

SURFACE PROPERTIES, CRYSTALLINITY AND OPTICAL PROPERTIES OF ANODISED TITANIUM IN MIXTURE OF β -GLYCEROPHOSPHATE (β -GP) AND CALCIUM ACETATE (CA)

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Anodic oxidation is an electrochemical method for the production of ceramic films on a metallic substrate. It had been widely used to deposit the ceramic coatings on the metals surface. This method has been widely used in surface modification of biomaterials especially for dental implants. In this study, the surface morphology, crystallinity and optical properties of titanium foil was modified by anodising in mixture of β -glycerophosphate disodium salt pentahydrate (β -GP) and calcium acetate monohydrate (CA). The experiments were carried out at high voltage (350 V), different anodising time (5 and 10 minutes) and current density ($10\text{-}70\text{ mA.cm}^{-2}$) at room temperature. Anodised titanium was characterised by using field emission scanning electron microscopy (FESEM), X-ray diffractometer (XRD), and UV-Vis spectrometry. The result of the experiment showed that surface morphology, crystallinity and optical properties depended strongly on the current density and anodising time. More porous surface and large amount of anatase and rutile was produced at higher current density and longer anodising time. Apart from that, it also revealed that the energy band gap of anodised titanium increases as the increasing of current density due to the presence of anatase and rutile TiO_2 .

Keywords: anodic oxidation, titanium, titanium dioxide, FESEM, band gap

INTRODUCTION

It is well known that titanium and its alloys have become one of the popular biomaterial for implants application due to its properties such as biocompatibility, promote osseointegration, good mechanical properties, low modulus of elasticity and high corrosion resistance [1-5]. Nowadays, there is an increasing trend in titanium implants especially for dental implants and prostheses [6]. The surface of implant plays a crucial role in the process of osseointegration. A number of efforts had been done by researchers on improving the

surface roughness, crystallinity and wettability of implant material in order to accelerate bone healing and enhance anchorage to the implant. Amount of bone-in-contact (BIC) is an important key to achieve long-term success of bone implant. Surface treatment of implant materials aims to maximise the BIC and promote the osseointegration [7]. Anodic oxidation provides modification in term of surface morphology, crystallinity and chemical composition of oxide layer [8]. The modified oxide layers can be 10 nm to 40 μm of titanium dioxide (TiO_2) layer. It is a simple method which is able to improve the

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mechanical properties, biocompatibility, crystallinity, corrosion resistance, adhesive bonding of oxide layer and provide higher clinical success rate [1,9-11]. The present study aims to investigate the surface morphology, crystallinity and optical properties of anodised titanium in the electrolyte of calcium acetate and β -glycerophosphate.

MATERIALS AND METHODS

Sample Preparation

High-purity titanium foils with dimension of 25 mm x 10 mm x 0.05 mm were wet hand polished with 1200 grit abrasive paper ($\sim 1 \mu\text{m}$) to remove native layer, and then immersed in an ultrasonic bath with acetone, rinsed with distilled water, and then dried using compressed air.

Anodisation

Anodic oxidation was done by using programmable power supply (Genesys 600-1.3, Densei- Lambda, Japan) in 400 ml electrolytic solution of β -GP (Sigma, $\geq 98.0\%$) and CA (HmbG, $\geq 90.0\%$) at room temperature (25°C). The experimental parameters used are shown in Table 1. The anodised foils were cleaned by dipping in distilled water, followed by drying in air.

TABLE 1. *Parameters used for anodic oxidation.*

Parameter	Values(s)
Electrolytes	0.02 M β -GP + 0.2 M
Concentration	CA
d.c voltage (V)	350
Current density (mA.cm ⁻²)	10, 30, 50, 70
Duration (min)	5, 10

Characterisation

The microstructures were examined by using FESEM (JFM-7600F, Joel) at an accelerating voltage of 2.0 kV. The mineralogical composition of the films was determined by using X-ray diffraction (D8 Advance, Bruker) at 45 kV and 40 mA, angle of incidence of 0.8° , scanning speed of $0.01^\circ 2\theta$. Absorbance spectra were recorded in the range 300-600 nm by using UV-Vis spectrophotometer (UV-1800, Shimadzu Corp.). The anodised titanium was placed across the sample radiation pathway while the uncoated titanium foil was put across the reference path. The absorption data were used for the determination of the band gap energy (E_g).

