. The oxide color is a result of the interactions of incident light waves, made up of a wide spectrum of frequencies, with the oxide surface and the substrate surface [3,29,31]. The phase shift between the reflected waves along with the oxide thickness, crystal structure (anatase and rutile), and stoichiometry of the oxide will determine if the light waves

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reinforce or cancel [3,29,31]. The thickness, crystal structure, and stoichiometry of the formed oxide can be altered with anodization parameters such as current density, electrolyte concentration, and voltage [3,29]. A non-stoichiometric and multi-phase crystalline oxide can produce different interference colors even though the oxide thickness and forming voltage (or current density) are equivalent [3,29]. The anodized layer on titanium implants is often amorphous without a subsequent heat treatment, which may cause discoloration of the oxide surface. Through adjusting anodization waveforms, it may be possible to achieve a crystalline surface oxide layer with a homogenous color and a nano-scale surface morphology without a subsequent heat treatment step.

Several research groups have suggested that nano-scale surface morphologies commonly associated with anatase and rutile oxide phases contribute to the inhibition of bacterial attachment compared to conventional micro-scale morphologies [9,19,20]. In addition, surface roughness and topography play fundamental roles in regulating shape, orientation, and adhesion of cells [32]. The pores found on some anodic oxide surfaces are of comparable sizes with biological entities, such as type I collagen, and they can induce biological interactions that do not occur on smooth flat surfaces [32]. Nanostructured surfaces are reported to possess unique properties that alter cell adhesion by direct (cell–surface interactions) and indirect (affecting protein–surface interactions) mechanisms. The literature shows that surface nano-topography appears to increase cell attachment, proliferation, and differentiation compared to the topography associated with dental and orthopedic implants [33–40].

Metallic ion release from mechanical processes or biochemical interactions between the implant and surrounding media are known to have a crucial role in the long-term success of dental and orthopedic implants [41,42]. Increased corrosion can affect the biocompatibility and mechanical integrity of the implant [43,44]. Titanium ions have been found in periprosthetic tissues, fibrous tissues and interfacial bone next to implants and may be the cause of inflammation and necrosis [41,44]. These conditions can lead to implant loosening, pain for the patient, and ultimately removal or revision surgery. Anodization of titanium in a sulfuric acid electrolyte has been shown to decrease the corrosion rate in Ringer's solution compared to non-anodized titanium [45]. Porosity was also found to be an important factor in corrosion resistance with increased porosity in the thicker surface oxides showing an increase in corrosion rate compared to the thinner oxides obtained at lower anodization voltages [45]. Decreasing the metal ion release by increasing the corrosion resistance and controlling the surface porosity may lead to greater long-term success of dental and orthopedic implants.

A previous anodization study from our laboratory evaluated the effect of sulfuric acid molarity on the formation of anatase and rutile into the anodized layer using a 5% duty cycle, pulsed potentiostatic waveform [46]. The results showed that the optimal sulfuric acid molarity for maximum anatase production for a dark green colored oxide was 2.8 M and 5.6 M for a gold colored oxide. In addition, the surface porosity of specimens anodized in each molarity was characterized as nano-sized surface roughness features [46]. The pulsed anodization waveform also produced smaller pore sizes and suggested higher anatase levels than those reported in previous potentiostatic and galvanostatic anodization studies [16,47,48]. The purpose of the present research was to investigate the effect of anodization waveform duty cycle on the formation of crystalline phases, surface transformations and corrosion resistance in Ringer's solution while maintaining a homogenous surface oxide color.

2. Materials and methods

2.1. Specimen preparation

Commercially pure titanium grade 4 (CPTi-4) sheet material with a thickness of 2.0 mm was supplied by Depuy-Synthes (West Chester,

PA) and produced by Metalwerks (Aliquippa, PA) for this research. Test specimens were cut to 2.54 cm wide and 2.54 cm in length using a metallurgical saw (Struers Cleveland, Ohio) with a constant flow of cooling fluid (5% Struers Corrozip-LF). A 3 mm hole was drilled through the specimens near one side to allow for electrical connection to the DC rectifier. All specimens were placed into an ultrasonic bath with a laboratory detergent, rinsed with distilled water and then rinsed with ethyl alcohol. Test specimens were dipped into a nitric acid-hydrofluoric acid solution (10:1 ratio) for a period of 30 s, rinsed with de-ionized water, and dried with a cold air stream prior to anodization. The pre-anodization dip of specimens in a nitric acid-hydrofluoric acid solution has been reported in previous studies and is used to clean the specimen of any remaining residues [46,49–51].

2.2. Anodization

Anodization on titanium specimens was conducted with a 300 V 10 A DC rectifier (Dynatronix, Amery, WI) in a cell which consisted of two titanium counter electrodes and 1 L of a sulfuric acid electrolyte at 5.6 M to produce gold colored specimens or 2.8 M to produce dark green colored specimens based on previous research [46]. A voltage controlled pulsed waveform with various duty cycles (DTCs) was applied to the dipped specimens to produce the desired anodization oxide colors. For the purposes of this study the duty cycle was defined as the on time divided by the total time, or period, of the applied waveform. The pulsed waveform consisted of a series of square waves (on time) whose amplitude equaled the applied voltage followed by a time period of no applied voltage (off time). The duty cycle was varied by changing the amount of on time while maintaining a constant off time of 99 ms for each duty cycle, except for the 100% DTC which had an off time of 0 ms. Therefore this procedure also resulted in a change of frequency of the waveform with a change in the applied duty cycle. For example, the frequency range for this study was calculated to be 5 Hz for the 100% DTC and 10 Hz for the 2% DTC. The rectifier software was limited to 15 voltage steps for each DTC. For each DTC, the applied voltage was increased in incremental 10 second steps ranging from 5 to 12 V, depending on the final forming voltage needed to achieve the desired oxide color. While the voltage was controlled, the current response for each pulse was the amount required to reach the applied voltage and was monitored on the rectifier output but was not captured. In the present study, the oxide color was determined by visual observation only. This procedure was utilized as to best represent the method commonly used in implant manufacturing facilities which compares anodized specimens to a standard macroscopic color specimen. Standard color specimens of gold and dark green were fabricated for visual comparison and are shown in Fig. 1.

The gold anodized specimens were labeled as group A and dark green specimens were labeled as group B. Waveforms of DTC 2%, 5%, and 8% were examined for group A specimens. While DTC waveforms of 2%, 5%, 8%, 25%, 50%, 75% and 100% were examined for group B specimens. A power analysis was conducted, and it was determined that three specimens per DTC were needed to determine significant differences ($\alpha = 0.05$) within the 95% confidence interval for anatase and rutile production. The specimens were electrically connected to the positive lead and commercially pure titanium counter electrodes were connected to the negative lead of the rectifier and fully immersed into the sulfuric acid electrolyte bath. The final forming voltage to produce the desired colors using each DTC was recorded using an oscilloscope (Agilent Technologies, Santa Clara, CA, DSO1012A).

2.3. Thin-film X-ray diffraction

Thin-film X-ray diffraction (Scintag, Franklin, MA, XDS2000) was used to determine the crystalline phases present in the surface oxide layer on all specimens. X-ray diffraction (XRD) scans were conducted at two-theta angles ranging from 23° to 30° at a continuous scan rate

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