

Physical and Chemical Properties of Anodised Titanium in Sulphuric Acid for Biomedical Application

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Abstract: Fabrication of bioactive titanium (Ti) by using anodic oxidation method for biomedical application as a high-performance material with good biocompatibility properties has been introduced since many years ago. The current study aims to investigate the physical and chemical properties of anodised Ti oxide layer in sulphuric acid at different applied voltages. High purity Ti films were anodised with varying voltages (50-200 V) in 0.3 M of sulphuric acid at 75 mA.cm⁻² current density for 10 min. Anodised Ti films were characterised for physical properties (colour, porosity, surface morphology, thickness) and chemical property (surface mineralogy). The anodised Ti produced using high voltage (200 V) appeared to be highly porous and demonstrated high crystallinity of rutile and anatase as well thicker oxide layer. From the results, the correlation between the physical and chemical properties can be used as a prediction of the properties of anodised Ti in sulphuric acid for a different parameter.

Keywords: Anodic oxidation, prediction, biomaterials, titanium thin films, colour

1. Introduction

The advanced of medicine and the increase in human life expectancy, there is now a greater need for biomaterials to remedy problems related to the reconstruction of tissues and organs, as well as problems related to injury or diseases attribute to ageing or trauma from accidents [1]. Biomaterials are used for the purpose of biomedical or clinical applications to treat diseases or injuries by replacing or reconstructing broken parts, tissues and organs, or by functioning in close contact with the tissue of live organisms especially humans [2]. Therefore, the development of bone-bonding materials with different mechanical properties is desired.

Titanium (Ti) is biocompatible, lightweight, and corrosion-resistant and has superior mechanical properties. Therefore, they have been widely used in biomedical implants and dental applications. These characteristics make them very suitable elements compared to other biomaterials [3-5]. Ti can be used as a material for an implant after undergoing a surface modification to modify the oxide of the material from bioinert to bioactive. Anodic oxidation is a promising technique that has the ability to enhance the physical and chemical properties of Ti without changing its microstructure. This method is able to produce anatase and/or rutile phases on the Ti surface in shorter time,

simplest, and cost-efficient compared to other methods such as alkaline treatment, gel oxidation, plasma spraying, and biochemical methods [6-7].

Anodic oxidation is a well-established method to produce different properties of an oxide layer on metals by altering the process parameters such as anode potential, temperature, type of electrolyte, and current [8-10]. It can be used to increase the thickness of oxide layer by transforming the bioinert Ti to bioactive Ti which able to enhance the corrosion resistance properties of the Ti and decrease the ion release, colouration, and porous (anatase and/or rutile) coatings [6]. Anodic oxidation technique also allows controlling the formation of the oxide layer which is thicker than formed naturally [11]. The properties of the implant surface play a crucial role in facilitating more sites for bone-like apatite nucleation [12]. These properties include porosity, roughness, high crystallinity, and wettability are ideal for enhancing the precipitation process [13].

In this present study, an oxide surface of Ti film was modified by anodic oxidation in sulphuric acid. The applied voltage was varied to investigate the effect of anodic oxidation on Ti films including the colour of anodic films, surface morphology, surface mineralogy and thickness. The prediction of anodised Ti properties based on the observations during anodic oxidation and its colour will be introduced.

2. Materials and Methods

2.1 Anodic Oxidation

High purity Ti films with dimensions 25 mm x 10 mm x 0.05 mm were wet hand-polished with 1200 grit silicon carbide (SiC) abrasive paper to remove its naturally formed oxide layer until a shiny metallic surface was obtained [14]. The Ti films were immersed in an ultrasonic bath containing acetone for 3 minutes and rinsed with distilled water prior to being dried with compressed air. Anodic oxidation is carried out in an electrochemical cell containing 0.4 L solution at ~ 25°C. The anode and cathode both are Ti film and the anodising are done with a programmable power supply (Genesys 600-1.3, Densai-Lambda, Japan). Sulphuric acid was used as an electrolyte (0.3 M) at different applied voltages (50-200 V) and a current density of 75 mA.cm⁻² for 10 minutes at room temperature. The anodised Ti films are cleaned by dipping them in 50 mL of distilled water 3 times, followed by drying them in still air.

