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Anodization and Titanium Surface Topography

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Abstract: ***Purpose: The aim of this study was to explore the effect of anodization on titanium surface topography (roughness) using different alectrolyte separately at different voltages. Materials and methods: Pure polished titanium discs were subjected to anodization, the anodization procedures were performed using two different electrolytes separately; 1 M H_2SO_4 or 0.05wt% HF in a beaker. A DC electrical power supply was used. Different voltages were used. Polished titanium surfaces were used as a control. Surface roughness was measured using profilometry. Topography was examined using scanning electron microscopy (SEM). Results: Surface roughness for anodization in HF electrolyte showed a steady increase in Ra value with each voltage increment to the maximum value of 110 V was observed. Highly significant differences were found between Ra values of titanium anodized at 110 V and the other groups (P<0.001). Interestingly, for anodization in H_2SO_4 electrolyte, the Ra value increased as the voltage value increased to reach its maximum value at 80 V, then declined at 110 V. It then increased again at 140 V but did not return to the peak value at 80 V. Conclusions: This research showed that a slight difference in voltage have significant impact on titanium surface topography and roughness increased with increased anodic voltage.***

Keywords: Dental implant, titanium, surface modification, anodization, roughness

1. Introduction

For the last 50 years, commercially pure titanium and titanium alloy have been successfully used for the fabrication of dental and orthopedic implants. Their success is related to their biocompatibility, mechanical properties such as high fracture toughness, corrosion resistance, passive oxide surface properties, ease of manufacturing, low modulus of elasticity and high strength to weight ratio. [1, 2, 3, 4].

Furthermore, the ability to alter the physical and chemical characteristics of the titanium surface, including changing the surface oxide composition, thickness, and morphology makes titanium a suitable material for the fabrication of dental implants. [5] The biocompatibility of pure titanium and titanium alloy are believed to be related to the ability of the titanium oxide layer to react with water ions and serum proteins [6, 1].

Many attempts have been made to modify dental implant surfaces in order to improve their biocompatibility, shorten healing times and improve surface characteristics that are involved in implant success. Topography of the biomaterial surface plays an important role in determining cellular response [3].

Surface roughness has an important role in enhancing bone healing and promoting biomechanical properties at the bone/implant interface through increasing the mechanical retention and allowing good stress distribution [7]. Rough surfaces are often used in clinical situations where acceleration and enhancement of osseointegration and bone interlocking is required such as in cases with poor bone quality or reduced bone volume [8].

For example, Sul et al., [9] in their study on different implant surfaces, found that electrochemical oxidation and acid etching of implant surfaces developed different surface properties in terms of surface chemistry, morphology, pore characteristics, oxide thickness, crystal structure, and roughness. They also suggested further studies which investigated the characteristics and details of implant surfaces in order to enrich the understanding of the process of osseointegration and to create new generations of implants. The development of an implant surface that could deliver drugs and growth factors to prevent infection and to enhance bone formation has also been suggested [10].

One of the methods of changing the implant surface is to use a process of anodization. Anodic oxidation is a simple procedure for increasing the oxide thickness of titanium. The formation of an oxide layer depends on temperature, current, electrolyte type and concentration and many other parameters [11, 12]. The oxide growth is formed by a balance between the formation and dissolution rate which is different between different electrolytes. For example an alkaline electrolyte may have rather low oxide formation ability whilst for some types of acid (like sulphuric acid and acetic acid) they can have a high oxide formation rate. [13]

Micro- or nano-porous surfaces can be produced by the anodization of titanium in strong acids (H_2SO_4, H_3PO_4, HNO_3, HF) at high current density ($200A/m^2$) or voltage

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(100 V). A thick oxide layer of more than 1000 Å on titanium can be achieved by this method. [8] However, Sul et al., [9] reported a double oxide type of surface consisting of an outer porous layer containing numerous pores and an inner barrier layer without pores. On some occasions they noticed crack propagation in this thick oxide layer. Kim et al., [10] found that the newly formed nano tubular structures formed by anodization were reported to be similar in shape and size regardless of the substrates used. This suggested that surface roughness of the titanium substrate used did not affect the shape and size of the nano-tubular layer prepared by the anodizing process. They also observed that the nano-tubular layer on an anodized titanium surface had a closed end. The end in contact with the titanium substrate was closed and the end with the electrolyte was open. Each of the tubes was connected through the sidewalls of the tubes. Sometimes a "breakdown phenomenon" could happen which resulted in irregular pores/craters. The pore size also became larger (up to 8 µm in diameter), because of interconnection of some of the pores to one another. [13] It is not only a nanotublar layer that can be obtained from anodization as Sjöström et al., [14] were able to achieve dot-like structures on pillar-like structures by using a through-mask anodization technique in which they coated a titanium disc with a thin layer of aluminum then anodized the surface with different stages.

