

# ANODIZATION OF TITANIUM ALLOY (GRADE-5) AND INFLUENCE OF ANODIC VOLTAGE AND ELECTROLYTIC CONCENTRATION ON MORPHOLOGY AND AESTHETIC APPEARANCE OF AN OXIDE LAYER

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**Abstract:** Titanium and its alloys are very useful nowadays, due to its sorcerous properties of high strength to weight ratio, high corrosive resistance, and biocompatibility; it is substantive as god metal. In the presented work the anodic film formation and variation in the aesthetic appearance of anodized titanium alloy (Ti6Al4V) surface are investigated at various levels of the applied potential difference across both terminal ends in an electrochemical circuit using sulfuric acid as an electrolyte. Various exercise sets of anodization (anodic voltage: 10 to 50 V, time of anodization: 4 minutes or 240 seconds per specimen, electrolyte concentration range: 0.5M to 4M, temperature of the electrolyte: at room temperature) were adopted as anodizing parameters, while altering the anodizing parameters different nano-porous structures were developed, Phase analysis revealed that 0.5M H<sub>2</sub>SO<sub>4</sub> leads anatase to rutile transformation. The effect of anodizing time on the surface roughness, morphology, and crystal structure of complex anodic films was studied. SEM (Scanning Electron Microscopy) analysis revealed, incremental change in the anodizing voltage leads deposition rate of the oxide layer or say thickness and also increase in pore diameter.

**Keywords—***Aesthetic appearance, Anodization, SEM.*

## 1. INTRODUCTION

Anodization is a process that leads to the formation of the oxide layer on the surface of the metal part, due to anodization interference in reflecting lights occurs which creates aesthetic change. The recognizable benefit of titanium anodization is the surface luster and surface finishing appears just as uniform as electropolishing, titanium anodizing gives the surface of variants in color. This can be used for marketing titanium parts as aesthetically unique and decorative. A.K. Sharma [1] investigated the effect of anodizing parameters such as voltage, the concentration of electrolyte used and temperature of electrolyte during anodization and optical properties on different operating conditions were analyzed when anodized titanium was used for space applications. He found that the colors of the oxide layers were changed with the change in the applied voltage and the slope between applied current density and time of anodization was rapid falls and after a particular value, it becomes a straight line approximately. Manjaiah et al. [2] investigated biocompatibility of titanium because of its ability to osseointegrate. He observed that an increase in applied voltage enhanced oxide deposition, this incremental change in the thickness of the oxide layer also increases resistance to flowage of the current through the circuit. At a particular value of the applied voltage, the thickness of the oxide layer reached to a critical value where the resistance has increased to an extent where only a few oxides of hydrogen ions were available to support continue oxide deposition.

Anodization using H<sub>2</sub>SO<sub>4</sub> as an electrolyte is an efficient way to develop nanoporous surface along with high surface roughness leads the apatite formation which is beneficial to osseointegration.

Trail et al. [3] suggested that the electrolytic conductivity increases with an increase in the temperature of the electrolyte; to perform this titanium grade-2 specimen was used. Anodization was performed at a temperature (25°C and 40°C) and anodizing time (5 and 10 minutes). During anodization, it was ascertained that at a higher temperature more current density and the less potential difference was obtained as compared to lower temperature. In the optical analysis, he observed that the oxide layer formed on the surface of the titanium alloy has a more homogeneous porous structure and oxide thickness at 25°C as compared to anodization performed at 40°C. Increase in time of anodization resulted in an incremental change in crystalline anatase.

Williamson et al. [4] explained that nano-sized pore formed during anodization is suitable for bone cell attachment and reproduction of cells when anodized titanium is used in orthopedic and dental implantation. In his investigation anodization of titanium was performed at various concentration levels of H<sub>2</sub>SO<sub>4</sub> as electrolyte and morphological analysis at varied voltage stages was observed. Indira et al. [5] reviewed the effect of anodization parameters including pH value of electrolyte, anodic voltage, the temperature of electrolyte and current density on the formation of TNT (Titanium Nano Tubes) because TNT formation plays a very important role in osseointegration when anodized

