FEASIBILITY STUDY OF PLASMA ELECTROLYTIC OXIDATION (PEO) ON TiO_2 NANOTUBES FABRICATION

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ABSTRACT

It is hard to find sufficient data on the formation of nanotube array in the surface of metal oxides by using plasma electrolytic oxidation process. One of the reason is because of the wide range of parameters and researchers are still doing research on this topic. In this research, the formation of TiO_2 nanotubular arrays in the surface of Ti6Al4V substrate by using plasma electrolytic oxidation technique will be observed. Results obtained meet the objectives of the present study which is to obtain TiO_2 nanotubes. The phenomenon of plasma discharge are as a result of dielectric breakdown that occurs when the applied voltage exceeds a certain threshold. The images of nanotubes are captured using FESEM and the analysis of elemental composition is done by EDX system. From the image obtained it can be concluded that only 43% of the substrate surface covered with nanotubular structure. The average diameter of the nanotubular structure is 95.6 nm and average tube wall thickness is 18.5 nm. The hardness for uncoated sample is 307.2 HV while average hardness for TiO_2 nanotubes is 426.4 HV. This proved that PEO coating enhances the hardness of a substrate. The adhesive strength obtained is ~199 mN. The scratch line drawn by the diamond indenter is not smooth and showed rise and fall peaks in the penetration depth graph. This is because of high surface roughness or non-uniformly distributed coating throughout the substrate surface.

ABSTRAK

Tiada data untuk kertas penyelidikan mengenai pembentukan morfologi nanotube pada permukaan oksida Titanium dengan menggunakan proses PEO. Salah satu sebabnya adalah kerana pelbagai parameter dan penyelidik masih lagi melakukan penyelidikan mengenai topik ini. Dalam kajian ini, pembentukan TiO_2 morfologi nanotube pada permukaan Ti6Al4V akan diperhatikan dengan menggunakan PEO. Hasil yang diperolehi daripada kajian ini telah memenuhi objektif iaitu untuk mendapatkan TiO_2 nanotube. Fenomena pelepasan plasma adalah akibat pecahan dielektrik yang berlaku apabila voltan yang digunakan melebihi voltan yang ditetapkan. Imej nanotube diambil dengan menggunakan FESEM dan analisis komposisi unsur dilakukan oleh sistem EDX. Dari imej yang diperolehi dapat disimpulkan bahawa hanya 43% permukaan substrat yang diselaputi dengan struktur nanotubular. Diameter struktur nanotubular adalah 95.6 nm dan ketebalan dinding tiub ialah 18.5 nm. Kekerasan untuk sampel yang tidak bersalut ialah 307.2 HV manakala kekerasan untuk TiO_2 nanotube adalah 426.4 HV. Ini membuktikan bahawa salutan PEO meningkatkan rintangan kekerasan sampel. Kekuatan cengkaman lapisan sampel yang diperolehi ialah ~199 mN. Garisan yang dilukis oleh indenter berlian tidak lancar dan menunjukkan kenaikan dan kejatuhan puncak dalam graf kedalaman penembusan. Ini kerana kekasaran permukaan yang tinggi atau salutan yang tidak seragam yang tersebar di seluruh permukaan substrat tersebut.

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LIST OF ABBREVIATIONS

AAO	Anodic Aluminum Oxide
ACAC	Acetylacetone
ALD	Atomic Layer Deposition
ASD	Anodic Spark Deposition
EDX	Energy Dispersive X-Ray
EG	Ethylene Glycol
EtOH	Ethanol
H_2O	Water
MAO	Micro-Arc Oxidation
MPO	Micro Plasma Oxidation
NH_4F	Ammonium Fluoride
PEO	Plasma Electrolytic Oxidation
PVA	Poly(vinyl alcohol)-titanium Alkoxide
FESEM	Field Emission Scanning Electron Microscopy
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
Ti6Al4V	Titanium Alloy
TI	Titanium Isopropoxide
TiO_2	Titanium Dioxide

CHAPTER 1

INTRODUCTION

1.1 Research Background

These days, in order to design and create modern devices, it requires a wide range of knowledge on the materials that are suitable to use for commercial applications. One of the emerging technology in materials science is nano-materials. Nano-materials' important role is to reach great performance of devices. The shape, geometry and nanostructures morphologies causes the devices to perform at optimum potential (Peighambardoust & Nasirpouri, 2013). Titanium and its alloy, Ti6Al4V are known for its outstanding properties such as good biocompatibility which is used in biomedical devices, great mechanical properties and good endurance against corrosion. The most studied compound in nanomaterial technology would be TiO_2. TiO_2 is also known as titanium dioxide or titania and this compound is often used in biomedical devices, photocatalysis, and dye-sensitized solar cells. First report about TiO_2 was stated by Zwilling et al. in 1999, the report explained on how to grow TiO_2 nanotubes in highly ordered arrays by a simple electrochemical technique via anodization of a titanium metal with optimized conditions. Due to the finding of that report, numerous new research activities has been done that focuses on modification, growth, properties and applications of the one-dimensional nanostructures.

One of the great trait of one-dimensional (1D) nanostructure is that they provide unorthodox electronic properties, for examples, high specific surface area, high electron mobility, high quantum confinement effects and high mechanical strength (Roy, Berger, & Schmuki, 2011). 1D nanostructures of TiO_2 can be obtained by various methods such as by thermal decomposition (Nakane, Shimada, Ogihara, Ogata, & Yamaguchi, 2007), sol-gel template (Ming Zhang, Bando, & Wada., 2001), atomic layer deposition (ALD) (Lee, Ju, Lee, Kim, & Lee, 2010), hydrothermal (Jasmeen, 2013) and anodization (Sreekantan, Saharudin, & Wei, 2011). Further overview about the various methods will be explained in Chapter 2. Regardless of the various synthesis techniques available, this paper will focus on a new method to obtained TiO_2 nanotubular arrays which is by using plasma electrolytic oxidation (PEO) method. It is hard to find sufficient data on the formation of nanotube array in the surface of metal oxides by using plasma electrolytic oxidation process. One of the reason is because of the wide range of parameters and researchers are still doing research on this topic. Therefore, this paper will introduce a new approach of different parameters and experimental conditions using PEO.

The most common method used for self-organized TiO_2 nanotube layers is a conventional electrochemical anodization. Anodization is a simple electrochemical oxidation reaction on a metallic specimen under a specific parameters set. This method has gained interest over the past 10 years. Over the last 3 years, the publication rate shows there are more than 1000 papers being published. This is because of the unique combination of the highly functional characteristics of TiO_2 with a nanoscale geometry that can be controlled. Figure 1.0 shows the conventional electrochemical anodization process. Besides titanium, this self-ordering anodization approach can be applied to a wide range of other metals and its alloys to form highly aligned oxide nanotube or pore structures (Mg (Turhan, Lynch, Jha, Schmuki, & Virtanen, 2010), Nb (Abdul Rani, Zoolfakar, Subbiah, Ou, & Kalantar-Zadeh, 2014; Sieber, Hildebrand, Friedrich, &

Schmuki, 2005; Wei, Lee, Shaw, & Schmuki, 2012), Zr (Berger, Jakubka, & Schmuki, 2008; Tsuchiya, MacAk, Ghicov, Taveira, & Schmuki, 2005), and Hf (Tsuchiya & Schmuki, 2005)).

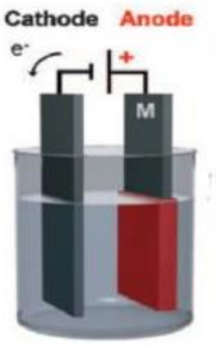


Figure 1.0: Conventional electrochemical anodization process (Roy et al., 2011).

PEO or also known as plasma oxidation electrolytic is the extended version of conventional electrochemical anodization. Both methods are carried out by using the same electrochemical process to produce oxide layers on metal surface in a respective electrolytes by the action of electricity. However, plasma electrolytic oxidation have some different features compared to anodization such as PEO required high voltage condition. During the process, the applied voltage can reach up to 1000 V different than anodization that uses low voltage. Furthermore, a glow, micro-arc discharge or spark discharge phenomenon can be seen on the surface of the samples during the process (Walsh et al., 2009). Further comparison between anodization and plasma electrolytic oxidation process will be explained in Chapter 2.

1.2 Problem Statement

In order to boost the properties of titanium dioxides nanotubes, titanium alloys have been subjected to various method of surface modification. One of the methods that is widely used to fabricate a self-ordered TiO_2 nanotubes is anodization. However, anodization coatings are not thick enough to offer effective protection against wear and corrosion. Hence, the introduction to plasma electrolytic oxidation (PEO) as an alternative to anodization. PEO uses eco-friendly electrolyte, forms thicker, denser and harder coatings. This relatively new surface coating technique, plasma electrolytic oxidation (PEO) process is mainly applied to light metals and its alloys to produce porous and adherent thick ceramic coating. There have been many research done on PEO and it is still a growing topic among researchers around the world due to the huge range of variables that can be manipulated and controlled. However, it has not been reported before on the fabrication of TiO_2 nanotubes by using plasma electrolytic oxidation (PEO) technique. For that reasons, this paper will introduce a new approach of different parameters and experimental conditions using PEO to obtain nanotubular arrays on titanium alloy, Ti6Al4V.

1.3 Objectives

The objectives of this research report are as follows:

a. To fabricate uniform coating of oxide on the surface of titanium alloy substrate, Ti6Al4V by PEO method.
b. To characterize formation of nanotubes via a technique of PEO.
c. To compare methods of PEO and anodization in the formation of nanotubes.

1.4 Structure of the report

This report consists of five chapters starting with Chapter One as the introduction of the project and ended with Chapter Five as the conclusion of the project. The structure of the report are categorized in chapter by chapter.

Chapter One is the introduction that gives brief explanation about the research project. It consists of background of the research, problem statement, objectives and structure of the report.

Chapter Two presents a literature review which covers background discussion of the various techniques available to achieved 1D nanostructures of TiO_2, an overview of TiO_2 nanotubes and its applications in the industry, the fundamental, process parameters, mechanism, and influences factors for plasma electrolytic oxidation (PEO) technique, and comparison between conventional electrochemical anodization and PEO.

Chapter Three describes the preparation of specimens and electrolytes, the experimental methods used, the process parameters, the analytical techniques used for characterization, and the procedures used to measure hardness and adhesion strength.

Chapter Four analyses the formation of TiO_2 nanotubes on the surface of the specimens, surface morphology and structures of the coatings using field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX). The TiO_2 nanotubes should be present in the images captured by FESEM. Evaluates the hardness and adhesion strength of the optimized PEO coating.

Chapter Five summarizes the results obtained in this research project and presents the main conclusions and suggest a few recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Titanium Dioxide (TiO_2) Nanotubes

Nanotubes composed of a number of materials such as carbon, oxides, and boron nitride. Carbon nanotubes was first discovered by (Iijima, 1991) via a method called plasma arcing. Plasma arcing involves the evaporation of one electrode as cations followed by deposition at the other electrode. The carbon nanotubes are formed by plasma arcing of carbonaceous materials, particularly graphite. Ever since the discovery of carbon nanotubes, many research have been done in exploring these exciting properties of the combination of extreme molecular geometry. This discovery has inspired many especially in the field study of nanotechnology and also in chemistry, physics and materials science (Roy et al., 2011). Carbon is the most explored nanotube material, however, other materials are considered as well such as sulfides and metal oxides. This material have been synthesized into a 1D geometries for examples as nanorods, nanowires, nanotubes, nanofibers and other nanostructures available (Rao & Govindaraj, 2011). Moreover, these 1D nanostructures have shown interesting new characteristics and properties. Although carbon being the most explored nanotube for microelectronic technology nowadays, inorganic nanotubes like oxides are mostly fabricated in the industry and its center of interest is on environmental applications, photochemical, biomedical, solar cells, and electrical appliances (Fernández-Garcia & Rodriguez, 2007).

Titanium dioxide or titania is also known as TiO_2 is the most comprehensively studied material among all other transition-metal oxides. There are over 40 000 publications about TiO_2 over the past 10 years which makes metal oxide as one of the most explored compounds in materials science. TiO_2 is known to have outstanding characteristics such as environmentally friendly, non-toxic, corrosion-resistant material and great biocompatibility which is used in medicine. The crystal forms of TiO_2 is a wide-bandgap semiconductor with a proper band-edge positions that allow its use for photocatalytic reactions and in solar cells. The electron-holes photogenerated can be used to split water into hydrogen and oxygen, or it can also be used for the remediation of hazardous wastes like toxic air contaminants or ground waters contaminants (Kudo & Miseki, 2009; Pozio, Casaccia, Anguillarese, & Galeria, 2015). TiO_2 exists in three main phases: anatase, rutile and brookite. As a bulk material, rutile is the stable phase, however, solution-phase preparation methods for TiO_2 generally favor the anatase structure. Surface energy is an important part of the total energy at very small particle dimensions and it has been found that the surface energy of anatase is lower than those of rutile and brookite (Zhang & Banfield, 2000). The nucleation and growth of the different polymorphs of TiO_2 depends on the reactants used (Li, Ishigaki, & Sun, 2007). Furthermore, TiO_2 nanotubular arrays have large surface areas with pore sizes that can be controlled, high uniform morphologies, and high oriented growth which makes this 1D nanostructure as one of the most promising efficient material for many applications. The potential applications of this metal oxides have been widened over the past 20 years towards appliances with increasingly advanced features such as electrochromic, photovoltaic, antifogging, and self-cleaning properties like biomedical devices, dye sensitized solar cells, smart-surface coatings, or sensors (Linsebigler, Lu, & Yates, 1995; Roy, Kim, Lee, Spiecker, & Schmuki, 2010; Sreekantan et al., 2011). In this report, the main objective is to achieve a self-organized TiO_2 nanotubular arrays using PEO. The following sections will explain several methods of obtaining 1D nanostructures of TiO_2 and a new approach of using PEO to achieve nanotube array of titanium alloy, Ti6Al4V.

2.2 Various synthesis techniques to obtain 1D nanostructures of TiO_2

There are many methods studied to synthesize 1D TiO_2 nanostructures, one of the method is by thermal decomposition of poly(vinyl alcohol)-titanium alkoxide hybrid nanofibers. According to Nakane et al. (2007) they obtained an anatase type of TiO_2 nanotubes by calcination of poly(vinyl alcohol)-titanium alkoxide hybrid precursor nanofibers in air. In this approach, the TiO_2 nanotubes as seen in Figure 2.0 below were obtained when the PVA nanofibers were submerged in a Ti tetraisopropoxide (10 wt%)-ethanol solution for 10 min. Once the nanofibers were washed and dried thoroughly, they were heated in an electric furnace at 500 °C in air. From the results obtained, the nanotubes showed high surface area and because of nitrogen adsorption isotherms, the mesopores can be seen on the nanotube wall.

