Surface Engineering of Titanium Using Anodization and Plasma Treatment

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Abstract. Ti64 alloy is a well-known material for biomedical applications due to high corrosion resistance and biocompatibility properties. Surface properties of implants plays a vital role in bone and cell growth in the human body. With the anodization process, we can increase the surface porosity, which will be adequate for surface fascination of the implant screw to the bone and appropriate mechanical properties. Hence, the present study attempted to improve the surface properties of Ti64 by anodization and plasma treatment that may be promising method to increase the biocompatibility of Ti materials. Anodization process is the cheapest one to improve the surface properties of Ti alloy and riskless process. To intensify the open pores on the Ti64 surface plasma treatment was performed. Also, the aim of this study was to improve the aesthetic appearance of the dental implants and reproduce interference of colours. With the help of UV-VIS spectrophotometer the colour and spectral reflectance were investigated. The oxide layer thickness, chemical composition and nanosurface roughness was measured. These results suggest the surface modification of Ti64 alloy by anodization can produce interference of colours and are dependent on the applied voltage, oxide layer thickness. The surface oxidation consisting of anatase and rutile phase and change in nanosurface roughness, may improve the biocompatibility of Ti64.

Keywords. Ti64; Nanosurface Roughness; Anodization; Oxide Film and XRD.

1. Introduction
Metallic biomaterials often require surface modifications in order to improve corrosion and wear resistance, biocompatibility, and surface wettability. Mechanical holding between two surfaces can be improved by modifying one or both surfaces to increase effective surface area by a mechanical modification methods such as sandblasting, shot peening, or laser peening. Osteointegration is defined as a "direct structural and functional connection between ordered living bone and the surface of a load-carrying implant." Using current materials and techniques, a titanium implant requires few months to osteointegrate together with surrounding tissue and bone. Although for successful implants that had continued for up to 17 years, proposing that the osteointegration has been imperfect for a long period of time [1]. Surface structure plays a significant role in the operational performance of dental implants. Average surface roughness (Sa) is a surface integrity descriptor that is most often used to quantify the
topography. As typically used, it does however have limitations and may not contain sufficient information to adequately describe and quantify the surface topography as relevant to dental implants. The physiological responses of the cells, bone which are in contact of the implant depend on the surface properties of the implant [2].

For dental and orthopedic implant applications, Titanium is a well-proven implantable material [3] as it is biocompatibility and has anti-corrosion surface properties. Furthermore, extremely porous titanium is a smart material for biomedical implantations because of its particular properties such as strength, weightlessness and high resistance to corrosion. Modulus of elasticity of porous titanium is alike to that of human bone and desired pore size helps in bone ingrowth.

Anodic oxidation was performed to create porous titanium oxide film on commercial Ti by Dikici et al. [4]. It was found that, the film with non-porous structured TiO$_2$ can be created by the anodic oxidation method which is transferred into anatase phase later annealing in air at 480°C for 2hrs. The TiO$_2$ film is good candidate for the photocatalytic degradation of harmful organic impurities in wastewater.

The bioactive spongy porous coating with nano surface structure and exceptional apatite formation capability on titanium were effectively attained by a hybrid process combining sand blasting, acid etching and anodization process, heat treatment and hydro-thermal treatment [5]. The processed samples have very good apatite creation capability due to the formation of nano anatase and brushite, which is having outstanding bioactivity.

Recently, selective laser metal (SLM) deposition is considered as a hopeful technology for manufacturing of scaffold Titanium implants with definite porosities. Wally et al. (2019) [6] found that it is possible to produce porous Ti64 structures with identical and graded porosity for dental implants by using SLM technique. Ti 64 with graded lattice structure of implants were fabricated by SLM technique, their biocompatibility results were showed that better osteointegration than the existing implants due to porous structure. This might be the efficient process for the fabrication of porous dental implants but the cost of the implants will be very high because of the powder cost and process is not commercialized still.

One go with lowest manufacturing cost by the anodization and plasma treatment of titanium implants which also have better results in terms of biocompatibility and bone tissue growth.

The plasma treatment has been confidently did on polymeric materials like polyethylene and polyethylene terephthalate to enhance biocompatible properties such as [7,8] wettability, roughness, cell adhesion, spreading and proliferation [9]. The plasma treatment is also done on metals to improve surface properties i.e. titanium implants to progress mechanical properties and biocompatibility [10].

