

# Surface Characterisation of Bioactive Titanium Formed Via Anodic Oxidation

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**Abstract**— Anodic oxidation (AO) is one of surface modification method that able to produce specific topographies and enhance bone growth of the titanium (Ti). Modifying the oxide layer of titanium from smooth (bioinert) to rough/porous (bioactive) surface makes this material able to be used as artificial implant for biomedical application. In this study, the effect of AO on the characteristics of titanium in different electrolytes is evaluated. Anodised Ti was prepared using AO method in two different electrolytes (acetic and sulphuric acid) with same concentration (0.3 M). The applied voltage were varied range 50 – 200 V, with constant  $75 \text{ mA}\cdot\text{cm}^{-2}$  of current density for 10 min of oxidation process at room temperature. The anodised titanium films were characterised using X-ray Diffractometer (XRD), field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). From this study, it is proven that the strong acid (sulphuric acid) is more effective to be used as electrolyte in order to produce rougher surface (formation of anatase and rutile) compared to weak acid (acetic acid) which able to produce small amount of anatase only.

**Keywords**—Anodic oxidation, titanium, biomaterials, thin film, titania

## I. Introduction

Titanium has been used widely in various industries including biomedical due to its desirable properties such as excellent mechanical properties, lightweight, high corrosion resistance and biocompatibility [1]. Some application of titanium in biomedical including in orthopedic field which used as artificial hip-joint implant and bone fixation as well in cardiac and cardiovascular where artificial heart valve and stents were made by using titanium [2]. Titanium is a bioinert material; therefore surface modification is needed to change this bioinert to bioactive material in order to enhance the tissue compatibility and mechanically interlocking between implant and bone [3].

The thin oxide layer (10 - 15 nm) on the surface of titanium can be formed naturally by exposing Ti to the air [4]. There are many types of surface modification techniques can be applied to titanium to produce bioactive titanium oxide layer (titania or  $\text{TiO}_2$ ) such as chemical treatment, sol-gel, chemical vapour deposition, thermal spray, ion implantation and deposition, anodic oxidation and many more [5].

anatase and/or rutile crystal structure films showed excellent apatite forming ability and able to produced compact apatite layer covering all surface of titanium after soaking in simulated body fluid (SBF) [7]. The comparison between these three natural polymorphs of titanium oxide; anatase, rutile and brookite, anatase is the most suitable form of photocatalytic activity while brookite normally difficult to obtain during the ceramic processing [8]. Rutile is the stable form of titanium oxide at ambient conditions which possesses unique semiconductor characteristics [9]. The crystalline oxides (anatase and rutile) present several unusual features that become attraction to researcher and industry such as good photocatalytic behavior, superhydrophilicity and biocompatible properties [10].

In order to enhance the interlocking of implant to bone, titanium must possess high crystal structure (anatase and/or rutile), porous and superhydrophilicity surface [11]. Recently, anodic oxidation has proven useful for producing titanium oxide ( $\text{TiO}_2$ ) coating on titanium substrate and able to enhance the bone conductivity. It works incorporate electrode reactions in combination of electric field metal driven and oxygen ion diffusion to the formation of an oxide film on anode surface. Anodic oxidation technique also allows controlling the formation of oxide layer which is thicker than formed naturally [12]. The anodic oxidation able to increase the thickness of oxide layer which also increase the corrosion resistance of the titanium films. The oxide layer is not only to increase the corrosion resistance (passive oxide layer) of the titanium but also to enhance the conditions of the titanium to be compatible with bone.

Anodisation is a simple techniques that are useful at low temperature for  $\text{TiO}_2$  production layers on titanium substrates and can be divided into two categories; oxidation at low voltage levels (<200V) and high voltage levels (>200V) [13]. Some studies had been done using  $\text{H}_2\text{SO}_4$  as an electrolyte followed by heat treatment and this studied concluded that this process is an effective method to prepare bioactive titanium [14]. After anodic oxidation processes, the surface of the sample was observed to be covered by porous  $\text{TiO}_2$  (anatase and/or rutile phase). The effect on structures and the properties of the anodic oxides depends on various process parameters. On the other hand, other researchers also compared the crystallinity of  $\text{TiO}_2$  thick film anodised in  $\text{H}_2\text{SO}_4$ . The results showed that phase formation, colour, thicknesses, and microstructures of the films depended strongly on the current density. The anatase phase was observed to form at low current density ( $5 \text{ mA}/\text{cm}^2$ ), and rutile phase was detected at current density more than  $60 \text{ mA}/\text{cm}^2$  [15]. It is also proven that, by increasing of anodizing time results the higher intensity of corrosion and formed high thickness oxide layer [16].