RESULTS AND DISCUSSION

Field Emission Scanning Electron Microscopy (FESEM)

Figure 1 displays FESEM images of the anodised films as a function of anodising time and current density. At low current density, such as 10 mA.cm^{-2} , the overall sample surface was relatively smooth even the anodising time increased to 10 minutes. For the sample anodised at 30 mA.cm^{-2} , small pores were formed on the surface. At 50 mA.cm^{-2} , small pores were formed after anodised for 5 minutes. In contrast, donut-shaped pores with large pore size were formed on the surface after anodising for 10 minutes. The sample for 70 mA.cm^{-2} showed much higher porosity than other samples. Larger donut-shaped pores were formed after anodising for 10 minutes. For the surface morphology of anodised titanium in accordance with the anodic oxidation conditions, larger pore size was observed with greater current density and anodising time. It also can be indicated that, under the same current density, prolonged anodising time leads to larger pores on the surface of titanium foils. The summary of microstructure at different voltage is tabulated in Table 2.

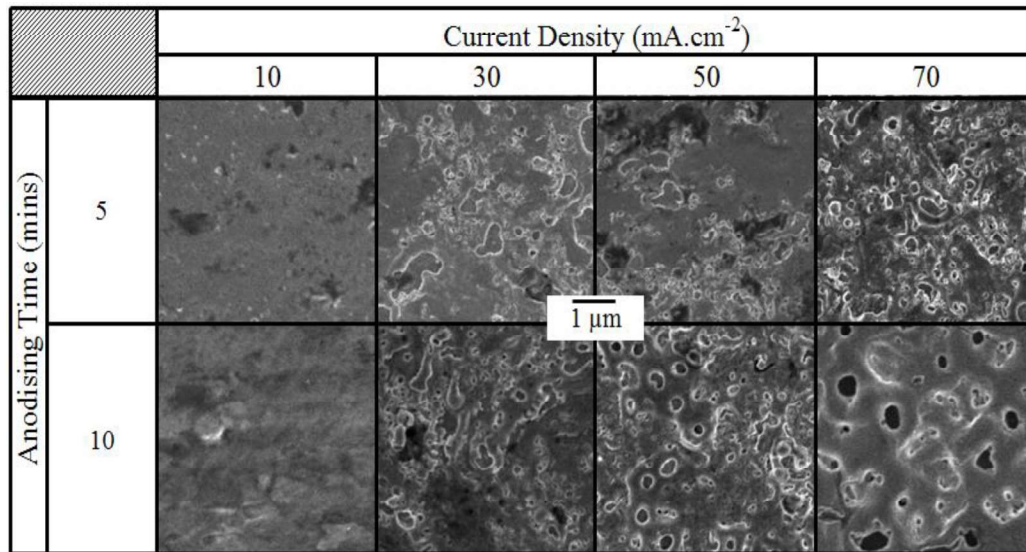


Fig. 1. FESEM micrographs of anodised surfaces at 10, 30, 50 and 70 mA.cm^{-2} for 5 and 10 minutes at 350V.

Table 2. The summary of effect of applied voltage on the microstructure of anodised films.

Current density (mA.cm^{-2})	Anodising time (minutes)	Microstructure		
		Pore No.	Surface Profile	Pore Size
10	5 & 10	No Appear	Even	No Appear
30	5&10	Few	Uneven	Small
50	5	Few	Uneven	Small
	10	Many	Uneven	Small
70	5	Many	Uneven	Small
	10	Many	Even	Larger

Surface Properties, Crystallinity and Optical Properties of Anodised Titanium in Mixture of β -Glycerophosphate (β -GP) and Calcium Acetate (CA) Avalanche theory can be used to explain the formation of porous surface on the anodised titanium. With increasing current density value, the oxide layer will grow until reach the dielectric breakdown limit and cause the sparking. Local melting occurs on the surface of anode resulted the formation of donut-shaped pores [8]. Rough and porous surface are the ideal condition for implant because it may increase the BIC and improve the cell adhesion to the surface, thereby it can achieve achieve better biomedical integrity. Rough and porous surface display a higher developed area than

a smooth surface therefore it enhance the bone anchorage and reinforces the biomechanical interlocking of bone with implant material [7,12]. Apart from that, rough and porous surface of implant also increases the surface energy thus improves the protein absorption, bone cell migration and proliferation and lastly promote the osseointegration [13].

X-ray Diffractometer (XRD)

Figure 2 and Figure 3 display XRD patterns of the anodised films under different anodising time and current density at 350 V. The summary of XRD is tabulated in the Table 3.