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titanium is used as a biocompatible material. Scanning electron microscopy and atomic force microscopy analysis showed that anodization of titanium was performed using sulphuric acid as electrolyte then within specific range of voltage very fine nanopores with a very small change in surface roughness was observed showing uniformity in structure. [6,7]. As well as the potential difference across terminal ends was increased, more oxygen ions diffusion would take place but suddenly the rate of diffusion was dropped due to a thick barrier of oxide layer was depleted on the metal surface which affects small current density at the surface where more diffusion of oxygen ions was commenced. [9] N. Masahashi et al. investigated that nano-sized pores appeared in oxide layer at minimum electrolyte concentration (0.1M) and surface area of pore increased with further increase in sulfuric acid concentration, incremental change in the electrolyte concentration ( $H_2SO_4$ ) prevailed that phase of titanium oxide changed from anatase to rutile. P. Mingthong et al. [10] explained in his surface analysis that if other parameters of anodization were kept constant microstructure of  $TiO_2$  was depend only on the concentration of the electrolyte, the surface study was performed by SEM and X-Ray powder Diffractometer to identify crystalline phase formation and revealed that anodized surface is more aqua phobic than the non-anodized surface. To obtain uniformity in pore formation and to enhance surface finish from metallic part such surface treatments were performed during anodization especially pickling and compact anodization but these type of treatments resulting in a reduction in endurance limit [11].

In summary previous researches showed that electrical variables like as current density, applied voltage, electrolyte concentration, the temperature of the electrolyte and duration for which current is passed through the circuit affect a lot to  $TiO_2$  formation. Due to this, pore density, pore size i.e. diameter and depth of pore as well as surface morphology also changed, thus it is concluded from literature that during the application of anodized titanium such as medical implantation, space applications or in any other purposes, these effective parameters should be critically analyzed and should be monitored during anodization.

## 2. EXPERIMENTAL PROGRAM

### 2.1 Sample Preparation

Titanium alloy grade-5 (Ti6Al4V) sheet of 0.4 mm thickness with specific surface finish was selected for anodization (elemental composition indicated in table 1), first of all, the specimen was abraded with SiC (Silicon carbide) abrasive paper of No. 200 to 1500 followed by  $SiO_2$  bath suspension resulting in a surface finish of 10-12 nm. The polished surface was cleaned ultrasonically in acetone suspension followed by immersion in  $HNO_3$  for 5 minutes and then washed by distilled water finally dried in hot air comes through the blower.

Table 1: Elemental composition of the Titanium specimen used for the anodization.

Element	Al	V	Ti
Composition	5.5-6.75%	3.5- 4.5%	Remaining

### 2.2 Anodization/oxide deposition

To attain porous structure on the surface of the specimen, titanium foil was cut in small size coupons having dimensions of 1cm x 1cm by masking the extra area using a tape or lacquer paint. The anodization was performed by using a schematic arrangement of two-piece electrode configuration setup of a conventional type using a D.C supply source. A schematic diagram is shown in fig 1. At first end, titanium specimen was connected as an anodic electrode (positive terminal), while on the other end, a commercial aluminum alloy sheet (same dimensions as titanium specimen) as a cathode (negative terminal). Various samples of electrolyte concentration ( $H_2SO_4$ ) of 0.5M to 4M were prepared individually and prepared total forty samples (five samples per concentration of electrolyte) of anodized titanium from operating voltage range of 10V to 50V. The temperature of electrolyte kept constant at 25°C (room temperature) by using mechanical stirrer to dissipate extra heat produced during the chemical reaction. Current flow in the circuit was recorded by the ammeter. Also to verify the flow of current at the end of each electrode multimeter was used.

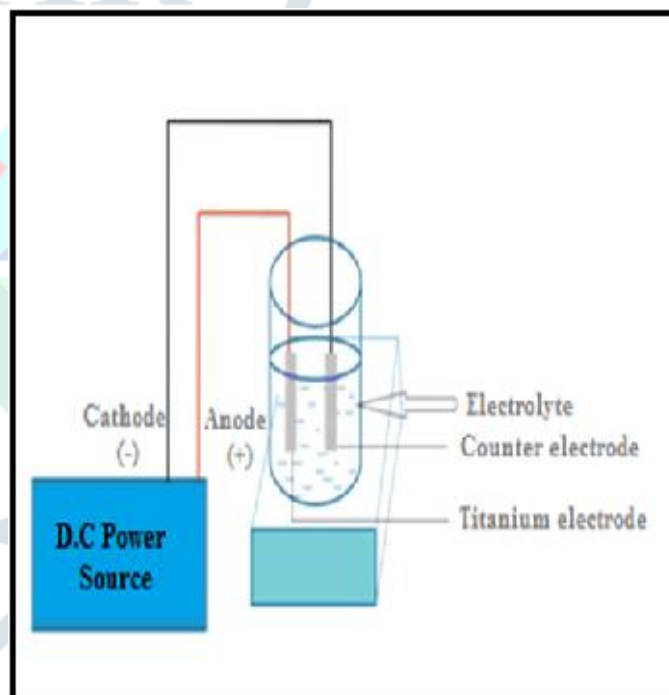


Figure 1: Schematic diagram of the anodization process

To investigate the effect of anodizing parameters like the change in concentration of the electrolyte, variation in anodic voltage and change in current density, many sets of experiments were performed, for this one parameter selected as variable and others were kept constant. For the consequence of the electrolytic concentration eight samples of solution lying in the concentration range of 0.5M to 4M (shown in table 2), were prepared by desegregating sulfuric acid and deionized water. During the anodization, the solution was agitated mechanically to dissipate heat which was evolved during the process. After anodization samples were rinsed in distilled water for 5 minutes and then keep out and dried at room temperature.