Therefore, combining anodization and plasma treatment applied to titanium material to enhance the surface roughness and biocompatible properties is considered in the current study. The consequence of plasma treatment on the Ti samples was examined and particular properties of the samples were analyzed therefore.

2. Experimental Setup

2.1. Plasma Treatment of Ti Plates

Ti64 (grade 4) 2mm thick and 25mmx25mm samples were prepared. The Ti64 samples were polished mechanically with different SiC grit papers. Afterwards the samples were sand blasted with 120µm SiO$_2$ from a distance of 10mm perpendicular to the specimen surface at a pressure of 0.35MPa for 5sec. The samples were then cleaned ultrasonically in acetone and distilled water for 15min, respectively. The specimens were then subjected to argon oxygen plasma treatment under atmospheric pressure to clean and activates the surface of the samples as shown in Fig. 1. The plasma treatment was performed at a discharge power of 200W with argon and oxygen for 3min with a standoff distance as 5mm. Anodization were conducted using DC voltage source. The Aluminium plate of 50mmx50mm and 5mm thick was used as cathode, Ti samples were used as anode electrode. Diluted sulfuric acid was used as electrolyte and maintained a proper distance between the anode and cathode. The anodic oxidation were carried out for a constant time of 2min for different voltages between 10V to 90V.
2.2. Reflectance Characteristics and TiO2 Layer Thickness
The colors of anodized samples were measured using UV-VIS spectrophotometer at an observation angle 20°-70°. The reflectance data was measured for a wavelength of 200-900nm. The oxide layer thickness of the anodized samples was calculated by the wavelength and the maximum reflectance with the following equations (1) and (2) [11]. The maximum reflectance for particular wavelength was chosen for measuring the refractive index.

\[ t = \frac{\lambda_{\text{max}}}{4n_o} \]  

(1)

\[ n_o^2 = 5.193 + \frac{2.441 \times 10^7}{\lambda_{\text{max}}^2 - 0.803 \times 10^7} \]  

(2)

Where; \( t \) - thickness of the oxide film in nm, \( \lambda_{\text{max}} \) - wavelength of highest film intensity absorption in nm, and \( n_o \) - film refractive index. The oxide layer refractive index varied with wavelength, which is obtained by the Eq (2).

2.3. Surface Characterization
The surface topography of anodized samples was measured by using atomic force microscope (AFM; Model: Nanosurf Easyscan 2) to understand the nanosurface roughness and porous structure. The X-ray diffraction (XRD; Model: RIGAKUD/MAX2500) was used to examine the surface phase compositions and their percentages of the anodized samples using CuKα radiations with scanning speed at a rate of 2°/min.

3. Results and Discussion
The interference of colors are attained on titanium during anodizing at various voltages in diluted sulfuric acid electrolyte. The oxygen is formed on the titanium plates and reacts with titanium to form TiO2. The thickness of the oxide layer increases with increase in quantity of voltage applied as a function of time. For variation in the voltage, oxide layer thickness increases/ grows but halts when the resistance has reached at a point where the current decomposed to a value at which only few OH- ions are existing to support to continue film growth. Generally, it is known that titanium anodization produces an inert transparent oxide film capable to produce interference of colors. This process is very simple and...
economical to produce stable oxide with different colors at room temperature within short time (2-3 min) [12]. The oxide film has a capability to refract, reflect, and observe the light. The light from the light source falling on to the TiO₂ oxide film is partly reflected and partly transmitted. The portion of transmitted rays attaining the titanium surface is again partially fascinated but mostly reflected to oxide film. A phase shift occurred through this method composed with many reflections. The amount of absorption is reliant on the thickness of oxide layer.

The different thickness of oxide film causes the disparities of luminous flux, reflective index and refractive index, harvests various precise colors of the anodized titanium. Golden yellow color is obtained at 40V-45V; seemed that the color oxide films are appropriate in dental clinic to colorize the titanium dental outlines of dentures. This will enhance the aesthetic of implants by anodization due to golden yellow color symphonic with the color of the teeth. The other colors produced by anodizing may be used for color coding of the abutments to recognize implanted size and type. The obtained results are further discussed in the following Sub-sections.

3.1. Refractive Index

Figure 2 illustrates the spectral reflectance curves of anodized samples at diverse voltages from 10V to 90V, which demonstrates that the reflectance index of titanium anodized at different voltage characterized tiny yellow to dark gray colors. The spectral reflectance of individually anodized samples were measure by using spectrophotometer. The oxide film thickness and the refractive index was calculated from λ_{max} using the Eq (1) and (2).

