



Surface characterization, shear strength, and bioactivity of anodized titanium prepared in mixed-acid electrolytes



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ABSTRACT

The present study focused on evaluation of anodized oxides prepared in four mixed acid electrolytes with and without phosphoric acid as a function of forming voltage. Specifically the oxide surface characteristics, the mechanical integrity, and the bioactive performance were evaluated for a range of forming voltages in each electrolyte. Surface analyses showed phosphorus incorporation into the oxide layer started at localized areas after a threshold forming voltage, but became more uniform at higher voltages. Oxide crystallinity and thickness were retarded by the phosphoric acid levels present in the anodization electrolytes. Surface roughness was shown to be electrolyte dependent as a function of forming voltage, and in general was shown to increase with increasing voltage. Samples anodized up to a forming voltage of 144 V did not show any oxide failure through shear strength testing with only epoxy delamination for three of the electrolytes. At 180 V, the oxide layers showed failure or partial failure at approximately 30–35 MPa, which is stronger than many values previously reported for anodized coatings in the literature. Additionally, oxide films prepared in phosphoric acid containing electrolytes showed greater bioactivity through enhanced apatite formation. These anodized coatings exhibiting enhanced bioactivity show promise for promoting faster osseointegration while providing better implant stability due to the superior coating adhesion strengths.

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1. Introduction

Titanium is widely used as an implant material due to its good mechanical properties and excellent biocompatibility. In an ambient environment in the presence of oxygen, titanium spontaneously forms a thin amorphous oxide layer. The amorphous oxide layer may be grown and eventually converted to a crystalline oxide form using an electrochemical process such as anodization. Both anatase and rutile crystalline phases of titanium oxide have been shown to enhance bioactivity [1–4]. Anodization techniques produce porous oxide implant surfaces with roughness levels ranging from a few nanometers to tens of microns, which have been shown to stimulate contact with osteoblast cells [5–8]. Additionally, anodization studies in electrolytes containing phosphoric acid have shown phosphorus uptake into the anodized layers [5,9–14]. Several of these studies have suggested that phosphorus uptake may provide additional improvements to the bioactivity response and possibly faster osseointegration [9,10,12,14].

Yet another important factor in the overall performance and long-term success of anodized titanium implant surfaces is the bond adhesion strength between the oxide layer and the titanium substrate. This

bond strength must withstand not only the initial surgical insertion and handling stresses, but also mechanical stresses applied during bone healing processes [15,16]. Plasma-sprayed hydroxyapatite (HA) coating techniques have recently been utilized to improve the osseointegration properties of titanium implants. However, the adhesion strength of these coatings has been reported to be weak and may lead to early implant loosening and failure [16–19]. Oxides created through anodization near or past the dielectric breakdown can produce relatively high bond strengths due to the generation of heat and spark discharge which has been shown sufficient enough to fuse the oxide to the titanium substrate [16,19]. However, only a limited number of studies were found that compare the adhesion strength of these anodized titanium coatings [19,29].

In a previous study in our laboratories, four acid electrolytes including sulfuric acid, phosphoric acid, oxalic acid, and hydrogen peroxide components were optimized to produce anodized titanium layers consisting of specific anatase and rutile oxide ratios at an endpoint forming voltage of 180 V [20]. The purpose of the present study was to compare and contrast the surface properties, mechanical integrity, and bioactivity of anodized layers produced in each of these electrolytes as a function of forming voltage. Specifically, the first objective was to evaluate the oxide crystallinity and thickness as well as the morphology, chemistry, and surface roughness at selected forming voltages in each electrolyte. The second objective was to compare the adhesion

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strengths of these anodized layers and their respective apatite forming ability in simulated body fluid.

2. Materials and methods

2.1. Specimen preparation

Commercially pure titanium grade 4 (CPTi-4) sheet with a thickness of 2.0 mm was supplied by Metalwerks (Aliquippa, PA). Test samples for all tests except shear strength were cut to 2.54 cm wide and 2.54 cm in length. An approximately 3.2 mm diameter hole was drilled at the top center for connection with the anodization rectifier. Shear strength samples were cut 3.8 cm in length and 2.54 cm wide with a 6.35 mm diameter hole for attachment to the mechanical testing frames. All samples were placed into an ultrasonic bath with a laboratory detergent, and rinsed with distilled water and ethyl alcohol. After cleaning, test samples were dipped into a nitric acid-hydrofluoric acid solution (10:1 ratio) for a period of 30 s to activate the surface as shown in previous studies [11,20,21], rinsed with distilled water, and dried using laboratory forced air.

2.2. Anodization procedure

Four mixed acid electrolytes containing sulfuric acid, phosphoric acid, oxalic acid, and hydrogen peroxide in varying molarities were used in this study as listed in Table 1. Anodization was performed in 500 ml of each electrolyte mixture using a DC rectifier (350 V, 10 A, Dynatronix, Amery, WI) and two titanium counter electrodes. The anodization waveform used a potentiostatic voltage in 12-V, 10-second steps. At the beginning of anodization, the test samples and electrolyte solutions were at room temperature, but the electrolyte temperature was not monitored or maintained throughout the anodization process. Samples in electrolytes A, B, and C were anodized up to a maximum forming voltage of 180 V, while those in electrolyte D were anodized to a maximum forming voltage of 300 V. Endpoint forming voltages were chosen based on the solutions becoming too reactive for the laboratory anodization setup. After anodization, samples were rinsed with distilled water and ethyl alcohol, and then blown dry. Sample groups were defined as an electrolyte and forming voltage combination.

