Nano Polishing of Titanium Alloy with Ionic Liquid

by

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CERTIFICATION OF APPROVAL

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Approved by,

(Associate Professor Dr. Patthi Hussain)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2016

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MUHAMMAD AIMAN BIN BAHTIAR)

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ABSTRACT

Nano polishing is a method of using electrochemical polishing to achieve nano size structure of a metal surface. The study was focusing on electrochemical polishing of titanium alloy using ionic liquid. Ionic liquid was used in comparison to the conventional ways of using hazardous solvent. Three parameters were varied such as voltage, rotational speed and polishing time for the experiment. The experiment was also performed to study the surface roughness and grain formation after the electrochemical polishing of the titanium alloy. Based from the surface roughness tester and Scanning Electron Microscopy (SEM) images, the surface roughness of titanium is proven to be decreased with the use of electrochemical process. A sample surface roughness was reduced to 54.4% from the initial surface roughness. The best parameters to conduct electrochemical polishing were low voltage and high rotation speed. The use of Atomic Force Microscopy (AFM) was preferable to show the 3 dimensional surface representation.

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CHAPTER 1

INTRODUCTION

1.1 Project Background

In recent years, titanium has been gaining popularity in a number of applications and in all sorts of industries. There are many application for titanium because of its physical and chemical properties which makes titanium a valuable metal. In order to increase strength and to withstand high temperatures, titanium is alloyed with aluminum, manganese, iron, molybdenum and other metals. Titanium alloy possesses high strength, lightweight and high corrosion resistance. In aerospace industries, titanium has been used as airplanes parts. The weight-to-strength-ratio of titanium produces lighter and low fuel consumption aircraft. In dentistry, titanium has been used as dental implant to replaces the root of a missing tooth. For automotive application, titanium is used to make engine parts. Noise and vibration can be solved by using the titanium parts. Titanium have been proven to increase horsepower, torque and improve fuel consumption. Ti-64Al-4V is by far the most common Ti alloy used for many application in the industry. However, despite the advantages of titanium, they are expensive than any other metals, because of the difficulty of the extraction process and difficulty of melting. On the other hand, the longer service live and higher mechanical properties counterbalance the high production cost.

Ionic liquid can be described as salts of mixture of salts which have the melting points below 100 °C. Ionic liquid are known for its properties such as good ion conductivity, thermal stability, non-flammability, high heat capacity, negligible volatility at room temperature, and strong polarizability and solubilizing effects [1]. Ionic liquids have huge advantages over other solvent that make them excellent for processing of metal

1.2 Problem Statement

Polishing is the final processing steps for many products. It is used to create a smooth surface and give higher mechanical properties for the products. Conventional method of polishing are by chemical and mechanical polishing. For example, chemical polishing can create a smooth surface by using hydrogen peroxide. However, this process is time consuming and require more work before a very smooth and flat result can be achieved. Conventional polishing was proven to be difficult and tedious process for titanium.

Electrochemical polishing or electropolishing has been used in various industries and products. The technology has been used in the production of spur gears in the automotive industries and the turbine blades in the aircraft industries. In the past years, the electrochemical polishing for titanium has been using aqueous solution as the electrolyte. However, the usage of aqueous such as perchloric acid faced a real challenges as it is potentially explosive. Moreover, the disposal of the acid is very costly and time consuming. Through an extensive research, ionic liquids has shown a promising result in electrochemical process with a better mechanical properties.

1.3 Objectives

This project aims to:

1. To achieve nano-polishing scale on titanium alloy using ionic liquid.
2. To investigate the effect of machining input parameters variation on the surface roughness on electrochemical polishing of Ti-6Al-4V using ionic liquid.

1.4 Scope of Study

The scope of the study is limited to investigate the variation of three input machining parameters which are voltage, rotation speed, and polishing time with an experimental method. In addition, the experiment will also study the effects of the input parameters on the surface roughness after the electrochemical polishing of the titanium alloys. On the other hand, the study is focused on using one type of ionic liquids as electrolyte during the polishing process which is l-butyl-3-methylimidazolium chloride.