The aims of this study was to explore the effect of anodization on titanium surface topography (roughness) using different alectrolyte (H_2SO_4 electrolyte; HF electrolyte separately) at different voltages.

2. Materials and Methods

Specimens preparation and polishing

Discs of 5 mm in diameter (± 0.1 mm) were punched out from 100 x 100 x 1 mm of annealed titanium sheets (99.6+%) (Goodfellow Cambridge Limited, Huntingdon, England). Discs were cleaned in an ultrasonic bath at room temperature with ethanol for 15 min then allowed to dry at room temperature.

Polishing

In order to have an accurate evaluation of surface changes (especially at nano-level) and for proper comparison between groups, a uniform clean surface was obtained (mirror polished surface) on one side of each disc. To facilitate polishing, discs were mounted within a specific ring using an epoxy resin system for embedding and impregnation of the specimens (Struers A/S, Ballerup, Denmark) and these were then polished with a Struers A/S machine.

The polishing procedure was conducted in three steps

The first step was conducted using a disc grinding paper (silicon carbide grinding paper), grit 500 (Paper), 200 mm diameters at 300 rpm, 25 N, for 1 min, under water flow.The second step was conducted using a MD Largo disc (MALOT), 200 mm diameter at 150 rpm, 30 N for 4 min with DiaPro Allegro/largo polishing liquid as a lubricant. The third and final step was conducted using a MD-Chem polishing cloth disc (MACHE) at 150 rpm, 30 N, for 5 min using OP-S 0.04 µm colloidal silica suspension with 10% H_2O_2.

A mirror surface image was obtained using this procedure. The discs were then cleaned in an ultrasonic bath at room temperature with ethanol for 15 min, and then with distilled water. Discs were then dried in an oven at 40 ˚C for 1 h and left to dry at room temp. The discs were stored in a sealed container.

Anodization

The anodization procedures were performed separately using two different electrolytes separately; 1 M H_2SO_4 or 0.05 wt % HF in a beaker. A DC electrical power supply was used (Thurlby-Thandar instrument (TTi) Ltd, England). The current was kept constant at 0.01 A and the voltage was allowed to increase until it reached the desired value. Different voltages were used (20 V, 50 V, 80 V, 110 V, 140 V) with additional voltages added for the H_2SO_4 electrolyte (70 V, 90 V). The temperature was monitored continuously and maintained around room temperature.

Titanium discs were connected one by one to the anode. Care was taken to cover all of the copper wire to prevent its contamination with the electrolyte. Only the titanium surfaces were exposed to the electrolyte to ensure a stable surface area ratio which was 1:10 time between anode and cathode. The cathode was formed from a platinum sheet. The distance between the cathode and anode was 3 cm.

Topographic inspection was conducted using a scanning electron microscope (SEM Tech Ltd, Bonsall, Derbyshire, UK). All samples were attached by adhesive to aluminum SEM stubs and examined at 20 kV in the secondary emission mode in a PC-controlled ISI 60 scanning electron microscope.

Non contact optical Proscan profilometry was used to measure the surface roughness (Proscan 2000, Scantron Industrial Products Ltd. Monarch centre, Taunton, England). Four discs per surface were measured. The measurements were conducted in an X and Y direction, and the scanned area was 2 x 2 mm. The measurement was taken for 20 lines in the Y axis; 250 spots in each line were measured twice. The final analysis was conducted in an area of 1.2 mm x 1.2 mm in order to avoid edge effects. Ra measurement was calculated for each sample: Ra: is the arithmetic mean of the absolute values of the surface point departures from the mean plane within the sampling area. [15]

3. Statistics

Statistical analysis was carried out using Excel and SPSS (Statistical Package for Social Sciences)

After verification of the normal distribution and the homogeneity of the variance, an analysis of the variance

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(ANOVA) was used to asses any significant differences among selected group. For multiple comparisons test (Post Hoc multiple comparisons) LSD (least significant difference) was used to determine the specific differences between the means of the group members.

The probability value (P-value) was considered significant at $P < 0.05$ and highly significant if $P < 0.01$.

4. Results

The morphology and the surface roughness of titanium discs was analysed, and found to be different from one to another after various surface modifications.

After anodization, the polished titanium discs retained a bright appearance but had different colours depending on the type of electrolyte and voltage used.

Anodization in H_2SO_4 electrolyte conducted using voltages of 20 V, 50 V, 70 V, 80 V, 90 V, 110 V, 140 V the titanium disc colour ranged from blue, faint green, yellow, deep purple, violet, deep green and shiny grey to deep green respectively.

Anodization in HF electrolyte conducted using voltages of 20 V, 50 V, 80 V, 110 V the titanium disc colour ranged from blue, faint green, deep purple, and green with slight yellow respectively.

