

Surface engineering of titanium for biomedical applications by anodizing

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Abstract

Competitive manufacturing implies fit for purpose and efficient manufacturing practices. Dental implants are biomedical parts that are manufactured from either Grade 4 or 5 Titanium alloy. In certain situations it may be beneficial for patient satisfaction purposes and for product identification marking to change the appearance (colour and reflectance) of the implant. In the present study, a TiO₂ based coating is applied on commercially pure titanium (Grade 4) alloy substrates by the anodizing process. The objective of this study was to engineer the aesthetic appearance of the dental implants while monitoring its effect on aspects as regards to biocompatibility and function. Chromaticity (colour and hue) and reflectance are investigated as a function of the anodizing process parameters (electrolyte voltage, current and electrolyte). Grade 4 titanium was anodized in diluted sulphuric acid electrolyte at various voltages. The reflectance of the anodized specimens was measured with a spectrophotometer. Surface roughness, oxide film thickness and chemical composition of the oxide phase were measured. By varying the electrolyte voltage between 5 V to 40 V different colour ranges were produced. It can be concluded that the surface colour of anodized titanium is dependent on the oxide layer thickness and therefore the applied voltage. Conventional surface roughness did not change and was similar to the virgin material. Elevated voltages resulted in a more crystalline oxide layer. The aesthetic appearance of titanium implants may be improved.

Keywords

Titanium grade 4, Anodization, surface roughness, reflective index and TiO₂, TiO₂ thickness and XRD spectra.

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1 INTRODUCTION

Titanium and its alloys are attractive because of their high strength to weight ratios, excellent corrosion resistance and fatigue properties. These properties along with its perceived biocompatibility make them especially useful for orthopedic and dental implants. However, titanium is a bioinert material that neither bonds to the bone tissue directly nor induces bone growth as compared with the stainless steel 316L, CrCoMo and calcium phosphate coated implants [1]. Therefore, various surface modification techniques have been developed and applied to titanium implants in an attempt to improve the bioactivity. Titanium falls within the group of neutral biomaterials that does not chemically bond with bone tissue. Because of the improvement in casting techniques of titanium alloys along with progress in CAD/CAM and electric discharge machining there has been renewed interest in the use of titanium and its alloys for fixed and removable prostheses [2]. Titanium has a dark iron like appearance that may be problematic as far as aesthetics are concerned when used in biomedical applications especially if it is exposed or visible in some way. A typical application is in the manufacture of dental implants. An ever increasing demand for dental implants for the restoration of oral functions such as chewing and oral communication and/or the restoration of aesthetic appeal has led to

the need for practical and effective ways to improve and maintain the function of implants but also with acceptable aesthetic appeal. Sections or components of the implant assembly may therefore be coloured to improve aesthetic appeal during implant exposure or tissue recession. A coloured collar may for example be inserted on the top of the implant for aesthetic purposes. The surface of this collar may have markedly different requirements than the coronal portion of the implant surface. This surface, albeit coloured, needs to be smooth to reduce dental plaque deposition and to facilitate easy cleaning. Manufacturers and physicians also require simple and effective techniques for product identification marking without having to resort to marking techniques that introduce additional foreign substances into the mouth cavity.

Anodizing is an electrolytic chemical oxidation process whereby the oxide layer thickness is engineered to thereby change the appearance (colour) of titanium. The thin passive oxide layer formed is usually more stable and thicker than the natural occurring oxide layer which is formed in contact with air. The anodic oxidation of the titanium surface for implant application is relatively inexpensive and may produce a uniform thickness throughout the surface area [3]. The anodic oxidation of titanium may also improve the corrosion resistance [4]. The implant corrosion resistance is

important because certain specific metal ions released during corrosion can induce a reaction around the implanted surface that may cause fixation failure. The corrosion resistance and biocompatibility of metals are largely the result of a passive oxide layer on the titanium surface [5]. The oxide layer and colouring is directly related to the anodizing voltage. The colours formed on the titanium surface are known as interference colours. There is no dye associated with the formation of these colours. This study was conducted to investigate the spectral reflectance, chromaticity, refractive index, oxide layer thickness, surface roughness and makeup of the oxide layer on anodized titanium at different voltages.