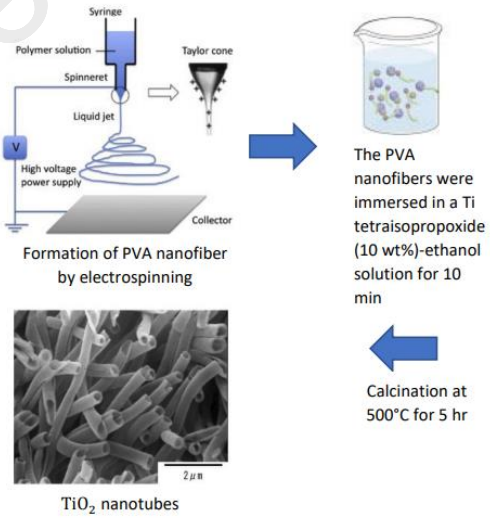


Figure 2.0: Synthesis of TiO_2 nanotubes formed by thermal decomposition of poly(vinyl alcohol)-titanium alkoxide hybrid nanofibers (Nakane et al., 2007).

Ming Zhang et al. (2001) obtained TiO_2 nanotubes and nanorods by the sol-gel template method. In this experiment, the nanotubes were successfully formed with a thick wall of 50 nm when the anodic alumina was immersed in the sol with solution of ethanol (EtOH), water (H_2O), acetylacetone (ACAC) and titanium isopropoxide (TI) mixed at molar ratio of 1:2:3:20 for 10 min. The long nanorods are achieved with diameters of 200 to 250 nm with molar ratio of 1:1:3:40. However from the first molar ratio, there were many broken nanotubes as shown in Figure 2.1 were found in this experiment with a wall thickness of 15 to 20 nm. From this experiment it can be concluded that the molar ratio of sol is very important in preparing the morphologies of the nanostructures for sol-gel template method. Due to hollow cores and high surface area, these nanostructure can be used for photocatalysis and as semiconductor electronic devices.

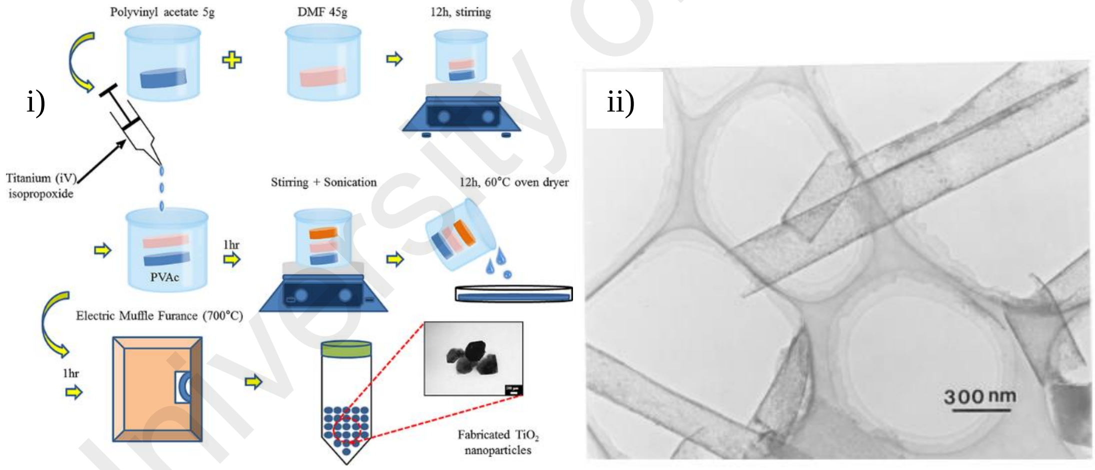


Figure 2.1: i) Synthesis of TiO_2 nanotubes and nanorods by the sol-gel template method and ii) TEM image of broken TiO_2 nanotubes with wall thickness of 15 to 20 nm (Ming Zhang et al., 2001).

According to an experiment done by Lee et al. (2010) titanium dioxide (TiO_2) nanotubes can be obtained via atomic layer deposition (ALD). The amorphous TiO_2 nanotubes were fabricated based on anodic aluminum oxide (AAO) membrane. In this approach, Lee et al. (2010) utilized titanium (IV) isopropoxide and water (H_2O) precursors and observed the chemicals reacted with each other. The nanotubes' thickness are controlled by the number of cycles of ALD. SEM and TEM are used to examine the morphology of the nanostructure. Figure 2.2 below shows the cross sectional image captured by SEM, showing the uniformly deposited of TiO_2 nanotubes in high aspect ratio with diameter of 50 nm.

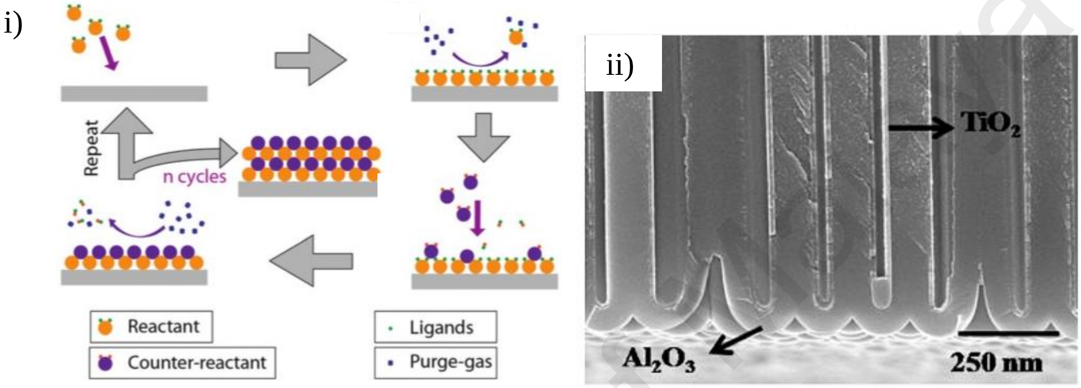


Figure 2.2: i) Synthesis of TiO_2 nanotubes via atomic layer deposition (ALD) and ii) Cross sectional SEM image showing the uniformly deposited of TiO2 nanotubes in high aspect ratio with diameter of 50 nm (Lee et al., 2010).

A study was conducted by Jasmeen (2013) to fabricate titanium dioxide nanotubes via microwave assisted hydrothermal treatment of TiO_2 powder in a concentrated sodium hydroxide (NaOH) solution. When the nanotubes derived from sol-gel method, an anatase phase TiO2 crystals with a diameter of 10 nm and a length of 85 nm was observed. From the study, it showed that the nanotubes displayed larger surface areas of 312.4 $m^2\ g^{-1}$ and higher pore volumes of 1.93 $cm^3\ g^{-1}$. Due to their high specific surface area, these nanotubes have a great potential for future use in industry especially for the preparation of catalysts, deodorants, and adsorbants (Jasmeen, 2013).

Even though there are various synthesis techniques for obtaining 1D nanostructures of TiO_2, most of the techniques produce single tubes, broken tubes or clustered tubes which unfortunately disregards the many advantages of the one-dimensional nanostructure. Due to that, self-organized nanotubes can be obtained via electrochemical anodization. Self-organized nanotubes are defined as when an array of oxide nanotubes aligned perpendicularly to the surface of the substrate. As shown in Figure 2.3 below, the length of the tube are well defined and are attached to the surface of the metal and they are electrically connected and easy to manage.

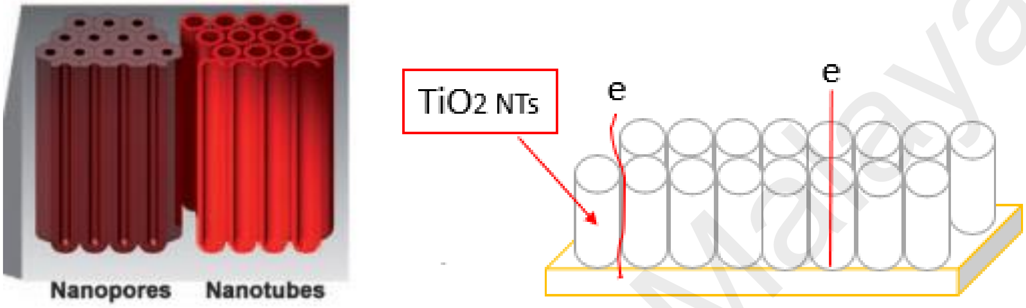


Figure 2.3: Self-ordered oxide nanotubes (Roy et al., 2011).

Sreekantan et al. (2011) did a study on the formation of TiO$_2$ nanotubes via anodization. The study was done to determine the effect of voltage, anodization time, cathode materials, and annealing temperatures on the formation of TiO$_2$ nanotubes. According to the report, TiO$_2$ nanotubes were obtained with an average diameter of 85 nm and an average length of 1.1 µm in glycerol 5 wt% ammonium fluoride (NH$_4$F) and 6 wt% ethylene glycol (EG) at 30 V for 60 minutes. The nanostructures become irregular, unstable and damaged at higher voltages and longer anodization time. Due to high dissolution rate (a measure of the actual release rate of the compound at the given particle size in an aqueous media) at the base of the nanotubes and low dissolution rate at the pore tip, the base of the nanotube walls become thin and can no longer support the long tubes and hence collapse. From the experiment to determine the effect of cathode materials using the same electrolyte, Sreekantan et al. (2011) discovered that the nanotubes formed using a stainless-steel cathode had a low aspect ratio (7.00) compared to the nanotubes formed using carbon (20.00), aluminum (20.00), and iron (21.33) cathodes. Aspect ratio is defined as the surface to volume ratio of nanoparticle. Nanoparticles show high aspect ratio indicates high surface energy or higher activity of the nanoparticle. The FESEM images of the TiO_2 nanotube arrays formed can be seen in Figure 2.4 below. From the results obtained, Sreekantan et al. (2011) determined that a stainless steel cathode produced short and non-uniform wall thickness of TiO_2 nanotube arrays. While carbon cathode produced high aspect ratio nanotubes with a diameter tube of 100 nm, and tube length of 2.0 µm. Even though both aluminum and iron cathodes produced high aspect ratios, they are less stable than those produced by using a carbon cathode. For that reason, carbon cathode is the most promising cathode material of all materials that are used for the experiment.

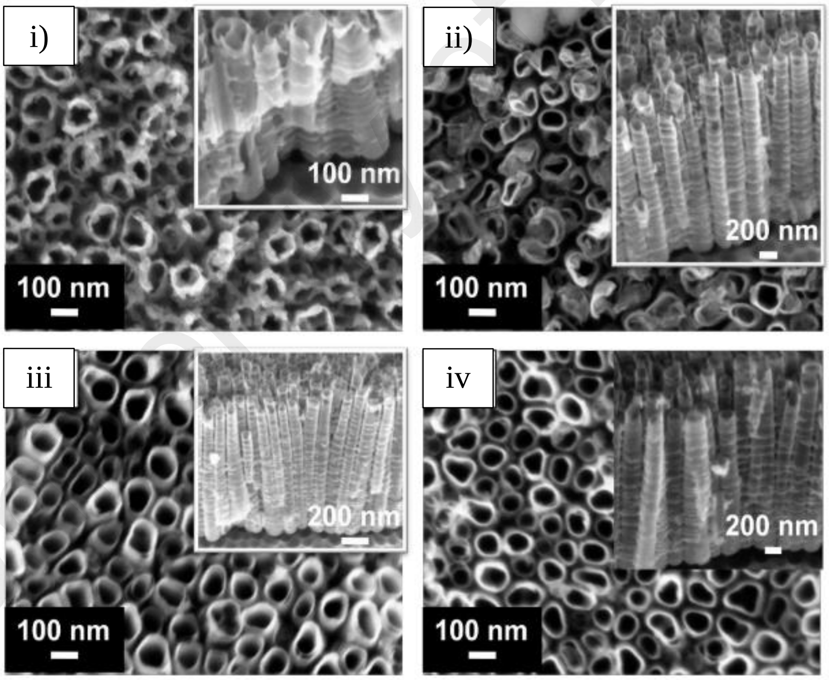


Figure 2.4: The FESEM images of the TiO_2 nanotube arrays formed using i) stainless steel, ii) aluminum, iii) carbon, and iv) iron cathodes in glycerol 5 wt% ammonium fluoride (NH4F) and 6 wt% ethylene glycol (EG) at 30 V for 1 hour (Sreekantan et al., 2011).

The nanotubes were annealed at different temperatures for 2 hours in an argon atmosphere to examine their crystalline structure. Anatase phase is produced when nanotubes were annealed at 400 and 500 °C, anatase and rutile phases are produced at 600 °C while annealing at 700 °C produced a highly rutile crystalline structure. Figure 2.5 below shows the FESEM images of TiO_2 nanotubes formed at 400, 500, 600 and 700 °C. From the FESEM images obtained, Sreekantan et al. (2011) concluded that annealing at low temperatures at 400 and 500 °C did not modify the structures of the nanotubes but the bottom structure of the nanotubes started to breaks at 600 °C and become more definite at 700 °C and the tube structure eventually collapses and forms a porous structure. Sreekantan et al. (2011) come to the conclusion that this morphology changes might be due to excessive amount of titanium ion diffusion along the nanotube walls, which encourages oxidation and hence thicken the oxide walls.

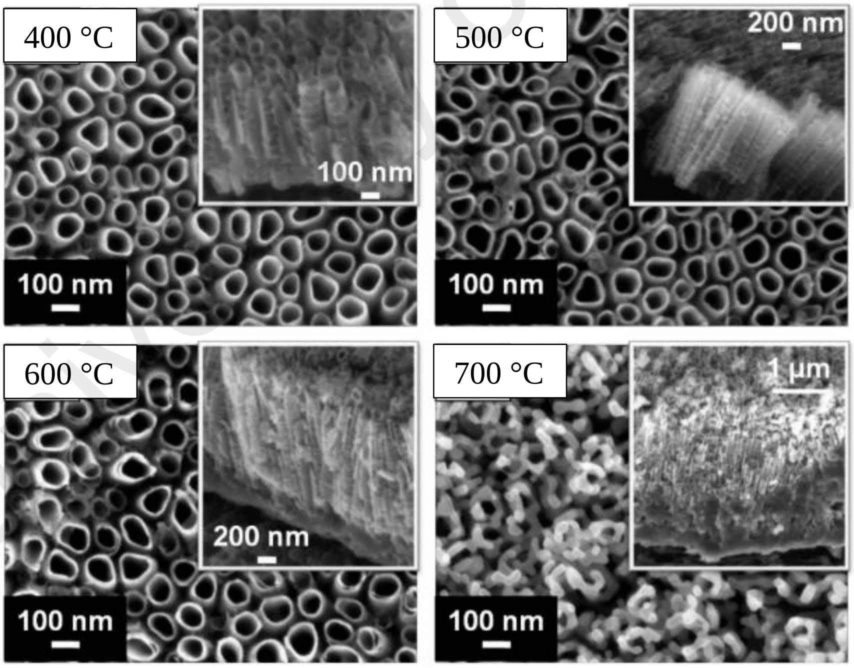


Figure 2.5: FESEM images of TiO_2 nanotubes formed at 400, 500, 600 and 700 °C in glycerol 5 wt% ammonium fluoride (NH4F) and 6 wt% ethylene glycol (EG) at 30 V for 1 hour (Sreekantan et al., 2011).