CHAPTER 2

LITERATURE REVIEW

Titanium is widely used mainly because of its high corrosion resistance, biocompability and mechanical properties in chemical and biomedical engineering [2]. Titanium also possess unique high strength-to-weight ratio, easy formability and fatigue resistance which make it reliable to be used in building rocket engine parts, fuel tanks and gas bottles [3].

In the periodic table, titanium is positioned on group 4 and period 4. It has an atomic weight of 47.9 and an atomic number of 22. Titanium is considered as a transition element, it has an incompletely filled d shell in its electronic structure [4]. Table 1 shows a chemical composition of the Ti-64Al-4V alloy [3].

Table 2.1 : Composition of Ti-6Al-4V [3].

Ti (wt.%)	Al (wt.%)	V (wt.%)	Sn (wt.%)	Cu (wt.%)	Fe (wt.%)	C (wt.%)
Basis	6.0	4.0	0.1	0.1	0.3	0.08

Depends on the room temperature microstructure, titanium alloys can be break down into 5 groups which are α + β, metastable β, or stable β, α, near-α. Regarding to the groups, there are three classification of titanium alloying elements: (1) β-stabilizers, such as Mo, V, Nb, Ta (isomorphous), Fe, W, Cr, Si, Co, Mn, H (eutectoid); (2) α-stabilizers, such as Al, O, N, C; (3) neutrals, such as Zr. The α and near-α titanium alloys shows high corrosion resistance but have low temperature strength. In comparison, the presence of the both the β and α phases make α + β alloys have higher strength. The thermal treatment, relative proportions of the β and α phases, composition and thermo–mechanical processing conditions affecting the properties of the materials. Superior corrosion resistance and low elastic modulus is the unique characteristic shown by the β alloys [4].

In dentistry, surface topography and geometry are essential for the short and long term success dental implant. The formation of fibrous soft tissue capsule around the implant and osseointegration are the two types of response after implantation. Osseointegration is the direct bone-implant contact without an intervening connective tissue layer. Modification of the titanium native surface is usually required to meet the requirement of response after implantation. Properties of titanium such as mechanical strength and bioinertness can be completely exploited by a surface modification based approach. Electrochemical methods are considered as simple and cheap method among the other methods of titanium surface modification which are known [5].

For the past years, mechanical polishing — occasionally incorporated with chemical polishing — is used for titanium castings. Compare to other dental alloys, mechanical polishing with abrasives and buff is proven to be difficult and tedious process for titanium. In addition, contamination of polished titanium surfaces can be caused by mechanical polishing. However, when applied with the suitable electrolyte and the suitable electrolytic conditions, electropolishing can microscopically produce a clean, bright and smooth appearance. As been applied in the industry, the usually used electrolytes based on perchloric acid and hydrofluoric acid is applied to titanium [6]. Most of the electropolishing process for titanium will used 3 types of electrolytes: (1) perchloric acid and glacial acetic acid (2) perchloric acid and methanol with or without organic additions (3) sulfuric acid in water or organic solvent with or without hydrofluoric acid. Methanol and hydrofluoric acid are highly toxic. Acetic acid, ethylene glycol monobutylether and butanol are examples of ordinary organic additions which are flammable and volatile colorless liquid with irritant smells [7].

Majority of industry sector using electroplating with aqueous solutions, either it is acidic or basic, although for a certain applications will be using organic solvents. More rare metals can be deposited using either plasma or chemical vapour deposition techniques (PVD and CVD). This permits covering of an extensive variety of substrates (metal, plastic, glass, ceramic, etc.) not only with metal but also with alloys or compounds (oxide, nitride, carbide, etc.) yet, the high production cost have limit it to markets with a high value products. An alternative liquid has been developed for the past 10 years, called an ionic liquid which is characterized as ‘an ionic material that is liquid below 100°C’. However, ionic meterials is also considered as having high melting points and in some cases, melting points down to 240°C. Ionic liquids have huge advantages over other solvent that make them excellent for processing of metal: (i) wide potential windows (ii) high solubility of metal salts (iii) avoidance of water and metal/water chemistry (iv) high conductivity compared to non-aqueous solvents. The application of ionic liquids does not restricted to the capability to electrodeposit metals that have until now been impossible to reduce in aqueous solutions but also the potential to engineer the redox chemistry and control metal nucleation characteristics. Approximately, more than 10^{18} ionic liquids have been discover as a potential and while this has become an advantage of flexibility, it also become a disadvantage as it adds extreme complexity to the optimization. Large, non-symmetric ions that have low lattice energy and low melting points existed in ionic liquid. Imidazolium, pyridinium and choline based are the most commonly used cations for metal finishing. The structures of these are shown in Figure 1.