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Basically, there are three types of polymorphs of titanium; anatase, rutile and brookite [6]. It is proven that

In the present study, an oxide surface of titanium was modified by anodising the commercially pure titanium (cp-Ti) in two different electrolytes of acetic and sulphuric acid. The applied voltage was varied to investigate the effect of

these acids in order to produce bioactive titanium. The oxide surface will be evaluated by using XRD, FESEM and AFM.

## II. Experimental Method

### A. Sample Preparation

A rectangular samples (with dimensions 25 mm x 10 mm and a thickness of 0.05 mm) made of a high purity titanium were used as substrates. The surfaces of the samples were polished using 1200 grit (~1  $\mu\text{m}$ ) silicon carbide (SiC) abrasive paper, followed by cleaning with acetone and distilled water, and drying using compressed air

### B. Anodic Oxidation

The anodic oxidation is done in an electrochemical cell containing 400 ml aqueous solutions of acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ , AO-A) and sulphuric acid ( $\text{H}_2\text{SO}_4$ , AO-S). The anode and cathode were titanium films and the anodising was done with a programmable power supply (Genesys 600-1.3, Densai-Lambda, Japan). The experimental parameters used are shown in Table I. The anodised titanium was cleaned by dipping in distilled water, followed by drying in still air. Figure 1 shows the schematic apparatus setup of anodic oxidation [17].

TABLE I. PARAMETERS USED FOR ANODIC OXIDATION

Parameter	Value (s)
Electrolytes	Acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ ), Sulphuric acid ( $\text{H}_2\text{SO}_4$ )
Concentration (M)	0.3
d.c voltage (V)	50, 100, 200
Current density ( $\text{mA}\cdot\text{cm}^{-2}$ )	75
Duration (min)	10

### C. Sample Characterisations

After anodic oxidation, the anodised titanium samples were washed with distilled water, dipping in acetone and

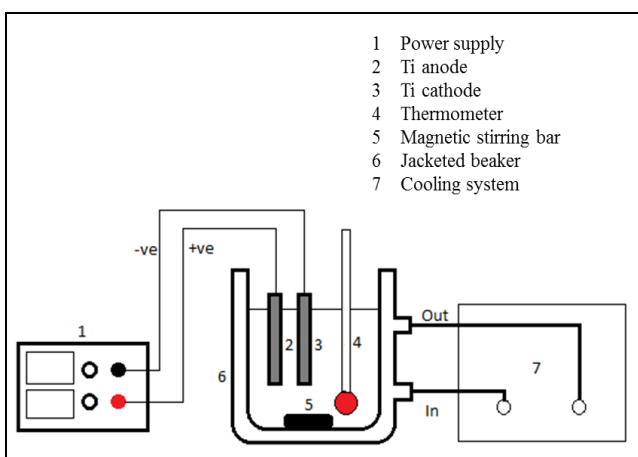


Figure 1. Schematic apparatus setup of anodic oxidation [17].

dried in still air before the analysis performs. The mineralogical composition of the films was determined using X-ray diffractometer (XRD; X'Pert<sup>3</sup> Powder, PANalytical, Netherlands) at 40 kV and 40 mA, angle of incidence of  $1^\circ$ , scanning speed of 0.067  $^\circ/\text{s}$ . The microstructures were examined by using field emission scanning electron microscopy (FESEM; JSM-7600F, Joel Ltd., Japan) at an accelerating voltage of 5 kV. The surface profile was determined by using atomic force microscopy (AFM; XE-100, Park System, South Korea) with 10  $\mu\text{m}$  scanning size, 250 – 850 nm wavelength, non-contact measurement mode and 3 mm distance between cantilever and sample.