Another study was done by Sarraf et al. (2017) on the formation of self-organized TiO_2 nanotubes via electrochemical anodization (Figure 2.6). Anodization was performed in an ammonium fluoride solution dissolved in a 90:10 ethane-1, 2-diol (ethylene glycol) and water solvent mixture. The process was performed at room temperature of 23 °C at a steady potential of 60 V for 60 minutes. From microscopic analysis, highly oriented arrays of TiO_2 nanotubes (Figure 2.7) were grown by annealing treatment for 90 minutes at 500 °C. However, the nanotubes were completely destroyed after further heat treatment at 700 °C. Scratch test analysis over a constant length ($1000\,\mu m$) indicated that the delamination was shifted from $247.4\ to\ 557.9\ \mu m$ while the adhesion strength was increased from $\sim 862\ to\ \sim 1814\ mN$ after annealing at 500 °C.

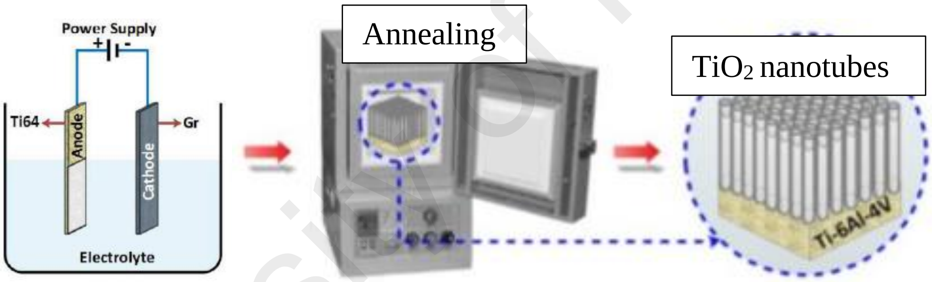


Figure 2.6: Synthesis of electrochemical anodization and heat treatment on the formation of TiO_2 nanotubes (Sarraf et al., 2017).

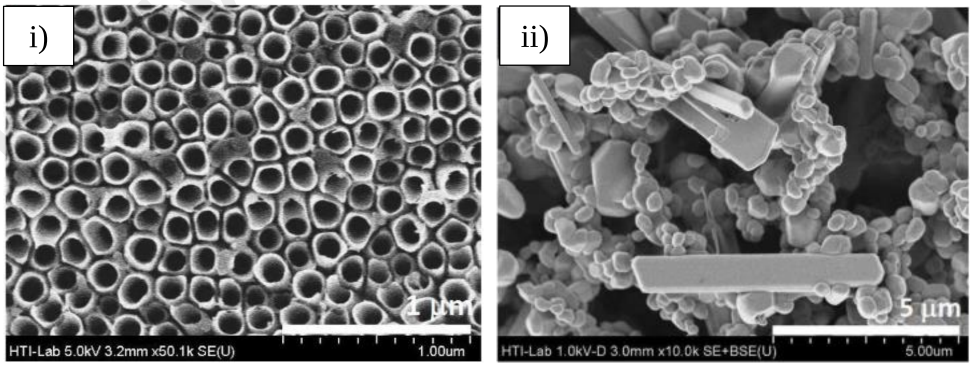


Figure 2.7: i) FESEM image of Ti64 surface after one pot of anodization with exposure of 60 minutes in 0.35% NH_4F electrolyte solution at 60 V and ii) FESEM

image of the detachment nanotubes after heat treatment at 700 °C for 90 minutes (Sarraf et al., 2017).

The diameter, tube length, and thickness of the nanostructure were varied according to the voltage, anodization time, cathode materials and annealing temperatures. Based on the overview explained above about the various synthesis techniques to obtain 1D nanostructures of TiO_2, most techniques produce single tube, broken tubes and clustered tubes which unfortunately disregards many advantages of this nanostructure. Plasma electrolytic is introduced as an alternative to anodization as PEO is done at a higher voltage therefore discharges or plasma are generated which influences the anodic structure of the substrate and because of the high potential, thick film coating can grow in a shorter time compared to anodizing. Further explanation about PEO method is explained in the next sub-chapter.

2.3 Plasma Electrolytic Oxidation (PEO)

Over the past few years, plasma electrolytic oxidation (PEO) had gained popularity among researcher as a novelty in research work of surface treatment on metallic components of complex geometric shape to produce porous and adherent layer. This novelty technology allows formation of thick, durable, homogenous, and strong adherent coating layer on lightweight metal and its alloys such as aluminum, magnesium, and titanium without changing the substrate as a whole at high temperature and without requiring complicated instrument and equipment. PEO is also known as micro-arc oxidation (MAO), anodic spark deposition (ASD), or micro-plasma oxidation (MPO) and is originated from anodization method (Clyne & Troughton, 2018). The universal contrast between conventional electrochemical anodization and micro-arc oxidation coating methods is shown in Table 2.1 below.

Table 2.1: Contrast between conventional electrochemical anodization and micro-arc oxidation coating methods (Jiang & Wang, 2010).

Coating methods	**Conventional anodizing**	**PEO**
Applied voltage (V)	10 ~ 50	150 ~ 800
Current density (A/dm^2)	0.5 ~ 2.5	5 ~ 20
Oxidation time (min)	10 ~ 60	Tens of mins
Electrolyte	Acid	Alkaline
Coating hardness (HV)	150 ~ 300	800 ~ 2000 (Al alloy) 300 ~ 600 (Mg alloy) 400 ~ 700 (Ti alloy)
Coating thickness (μm)	0.1 ~ 3	Up to 200
Wear resistance	Low	High
Corrosion resistance	Low	High
Environmental-friendly	Electrolyte containing acid, leads to pollution	Eco-friendly, brings no harm when dispose the electrolyte

The PEO process shares the same configuration as conventional electrochemical oxidation but operated at much higher voltage that can reaches up to 1000 V. The applied voltage will keeps on increasing from small value of volts to high value of volts, which is different than conventional anodization method that uses low voltage. The phenomenon of plasma discharge are as a result of dielectric breakdown that occurs when the applied voltage exceeds a certain threshold. The high voltage used in PEO technique helps create plasma discharges, which alters the coating during the development process that lead to a ceramic surface coating. Throughout the process, the color of plasma discharges changes from white to yellow and eventually to orange while density decreases and intensity increases.

Plasma or micro-arc release large quantities of heat which lead to formation of crystallization that introduces nanocrystals on the oxide layer of a substrate. The hardness of the protective layer can increases up to four times harder than hard anodized coatings and that is why PEO coating is known to provide an improved performance of wear and corrosion resistance. Even though traditional anodization creates a great breakthrough in improving the wear performance of metals, according to a study done by Shrestha et al. (2007), anodic oxide layers can form with cracks, which makes them vulnerable to extreme changes of temperature. Based on Figure 2.8 below, PEO coating showed a uniform coverage and good edge retention while hard anodized showed cracks extending down to the edge of substrate. The microstructure oxidized coatings from the PEO method take on an irregular form that protects them from cracking and improves the performance during extreme temperatures.

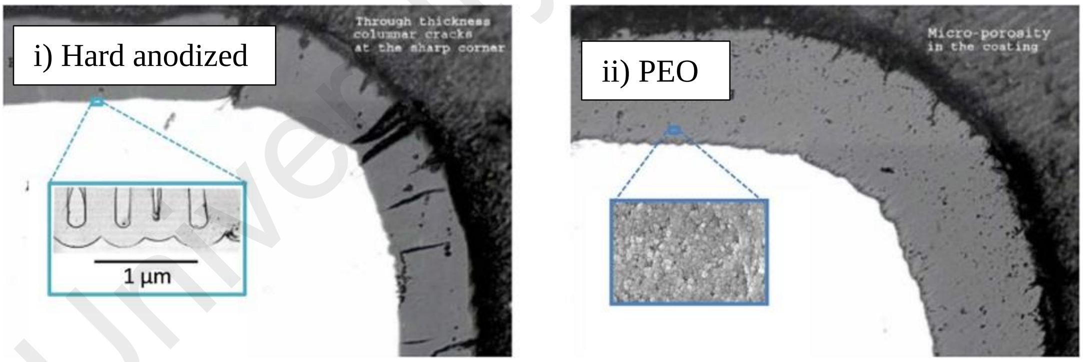


Figure 2.8: Optical micrograph of i) hard anodized coating, ii) PEO coating (Shrestha & Dunn, 2007).

The coatings produced from PEO technique provides better characteristics compared to the conventional anodization (Dehnavi, Luan, Shoesmith, Liu, & Rohani, 2013). Conventional anodization coatings are not thick enough to offer effective protection against wear and corrosion and thus this coating are mainly used for decoration purpose only. PEO technique is capable of producing thicker coatings with higher hardness, great bonding strength with the substrate, and a better wear and corrosion resistance as compared to the conventional electrochemical anodizing method. PEO process exhibits great success in posing improved surface oxidation treatment of lightweight metals and its alloys such as titanium, magnesium and aluminum, substituting the conventional anodizing processes that used acid based electrolyte. Waste products from the conventional electrochemical anodization are extremely hazardous because of the usage of acid electrolyte bath. For example, during the anodiziation of aluminum, aluminum hydroxide and degraded sulphuric acid are produced and they both create fumes that are harmful to the environment and are challenging to practice safely. While PEO technique uses 99% distilled water, produces no toxic wastes, and is ecologically friendly because of the usage of alkaline electrolytes, there is no toxic release involved in the process, and thus this technique meets the surface modification technology requirements which is green environment-friendly. The following sub-chapter will introduces the process parameters, mechanism, and influences factors for PEO technique.

2.3.1 Process parameters of PEO technique

Figure 2.9 below shows a typical equipment setup for PEO process. DC power supply is connected to both anode and cathode electrodes. The counter electrode (cathode) is the electrolyte tank made of stainless steel and is insulated and water cooled. The sample of the experiment is submerged in the electrolyte solution. A mixer is used to continuously stir the electrolyte to ensure a uniform electrolyte concentration and dissipation of heat generated during the PEO process.

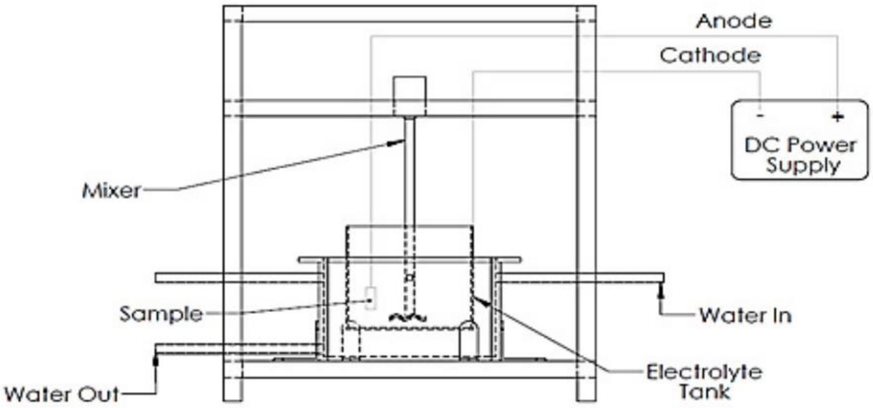


Figure 2.9: Schematic diagram of plasma electrolytic oxidation process (Adeleke, S. A., Bushroa, A. R., Sopyan, 2017).

2.3.2 Mechanism and structure compositions of PEO technique

When the metal substrate is placed in the electrolyte, the surface of the substrate will instantaneously produces an insulated layer of oxide film. Once the applied voltage surpasses a critical value (microarc stage in Figure 2.10), the fragile fragments of the oxide film will broke down and causes the formation of micro-discharge phenomena. A schematic diagram of the discharge phenomena and changes of the coating structure during micro-discharge oxidation process is shown in Figure 2.10 below.

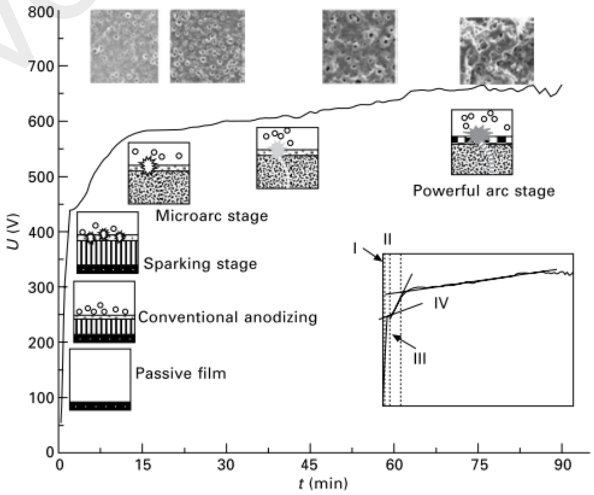


Figure 2.10: Schematic diagram of discharge phenomena and changes of coating structure during PEO (Jiang & Wang, 2010).

At the initial stage of PEO process, the voltage linearly increase with time and when the applied voltage increases, a large number of gas bubbles can be seen. This also occurs in the traditional anodization with the formation of porous insulation film with a columnar structure perpendicular to the substrate. Dielectric breakdown happens at the weak regions of the oxide film when the voltage exceeds a critical value. The color of the sparks produced gradually changes from white to yellow to orange-red. In the yellow to orange-red sparks stage also known as the micro-arc stage, the growth rate of coating is faster compared to the white sparks stage. The coating thickness increases as the voltage value increases and the growth of coating in PEO process occurs on the above and below of the substrate’s surface simultaneously compared to anodization, the coating is only on the top surface of the substrate.

In Region I of the Figure 2.10, voltage linearly decrease with time, corresponding to the traditional anodizing stage which forms thin insulating film. In Region II, the voltage slowly increase with the decreased oxide film growth rate, which is attributed to the competition of anode coating growth and dissolution. Region III is when the voltage increases rapidly to exceed the voltage limit, a large number of dispersed discharge channel are produced as a result of micro-regional instability caused by breakdown and are accompanied by a large release of oxygen. Lastly in Region IV, the voltage remains stable and at the end of the stage, the strong arc discharge appears.

In general, the PEO coating consist of a three layers such as porous layer at the top, a compact layer at the central and a thin inner layer. The layers at the central and inner are compressed and adhered well to the substrate (Walsh et al., 2009; Wirtz, Brown, & Kriven, 1991). The surface morphologies can be characterized on many aspects such as by their microcracks, micropores and dimples. The PEO ceramic coatings are composed of both predominant substrates metal oxides and also the complex oxides and compounds that involves in the electrolytes such as Ti6Al4V alloy in aluminate electrolyte bath (Qin, Xiong, Li, & Tyagi, 2016), TiO_2 on Mg alloy in phosphate solution containing titania sol (J Liang, LT, & JC, 2007) and MgF_2 on Mg alloy with KF in the electrolyte solution (Jun Liang et al., 2005).