Figure 1 shows the mean Ra values for anodized surfaces. For anodization in HF electrolyte, a steady increase in Ra value with each voltage increment to the maximum value of 110 V was observed. Highly significant differences were found between Ra values of titanium anodized at 110 V and the other groups ($P<0.001$). Interestingly, for anodization in H_2SO_4 electrolyte, the Ra value increased as the voltage value increased to reach its maximum value at 80 V, then declined at 110 V. It then increased again at 140 V but did not return to the peak value at 80 V.

To explore the accuracy of this threshold voltage and to ensure that it was not an artefact, additional different voltages were tested (70 V, 90 V). Figure 2 shows that the steep increases in Ra value started at 70 V and mantained a relatively similar value before starting to decrease at 110 V.

SEM

SEM images for anodized titanium surfaces in both electrolytes revealed they are similar to the untreated polished surface (Figure 3; 4), but at higher magnification the 140 V anodized surfaces (x 1500) show cracks, separated and interconnecting deep holes on its surface and at higher magnification the nano-tubule like surface started to appear.

5. Discussion

Anodization of titanium surfaces using HF electrolyte led to a steady increase in Ra value with each voltage increment, same results was seen for anodization in H_2SO_4 electrolyte, with exception that the Ra value start to decline after 80 V, hen increased again at 140 V but did not return to the peak value at 80 V.

In anodization procedures, initial attempts were to anodize using different acids that usually used for etching. [16] However, a good range of different voltages could not be obtained for HCl or HNO_3, therefore HF acid and H_2SO_4 were used for anodization. For HF acid electrolyte, the voltage could not be increased above 110V.

Care was taken to ensure that the surface modification with anodization procedure was just due to anodization and not to etching. There was no problem in the case of H_2SO_4 as it was known that it did not react with titanium at room temperature. [17] For HF acid, a pilot study was conducted to ensure that the concentration used (0.05 wt %) did not have an effect on the titanium surface for the time provided.

The results showed that a range of treatments of titanium produced different surface topographies, as first indicated by Xavier et al., [18] significant differences in surface roughness were obtained.

According to the results from this research, it can be concluded that anodizations produced smooth surfaces making them good surfaces to manufacture supra-gingival part of dental implant.

In order to generate accurate base-line data and have accurate comparisons of the modified surfaces, standard polished surfaces were produced to use as control. [19] These polished surfaces appear extremely smooth to the naked eye with a shiny mirror surface, and Ra value= 0.047 µm. This is close to the Ra values found by Nagassa et al., [20] of 0.053 µm for their polished titanium surfaces.

Anodization

Anodized surfaces are a relatively recent development in commercially available implants. It is a method for modifying a titanium surface and has been shown to enhance osseointegration effects. [21] In the anodization procedure two different electrolytes were used; H_2SO_4 as it is a powerful electrolyte vehicle that increases the oxide layer on titanium surface, [13] and HF acid as it has been suggested that anodization in the presence HF acid incorporates fluoride in to the titanium surface, [10, 19] which subsequently may have an inhibitory effect upon bacteria.

Anodic oxidation is a controlled procedure for increasing the titanium surface oxide thickness, and the oxide thickness increases in a linear relationship with the applied voltage. [5, 11] Increases in oxide thickness correlate with changes in titanium surface colour according to the applied voltage and type of electrolyte used, which is in agreement with Sul et al., [13]. In this research it was possible to measure just the surface roughness for these surfaces. As expected the roughness increased with increased voltage [22] Changes in average

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surface roughness were consistent with changes in porosity of the anodized implant.22 This elevation in surface roughness was relatively small, and Lausmaa [23] showed that anodic oxidation increases roughness at a sub-micron level.

Interestingly, in anodization in H_2SO_4 electrolyte, the surface roughness continued to increase in a linear relation up to a specific voltage. The Ra value then decreased before increasing again. This phenomenon was reported by Sul et al., [22] and is explained by an increase in the pore size and shape changing the surface roughness to wavy. It has been mentioned that the SEM images have limited magnification ability, and those surface changes associated with anodization were in such a small scale. This explains why the SEM pictures for anodization do not show the expected pore configuration. Only when the anodization voltage reached 140 V in H_2SO_4 electrolyte, did a blurred image of pores appeared. This image can be explained because the pore size increases with increasing voltage and the pores become larger due to interconnection of some pores with each other. [22]

6. Conclusions

This research showed that a slight difference in voltage have significant impact on titanium surface topography.Modification of titanium surfaces using anodization produced slight changes in surface roughness.

In anodic oxidation, roughness increased with increased anodic voltage, and for anodization using H_2SO_4 electrolyte, showed a threshold voltage after which surface roughness decreased.