2.2 Characterisation

The colour of anodic films was recorded using a digital camera (iPhone 5s, Apple) [15]. The mineralogical composition of the anodised films was examined using glancing angle X-ray diffraction, GAXRD (X'Pert³ Powder, PANalytical, Netherland) at 40 kV accelerating voltage and 40 mA of current, angle of incidence of 1°, 0.067°/s scanning speed. The surface morphology was determined by using field emission scanning electron microscopy, FESEM (JSM-7600F, Joel Ltd., Japan) at accelerating voltage of 7 kV. Meanwhile, the focused ion beam, FIB (Dual beam, Helios NanoLab 650, FEI) was used for cross-sectional imaging (thickness). The pores size was determined by using ImageJ software.

3. Results and Discussion

3.1 Colour of anodic films

Ti exhibits various colour because of thin film interference of passive layer. Numerous studies have been done on Ti and its alloys to study the colour of the metals and suggested that the colour of the thin film is strongly dependent on the thickness of the oxide layer and incident angle of light beam [16-17].

Fig. 1 set outs the visual appearance of anodised Ti prepared using sulphuric acid as a function of applied voltage. According to multi-beam interference theory, the colouring resulted from the interference between the light beams that are reflected from (a) the film surface and (b) the film-substrate interface [18]. The colour of anodic films can be classified into two groups based on the arcing during anodisation and its effects: non-arcing (blueish yellow) and arcing (dark purple and grey).

In this study, the colour variations of anodised Ti films were influenced by the applied voltage. The films resulted in a greater intensity of arcing in short time at a high current density that leads to micro-arc sparking occurred. This happens due to the higher electrical conductivity of the solution that trigger by higher cell potential (voltage) that raised the temperature on the anode. High temperature can melt the oxide layer that known as localised heating phenomenon. Further anodisation will lead to micro-arc sparking. This phenomenon exists due to the exposure of films substrate to the electrolyte and excessive ions migration from the (rapid electrolyte to exposed Ti Substrate. Meanwhile, the arcing process resulted from the dielectric breakdown reduction in the resistance of an electrical insulator) [19]. Table 1 displays the summary of the colour of anodised Ti films in sulphuric acid.

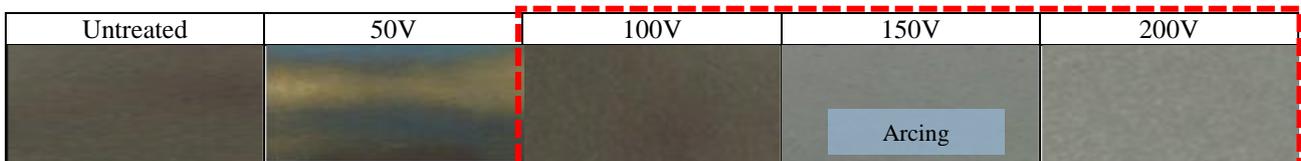


Fig. 1 Colour of anodised Ti films as a function of applied voltages (50-200V).

Table 1 Summary of anodised Ti colour

	Voltage (V)	Arcing ability	Colour	Observation at anode
Non-arcing	50	Weak	Blueish yellow	<ul style="list-style-type: none"> Few bubbles were produced and stick on the film No white-subsurface due to no arcing occurs
	100	Strong	Dark purple	<ul style="list-style-type: none"> Numerous bubbles were produced and actively moving to air Thin white-subsurface
Arcing	150	Very strong	Grey	<ul style="list-style-type: none"> Numerous and excessive bubbles produced and intensely moving to air Thick white-subsurface Breakdown voltage observed
	200	Very strong	Whitish grey	<ul style="list-style-type: none"> Numerous and excessive bubbles produced and intensely moving to air Thick white-subsurface Breakdown voltage observed Micro-arc sparking occurred

Table 2 Prediction of anodised Ti properties

Colour	Observations	Possible properties
Blue, yellow, bright purple, brown	~ Onset formation of O ₂ bubbles ~ Bubbles attached on Ti surface ~ No arcing ~ Voltage dominant	~ Smooth and dense morphology ~ No or low crystallinity of anatase ~ Thinner oxide ~ Lowest porosity
Bluish purple, purple	~ More O ₂ bubbles formed ~ Bubbles are moving upward to the air ~ Arcing and dielectric breakdown occurred ~ Thin formation of white substance at interface electrolyte, Ti film and air ~ Voltage dominant	~ Uneven morphology ~ Low anatase and no rutile ~ Thin oxide ~ Low porosity
Grey	~ Numerous O ₂ evolutions ~ Bubbles are moving rapid and intense to the air ~ Arcing and dielectric breakdown occurred ~ Thick formation of white substance ~ Current density dominant	~ Consistent morphology (donut-shape) and small pores boundaries ~ High anatase and/or low rutile ~ Thick oxide ~ High porosity
Whitish grey	~ Enormous O ₂ evolutions ~ Bubbles are moving rapid and intense to the air ~ Arcing and dielectric breakdown occurred ~ Thicker formation of white substance ~ Micro-arc sparking observed ~ Current density dominant	~ Even morphology (melted donut-shape) and wider pores boundaries ~ High rutile and low anatase ~ Thicker oxide ~ Higher porosity