2.3.3 Influence factors for PEO technique

Plasma electrolytic oxidation technique is influenced by two major factors such as intrinsic (substrates, pH, and electrolyte compositions) and extrinsic (power source, electrical parameters, additives, oxidation time, and electrolyte temperature) factors. The types of substrate materials, electrical parameters, and composition of electrolyte used during the PEO process play an important role in obtaining the desired coatings with unique microstructure and phase component. The power source for PEO technique plays a significant role in the preparation of a high quality coating desired for commercial applications. Over the years, there are various types of power sources used for PEO process such as AC sources (Arrabal et al., 2008; X. Wang, Zhu, Li, Liu, & Li, 2009), DC sources (Kuhn, 2003; Z. Shi, Song, & Atrens, 2006), and bipolar pulsed sources (Jin et al., 2006; Timoshenko & Magurova, 2005). The flexibility of electrical conditions enables to control the surface discharge characteristics over a wide range that are related to the microstructures and coating growth. The main compositions and properties of the PEO coatings depend on the types of substrate materials. The dominant component deposited on lightweight metals substrates such as Al, Mg, Ti, and their alloys are Al_2O_3, MgO and TiO_2 respectively. Hence, different types of substrates metal possess different properties of the coating. The average coating thicknesses on these metals substrates are around 300 μm on Al alloy, 150 μm on Mg alloy and 200 μm on

Ti alloy. While the hardness values ranges from 800 to 2000 HV on Al alloy, 300 to 600 HV on Mg alloy, and 400 to 700 HV on Ti alloy (Jiang & Wang, 2010).

The concentration and compositions of electrolyte greatly influence the properties of PEO ceramic compact coatings. Different types of electrolytes produce different types of microstructure, growth rates, phase compositions and element distribution of the coating. In general, PEO electrolytes are alkaline and to meet the requirement for dielectric breakdown, phosphates (X. Shi, Wang, Wang, & Ge, 2009; Shin, Ko, & Shin, 2011), silicates (Becerik, Ayday, Kumruoğlu, Kurnaz, & Özel, 2012), and aluminates (Da Forno & Bestetti, 2010) are most commonly used as the electrolytes base. These three groups of electrolytes provide a few advantages to the PEO process such as allowing the sparking voltage to be reached easily in a short time, the components present in the electrolyte such as PO_4^{3-}, SiO_3^{2-} and AlO_2^- are combined easily into the coatings by deposition and polyreactions, increases the growth rate, and environmentally friendly usage. The acid electrolytes such as concentrated phosphoric acid and sulfuric acid are infrequently used in the PEO process due to their abundant environmental pollution. A few studies was done to determine the coating phase constituents formed on Ti alloy, Ti6Al4V in phosphate, silicate and aluminate based electrolytes. It has been proved that complex electrolyte compositions are commonly desirable for experiments and commercial applications. Table 2.2 below shows the different electrolyte groups used on Ti alloy substrate, phase compositions formed and the potential applications from the PEO process.

Table 2.2: Different electrolyte groups used on Ti alloy, Ti6Al4V substrate, phase compositions formed and the potential applications from the PEO process.

Substrate	**Electrolyte group**	**Electrolyte composition**	**Coating phase composition**	**Applications**	**References**
Ti6Al4V	Phosphate	$(NaPO_3)_6$, NaF, $NaAlO_2$	$AlPO_4$ dominated, TiO_2	Biomedical, corrosion resistance	(Y. Wang, Lei, Jiang, & Guo, 2004)
Ti6Al4V	Silicate	Na_2SiO_3, $(NaPO_3)_6$, $NaAlO_2$	Rutile dominated, anatase	Wear and corrosion resistance	(Y. M. Wang, Jiang, Lei, & Guo, 2006)
Ti6Al4V	Aluminate	$NaAlO_2$, Na_2CO_3	Al_2TiO_5	Wear and corrosion resistance	(Y. M. Wang, Jiang, Lei, & Guo, 2005)

The temperature of the electrolyte can prominently affect the PEO process. Low temperature will causes weak oxidation process, thus resulting in low hardness and less thickness of the PEO coatings. While high temperature will enhancing the dissolution of oxide film, resulting in the decreasing of the hardness and the coating thickness. For that reason, the optimum processing temperature should be controlled in the range of 20 to 40 °C. A study done by Habazaki et al. (2012) was to investigate the effects of different temperatures of the electrolyte on the formation and characterization of PEO coatings on Ti alloy. The experiment was carried out on Ti alloy, Ti-15-3 in electrolyte bath of 0.15 mol/L $K_2Al_2O_4$, 0.02 mol/L Na_3PO_4 and 0.015 mol/L NaOH, at two different temperatures of 5 °C and 40 °C respectively. Based on Habazaki et al. (2012)

observations from the results obtained, at lowest temperature of 5°C, there is a high concentration of α-Al_2O_3 phase at the yielded PEO coating, it also exhibited lower uniformity, porosity and density, and showed more improved wear resistance compared to the results obtained from high temperature of 40 °C (Habazaki, Tsunekawa, Tsuji, & Nakayama, 2012).

In addition, the coating thickness increase linearly as the oxidation time increases, while the rate of growth decreases. This is because different oxidation time causes different results of coating properties (such as roughness, hardness, adhesion, thickness, and wear and corrosion resistance). A study was done by Gu et al. (2012) on the effect of oxidation time on the corrosion behavior of micro-arc oxidation coatings on Mg alloy in simulated body fluid. The substrates were fabricated on AZ31 Mg alloy in electrolyte solution of 30g/L sodium phosphate at applied voltage DC source of 325 V, current density of 150 Ma/cm^2, with four different oxidation time at 1, 3, 5 and 8 minutes. Gu et al. (2012) concluded that the oxidation time had very small influence on the phase compositions and that the coatings predominantly consisted of Mg, MgO, $MgAl_2O_4$ and $Mg_3(PO_4)_2$. Results showed that as the oxidation time increases, the diameter of the micropores in the PEO coating surface also increases. The substrate at 5 minutes showed the thickest layer and have a relatively smooth and uniform microstructure with less micropores. At oxidation time of 8 minutes, the coating thickness decreased and showed rough surface on the coating of the substrate. Gu et al. (2012) concluded that oxidation time at 5 minutes had the highest electron chemical impedance and lowest corrosion current density compared to other oxidation times. Due to the compact, uniform and smooth coating morphologies, the substrate coated at 5 minute had the highest corrosion resistance (Gu, Bandopadhyay, Chen, Guo, & Ning, 2012).

Furthermore, adding different additives in the electrolyte solution can prominently affect the PEO process, and hence resulting in different coating qualities. Jun Liang et al. (2005) investigated the effect of potassium fluoride (KF) in electrolyte solution of Na_2SiO_3-KOH on the structure and properties of PEO coatings on Mg alloy. Results showed that the addition of potassium fluoride increase the conductivity of the electrolyte, decrease the applied voltage during the PEO process and alter and the spark discharge characteristics. The addition of KF also causes the surface roughness and pore diameter to decrease, coating compactness to increase and changes in phase compositions. As a whole, addition of additives in PEO process enhanced the hardness and wear resistance of the coatings.

2.4 Summary

There are numerous methods to obtain a 1D nanostructure of TiO_2 such as by anaodization, atomic layer deposition, thermal decompostition and sol-gel template method. However, it has not been reported before on the formation of TiO_2 nanotubes using plasma electrolytic oxidation technique. This is because the PEO process is quite complex and have a wide range of parameters and process conditions that can be manipulated. Plasma electrolytic oxidation is a very unique, cost-effective, easy usage of equipment and environmentally friendly surface treatment for lightweight metals and its alloys. PEO process are mainly focuses on improving the wear protection and corrosion resistance of a substrate. The PEO process has been recognized by the researchers as a novelty technology for over 30 years and is significant to the industry for commercial applications. Researchers proved that PEO technique has a number of complex and unique characteristics which makes them an interesting topic to study. PEO have many process variables that can be studied and they are very versatile compared to other method of surface treatments. It is also proven that this technique improve the coating thickness, hardness, adhesion, and wear and corrosion resistance compared to the traditional anodization method. Due to that, PEO coatings can be tailored effectively to be used in commercial applications that meet the industry requirements. The influence factors for PEO such as types of substrate materials, electrical parameters, electrolyte compositions, oxidation time, and mechanism of the technique greatly affect the coatings of PEO. For that reason, this research is done to study whether or not these parameters have a significant influence on the composition, structure and morphology coating of the formation of TiO_2 nanotubes via plasma electrolytic oxidation technique.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter is to briefly explain the research flow of the project. The project is introduced with the preparation of substrate materials, concentration of electrolyte, PEO experimental set up, and PEO parameters such as voltage applied, oxidation time, electrolyte compositions, and cathode materials. Further explanation can be found in the next subchapter. After the PEO coating is done, the substrate will be studied under Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray (EDX) machines to identify the presence of TiO_2 nanotubes. EDX is used to investigate the metal compositions on the surface of the substrate’s coating. Once the image of nanotubes is obtained, the project will then proceed to the next step of analysis which are hardness and scratch adhesion tests to identify the value of hardness and adhesion strength of the coatings. These results will then be compared to the uncoated substrate and general adhesion strength of PEO coatings. The flow work of the project can be seen in the Figure 3.0.

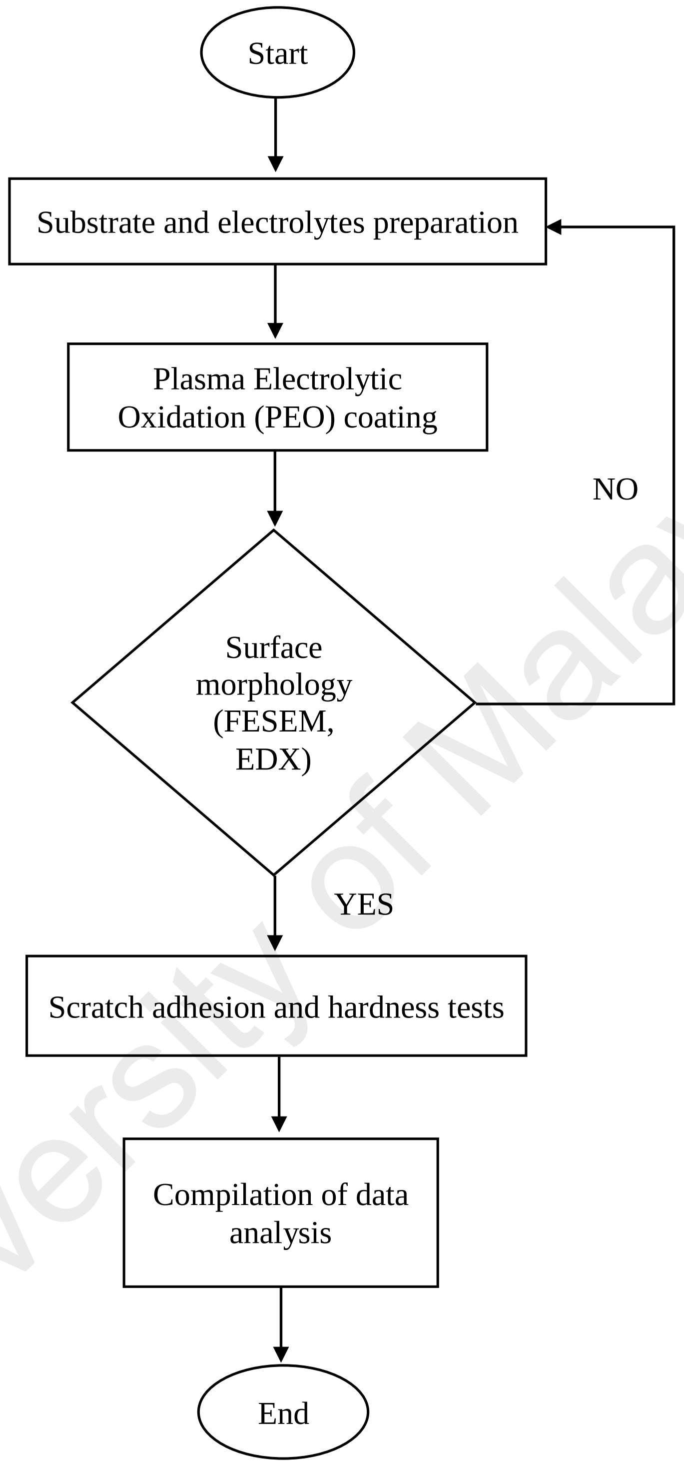


Figure 3.0: Research flow work

3.2 Material and equipment

3.2.1 Substrate preparation

The substrate used in the this study was titanium alloy, Ti6Al4V of 2 mm thickness that was obtained from Cenco Science Special Materials Co. Ltd, Malaysia. The substrates were wire cut using electrical discharge machine (EDM) into small specimens with dimensions of 15 mm x 15 mm. Table 3.1 below shows the chemical composition of the Ti6Al4V alloy Grade 5.

Table 3.1: Chemical composition of Ti6Al4V substrate (Grade 5).

Element	**Ti**	**Al**	**V**	**O**	**C**	**Fe**
Weight (%)	90.1	5.65	3.93	0.11	0.08	0.13

The substrates were then grounded with silicon carbide (SiC) abrasive papers with 3 grades of 800, 1200 and 2000 grit. After that, the substrates were cleaned in ultrasonic bath for 10 minutes, degreased with acetones and distilled water to remove dirt and any surface contamination and dried in air thoroughly. Figure 3.1 illustrates the apparatus used for grinding the substrate and cleaned in ultrasonic bath.

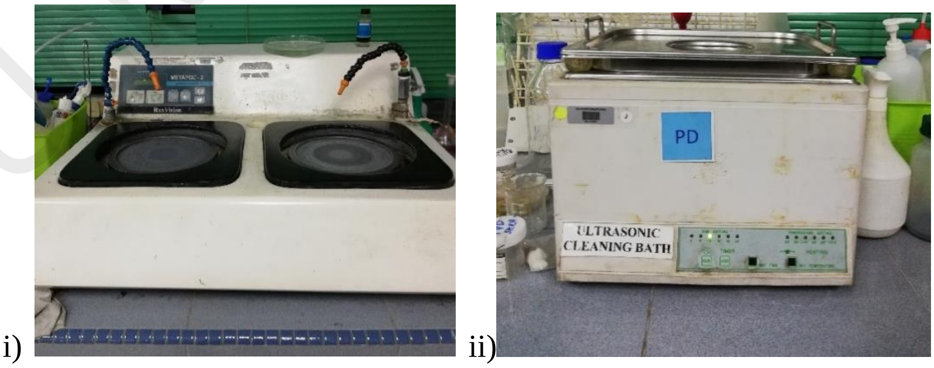
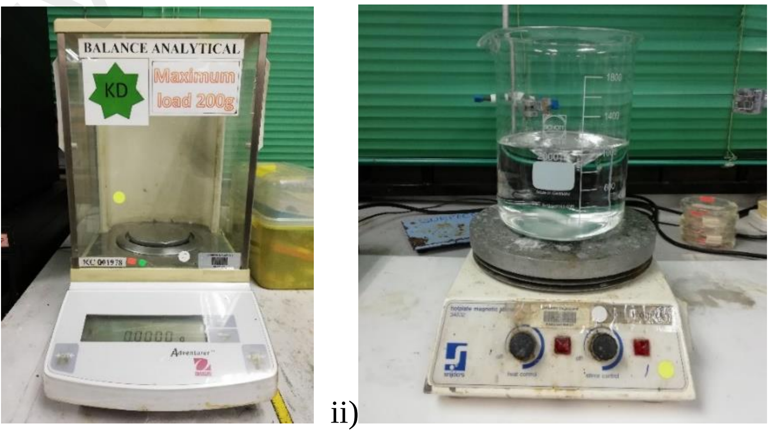


Figure 3.1: Apparatus used for substrate preparation; i) Grinding machine, ii) Ultrasonic cleaning bath machine.