Table 2: Anodization process parameters

Sr. No.	Parameters	Range
1.	Voltage	10 V-50 V
2.	H <sub>2</sub> SO <sub>4</sub> Molarities	0.5M to 4M
3.	Time	240 s
4.	Temperature	25°C

The different test conditions were applied during the anodization resulting in variation in pore formation and have different morphology of oxide layer obtained on titanium specimen. Scanning electron microscopy revealed that after anodization very fine pores like nanotubes were distributed on the entire surface of the specimen. Effect of variation in anodic voltage prevailed aesthetic appearance (refer table 3), as well as the substantial topography and morphology of the oxide layer, were altered at a different level of voltages. Effects of variation in concentration of sulfuric acid and the current density were observed (refer table 2) during the entire process. The actual process set up used for deposition of the oxide layer is shown in fig. 2, have the following components:

1. D.C. supply source
2. Transformer to control the supply
3. Anode and cathode set up with electrolyte
4. Multimeter to verify voltage at both terminals
5. Ammeter.

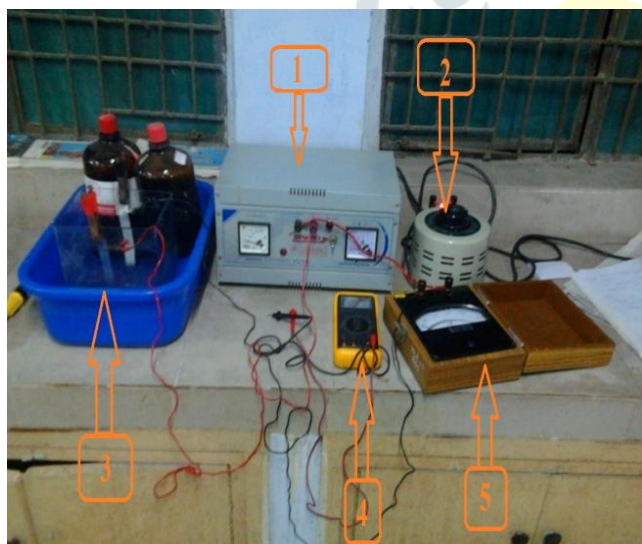


Figure 2: Experimental set up used in the anodization process

### 3. SAMPLES CHARACTERIZATION

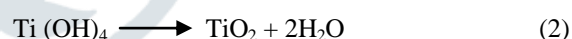
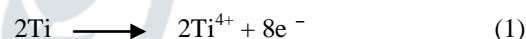
The morphological analysis of the oxide layer was performed by Field Emission Scanning Electron Microscopy (Carl Zeiss-Ultra Plus, FE-SEM). Images obtained from SEM were accessible to identify the number of pores, type of distributions, individual pore surface area, maximum pore size, pore density and the percentage of porosity. The surface roughness was examined by SURFEST SJ-210 (MITUTOYO) portable surface roughness tester.

## 4. RESULTS AND DISCUSSIONS

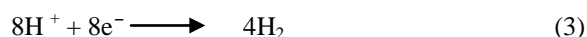
### 4.1 oxide layer mechanics

Multicolor images of the titanium oxide samples anodized in optimum concentration of 0.5 M and 1 M of sulfuric acid at various levels of anodic voltages are presented individually in table 3, which clearly showed that the aesthetic appearance of the anodized titanium plate is a function of voltage across terminals, at different operating voltages colors of the oxide layer were changed in each step. Different colors intensities produced during the process are not pigments or dyes. The colorful surface was obtained due to the interference phenomenon of reflected light, because when rays of light were fallen on anodized surface then due to different pores on surface of oxide layer reflection of light takes place at different angles for each anodized specimen processed under different variable conditions then different scattered images were produced showed different colorful surfaces for each oxide layer. The formation of the oxide layer is quite complex because some basic concepts of chemistry are involved in this process, so it is our need to understand these steps. The anodic layer generally called as an outside layer which is exposed to the electrolyte (H<sub>2</sub>SO<sub>4</sub>) has a large amount of OH<sup>-</sup> ions as compared to the inner layer and is considered to be Ti(OH)<sub>4</sub>. The inner layer, where the removing of hydrogen occurred, is represented as titanium oxide. Actually, there is variation in electrolyte concentration across the film, which can be written as TiO<sub>2</sub>.xH<sub>2</sub>O, to comprise the inner and outer anodic oxide layer. The chemical changes happened at the positive terminal are:

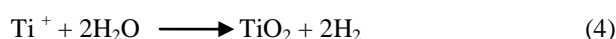
Removing of oxygen and electrons during oxidation from titanium surface,



The terminal at negative polarity evolve hydrogen,



Addition of equations from (1) to (3), the overall process of oxide formation is given:



By anodization method, the deposition of titanium dioxide on the titanium substrate contains mostly of rutile phase of TiO<sub>2</sub>. The formed oxide layer is corrosion resistant, the thickness of the layer increased continuously with an increase in anodic voltage but the thickness incremental rate is reduced with time due to barrier formation of oxides which opposes current density, however, hydrogen gas escaped during the process and titanium becomes heated because heat evolved by the chemical reaction occurred at the anode, equation 4 clearly justify it.



Table 3: Aesthetic appearance of titanium oxide at corresponding value of anodic voltage.

1 M of H <sub>2</sub> SO <sub>4</sub>			0.5 M of H <sub>2</sub> SO <sub>4</sub>		
Voltage	Color	Image	Voltage	Color	Image
10 V	Dull golden		10 V	Golden	
20 V	Dark Blue		20 V	Dark Blue	
30 V	Sky Blue		30 V	Sky Blue	
40V	Light Sky Blue		40V	Blue Froza	
50 V	Silvery		50 V	Silvery	

Table 3 shows, a small change in concentration of the electrolyte affects a little bit in the aesthetic appearance of the oxide layer at the corresponding voltage level, but on another side, if a change in electrolytic concentration is large, then at same voltage oxide layer became differ in color.

**4.2 Scanning electron microscopy**

SEM images of the oxide layer exhibit that pores are distributed on the entire surface which has crater type morphology, characteristics of pores formed i.e. shape, diameter, depth, and pore density depends on

the potential difference among electrodes as well as the concentration of the electrolyte, as indicated in fig. 3. It is observed that pore diameter varied in a continuous manner as voltage level increased, clearly depicted in SEM micrographs, as potential difference varied from 10 V to 50 V pore size also increased in the same manner from fig. 3; a to d. On the other hand, if voltage and time variables are kept constant (refer table 2) and electrolytic concentration (H<sub>2</sub>SO<sub>4</sub>) is reduced from 1 M to 0.5 M, very fine pores with high pore density and small pore diameters were produced, which enhanced the biocompatibility of anodized titanium.

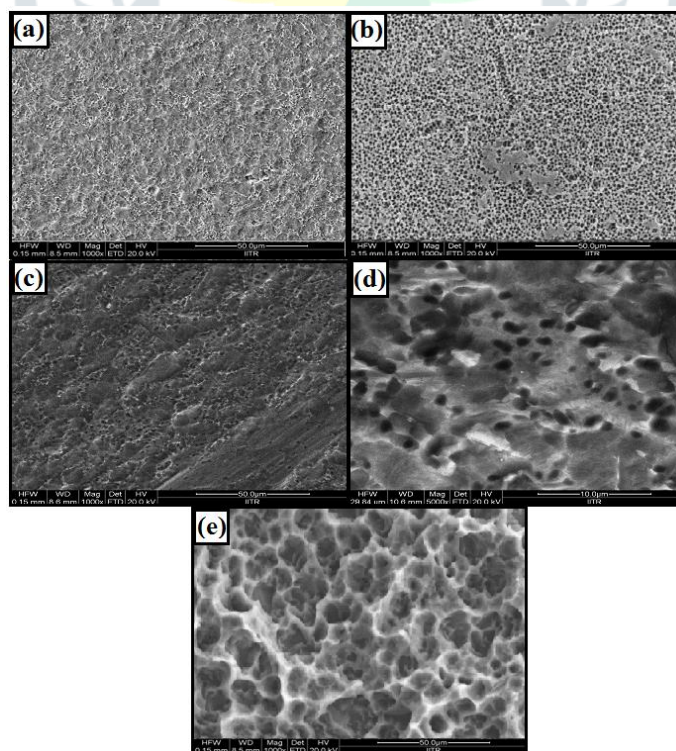


Figure 3: Selected SEM images to represent the type of pore formation at the different level of voltages (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V and (e) dissolution of oxide at 80 V respectively.