Based on the results reported in present and previous studies conducted by the author [14-15, 20-21], the prediction of the properties of the anodised Ti in sulphuric acid such as its morphology and mineralogy can be made based on the anodic oxidation reactions and the colour of the films as shown in Table 2. So far, this prediction is eligible for two types of electrolyte only (sulphuric and acetic acid). Others electrolyte must undergo anodic oxidation to confirm and validate the suitability and reliability of this prediction.

3.2 Surface morphology (FESEM)

Fig. 2 shows the surface morphology of anodised Ti produced at voltages of 50, 100, 150, and 200 V. It can be observed that the porosity of the oxide layer increased with applied voltage. Besides that, the number of pores and its size increased with increasing of applied voltage. The formation of pores on Ti surface occurred due to the oxygen gas evaluation, where the oxygen ion transferred into Ti interface and migration of Ti⁴⁺ ion from the Ti substrate to the film-electrolyte interface at the anode. The effect of applied voltage on the morphology of the

films is tabulated in Table 3 and the pore size was calculated by using ImageJ software.

3.3 Surface mineralogy (GAXRD)

The mineralogical of anodised Ti at different voltages of 50-200 V is illustrated in Fig. 3. The anatase phase (JCPDS No.: 3-7543) revealed in GAXRD results in the early stage of anodisation. Rutile phase (JCPDS No.: 7-6757) was detected starting at 150 V. As the arcing activity become more intense, the X-ray peaks (major peak) of anatase or rutile gradually increased. At low voltage (50 V), the low crystallinity of anatase is observed indicates that thin coating of anatase formed on the surface of the film. By increasing the applied voltage to 100 V, the intensity of anatase peaks (25°2θ is major peak of anatase) increased gradually. Mixtures of anatase and rutile phases were observed at 150 V to comprise the oxide layer. Further anodisation (200 V), greater amounts of rutile over anatase were present since the micro-arc sparking occurred during the process. It is well known that the anatase transforms to rutile at a temperature > 600 °C [22].

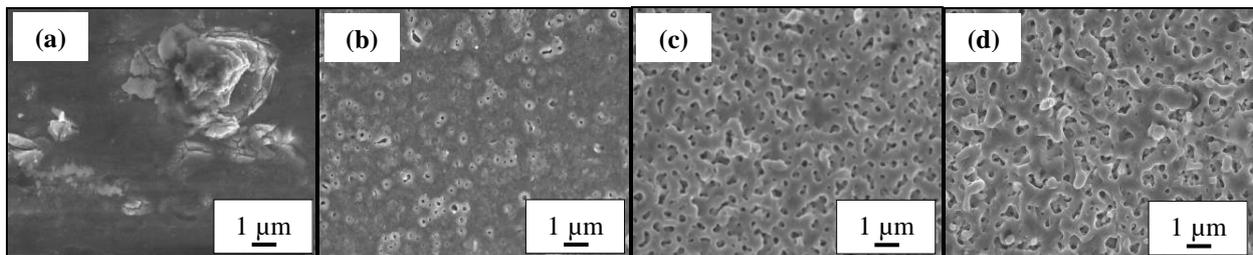


Fig. 2 FESEM micrographs of anodised Ti obtained at different applied voltages: (a) 50V, (b) 100V, (c) 150V, and (d) 200V.

Table 3 Summary of surface morphological of anodised Ti at voltages of 50-200V

Voltage		Type of Morphology	Pore no.	Pore distribution	Pore size (μm)		
Type	(V)				Mean	Min	Max
Low	50	Smooth and open cracks	Few	Uneven	NA		
High	100	Various porosity	Many	Uneven	0.170	0.078	0.404
Very high	150	Consistent porosity	Many	Even	0.396	0.215	0.866
	200	Consistent porosity	Many	Even	0.402	0.110	0.850