3.2.2 Electrolytes preparation

Various electrolytes were prepared in this study in order to identify its influence on the composition and morphology of the coating. Four aqueous electrolytes were prepared in this study to investigate the formation of TiO_2 nanotubes. An alkaline phosphate electrolyte were prepared by dissolving 3.86 g/L ammonium fluoride NH_4F, 900 mL/L ethylene glycol Ehane-1, 2-diol, 100 mL/L distilled water H_2O, and 10 g/L trisodium orthophosphate $Na_3PO_4.12H_2O$ together. Ammonium fluoride and ethylene glycol were used because fluoride ions in electrolyte is a great contributor to develop TiO_2 nanotubes (Sarraf et al., 2018) and sodium phosphate is used because it has been extensively used owing to its ability to ionize easily in water and good conductivity (Venkateswarlu, Suresh, Rameshbabu, Bose, & Subramanian, 2011). Another set of electrolyte were prepared by dissolving ammonium fluoride, ethylene glycol and distilled water at pH value of 6. The electrolytes were stirred with a magnetic stirrer on a hot plate to obtain a homogenous solution. Figure 3.2 displays the apparatus used for the preparation of electrolytes. Table 3.2 below shows the electrolyte compositions and pH values used in the experiment. The pH of the electrolyte were measure using pH meter (HANNA 211).



i) ii)

Figure 3.2: Apparatus used for electrolytes preparation; i) Weighing balance, ii) Hot plate magnetic stirrer.

Table 3.2: Electrolyte composition of PEO experiment.

Substrate	Electrolyte compositions	pH values
Ti6Al4V	3.86 g/L NH_4F 900 mL/L Ethane-1, 2-diol 100 mL/LH_2O	6
Ti6Al4V	3.86 g/L NH_4F 900 mL/L Ehane-1, 2-diol 100 mL/LH_2O 10 g/L $Na_3PO_4.12\ H_2O$	13

3.2.3 PEO parameters

In the present study of using neutral organic compound and alkaline phosphate electrolytes, DC supply unit is used as the power source for PEO coating. The applied voltage for all electrolytes are set at the same value which is at 350 V with constant current of 1 A. The temperature of the electrolyte remains in the range of 30 to 35 °C and is maintained with the aid of water coolant passing through a hosepipe during PEO treatment. The temperature needs to be monitored in between that range because it can affect the coating morphology. Thermocouple is used to measure the electrolyte temperature. The oxidation time is different for all four experiments which is at around 10 to 45 minutes. A cylindrical stainless steel tank with a diameter of 140 mm is used as the container and as the counter electrode (cathode) for PEO because it allows a symmetrical electrical field that resulting in uniform coating thickness. Carbon cathode is used as the second material of cathode and from review of literatures, it is the most promising material for cathode in anodization as it produces high aspect ratio, large tube diameter and longer tubes of TiO_2 nanotubes. Therefore, in the present study, stainless steel and carbon are used as the cathode materials to study the formation of TiO_2 nanotubes using PEO method. Table 3.3 below displays the details of the PEO parameters used in the present study.

The Ti6Al4V substrate is used as the anode and is then immersed in the electrolyte. Once all materials and set up is done, the PEO treatment is start at the applied voltage of 350 V and current of 1 A. The oxidation time is observed throughout the PEO process, and recorded once the applied voltage is reach its limit and spark discharge can be seen from the treatment. After the PEO process, the specimens were removed from the electrolyte and cleaned thoroughly with distilled water and air dried at room temperature for further analysis.

Table 3.3: Specifics of the PEO parameters used in the present study.

Substrate no	**Substrate**	**Electrolyte compositions**	**pH values**	**Voltage (V)**	**Current (A)**	**Oxidation time (minutes)**	**Cathode materials**
1	Ti6Al4V	3.86 g/L NH_4F 900 mL/L Ethylene glycol (Ethane-1, 2-diol) 100 mL/LH_2O	6	350	1	10	Stainless steel
2	Ti6Al4V	3.86 g/L NH_4F 900 mL/L Ethylene glycol	6	350	1	12	Carbon/Graphite

		(Ethane-1, 2-diol) 100 mL/LH_2O					
3	Ti6Al4V	3.86 g/L NH_4F 900 mL/L Ethylene glycol (Ethane-1, 2-diol) 100 mL/LH_2O 10 g/L $Na_3PO_4.12\ H_2O$	13	350	1	45	Stainless steel
4	Ti6Al4V	3.86 g/L NH_4F 900 mL/L Ethylene glycol (Ethane-1, 2-diol) 100 mL/LH_2O 10 g/L $Na_3PO_4.12\ H_2O$	13	350	1	45	Carbon/Graphite

3.3 Surface morphology and characterization of the PEO coatings

The coatings produced from PEO process are the results of different combination of electrolyte compositions, applied voltage, oxidation time and cathode materials. In order to investigate the presence of TiO_2 nanotubes, a specific machine is to be used to capture the image of the respective nanostructure and that machine is called Field

Emission Scanning Electron Microscopy (FESEM). As for the metal characterization of TiO_2 nanotubes can be done by using Energy Dispersive X-Ray (EDX). A few mechanical tests will be done to study and compare the hardness and scratch adhesion strength of the coatings. The procedures for each of these morphologies and mechanical characterization are presented in subchapters below.

3.3.1 FESEM and EDX

Researchers in chemistry, biology and physics fields employed this technique on various object to study the surface morphologies of the material. Field emission electron microscopy (FESEM) is used to observe small structures of up to 1 nanometer on the surface of the materials studied. FESEM is a microscope that uses a focused beam of electrons instead of light to generate an image of the specimen. The mechanism of FESEM is the electrons interact with the atoms embracing the specimens to produce signals that contain information about the surface composition, topography and other properties. In this project research, the FESEM measurements of studying the characteristics of the TiO_2 nanotubes were performed using FEI Quanta 450 FEG FESEM machine (Figure 3.3) at an accelerated voltage of 15-20 kV.

Figure 3.3: FEI Quanta 450 FEG FESEM machine.

In FESEM, electrons are liberated by a field emission source and speeded up by applying high electrical field gradient. To generate a narrow scan beam that projected on the specimen, the primary electrons are focused and ricocheted by electronic lenses with high vacuum column. The secondary electrons is detected by a detector and creates an electronic signal that is amplified. It is then later changed to a video scan-image that will be processed further and observed on a monitor. Figure 3.4 illustrates the schematic diagram of FESEM.

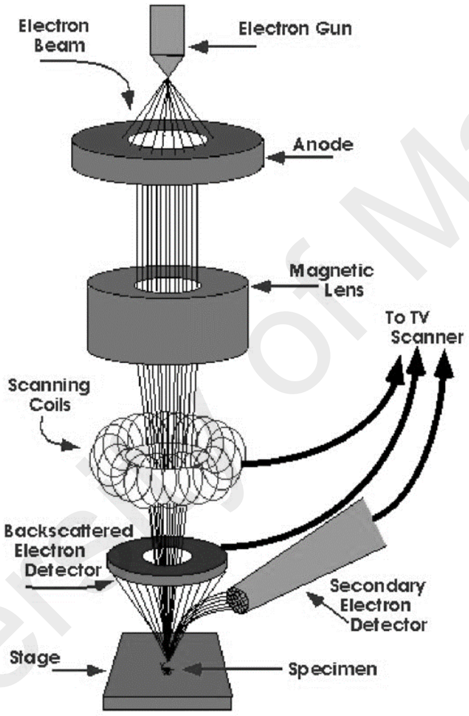


Figure 3.4: Schematic diagram of FESEM (Billah, 2014).

Energy Dispersive X-Ray spectroscopy (EDX/EDS) analysis can be done from FESEM system as it is equipped along with the machine as shown in Figure 3.4. EDX is defined as a system for elemental analysis or chemical characterization of a specimen. Both of these systems enables to study the relationship between morphological properties and elemental compositions of a sample. EDX mechanism is composed of electron beam that is used in FESEM, a detector that is used to convert the beam energy into voltage signals that will be measured by using a pulse processor, and an analyzer to process and analyze the data collected. The alteration of outer shell electrons releasing energy in the form of an X-Ray can be seen in Figure 3.5 below.

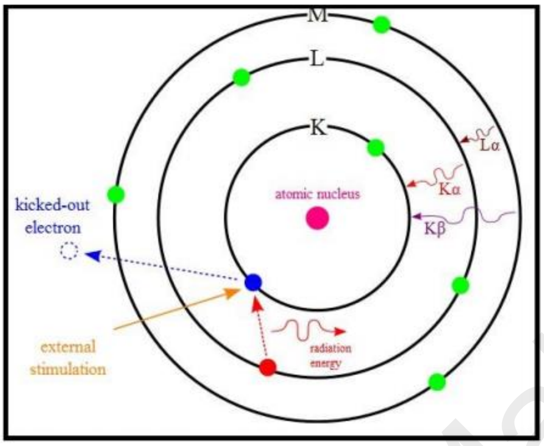


Figure 3.5: Movement of energy released by the outer shell electrons in the form of an X-Ray (Oliveria, 2017).

EDX system depends on the interaction between electromagnetic radiation and a specimen. A high energy electrons is moving fast and is then focused into the specimen to simulate the emission characteristics of an X-Ray. The beam enters the surface of the specimen and thus stimulate the electrons that is bound tightly together. The openings produced in the inner shell are then immediately filled up by the movement of energy released by the outer shell electrons in the form of an electromagnetic radiation. Hence the energy released in the form of an X-Ray is measure using energy dispersive spectrometer to allow the study of elemental composition and surface morphology of the specimen.

3.3.2: Micro-hardness and micro-scratch adhesion tests

Micro-hardness test is widely used on a thin material with applied loads at 1 kg and below. This test is evaluated by measuring the area of indentation instead of the depth of a hardness of a material. In this test, a diamond indenter (Figure 3.6) of a specific geometry is pressed into the surface of the substrate under 2.942 N. The load is applied smoothly and the indenter is held in place at 5 seconds. Once the load is removed, a diamond or diagonal shape will appears indicated indentation worked thus, the hardness of a substrate can be measured. In general micro-hardness test produce indentations of about 50 µm and work under forced of 200 gf or 2 N. Averages of five measurements are taken on each specimen recorded and standard deviation is identified. Formula of standard deviation is as follow (Wiki Groen Kennisnet, 2014).

$$\sigma = \sqrt{\frac{\sum(x-\bar{x})^2}{n}}; \qquad 3.1$$

where σ = standard deviation, $\sum =$ the sum of, $\bar{x}$ = the mean. Coefficient of variation is estimated to get an approximate answer. Formula for CV is (Wiki Groen Kennisnet, 2014).

$$CV = \frac{\sigma}{\bar{x}} \qquad 3.2$$

where σ = standard deviation and $\bar{x}$ = the mean. If the coefficient of variation is more than 1 it indicates the variation is relatively high, while coefficient of variation less than 1 indicates low variation. This means the distributions with a high CV are considered to be high variance while low CV are considered to be low variance.

Figure 3.6: Micro-hardness tester.

A scratch test is performed by using a micro-scratch tester (Micro Materials LTD., Wrexham, UK) as shown in Figure 3.7 below. Micro-scratch test is defined as to measure the adhesive strength of the PEO coatings under applied loads ranging from 0 to 3000 mN. The setup of this testing is the indenter is drawn across the coated surface at a fixed rate of 1.2 µm/s with the length of the scratch at about 1000 µm. In this micro-scratch test, two critical loads are applied (1500 N) to quantify the adhesive strength of the coating of the substrate. Critical load (L_c) also defined as the load that caused the coatings to disengage completely from the substrate. After the scratch test was done, a few graphs are obtained such as the penetration depth, frictional curve and function of critical load applied to determine the magnitude of (L_c). The scratch tracks were observed under light microscope.

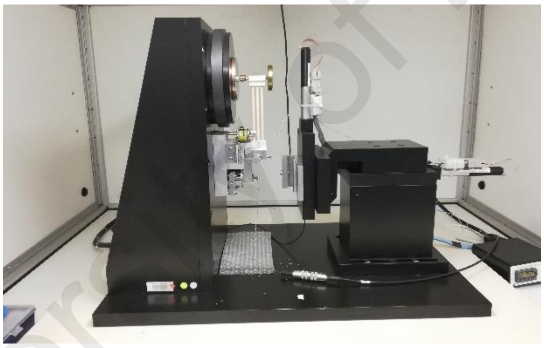


Figure 3.7: Micro-scratch tester.

3.4 Summary

In this chapter, the preparation of substrate, electrolytes, equipment and experimental set up was presented with adequate explanation and schematic diagrams. Various parameters are used in order to study whether or not it have a significant influence on the composition, structure and morphology coating. The procedures and experimental conditions are essential to the project in order to achieve objectives mentioned in Chapter One. With proper preparation and precaution, objectives can be obtained. The equipment for data analysis is described as well such as FESEM and EDX for surface coating morphology and compositions. The procedures for mechanical testing are presented in a very simple explanation. It is important to understand the mechanism of the tests done on the PEO coatings.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter is to present the results obtained which is TiO_2 nanotubular array by plasma electrolytic oxidation method and discussion about the influences of the electrolyte, oxidation time, cathode materials, and applied voltage for the PEO technique on Ti6Al4V alloy. Discussions include the metal composition obtained from FESEM and EDX analysis, hardness and adhesion strength from micro-hardness and micro-scratch tests. The failure of other experiments was also discussed as well.