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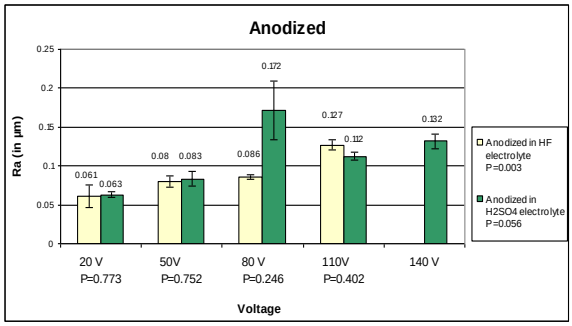


Figure 1: Average Ra value (in µm) and standard deviation of titanium surfaces anodized in 1 M H_2SO_4 electrolyte and 0.05 wt % HF electrolyte separately at different voltages as quantified by profilometry. P values in legend represent the significance between different voltages in the same electrolyte. P values in X axis represent the significance between the two electrolytes in same voltage group

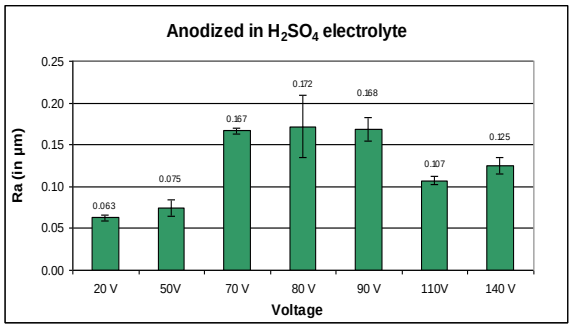


Figure 2: Average Ra value (in µm) and standard deviation of titanium surfaces anodized in 1 M H_2SO_4 electrolyte at different voltages quantified by profilometry

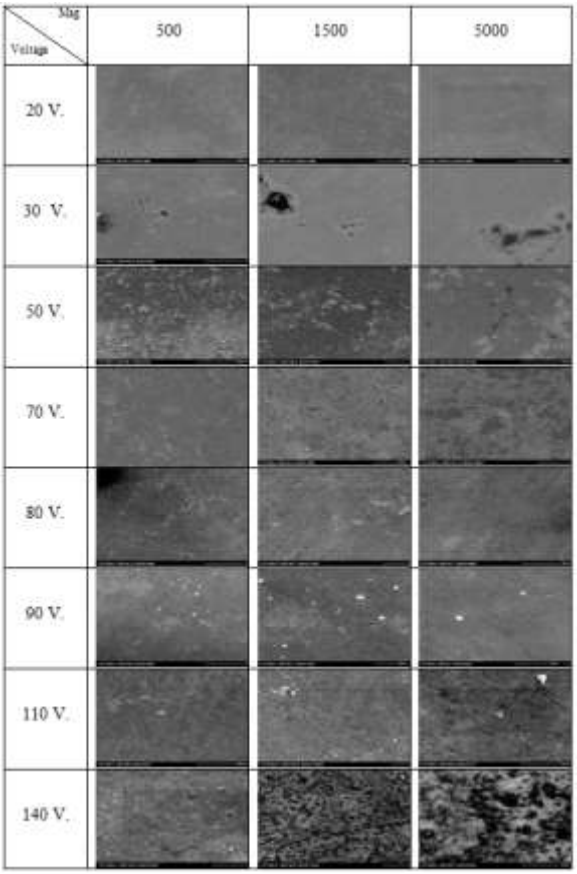


Figure 3: SEM images of titanium surfaces anodized in 1 M H_2SO_4 electrolyte with different voltages and at different magnifications

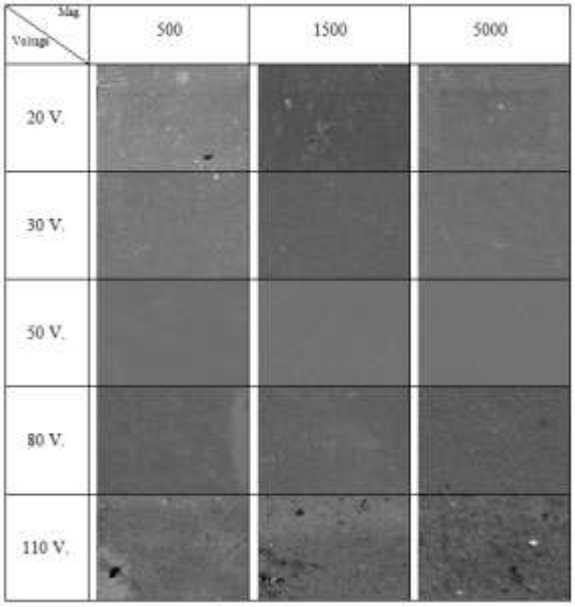


Figure 4: SEM images of titanium surface anodized in 0.05 wt% HF electrolyte with different voltages and at different magnifications

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