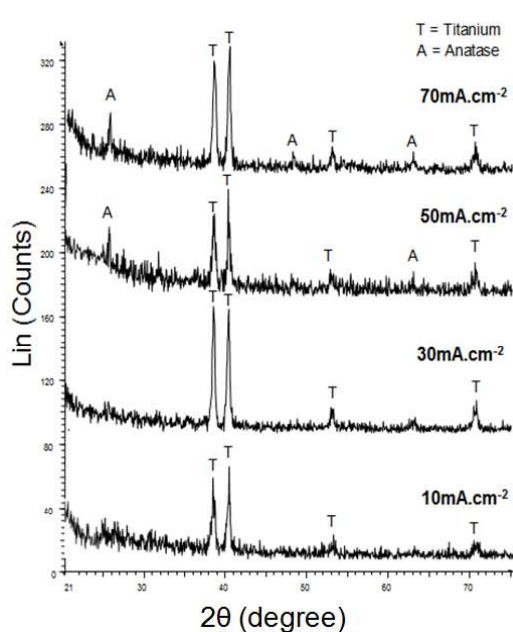


Fig. 2: XRD patterns of the anodised samples at 10, 30, 50 and 70 mA.cm^{-2} for 5 min.

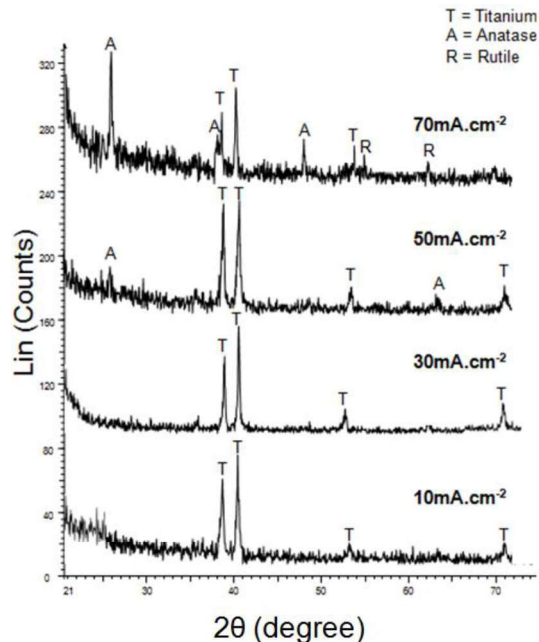


Fig. 3: XRD patterns of the anodised samples at 10, 30, 50 and 70 mA.cm^{-2} for 10 min.

TABLE 3: Summary of GAXRD for Figure 2 and Figure 3

Anodising Time (5 minutes)	Anodising Time (10 minutes)
- Anatase phase was not detected at current density $\leq 30 \text{ mA.cm}^{-2}$ - Small amount of anatase formation at current density of 50 mA.cm^{-2} - More anatase phases were detected at higher current density (70 mA.cm^{-2}) - Rutile phase was not detected for all samples	- Anatase phase was not detected at current density $\leq 30 \text{ mA.cm}^{-2}$ - Small amount of anatase formation at current density of 50 mA.cm^{-2} - More anatase phases were detected at higher current density (70 mA.cm^{-2}) and the peak intensity of anatase is higher than 50 mA.cm^{-2} - Rutile phases were detected at high current density (70 mA.cm^{-2})

These results showed that the amount of anatase and rutile increased with the increasing of current density and anodising time. This is due to higher current density and longer anodising resulted localised heating. Subsequently, local temperature will rise and can be up to thousand Kelvin [8]. It is reported that anatase and rutile phase of TiO_2 will be

formed at high temperature. Liet *al.* [14] claimed that rutile TiO_2 becomes more stable than anatase TiO_2 at higher temperature. Therefore, rutile TiO_2 can be formed at higher current density. It is firmly believed that the films with anatase and rutile surfaces are better than amorphous structure in promoting osseointegration and important for the success of implant integration.

Anatase and rutile surfaces provide better torque resistance value and better cellular responses if compared to the amorphous surfaces. Moreover, adhesion, proliferation, expression of osteoblastic markers and mineralised are increased due to the crystalline surfaces such as anatase and rutile type [15].

UV-Vis Spectrometry

The energy band gap of the anodised titanium had been calculated with the help of absorption spectra. Tauc relation was used to calculate the energy band gap from absorption spectra [16].

$$\propto hv = A(hv - E_g)^n$$

where, α = absorption coefficient, $h\nu$ = photon energy, A =constant, E_g =energy band gap and $n=1/2$ for direct band gap.