4.2 TiO_2 nanotubes

In total there are four metal substrates used for plasma electrolytic oxidation technique in the present study. However, only one specimen manage to achieve the objective of this project which is the formation of TiO_2 nanotubular array using PEO method. In general, the formation of titanium dioxide nanotubes in F^- electrolytes is a result of hydrolysis process of titanium metal to form TiO_2, chemical dissolution of TiO_2 at oxide interface, and dissociation of NaF. When the applied voltage is higher than the breakdown voltage, the spark discharge rapidly build up on the substrate surface which leads to the dissolution of Ti. The development of homogenously distributed pores is due to the chemical dissolution. At this stage, a random local dissolution of the TiO_2 surface generated the nanopores. The dissolution of Ti^{4+} ions is when the strain energy increases, causes F^- ions to migrate to a higher strain energy region and hydrogen ions to migrate to maintain electrical neutrality. The formation of the nanotubes is the consequences of the voids and pores that grow simultaneously. These nanostructures are generally formed in anodization stage during PEO process in fluorine electrolyte composition. The chemical formulation of how TiO_2 is achieved in this project is as follows (Asekunle, 2018):

$$Ti \rightarrow Ti^{4+} + 4e^- \tag{4.1}$$

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{4.2}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \tag{4.3}$$

$$Ti + 4OH^- \rightarrow TiO_2 + 2H_2O + 4e^- \tag{4.4}$$

The presence of fluorides in the electrolyte greatly influenced the anodization process as it generates water soluble $[TiF_6]^{2-}$ species. The reaction between the ejected Ti^{4+} ions at the oxide interface and chemical occurrence to produce TiO_2 is as follows (Asekunle, 2018) :

$$Ti^{4+} + 6F^- \rightarrow {TiF_6}^{2-} \tag{4.6}$$

$$TiO_2 + 6F^- \rightarrow [TiF_6]^{2-} + 2H_2O \tag{4.7}$$

The electrochemical behaviors of a sample depends on the concentration of the fluoride compound. If the electrolytes containing fluoride concentrations is below 0.05 wt%, the electrochemical behaviors is the same as electrolyte with no fluoride. While fluoride concentrations above 1 wt%, fluoride ions will react immediately with the Ti^{4+} ions and extend the generation of $[TiF_6]^{2-}$ species causing the elimination of oxidation phase. This study uses 0.35 wt% of fluoride concentration in electrolyte resulting in the development of TiO_2 nanotubular structure after 10 minutes of PEO process. Compared to the anodization done by (Sarraf et al., 2017), the self-organized nanotubes are obtained after heat treatment at 500 °C for 90 min while PEO does not required to undergo heat treatment due to high potential that causes plasma to be generated. The oxidation time is shorter in PEO method compared to anodization and it is also because of the high potential used.

There are many features to discuss on why other substrates did not manage to obtain nanotubular structures. One of it is because of oxidation time, longer oxidation time at 45 minutes results in thicker coating compared to oxidation time at 10 minutes. Oxidation deposition time prominently affect the PEO coating because of the longer duration of oxide phase and since there is no nanotubes presence under FESEM analysis, there is a high possibility that the nanotubular structure collapsed due to excessive amount of titanium ion diffusion along the nanotube walls which encourages oxidation and hence, thickens the oxide walls and thick coating developed instead. Current density also decreases as a result of the development of a compact oxide film which eventually enhances the resistance.

An alkaline phosphate electrolyte produces thick PEO coating, however there is no presence of nanotubular structure on the substrate. Electrolyte composition plays a major role in developing of TiO_2 nanotubes. If the electrolyte is not compatible, there will be no spark discharge in the electrolyte, no dielectric breakdown occurs, thus only anodization is happening instead of plasma electrolytic oxidation and this indicates that the PEO process failed. Ethylene glycol and ammonium fluoride has been used by many researchers in anodization method and most of the results obtained are nanostructure, however this electrolyte composition has never been done by PEO method. At 350 V voltage, 10 minutes of oxidation time, stainless steel as cathode, in 0.35 wt% of fluoride concentration, there is a presence of TiO_2 nanotubes on the substrate.

4.3 Surface morphology and mechanical characterization

Figure 4.0 below shows the FESEM images of TiO_2 nanotubes formed by PEO in a titanium alloy, Ti6Al4V in 0.35 wt% of fluoride concentration. The figure obtained at 200x magnification showed that nanotubes formed on the smooth surface. In this case study, only 43% of the smooth surface has the presence of TiO_2 nanotubes. The reason why nanotubes are not fully formed on the surface is because of the concentration of the electrolyte solution, applied voltage or oxidation time that could be held longer than 10 minutes. The area marked with white box indicated the area magnified at 200 000x magnification to study the nanotubular structure. As shown in the figure, it is clear that the nanotubes formed after PEO process at 10 minutes with an average diameter of 95.6 nm and average tube wall thickness of 18.5 nm. The measurements of nanotubes diameter and tube wall thickness was done by using a software ImageJ. In comparison with anodization method done by Sreekantan et al. (2011), the average diameter of the nanotubes is 100 nm and the average thickness is between 5-10 nm. The wall thickness obtained by Sreekantan et al. (2011) is very thin, it eventually collapses in unstable regions as they cannot support themselves. The wall thickness of the nanotubes formed by anodization is not uniform compared to the current study, the wall thickness formed by PEO is uniform and thick and that makes the structure strong and able to support the nanostructure.

Due to high applied voltage, the chemical dissolution dominates over field-assisted dissolution thus causing the oxide layer to thicken and enhances the size of the pores. As the pores continue to grow and propagate, the hollow cylindrical oxide particles eventually develop into nanotubular structure during oxide interface state. The rate of electric field dissolution at the barrier layer inside the nanotubes is high due to high applied voltage. For that reason, longer nanotubes would be produced and enhances the properties of the coating.

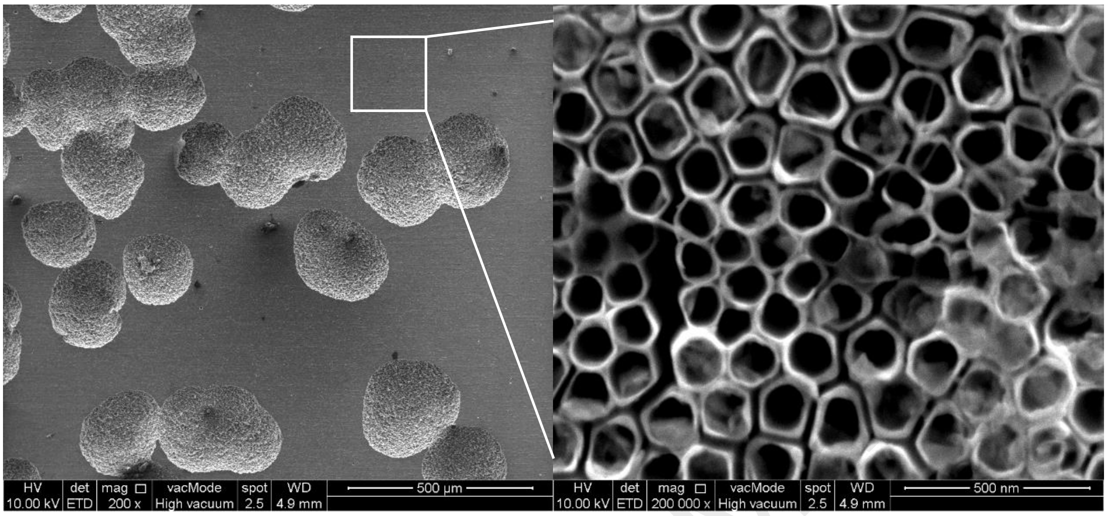


Figure 4.0: FESEM images at two different magnifications of TiO_2 nanotubes formed by PEO of a titanium alloy, Ti6Al4V in 0.35 wt% of fluoride concentration.

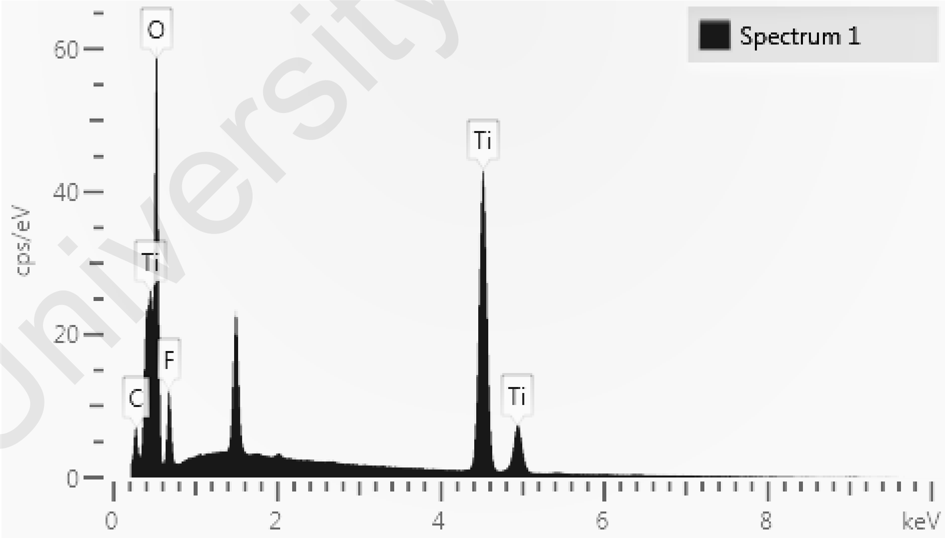


Figure 4.1: EDX profiles of the TiO_2 nanotubes.

Qualitative analysis is used in this case study in order to identify which elements are present in the substrate. The elements are identified from their characteristics X-ray peaks. The basic law to analyze the compound elements with EDX is Moseley's Law (Hafner, 2006). Moseley's Law is when the energy of the characteristics radiation within a given series of lines (K, M or L lines) varies monotonically with atomic number. If the energy of a given line is measured, the atomic number of the line produced by that element can be determined. In this case study, the line type from the EDX analysis is K series indicates light elements emit X-rays of the K series only. Compared to L line is when intermediate elements emit X-rays and heavy elements emit X-rays of the M series or L and M series. Figure 4.1 above shows the EDX profiles of the TiO_2 nanotubes for 10 minutes of PEO process at 350 V in 0.35 wt% fluoride electrolyte. Wt% is defined as the weight percentage of an element measured divided by the weight of all elements in the sample multiplied by 100. Weight percentage, wt% gives the concentration of the element in terms of mass fraction of that element in the sample. While atomic % is defined as the number of atoms of that element, at its weight percentage, divided by the total number of atoms in the sample multiplied by 100. O and Ti are the highest peaks at 30.33 wt% and 61.71 wt% respectively indicate that oxidation of substrate is the predominant during PEO process. The composition of C and F are from the chemical reaction between the substrate and electrolyte. Based on the Table 4.1, the EDX analysis showed no foreign chemical compound is present during the PEO process. A simple calculation is done to obtain the empirical formula of TiO_2.

Calculation:

Ti: 61.71 wt%, O: 30.33 wt%, F: 6.22 wt%, C: 1.74 wt%

Divide each by their atomic weights and summation;

Ti = $\frac{61.71}{47.87g} = 1.289$ F = $\frac{6.22}{19g} = 0.327$

O = $\frac{30.33}{16g} = 1.896$ C = $\frac{1.74}{12.01g} = 0.145$

Divide each by the summation (3.657);

Ti = $\frac{1.289}{3.657} = 0.35$ F = $\frac{0.327}{3.657} = 0.089$

O = $\frac{1.896}{3.657} = 0.52$C = $\frac{0.145}{3.657} = 0.040$

$\mathbf{0.35 \times 4 = 1.4,\ 0.52 \times 4 = 2.08\ \therefore\ \boldsymbol{TiO_2}}$

Table 4.1: EDX elemental analysis.

Element	Line Type	Wt%	Atomic %
C	K series	1.74	3.96
O	K series	30.33	51.85
F	K series	6.22	8.95
Ti	K series	61.71	35.23
Total		100.00	100.00

The values of hardness are tabulated as shown in Table 4.2 and Figure 4.3 displays the standard deviation of hardness of all the substrates that are deposited via PEO method. The average hardness value for Substrate 1, TiO_2 nanotubes is 426.4 HV compared to the average hardness of uncoated specimen at 307.2 HV. This might due to the compatibility of the electrolyte used for Substrate 1 which is the interaction between ethylene glycol and ammonium fluoride with stainless steel as the cathode via PEO method. It is proven that PEO coating improved the hardness of the substrate as the value increases. In general, the hardness of uncoated titanium alloy is in range of between 200 to 300 HV. In this case study, the hardness obtained for TiO_2 nanotubes increases from 300 HV to 426.4 HV. This study was done to not only identify the formation of nanotubes but also to study the mechanical characterization of the sample. From the results obtained, it can be concluded that PEO coating enhances mechanical properties and improved the hardness of a material.

Substrate 4 in electrolyte of ethylene glycol, ammonium fluoride and sodium phosphate with graphite cathode shows high hardness at average of 488.8 HV due to its thick coating produced on the substrate and surface course which is beneficial to reduce wear. Coatings produced with higher porosity have lower hardness that is why the coating hardness of a sample strongly depending on the coating compactness. The more compact of the coating, the higher the hardness. Therefore, porosity levels is important to be controlled to improve the hardness coating of a sample. These can be done by manipulating the process parameters such as electrolyte composition and current density. Other factors that affecting the hardness of a coating is the crystalline and amorphous phases which are resulted from the high temperatures that the coating reached locally. These phases can give rise to coatings of high hardness and wear resistance.

Table 4.2: Hardness values of all the substrates in the study under PEO method.

Substrates	**Uncoated substrate**	**Substrate 1** (Thin coating)	**Substrate 2** (Uneven coating)	**Substrate 3** ($\mathbf{TiO_2}$ nanotubes)	**Substrate 4** (Coarser & rougher coating)
Average hardness (HV)	306.6	307.6	399.2	426.4	488.8
Standard deviation, σ	14.19	23.0	53.54	7.34	94.94
Coefficient of variation (%)	5	7	13	2	19

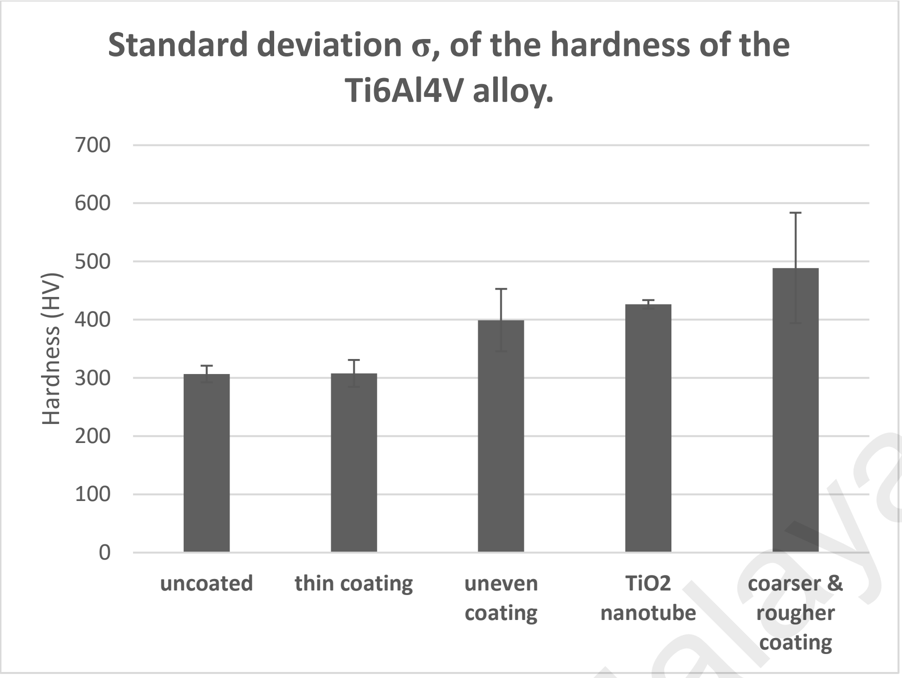


Figure 4.2: The standard deviation of hardness of all the substrates that are deposited via PEO method.