2 MATERIALS AND METHOD

Grade 4 titanium was used as workpiece material for this study. The samples for anodizing were cut from 2 mm grade 4 titanium plates. The chemical composition is given in the **Error! Reference source not found.** The samples were cut to dimensions of 25 mm × 35 mm and then degreased by acetone and acid washed with 40% HNO₃ solution for 20 s according to ASTM B600. The samples were then washed twice with distilled water to remove the traces of acid. The samples (surface roughness, Ra = 1.28 μm) were anodized in 20% concentrated sulphuric acid (H₂SO₄) electrolyte bath for 2 min for various constant voltages using a potentiostat. The anodizing voltage was varied in the range of 5 - 40 V, with incremental step of 5 V. After anodizing the samples were washed twice again with distilled water. The colours (irradiance and reflectance) of the anodized samples were measured with a UV spectrophotometer (Varian model Cary 5000 UV-VIS-NIR) with an observation angle of 20 - 70 degrees. The spectral reflectance was recorded for wavelength's varying between 200 to 2000 nm. The thickness of the anodized layer was determined by noting at what wavelength the maximum % spectral reflectance occurred and then applying equations Eq (1) and (2)[3].

$$t = \frac{\lambda_{\max}}{4n_o} \quad (1)$$

$$n_o^2 = 5.193 + \frac{2.441 \times 10^7}{\lambda_{\max}^2 - 0.803 \times 10^7} \quad (2)$$

Where; t is the thickness of the film in nm, λ_{max} is the wave length of maximum film intensity absorption in nm, and n_o is the film refractive index. Oxide film refractive index varies with wavelength which can be obtained from the Eq (2).

Element	C	N	Fe	H	O	Ti
% by weight	0.010	0.01	0.20	0.002	0.30	Bal

Table 1 - Chemical composition of grade 4 titanium plate

The surface roughness of the anodized samples was measured by using a Hommel surface profilometer (HOMMEL-ETAMIC T8000). The centerline average surface roughness of the samples was measured with 0.8 mm cut off value and 15 mm traverse length. An average surface roughness (arithmetic surface roughness, Ra) was measured at six different locations in both the longitudinal and transverse directions of the anodized surface. The chemical composition of the samples was measured by Energy dispersive spectroscopy (EDS) whereas the crystal structure was determined by X-ray diffraction (XRD) with a thin film collimator (X'pert Pro MRD, Philips Ltd, Eindhoven Netherlands). The step size used in the scan was 0.02° over the range of 10° - 90°. The spectra was recorded using Cu Kα radiation (0.154056 Å) generated at an acceleration voltage of 40 KV and a current of 40 mA.

3 RESULTS AND DISCUSSION

3.1 Colour

Table 2 shows the created colours on the titanium during the anodizing at different voltages in diluted sulphuric acid. When the titanium immersed in an electrolyte the current is drawn, the oxygen is generated at the anodic surface and combines with the titanium to form a titanium oxide. This oxide layer thickness increases in relation to the amount of voltage applied with the time. As oxide layer thickness its resistance to the passage of current also increases [3]. For any applied voltage the oxide layer grows and then stops when the resistance has increased to a point where the current is decayed to a value at which only few OH⁻ ions are available to support continued film growth. The colour of the anodized titanium samples at different voltage determined by the naked eye are given in the Table 2. It is generally known that titanium anodize produce an inert transparent oxide film capable to generating interference colours. This is the simplest method and economic, it utilized ordinary chemicals to produce stable oxide with different colours at room temperature within 2min [4]. The produced colours are no pigments or dyes. The interference colours are produced by thin transparent film on a reflective surface. The film has an ability to reflect, refract and observe the light. The white light falling on the film is partially reflected and partially transmitted. The transmitted fraction reaching the metal surface is again partly absorbed but largely reflected back to oxide film. A phase shift occurs during this process together with multiple reflections. The degree of absorption is dependent on the oxide layer thickness. The different thickness of oxide film causes the variations of luminous flux, refractive index and reflective index, produces various specific colours of the anodized titanium. Figure 1 illustrates that when the colours of titanium anodizes at different voltage at 5 to 40V, the spectral reflectance indexes varies specifically. It is determined that the colour and thickness of the oxide is dependent on

the voltage applied. Golden yellow colour is obtained at 40 V; it seemed that the colour films are applicable and practically in dental clinic to colorize the titanium dental frameworks of dentures in order to enhance the aesthetic of implants by anodization due to golden yellow colour harmonious with the colour of the teeth. The other colours produced by anodizing may be used for colour coding of the abutments to recognize implanted size and type. Even they probably used in the applications of jewels, with crucial requirements of good reliability of hue on differently finished surfaces.