2.3. Thin-film X-ray diffraction

Thin-film X-ray diffraction (XRD) (Scintag, Franklin, MA, XDS2000) was used to determine the crystalline phases present in the anodized layers for each sample group. Samples were rotated 1° away from the copper X-ray source (1.54 Å Cu-K α) to enhance the X-ray interaction volume with the anodized layer. XRD scans were conducted in duplicate at two-theta angles ranging from 24° to 30° at a continuous scan rate of 2°/min. Anatase and rutile have their highest intensity diffraction peaks within this scan range at 25.3° and 27.5°, respectively. Jade software (Jade 9 MDI, Livermore, CA) was used to identify diffraction peaks and extrapolate the peak intensities.

2.4. Anodized layer thickness

One representative sample from each group was cross-sectioned along the transverse axis at a slow speed with constant cooling water

flow. Transverse sections were mounted in a conductive media (Polyfast, Struers, Cleveland, Ohio), and mechanically polished (TegraSystem, Struers, Cleveland, Ohio) through a series of steps to a final surface finish of 0.02 μ m with diamond paste. Cross-sectional layer thickness was measured using scanning electron microscopy (SEM, Zeiss, Jena, Germany, Supra 40) at 5000 \times or 10,000 \times with a 3 kV accelerating voltage. Five measurements were made on triplicate images for a total of fifteen thickness measurements for each sample group.

2.5. Anodized layer surface analyses

2.5.1. Surface porosity

Triplicate high resolution (2046 \times 1536 pixels) SEM surface images were taken at 5000 \times at randomized locations using a 3 kV accelerating voltage. Clemex Image analysis (Clemex Montreal Canada, Vision Professional Edition 6 Software) was used to determine the average and maximum surface pore areas for each sample group. The lower limit of pore measurement was set such that 5 pixels were required to distinguish a pore.

2.5.2. Surface roughness

Representative samples for selected forming voltages in each electrolyte were measured for surface roughness using an atomic force microscope (AFM, Bruker, Santa Barbara, CA, Bioscope Catalyst) in ScanAssyst mode (0.25 Hz, and 512 samples/line). The total scan area for each sample was 100 μ m \times 100 μ m, which was subsequently divided into sixteen 25 μ m \times 25 μ m sections for analyses. Gwyddion software (Version 2.41) was utilized to calculate surface roughness average (R_a) values. Since unequal variance was shown in the dataset, a Welch's one-way ANOVA ($\alpha = 0.05$) was performed on all anodized sample groups from each electrolyte and compared to an un-anodized titanium control sample. If significant differences were found, a *post hoc* Games-Howell test was used to compare the surface roughness values of sample groups from each electrolyte.

2.6. Anodized layer chemistry

Representative samples at selected forming voltages in phosphoric acid containing electrolytes were also examined for phosphorus uptake using energy dispersive spectroscopy (EDS) (EDAX, Mahwah, NJ, TEAM EDS Software Suite). EDS spectra were collected from the surfaces at 500 \times magnification using a 15 kV accelerating voltage. A standard less quantitative chemistry calculation was performed with a 200 s acquisition time in order to determine the phosphorus concentration present within the anodized layer. Additionally, cross-sectional (2500 \times) EDS maps were collected from selected sample groups in phosphoric acid containing electrolytes to examine the depth of and the spatial distribution of phosphorus uptake within the anodized layers.

2.7. Anodized layer shear strength

The ASTM F1044-05 [22] standard testing method was used to determine the shear strength of anodized layers from selected sample groups in each electrolyte ($n = 5$). A minimum of 2.84 cm 2 area, as specified in ASTM F1044-05, of the anodized sample surface from each group was bonded to an un-anodized titanium control sample using FM1000 (Cytec Engineered Materials, Tempe, AZ). The FM1000 epoxy glue was provided in the form of wafer with a thickness of 0.254 mm. The sandwich composite, consisting of the anodized sample surface, the epoxy wafer, and the un-anodized titanium surface, was then cured at 175 °C for 150 min as suggested by the manufacturer. Careful alignment of the sandwich composite components was maintained throughout the curing process. The bonded composites were allowed to air cool down to room temperature. The sandwich composites were then secured into a sample holder on the load frame and subjected to

Table 1
Mixed-acid electrolyte compositions.

Electrolyte	Sulphuric acid	Phosphoric acid	Hydrogen peroxide	Oxalic acid
A	3.5 M	0.1875 M	0.75 M	0.25 M
B	5.6 M	–	–	–
C	1.4 M	0.03 M	0.75 M	–
D	0.7 M	0.5 M	–	–

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