Standard deviation is used to show how much variation from the mean exists. A low standard deviation is defined as the data points that is close to the mean value. While a high standard deviation is defined as the data points that are spread out over a large range of values. Standard deviation of coating hardness correlate with the structural homogeneity of PEO layers. From the data obtained in Figure 4.2, Substrate 1 have the lowest standard deviation while Substrate 4 displays the highest standard deviation which is might be due to the homogeneity of PEO coating on the surface. The thickness of Substrate 4 is higher and the coating is more compact compared to Substrate 1 but it showed non-homogeneity of PEO layers on the surface and that is why Substrate 4 has high deviation due to the reaction between electrolyte and the graphite cathode. The presence of the graphite produce an increase in the thickness of the coating compared to Substrate 3. This behavior can be linked with the electrical conductivity of the graphite particles that influence the discharge process during PEO process and produce an increase in the thickness of the coating. The porosity levels of Substrate 1 is lower compared to Substrate 4. This is due to the electrolyte composition which contains phosphate and longer oxidation time at 45 minutes hence, the coating of Substrate 4 is thicker and more compact to Substrate 1. However the presence of nanotubes can only be seen in Substrate 1 and it is proven that the hardness is improved compared to uncoated substrate.

As for the adhesion strength results, this test is important to determine the stability and durability of the film coatings produced. Cohesion and adhesion of the coating is closely related to its wear and abrasion resistance during sliding in an increasing load mode because in both cases the failure originates in the coating. This failure is due to the external force applied via wear or abrasive particles or sliding indenter during scratch test (Nohava, 2009). Scratch tests were performed on the substrates to investigate the failure modes of the coating. Figure 4.3 shows the scratch test done on the surface of the PEO coating of Substrate 1 the one with the presence of nanotubes. The diamond indenter is drawn over the surface as seen in Figure 4.3, the scratch direction is from right to left with loads of 1500 mN until failure occurs at the critical load. The coating was in the elastic to plastic state at the beginning of the test. As the load increase progressively, the diamond indenter gradually sinks into the coating and as shown in Figure 4.3, a linearly change of penetration depth throughout the coated layer can be seen. The coating fails at early stage during the scratch test and the indenter causes progressive plastic deformation. As the scratch load increases, delamination trackside appeared. Delamination occurred because of insufficient adhesion between the coating and substrate. This phenomena is called delamination when the coated layer separates from the substrate. In this case study, the delamination results from the flaws at the interface that is why the line drawn on the coating is not smooth which indicates failure happened. This could be due to high surface roughness and unwanted bumps and holes as there is a slightly height difference between PEO coating and nanotubes layers. Based on Figure 4.3 below, the coating on the alloy completely fails at early stage at 184 μm with critical load of ~199 μm (adhesion strength). Since titanium alloy have high strength compared to titanium, they provides better support for the coating and produces higher critical loads (Dikova et al., 2016).

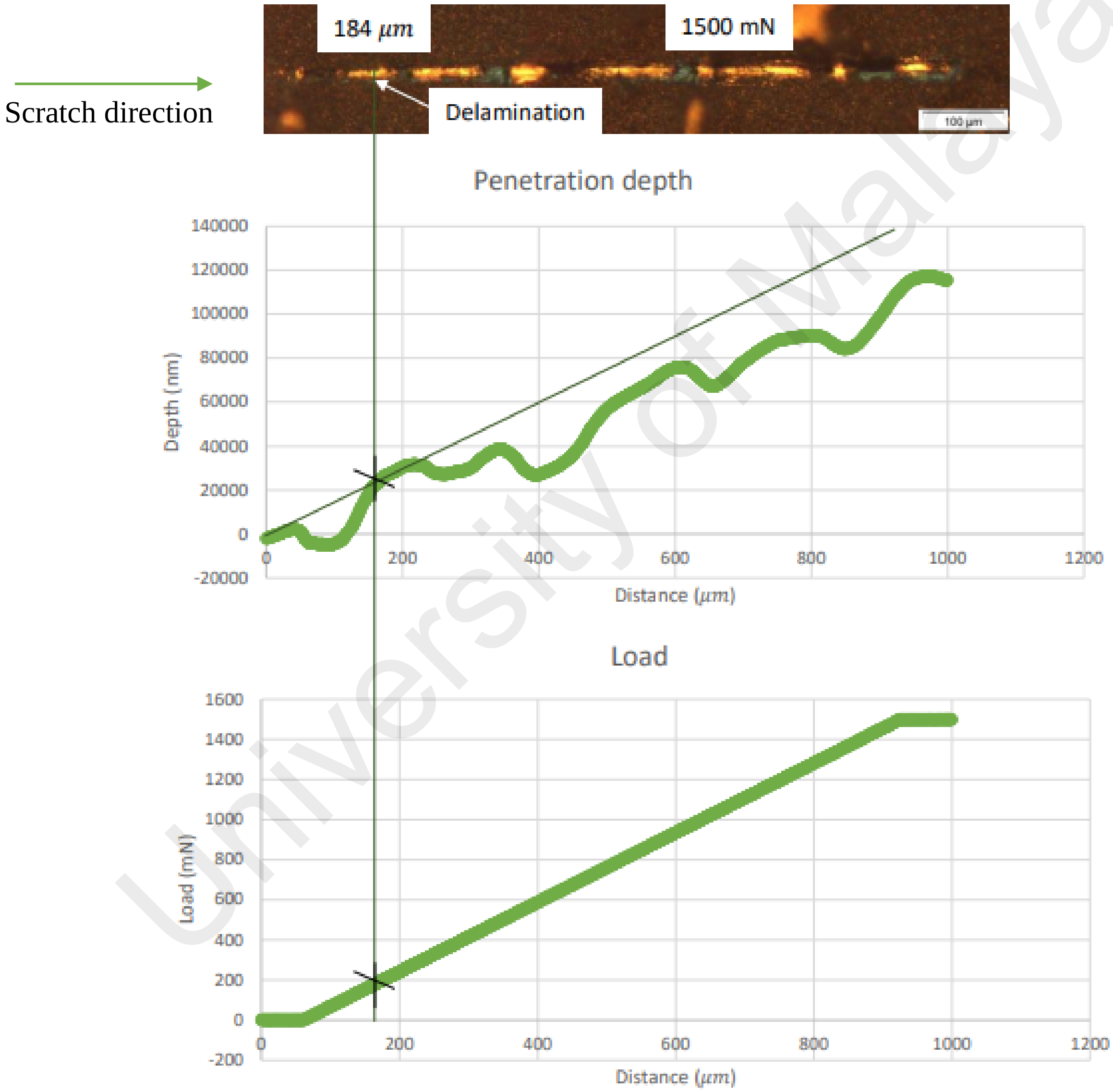


Figure 4.3: Scratch test on the PEO coating of Substrate 1.

Figures 4.4 displays the results of scratch test done on Ti6Al4V substrate via anodization method (Sarraf et al., 2017). According to the scratch test, the adhesion strength of the coating at 1000 mN is 862 mN. In anodization the results is three times higher than PEO coating. This is might be due to the 43% of nanotubes on the substrate via PEO method. The surface roughness on PEO is higher than anodization and since this is still a feasibility study, the parameters used in the experiment is still not optimized yet and still in studying in order to identify its influence on the coating properties.

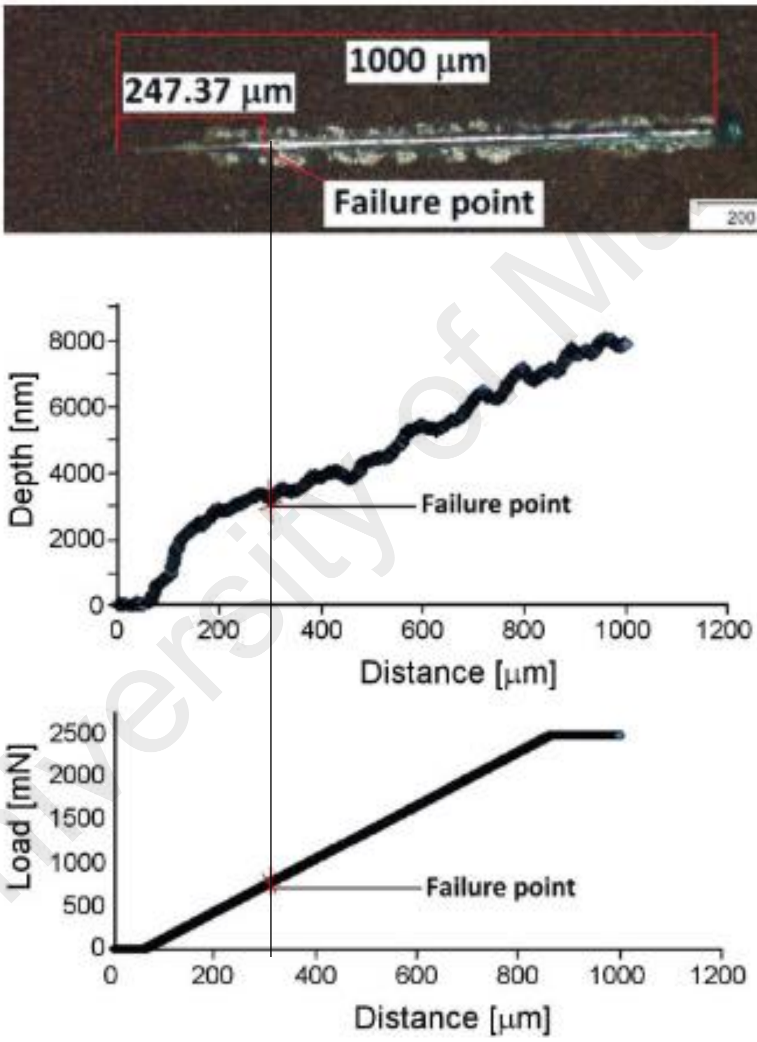


Figure 4.4: Scratch test done on Ti6Al4V substrate via anodization method (Sarraf et al., 2017).

There are a few factors influencing the failure modes observed on the surface coatings. Internal factors such as applied load, loading rate, scratch speed, shape of indenter and machine calibration greatly influences the failure modes mechanism. External factors such as material of the substrate, properties of the coating, surface roughness, and coefficient of friction. In this study, the failure was seen to occur a few times along the coated layer, this may be due to the interaction between the coating and the substrate. In general, Ti is known to be ductile while oxide film is brittle. When the diamond indenter contacts the coated layer during scratch test, failure modes started to happen probably due to high surface roughness of the film coating or compressive stresses created ahead of the moving diamond indenter. The rise and fall of the diamond indenter penetration depth is the consequences of the tensile crack formed at the weak region of the coated layer. Coating thickness influenced the adhesion strength. As the coating process progresses, significant changes take place in the inner layer structure as result of diffusion processes and adhesion is improved.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study aims to produce TiO_2 nanotubes by using plasma electrolytic oxidation (PEO) technique because it has not been reported before. PEO is derived from conventional anodization method and studies have showed that by anodizing Ti and its alloy it can produce 1D nanostructures hence, the innovation of this study which is to utilize PEO process to produce TiO_2 nanotubular arrays. The materials are prepared with careful and accurate measurements as it will affect the results. The analysis were done by using equipment and software to get accurate data. Previous chapter had discuss the results and the factors influence the coating such as electrolyte composition, oxidation time, cathode materials and other PEO conditions to obtain the objective of the project. In summary, these factors greatly affect the formation of nanotubes on the Ti alloy, Ti6Al4V surface. The fluoride ions is a great contributor to develop the nanotubular array of TiO_2 in electrolyte solution. Low concentration of fluoride causes the same results as electrolyte with free fluoride. While high concentration of fluoride produces compact thick coating instead of nanotube due to the oxidation interface. Compatibility of electrolyte significantly affect the surface morphology of PEO coating. If the electrolyte is not compatible, there will be no micro-discharge produced hence, indicates no PEO process is happening to the anode electrode. Micro-discharge phenomena is important as that phenomena is what makes this surface treatment special and unique to study compared to anodization that did not produce any plasma discharge and uses constant low voltage. High voltage causes the Ti ions to react rapidly with the electrolyte compound during chemical dissolution of Ti^{4+} ions. The phenomenon of plasma discharge are as a result of dielectric breakdown that occurs when the applied voltage exceeds a certain threshold. The images of nanotubes are captured using FESEM and the analysis of elemental composition is done by EDX system. From the image obtained, it is clear that the nanopores is present on the Ti6Al4V substrate. Only 43% of the substrate surface covered with nanotubular structure this is may be due to short oxidation time. Longer oxidation deposition time leads to thicker and uniform coating. The average diameter of the nanotubular structure is 95.6 nm and average tube wall thickness is 18.5 nm. The hardness for uncoated sample is 307.2 HV while average hardness for TiO_2 nanotubes is 426.4 HV. This proved that PEO coating enhances the hardness of a substrate. The coating fails at early stage during the scratch test when loads of 1500 mN is applied. The adhesion strength of PEO coating at 1000 mN is at ~199 mN. Since titanium alloy is ductile material with higher strength compared to titanium, they provide better support for the coating and produces higher critical loads. The scratch line drawn by the diamond indenter is not smooth and showed rise and fall peaks in the penetration depth graph. This is because of high surface roughness or non-uniformly distributed coating throughout the substrate surface.

5.2 Recommendations

Even though the objectives of the present study are achieved, there are a number of issues and challenges throughout the entire process of completing this project. The nanotubes obtained from this study is only at 43% maybe in the future research, aim to obtain 100% of nanotubes covered on the coated layer. Next is further study on the mechanical and chemical characterization of the nanotubes. A few more tests can be done to investigate the coating characteristics, for example, nanoindentation, wettability, and tribological properties. This would be a great value and novelty discovery as other researchers can refer for further studies and analysis. Corrosion test can be done as well in the future to study their wear and corrosion resistance behavior. Furthermore, different substrate material can be studied such as Mg and its alloy or Al and its alloy to study the metal composition and its reaction towards fluoride in the electrolyte solution. There are many variables that can be studied in this topic as it have a wide range of parameter that can be manipulated and results obtained are usually different and showed improvement compared to conventional chemical anodization method.