![Figure 2](image.png)

**Figure 2.** Spectral reflectance versus wavelength for different applied voltage 10V-90V.

Figure 3 illustrates the variations in the refractive index versus the applied anodizing voltage. It’s observed that, the layer thickness increases with increasing applied voltage, which implies decrease in the refractive index of the oxide film. This may be due to the increasing of anodizing voltage which is responsible for decreasing density and compression of the anodic film [7]. The highest refractive index was obtained for the lowest applied voltage (10V) sample. In principle, the oxide layer thickness will be increases constantly with increased applied voltage for a fixed time. When the Ti start to react with oxygen, the color will be altered, the current density decreases intensely and the film is basically stable. Few researchers have examined the relationship of atmospheric plasma treatment on titanium sample to
enhance the biocompatibility. The plasma treatment of titanium improves the cell adhesion and osteogenic differentiation. Atmospheric plasma treatment imparts hydrophilicity to the surface of pure titanium and eliminates impurities from it. The plasma treatment induces adhesion bone marrow cells and protein to the material and trigger the surface tissue formation [13,14]. Based on this, plasma treated plus anodized samples may have high adhesion of cell growth and higher biocompatibility of the titanium material. It may improve the higher degree of tendency of bone contact with the implants and tissue growth.

![Figure 3. Refractive index of anodized samples.](image)

3.2. Surface Topography
Figure 4 describes the increase in nanosurface roughness with applied anodization voltage. The TiO$_2$ layer with 3D structures consisting of numerous open pores was made on the surface of the titanium plate during anodization. The rate of oxide layer growth is slow up to 50V, hence less peak and valley were observed in 3D topographical images (Fig. 5). Further, the valleys and peaks are more caused by the formation of volcano shaped oxide layer completely covering surface area of the titanium specimen. It has increased size and number of open pores on the surface of specimen with higher applied voltage, caused for increase in the nanosurface roughness. Atomic force microscope images clearly notices differences among the oxidized samples for varying voltage. It can observed that, sharp peaks and valleys in a range of width, with a roughness Sa of 9nm to 33nm. Due to anodic reaction, the oxide layer becomes thick. This is because of oxygen ion diffusion moved into the titanium interface, a migration of Ti$^{4+}$ ions from the titanium plate to electrolyte interface at the anode. The anodic oxidation is capable to change the surface roughness from smooth to rough by creating pores on the surface of the plate. The sulfuric acid is more effective to produce pores on the titanium plate compared to other acids. The formation of apatite is more in anodized specimen in sulfuric acid [15]. The increase in the apatite formation will enhance the bonding between the implant and bone when inserted into human body [16].
3.3 Phase Analysis

Figure 6 describes the phase pattern of the anodized sample at 80 voltage. The XRD pattern endorses the presence of TiO$_2$ on the anodized surface. The XRD pattern clearly shows us the presence of anatase and rutile structure on the anodized samples. The rutile peak intensity were relatively higher than that
anatase peak. Based on the published results, the structure of the oxide layer formed on titanium plate has characteristically stated to be amorphous at low voltage (<20V) and crystallization takings place at greater voltage (80V) [17] which are dominant phases with biocompatibility. This crystalline structure may be beneficial for bone growth and less healing time. Cells and bacterial growth will be high when compared to the amorphous structure.

Figure 6. Phase pattern of Anodized Titanium sample at 80V.

4. Conclusions
Anodization, an electrochemical process, was employed for oxidation of a titanium alloy. It concludes that colors of the samples and the anodization voltage can be related to one another. It is found that uniform interference of colors obtained by anodization process. These data may employed for dental implant aesthetic appearance and coding the size of abutments, screw diameter etc. Significant improvement in surface roughness was obtained for an increased voltage. The amount of surface roughness increased for 90V by 71% compared to 10V. Nanosurface roughness is on par with increased oxide layer thickness. The atmospheric plasma treatment and anodization may have significant influence on porous structure on titanium plates. The phase analysis evidently reveals the existence of two different anatase and rutile crystalline phases on the anodized titanium surface.

5. Future scope
The work needs to be continued to evaluate the biological properties of anodized samples for different applied voltages. In addition, the effect of atmospheric plasma treatment on the biocompatibility of titanium will be further investigated.

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