Voltage (V)	colours
5	Tiny yellow
10	Dark golden
15	Dark brown
20	Purplish blue
25	Shallow blue
30	Sky blue
35	Grayish yellow
40	Yellowish gold

Table 2 - The correlation of colours to volts of anodized titanium

3.2 Refractive index and Thickness

Error! Reference source not found. shows the spectral reflectance of each sample obtained by the spectrophotometer. The thickness of the anodic film and the refractive index was calculated from λ_{max} using the Eq (1) and (2). **Error! Reference source not found.** shows the changes in the refractive index versus the anodizing voltage. It can be seen that the increase in the anodizing voltage increases the anodic film thickness which implies a decrease in the refractive index of the layer. This is because of increasing anodizing voltage, the density and compression of the anodic film is decreased [6]. The highest refractive index obtained was 1.457 for the sample at 5 V while the lowest refractive index was 1.421 for the sample at 40 V. **Error! Reference source not found.** presents the variation in film thickness as a function of the anodizing voltage. In essence the anodic film thickness increases linearly with increasing applied voltage for a constant anodizing time. Initially a high current density is realized with the application of the constant voltage that drops quickly almost immediately from its maximum value to then stabilize and eventually to become constant. Once the initial growth has occurred and the color changed the current density reduces dramatically and the film is essentially stable.

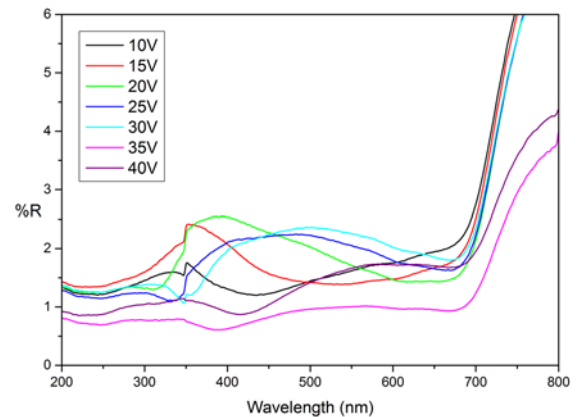


Figure 1 - Reflectance spectra of interference colors obtained as a function of voltage from 10 to 40 V

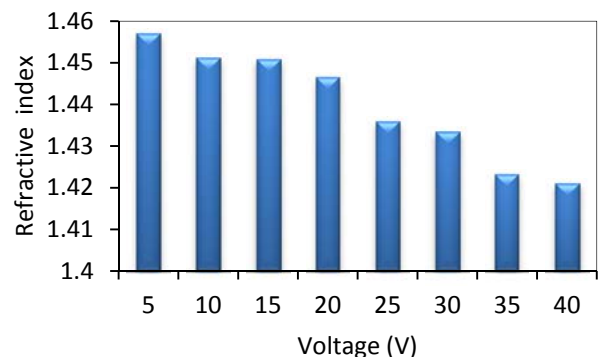


Figure 2 - Changes in the refractive index of anodized samples

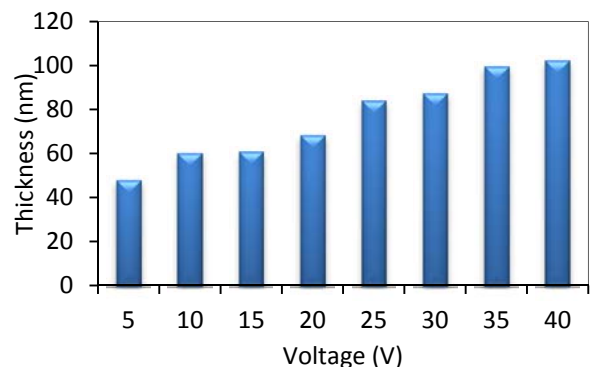


Figure 3 - Changes in thickness of anodized samples Vs. anodizing voltage

3.3 Surface Roughness

Figure 4 shows the surface roughness of the anodized samples at different applied voltages. The data shows that in essence the roughness (R_a) remained constant and is similar to the unanodized virgin sample. This shows that even though there was a change in the color of the surface and growth of the oxide layer there was no changes in the surface roughness after 2 min of anodizing. This conclusion is of course only valid for the length scale considered as applicable to the standard roughness measurement as conducted. At reduced

length scales there may be changes in the surface roughness due to the oxide layer growth due to secondary oxide particles [7]. Zhu et al. [8] also considered oxygen (O₂) bubble generation during anodizing of aluminum that result in the formation of a porous surface morphology. O₂ bubble formation may therefore play a significant role in reduced length scale roughness and should be considered for future investigation.