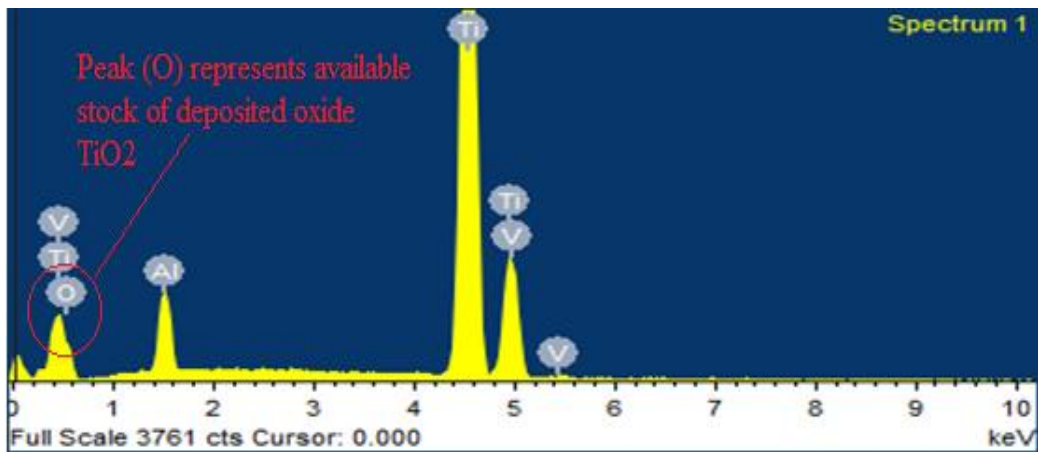


Figure 4: Energy Dispersive X-Ray Spectroscopy of the anodized sample.

### 4.3 surface roughness

EDS (Energy Dispersive X-Ray Spectroscopy) in figure 4 represents an oxide layer deposited on titanium substrate after anodization. It means oxide deposition offers a poor surface finish. Figure 5 represents the surface roughness is a function of anodic voltage, it means as the potential difference across the terminals increases the surface roughness also increased (shown in figure 5), the graphical representation shows slope

of the line is upwards it means surface roughness is in direct relation with anodic voltage as well as the concentration of the electrolyte. Reference non-anodized specimens have a surface finish of 12 nm (approximately) but during anodization change in voltage affects surface roughness in a direct manner except for this concentration of electrolyte also have the same relationship with the surface roughness.

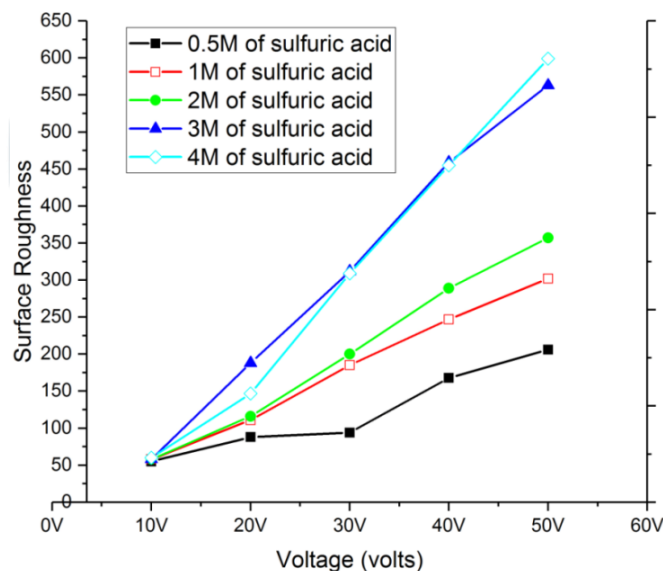


Figure 5: surface roughness v/s anodic voltage.

## 5. CONCLUSIONS

From the above observations, it can be concluded that:

- Anodization commences immediately with the current draws through the circuit when titanium immersed in the electrolyte, oxygen is generated at the anodic surface that then subsequently combined with the titanium to form titanium oxide. The oxide layer thickness deposited on the titanium alloy specimen is linearly dependent on applied anodizing voltage.

- It is observed that oxide layer thickness also depends on time for which anodization takes place, if the anodizing voltage is constant then the thickness of oxide layer depends on the time of anodization except this as the thickness of oxide layer increases the resistance of the oxide layer also increases.
- Inter-pore distance and pore diameter increase with an increase in anodizing voltage but beyond a critical value of the current density oxide layer, dissolution takes place.

- To obtain fine nanopores with high surface roughness optimized value of the concentration of the electrolyte is 1 Molar for sulfuric acid above this value surface roughness increased steeply.

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