References

Abdul Rani, R., Zoolfakar, A. S., Subbiah, J., Ou, J. Z., & Kalantar-Zadeh, K. (2014). Highly ordered anodized Nb2O5nanochannels for dye-sensitized solar cells. *Electrochemistry Communications*, *40*, 20–23. https://doi.org/10.1016/j.elecom.2013.12.011

Adeleke, S. A., Bushroa, A. R., Sopyan, I. (2017). Characteristics Features of Plasma Electrolytic Treated Layers in Na3Po4 Solution. *Procedia Engineering*. https://doi.org/10.1016/j.proeng.2017.04.149

Arrabal, R., Matykina, E., Viejo, F., Skeldon, P., Thompson, G. E., & Merino, M. C. (2008). AC plasma electrolytic oxidation of magnesium with zirconia nanoparticles. *Applied Surface Science, 254*(21), 6937–6942. https://doi.org/https://doi.org/10.1016/j.apsusc.2008.04.100

Asekunle, A. S. (2018). *Development of bovine hydroxiapatite coating on Ti6Al4V implant by plasma electrolytic oxidation.* University of Malaya.

Becerik, D. A., Ayday, A., Kumruoğlu, L. C., Kurnaz, S. C., & Özel, A. (2012). The effects of Na 2SiO 3 concentration on the properties of plasma electrolytic oxidation coatings on 6060 aluminum alloy. *Journal of Materials Engineering and Performance*, *21*(7), 1426–1430. https://doi.org/10.1007/s11665-011-0022-1

Berger, S., Jakubka, F., & Schmuki, P. (2008). Formation of hexagonally ordered nanoporous anodic zirconia. *Electrochemistry Communications*, *10*(12), 1916–1919. https://doi.org/10.1016/j.elecom.2008.10.002

Clyne, T. W., & Troughton, S. C. (2018). A review of recent work on discharge characteristics during plasma electrolytic oxidation of various metals. *International Materials Reviews*, *0*(0), 1–36. https://doi.org/10.1080/09506608.2018.1466492

Da Forno, A., & Bestetti, M. (2010). Effect of the electrolytic solution composition on the performance of micro-arc anodic oxidation films formed on AM60B magnesium alloy. *Surface and Coatings Technology, 205*(6), 1783–1788. https://doi.org/https://doi.org/10.1016/j.surfcoat.2010.05.043

Dehnavi, V., Luan, B. L., Shoesmith, D. W., Liu, X. Y., & Rohani, S. (2013). Effect of duty cycle and applied current frequency on plasma electrolytic oxidation (PEO) coating growth behavior. *Surface and Coatings Technology*, *226*, 100–107. https://doi.org/10.1016/j.surfcoat.2013.03.041

Dikova, T., Assist, C., Nikolova, M., Assist, C., Yankov, P. E., Medicine, D., … Str, S. (2016). ADHESION ANALYSIS OF TITANIUM OXIDE NANOCOATINGS ON, *2*, 42–47.

Fernández-Garcia, M., & Rodriguez, A. (2007). Metal Oxide Nanoparticles, (October).

Gu, Y., Bandopadhyay, S., Chen, C., Guo, Y., & Ning, C. (2012). Effect of oxidation time on the corrosion behavior of micro-arc oxidation produced AZ31 magnesium alloys in simulated body fluid. *Journal of Alloys and Compounds*, *543*, 109–117. https://doi.org/https://doi.org/10.1016/j.jallcom.2012.07.130

Habazaki, H., Tsunekawa, S., Tsuji, E., & Nakayama, T. (2012). Formation and characterization of wear-resistant PEO coatings formed on β-titanium alloy at different electrolyte temperatures. *Applied Surface Science*, *259*, 711–718. https://doi.org/https://doi.org/10.1016/j.apsusc.2012.07.104

Hafner, B. (2006). Energy Dispersive Spectroscopy on the SEM: A Primer. *Characterization Facility, University of Minnesota*, 7–10. https://doi.org/10.1093/SER/mwj030

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature*, *354*, 56. Retrieved from https://doi.org/10.1038/354056a0

Jasmeen, N. (2013). Synthesis of Titanium Oxide Nanotube via Hydrothermal Method and Recovery of Palladium by means of it, *2*, 2–5.

Jiang, B. L., & Wang, Y. M. (2010). Plasma electrolytic oxidation treatment of aluminium and titanium alloys. *Surface Engineering of Light Alloys*, 110–154. https://doi.org/10.1533/9781845699451.2.110

Jin, F., Chu, P. K., Xu, G., Zhao, J., Tang, D., & Tong, H. (2006). Structure and mechanical properties of magnesium alloy treated by micro-arc discharge oxidation using direct current and high-frequency bipolar pulsing modes. *Materials Science and Engineering: A*, *435–436*, 123–126. https://doi.org/https://doi.org/10.1016/j.msea.2006.07.059

Kudo, A., & Miseki, Y. (2009). Heterogeneous photocatalyst materials for water splitting. *Chemical Society Reviews*, *38*(1), 253–278. https://doi.org/10.1039/b800489g

Kuhn, A. (2003). *Plasma anodizing of magnesium alloys*. *Metal Finishing* (Vol. 101). https://doi.org/10.1016/S0026-0576(03)90261-3

Lee, J., Ju, H. K., Lee, J. K., Kim, H. S., & Lee, J. (2010). Atomic layer deposition of

TiO2nanotubes and its improved electrostatic capacitance. *Electrochemistry Communications*, *12*(2), 210–212. https://doi.org/10.1016/j.elecom.2009.11.026

Li, J.-G., Ishigaki, T., & Sun, X. (2007). Anatase, Brookite, and Rutile Nanocrystals via Redox Reactions under Mild Hydrothermal Conditions: Phase-Selective Synthesis and Physicochemical Properties. *The Journal of Physical Chemistry C*, *111*(13), 4969–4976. https://doi.org/10.1021/jp0673258

Liang, J., Guo, B., Tian, J., Liu, H., Zhou, J., & Xu, T. (2005). Effect of potassium fluoride in electrolytic solution on the structure and properties of microarc oxidation coatings on magnesium alloy. *Applied Surface Science*, *252*(2), 345–351. https://doi.org/https://doi.org/10.1016/j.apsusc.2005.01.007

Liang, J., LT, H., & JC, H. (2007). Preparation and characterization of oxide films containing crystalline TiO2 on magnesium alloy by plasma electrolytic oxidation. *Electrochimica Acta*, *52*(14), 4836–4840. https://doi.org/10.1016/j.electacta.2007.01.059

Linsebigler, A. L., Lu, G., & Yates, J. T. (1995). Photocatalysis on TiO2 Surfaces_ Principles, Mechanisms, and Selected Results.pdf, 735–758. https://doi.org/10.1021/cr00035a013

Ming Zhang, Y., Bando, K., & Wada. (2001). Sol-gel template preparation of TiO 2 nanotubes and nanorods, 167–170.

Nakane, K., Shimada, N., Ogihara, T., Ogata, N., & Yamaguchi, S. (2007). Formation of TiO2nanotubes by thermal decomposition of poly(vinyl alcohol)-titanium alkoxide hybrid nanofibers. *Journal of Materials Science*, *42*(11), 4031–4035. https://doi.org/10.1007/s10853-006-0241-2

Nohava, J. (2009). Characterization of thermal spray coatings by instrumented indentation and scratch testing: Part 1. *CSM Instruments, Advanced Mechanical Surface Testing*, (28).

Peighambardoust, N. S., & Nasirpouri, F. (2013). Manipulating morphology, pore geometry and ordering degree of TiO2nanotube arrays by anodic oxidation. *Surface and Coatings Technology*, *235*(September), 727–734. https://doi.org/10.1016/j.surfcoat.2013.08.058

Pozio, A., Casaccia, C. R., Anguillarese, V., & Galeria, S. M. (2015). Effect of Tantalum Doping on TiO2 Nanotube Arrays for Water-Splitting, (January), 1–12. https://doi.org/10.1007/s00421-013-2805-6

Qin, Y. K., Xiong, D. S., Li, J. L., & Tyagi, R. (2016). Compositions and tribological properties of PEO coatings on Ti6Al4V alloy. *Surface Engineering*, (May 2017), 1–7. https://doi.org/10.1179/1743294414Y.0000000412

Rao, C., & Govindaraj, A. (2011). Nanotubes and Nanowires, *113*(December), 375–392. https://doi.org/10.1039/9781849732840

Roy, P., Berger, S., & Schmuki, P. (2011). TiO2nanotubes: Synthesis and applications. *Angewandte Chemie - International Edition*, *50*(13), 2904–2939. https://doi.org/10.1002/anie.201001374

Roy, P., Kim, D., Lee, K., Spiecker, E., & Schmuki, P. (2010). TiO2nanotubes and their application in dye-sensitized solar cells. *Nanoscale*, *2*(1), 45–59. https://doi.org/10.1039/b9nr00131j

Sarraf, M., Dabbagh, A., Abdul Razak, B., Mahmoodian, R., Nasiri-Tabrizi, B., Hosseini, H. R. M., … Sukiman, N. L. (2018). Highly-ordered TiO2nanotubes decorated with Ag2O nanoparticles for improved biofunctionality of Ti6Al4V. *Surface and Coatings Technology*, *349*(April), 1008–1017. https://doi.org/10.1016/j.surfcoat.2018.06.054

Sarraf, M., Razak, B. A., Crum, R., Gámez, C., Ramirez, B., Hayaty, N., … Basirun, W. J. (2017). Adhesion measurement of highly-ordered TiO 2 nanotubes on Ti-6Al-4V alloy, 311–321.

Shi, X., Wang, Q., Wang, F., & Ge, S. (2009). Effects of electrolytic concentration on properties of micro-arc film on Ti6Al4V alloy. *Mining Science and Technology (China)*, *19*(2), 220–224. https://doi.org/https://doi.org/10.1016/S1674-5264(09)60042-9

Shi, Z., Song, G., & Atrens, A. (2006). Influence of anodising current on the corrosion resistance of anodised AZ91D magnesium alloy. *Corrosion Science*, *48*(8), 1939–1959. https://doi.org/https://doi.org/10.1016/j.corsci.2005.08.004

Shin, K. R., Ko, Y. G., & Shin, D. H. (2011). Effect of electrolyte on surface properties of pure titanium coated by plasma electrolytic oxidation. *Journal of Alloys and Compounds*, *509*, S478–S481. https://doi.org/https://doi.org/10.1016/j.jallcom.2011.02.056

Sieber, I., Hildebrand, H., Friedrich, A., & Schmuki, P. (2005). Formation of self-organized niobium porous oxide on niobium. *Electrochemistry Communications*, *7*(1), 97–100. https://doi.org/10.1016/j.elecom.2004.11.012

Sreekantan, S., Saharudin, K. A., & Wei, L. C. (2011). Formation of TiO2 nanotubes via anodization and potential applications for photocatalysts, biomedical materials, and photoelectrochemical cell. *IOP Conference Series: Materials Science and Engineering*, *21*(1). https://doi.org/10.1088/1757-899X/21/1/012002

Timoshenko, A. V, & Magurova, Y. V. (2005). *Investigation of plasma electrolytic oxidation processes of magnesium alloy MA2-1 under pulse polarisation modes*. *Surface and Coatings Technology* (Vol. 199). https://doi.org/10.1016/j.surfcoat.2004.09.036

Tsuchiya, H., MacAk, J. M., Ghicov, A., Taveira, L., & Schmuki, P. (2005). Self-organized porous TiO2 and ZrO2 produced by anodization. *Corrosion Science*, *47*(12), 3324–3335. https://doi.org/10.1016/j.corsci.2005.05.041

Tsuchiya, H., & Schmuki, P. (2005). Self-organized high aspect ratio porous hafnium oxide prepared by electrochemical anodization. *Electrochemistry Communications*, *7*(1), 49–52. https://doi.org/10.1016/j.elecom.2004.11.004

Turhan, M. C., Lynch, R. P., Jha, H., Schmuki, P., & Virtanen, S. (2010). Anodic growth of self-ordered magnesium oxy-fluoride nanoporous/tubular layers on Mg alloy (WE43). *Electrochemistry Communications*, *12*(6), 796–799. https://doi.org/10.1016/j.elecom.2010.03.036

Venkateswarlu, K., Suresh, S., Rameshbabu, N., Bose, A. C., & Subramanian, S. (2011). Effect of Electrolyte Chemistry on the Structural, Morphological and Corrosion Characteristics of Titania Films Developed on Ti-6Al-4V Implant Material by Plasma Electrolytic Oxidation. *Key Engineering Materials*, *493–494*, 436–441. https://doi.org/10.4028/www.scientific.net/KEM.493-494.436

Walsh, F. C., Low, C. T. J., Wood, R. J. K., Stevens, K. T., Archer, J., Poeton, A. R., & Ryder, A. (2009). Plasma electrolytic oxidation (PEO) for production of anodised coatings on lightweight metal (Al, Mg, Ti) alloys. *Transactions of the IMF*, *87*(3), 122–135. https://doi.org/10.1179/174591908X372482

Wang, X., Zhu, L., Li, W., Liu, H., & Li, Y. (2009). Effects of half-wave and full-wave power source on the anodic oxidation process on AZ91D magnesium alloy. *Applied Surface Science*, *255*(11), 5721–5728. https://doi.org/https://doi.org/10.1016/j.apsusc.2008.12.082

Wang, Y., Lei, T., Jiang, B., & Guo, L. (2004). Growth, microstructure and mechanical properties of microarc oxidation coatings on titanium alloy in phosphate-containing solution. *Applied Surface Science*, *233*(1), 258–267. https://doi.org/https://doi.org/10.1016/j.apsusc.2004.03.231

Wang, Y. M., Jiang, B. L., Lei, T. Q., & Guo, L. X. (2005). Microarc oxidation and spraying graphite duplex coating formed on titanium alloy for antifriction purpose. *Applied Surface Science*, *246*(1), 214–221. https://doi.org/https://doi.org/10.1016/j.apsusc.2004.11.010

Wang, Y. M., Jiang, B. L., Lei, T. Q., & Guo, L. X. (2006). Microarc oxidation coatings formed on Ti6Al4V in Na2SiO3 system solution: Microstructure, mechanical and tribological properties. *Surface and Coatings Technology*, *201*(1), 82–89. https://doi.org/https://doi.org/10.1016/j.surfcoat.2005.10.044

Wei, W., Lee, K., Shaw, S., & Schmuki, P. (2012). Anodic formation of high aspect ratio, self-ordered Nb2O5nanotubes. *Chemical Communications*, *48*(35), 4244–4246. https://doi.org/10.1039/c2cc31007d

Wirtz, G. P., Brown, S. D., & Kriven, W. M. (1991). CERAMIC COATINGS BY ANODIC SPARK DEPOSITION. *Materials and Manufacturing Processes*, *6*(1), 87–115. https://doi.org/10.1080/10426919108934737

Zhang, H., & Banfield, J. F. (2000). Understanding Polymorphic Phase Transformation Behavior during Growth of Nanocrystalline Aggregates: Insights from TiO2. *The Journal of Physical Chemistry B*, *104*(15), 3481–3487. https://doi.org/10.1021/jp000499j