## III. Results and Discussion

### A. Mineralogical of Samples

Figure 2(a) and Figure 2(b) show the XRD patterns of the anodised titanium films under different applied voltage and type of electrolyte at current density of  $75 \text{ mA}\cdot\text{cm}^{-2}$ . It can be seen from the Figure 2(a) and Figure 2(b) that there were significant effect of applied voltage and type of electrolyte used in formation of anatase and/or rutile phase on the titanium film surface. Anatase was detected when the applied voltage of oxidation process more than 200 V and 100 V for AO-A and AO-S respectively

During the anodic oxidation, micro-arc sparking occurred on 200 V of AO-S sample. This leads to formation of mixture anatase and rutile on titanium film surface. It is also observed that the crystalline structure of anatase phase are higher for AO-S compared to samples AO-A at 100 V. From Figure 2(b), mixture of anatase and rutile was observed on the sample formed in  $\text{H}_2\text{SO}_4$  electrolyte solution at 200 V. This happened due to localised heating occurred which leads to micro-arc sparking resulted rutile phase becomes more stable than anatase. A weak acid (acetic acid) is able to form a thin anatase structure under low voltage (<200 V). Meanwhile, a high voltage ( $\geq 200$  V) was used to formed high crystalline structure of anatase on titanium film surface. Furthermore, different type of electrolyte being used for anodic oxidation process with same applied voltage and current density produced different crystalline structure on the samples. The results as shown in Figure 2(a) and Figure 2(b) indicated that the amount of anatase and rutile increased with increment of applied voltage for both electrolytes.

In anodic oxidation, oxygen from the acidic electrolyte is produced at the anode and this can react with the metal to thicken the metal oxide layer ( $\text{Ti}^{4+}$  ions). The result indicated that the higher the voltage, the thicker (more porous) the oxide layer and amount of anatase produced. Sulphuric acid (fully ionise) also have better corrosiveness when used as electrolyte compared to acetic acid (not fully ionise) due to its proton (hydrogen ion) capabilities to be transferred to a water molecule to produce hydroxonium ion. The summary of XRD analysis was tabulated in Table II.

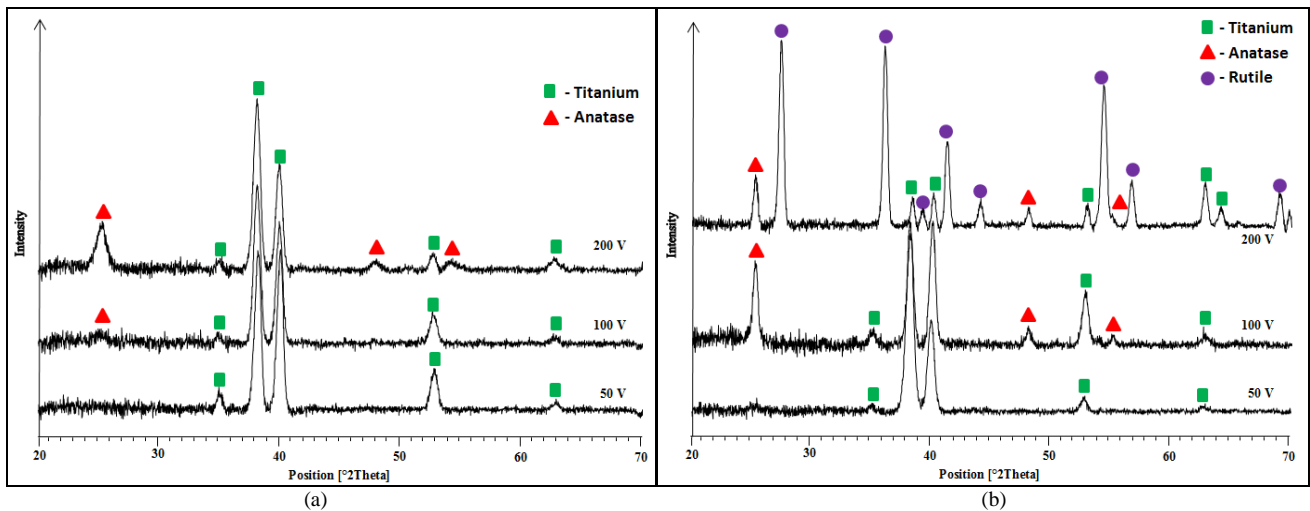


Figure 2. XRD analysis of anodised samples at  $75 \text{ mA.cm}^{-2}$  in; (a)  $\text{C}_2\text{H}_4\text{O}_2$  and (b)  $\text{H}_2\text{SO}_4$ .