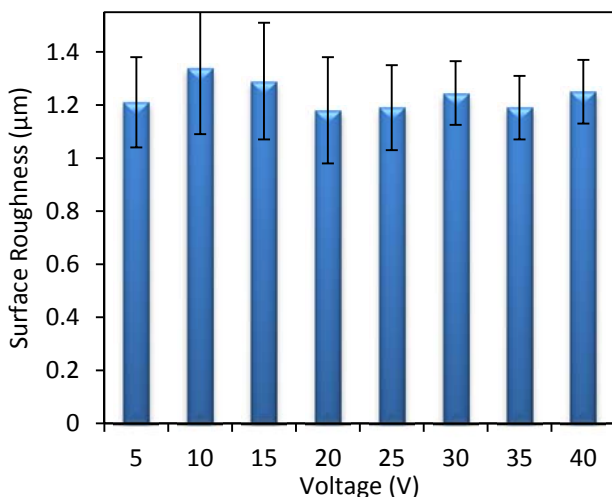


Figure 4 - Effect of Anodizing voltage on surface roughness

3.4 Crystal structure

The XRD pattern shown in **Error! Reference source not found.** reveals the amorphous structure of the oxide films in the anodized sample at an applied voltage of 10 V and 40 V. The oxide film (TiO₂) formed by the diluted sulfuric acid (H₂SO₄) electrolyte forms a rutile structure on the surface of the titanium. As observed from the XRD spectra the intensity of the titanium phase is decreased for higher anodizing voltage (40 V) compared to the low anodizing voltage (10 V). The oxide layer formed for the 40 V anodized sample has a higher TiO₂ content compared to the 10 V anodized sample (see quantitative analysis Table 3). The increased oxide layer may enhance the biocompatibility of the implant with the surrounding tissues and helps to grow the cells at a faster rate [7]. In general, at low voltage the oxide film was amorphous but with increasing voltage the structure of the oxide film may change from amorphous to a crystalline oxide. The crystalline oxide (anatase) of titanium are reported to be beneficial bone growth and response to the surrounding tissues compared to the amorphous structure [9].

Phase name	Content(%) 10 V	Content(%) 40 V
Titanium Oxide	---	26.40
Rutile	0.32	7.02
Titanium	99.68	66.57

Table 3- Quantitative analysis of XRD results

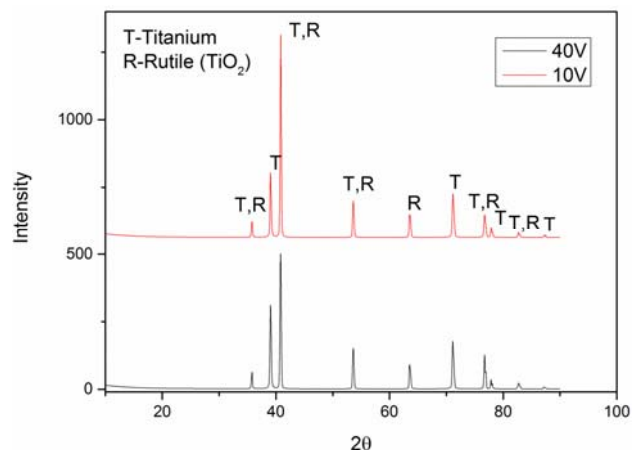


Figure 5 - XRD spectra of anodized sample at 15V and 40 V

4 CONCLUSIONS

1. Titanium Grade 4 was anodized in dilute sulfuric acid electrolyte at various voltages. The following conclusions are drawn.
2. Different interference colors are produced with different voltages. This is similar as demonstrated by various other investigations.
3. The refractive index of the anodic film decreased, which showed that the density of the anodic film has decreased. The thickness of the anodic film increased by increasing the anodizing voltage.
4. The XRD spectra showed that the oxide layer is stable. The crystalline TiO₂ structure that is a characteristic of the higher voltage anodizing may enhance bone growth and better bonding between the surrounding tissues in biomedical implant use.
5. Anodizing did not significantly change conventional surface roughness. The effect on reduced length scale roughness is still unclear and should be investigated in more detail as there is evidence that suggests that the biomedical behavior of titanium implant surfaces may be a function of roughness at different length scales.

5 ACKNOWLEDGMENTS

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