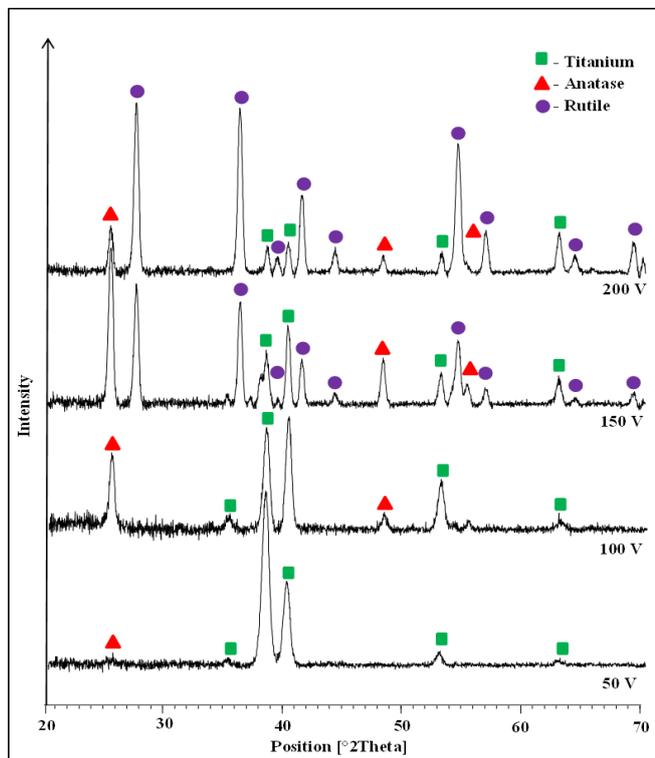


Fig. 3. GAXRD patterns of anodised Ti.

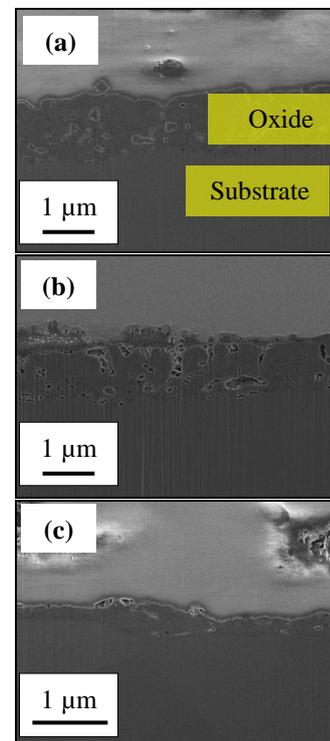


Fig. 4 FIB micrographs of anodised Ti: (a) 100V, (b) 150V, and (c) 200V.

Table 4 Summary of GAXRD results and observation on bubbles during anodisation process

Voltage		Type of mineralogy	Oxygen gas (bubble) at anode	
Type	(V)		Amount	Condition
Low	50	Low anatase	Few	Stick on Ti surface
High	100	High anatase	Many	Some evolve to air (steadily)
Very high	150	Very high anatase + high rutile	Enormous	Continuously evolve to air (rapid)
	200	Low anatase + very high rutile		

The summary of GAXRD results and observation on bubbles formed during anodic oxidation process is tabulated in Table 4.

3.4 Thickness of oxide layer (FIB)

Fig. 4 shows that FIB images of the cross-section tilted at 54° of the anodised films. The images consist of two layers (substrate and oxide layer). The images revealed that the thickness of anodised Ti films increased with increasing of applied voltage. At some point (150-200 V), the thickness of the films almost similar even though anodisation reactions not same. The images set out that the thickness of anodised films at 100 V, 150 V

and 200 V are $0.44 \pm 0.20 \mu\text{m}$, $1.00 \pm 0.18 \mu\text{m}$, and $1.00 \pm 0.23 \mu\text{m}$ respectively. The FIB images show that the microstructure (pores or void) of both specimens (150 and 200 V) are different despite having similar thickness.

4. Conclusions

As for conclusions, the applied voltage has a significant influence on the properties of anodised Ti such as colour, surface morphology, mineralogy, microstructure, and thickness. With the increase in applied voltage, the oxide layer of the film was observed become porous, rougher and thicker. The correlation between the reactions during the anodic oxidation and the

colour of anodic films can help to predict the surface morphology, surface mineralogy, surface profile, and thickness of its oxide layer. The findings indicate that both the observation and the colour of anodic films are needed to have a better prediction of the properties of the films. Proper parameters combination of anodic oxidation such as applied voltage, current density, type of electrolyte, concentration of electrolyte, treatment duration and much more can influence the intensity of arcing process, which can affect the properties of the films.

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