TABLE II. SUMMARY OF XRD ANALYSIS

Voltage (V)	AO-A	AO-S
50	No anatase and rutile form	
100	Very low of anatase formed	High crystalline of anatase observed
200	Better anatase was detected than 100 V	Mixture of anatase and rutile were identified

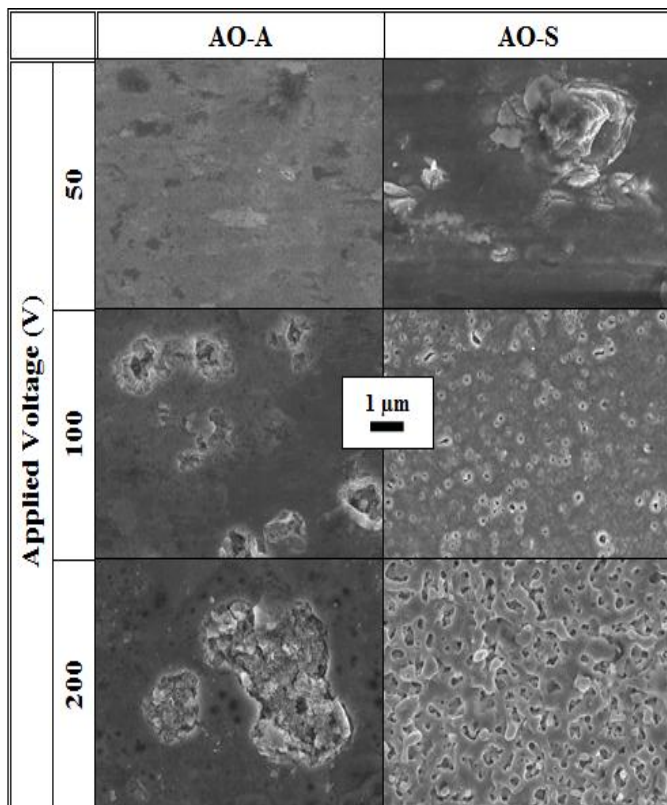


Figure 3. FESEM micrographs of anodised titanium in  $\text{C}_2\text{H}_4\text{O}_2$  (AO-A) and  $\text{H}_2\text{SO}_4$  (AO-S) at  $75 \text{ mA.cm}^{-2}$ .

### B. Surface Morphological of Samples

Figure 3 shows the surface morphologies of the anodic films obtained from oxidation process in different electrolyte and applied voltage observed by FESEM. For sample prepared using AO-A, a smooth and clear polishing effect can be seen at 50 V. Applied voltage of 100 V is the onset of anodising effect where some craters are formed on certain area of titanium surface. The anodising effect (crater) becomes bigger and there are many pores observed on the sample surface with increment of applied voltage up to 200 V.

After anodic oxidation in  $\text{H}_2\text{SO}_4$ , the anodising effect is seen on titanium surface at 50 V. There are many pores observed on the titanium films at 100 V, where mixture of small open and close pores were formed covering the surface of the specimen. At 200 V, an oxide layer with three-dimensional oxide structure consisting of numerous open pores formed on the surface of titanium sample. During this process, gas evolution and spark discharged occurred. It is increased the size and number of pores formed on the sample, which increased the surface roughness of the specimen.