Next, graph $(\alpha h\nu)^2$ versus $h\nu$ is plotted in order to calculate the energy band gap from absorption. The extrapolation of the straight line to x-axis gives the value of energy band gap. Figure 4 present the graph $(\alpha h\nu)^2$ versus $h\nu$ for anodised titanium at 350 V and 70 mA.cm⁻² for 10 minutes. The value of energy band gap for this sample is 2.9 eV. On the other hand, Figure 5 displays the value of energy band gap at different current density at 350 V for 10 minutes. The energy band gap for anodised titanium at current density of 10 mA.cm⁻², 30 mA.cm⁻², 50 mA.cm⁻² and 70 mA.cm⁻² at 350V were 2.2 eV, 2.3 eV, 2.55 eV and 2.9 eV, respectively. It is observed that, the energy band gap of anodised titanium increases with the increasing of current density. It is reported that the energy band gap of anatase and rutile are ~3.2eV and ~3.0eV, respectively [17]. With the increase of current density, the amount of anatase and rutile in the anodised titanium was increased too. Therefore, the energy band gap was increased as increasing of current density. However, the energy band gap for anodised titanium did not reach the theoretical value (~3.2eV for anatase and ~3.0eV for rutile). This is because the anodised titanium still

consists of amorphous structure on the surface of coating. This reason is supported by result of XRD. The higher band gap indicated that the surface more active during the photocatalysis. It is reported that, the hydroxyl groups (OH⁻) will be produced during the photocatalysis. Hydroxyl groups can be considered as active sites for apatite formation. The increase of Ti-OH sites will activate the nucleation of apatite and promote the osseointegration [18].

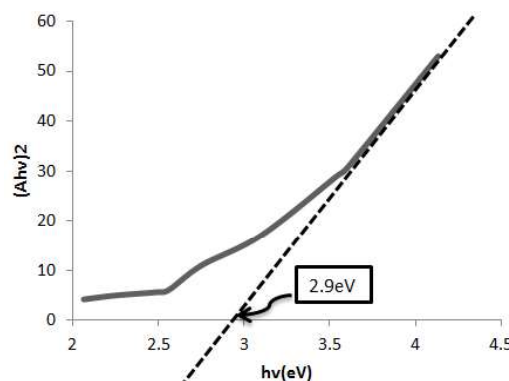


Fig. 4: Plot of $(Ah\nu)^2$ versus $h\nu$ for the anodised titanium at 350V and 70mA.cm⁻² for 10 minutes.

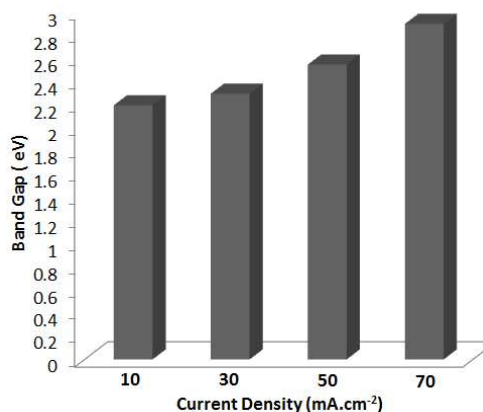


Fig. 5: Energy band gap at current density of 10-70 mA.cm⁻².

CONCLUSIONS

As a conclusion, anodic oxidation is able to improve the surface morphology and

crystallinity of the titanium by adjusting the current density and anodising time. Porous surface with large amount of anatase and rutile TiO_2 were formed at high current density (70 mA.cm^{-2}) with 10 minutes anodising time. FESEM results showed that, the donut-shaped pores were formed at 70 mA.cm^{-2} . Moreover, XRD results indicated that the anatase TiO_2 of titanium was formed when the current density $\geq 50 \text{ mA.cm}^{-2}$. Rutile TiO_2 was detected at 70 mA.cm^{-2} . It also can be concluded that, the energy band gap of anodised titanium increases as increasing of current density due to the presence of anatase and rutile TiO_2 on the surface of anodised titanium. The highest band gap was 2.9 eV which produced at 350 V and 70 mA.cm^{-2} . The value of band gap is closed to the theoretical value. Consequently, it was demonstrated that desired surface morphology, crystallinity and optical properties can be achieved easily via anodic oxidation.

ACKNOWLEDGMENT

The authors gratefully acknowledge the supported by Universiti Tun Hussein Onn Malaysia and Ministry of High Education Malaysia for their Research Acculturation Collaborative Effort (RACE Vot 1442) for support in providing the grant implement “*In Vitro* Bioactivities (UV Light Exposures) On Surface Layer of Anodised Titanium for Biomedical Application” project.

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