The oxide layer became thicker after the oxidation reaction increasing due to the oxygen ion diffusion ( $\text{O}_2$  ions) transferred into the titanium interface and migration of  $\text{Ti}^{4+}$  ions from the titanium substrate to the film/electrolyte interface at the anode. From the Figure 3, it shows that the anodic oxidation able to change smooth surface of titanium to rough surface by increasing the applied voltage of the system. Apart from that, strong acid (sulphuric acid) is more efficient to produce rougher surface compared to weak acid (acetic acid). The three-dimensional oxide structure at 200 V of AO-S provided better nucleation site for apatite formation when soak in simulated body fluid [17]. This will enhance the interlocking of implant to bone when implanted inside human body as artificial implant. From these results, it shows that AO-A need higher potential energy to breakdown the dielectric layer to produce more porous surface for high crystalline of anatase and/rutile to be formed on titanium surface and vice versa for AO-S.

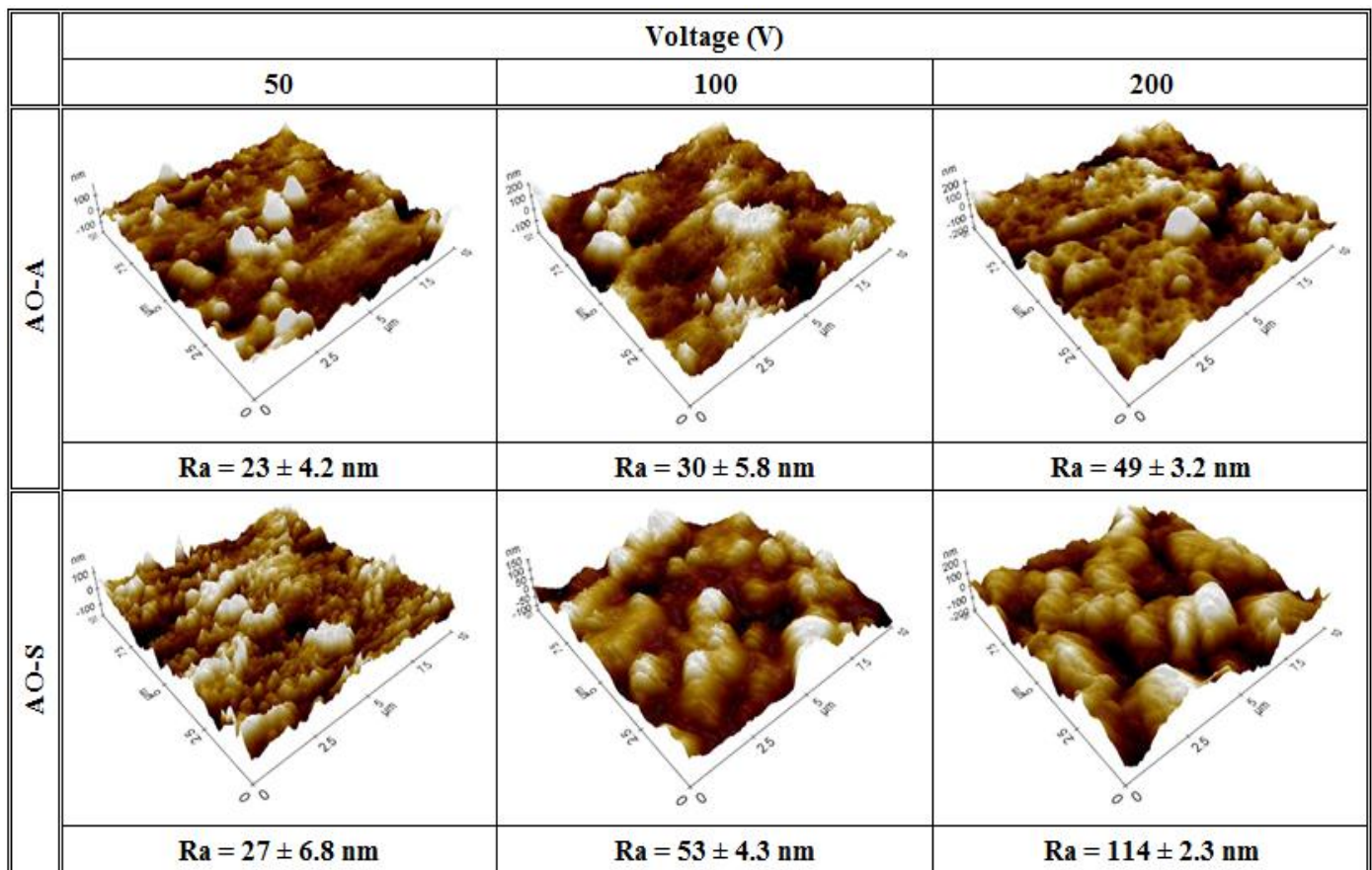


Figure 4. AFM images of anodised titanium in  $C_2H_4O_2$  (AO-A) and  $H_2SO_4$  (AO-S) at  $75 \text{ mA.cm}^{-2}$ .

### C. Surface Profile of Samples

Numerous open pores formed on the surface of titanium under certain conditions and increment of pore size also the existence of white subsurface leads increment of surface roughness (Ra). From Figure 4, At 50 V of AO-A, there are some scratches valley (effect from polishing) still visible on three-dimensional AFM images. The amount of oxide formed on the titanium surface for AO-A was increased with increment of applied voltage and makes the polishing effect unseen. The shape of oxide also changed from small and shard oxide at 50 V to dented (volcano shaped), uneven and big oxide at 200 V which covered all surface of the titanium. The surface roughness of the specimen also increased when the applied voltage was increased. This result supported by the XRD and FESEM results.

For AO-S, at 50 V there are numerous small and sharp oxides formed on the titanium surface and the polishing effect is unseen on this sample. This oxide change to big and scatter oxide when the applied voltage increased to 100 V. There are some black spots on the sample surface due to open pores as shown in Figure 2 of FESEM result. At 200 V, the big oxides merge to formed network of oxide and black spots became more seen compared to 100 V due to overlap oxides, number of open pores increased and covered almost all area of the titanium surface.

Figure 4 indicated that the surface roughness (Ra) of AO-A slightly increased when the applied voltage increased from  $23 \pm 4.2 \text{ nm}$  (50 V) to  $49 \pm 3.2 \text{ nm}$  (200 V). While for AO-S, the Ra increased drastically from  $27 \pm 6.8 \text{ nm}$  at 50 V to  $114 \pm 2.3 \text{ nm}$  (200 V). There is a huge different of Ra

value for AO-A and AO-S at voltage 100 V and 200 V. This happened due to type of electrolyte been used. The electrolyte itself had different oxygen ion diffusion potential, where AO-S have better ionise than AO-A as mentioned in previous analysis.

## IV. Conclusions

In conclusion, this paper presented works on preparing bioactive titanium from bioinert by performed surface modification via simple anodic oxidation process, which able to convert the amorphous oxide of titanium into an anatase or mixture with rutile. From this study, it shows that the sulphuric acid is and optimal electrolyte when the aim of the study is to obtain anatase crystalline on the titanium film compared to acetic acid. This electrolyte able to formed porous surface with anatase even at some cases up to mixture with rutile crystalline without performing and additional treatment (heat or alkaline treatment) or technique for conversion of an amorphous oxide.

From the study, both AO-A and AO-S sample are greatly affected by high potential of anodising (applied voltage). Different types of electrolyte also lead to differed result even the other parameters are same. The applied voltage and type of electrolyte of anodic oxidation affects the surface morphology and crystallinity of the titanium. Porous surface and anatase and/or rutile was formed on the titanium surface when the applied voltage  $\geq 100 \text{ V}$  for AO-S. While for AO-S, this electrolyte only able to produce small amount of anatase even the applied voltage is 200 V, which needs other treatment to enhance the surface properties of the titanium.

Finally, the applied voltage and type of electrolyte of anodic oxidation plays an important role in the formation of anatase of Ti specimen. The surface roughness of the Ti specimens was increased with increment of applied voltage. More porous surfaces of Ti will lead more sites for apatite formation. It can be conclude that, the surface morphology and profile of Ti films were strongly affected by the applied voltage and type of electrolyte to meet clinical need by changing the smooth surface of Ti to rough/porous, where this kind of surface able to provide more site for apatite formation when implanted inside human body as biomaterial.

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