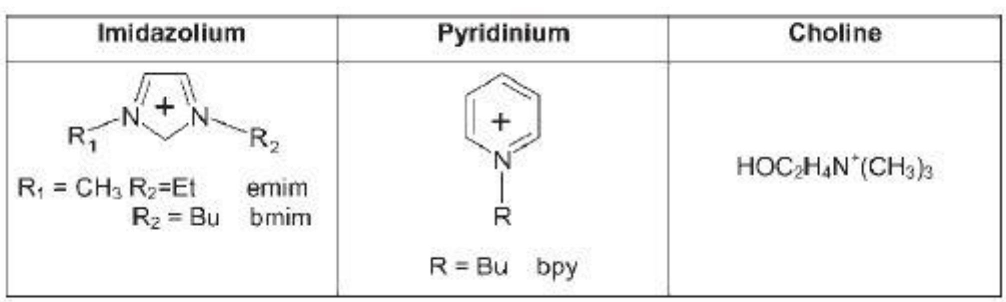

Figure 2.1 : Types of Ionic Liquid [8].

Ionic liquids have two types of generation which are called first and second generation liquids, which have been identified through their anionic species. The first generation liquids have complex anions formed between a Lewis basic anion, e.g. Cl2 with a Lewis acid metal salt or a Brønsted acid hydrogen bond donor. Second generation ionic liquids have discrete anions such as BF4 2, PF6 2 and SCN2. The latest studies have concentrate on the second generation ionic liquids as they proves to have advantages than the first generation ionic liquid. The second generation ionic liquid proven to have lower viscosities and are chemically easier to describe, because it consists of one type of anion. The studies are focusing on imidazolium, pyridinium and quaternary ammonium salts. Once again, the chosen cation is ethyl, methyl imidazolium as they have low viscosity and concomitant higher conductivity [8] [9].

CHAPTER 3

METHODOLOGY

3.1 Project Activity

Figure 3.1 shows the project flow chart which indicates the key activities that had been done throughout the project.

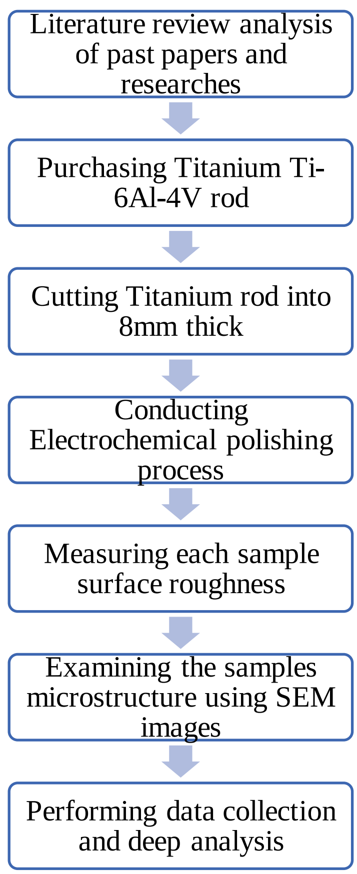

Figure 3.1 : Project Flow Chart

3.2 1-butyl-3-methylimidazolium chloride

There were a few advantages of using ionic liquid. Ionic liquid had a good ionic conductivities compared to organic solvent. The ionic liquid also had high viscosity at room temperature. The liquid existed as liquid in room temperature and had low melting point. Through the research, the liquid was stable up to temperature of 423°C. The most important property of ionic liquid was the electrochemical window. The ability of electrochemical potential, range over which the electrolyte was neither reduced nor oxidized at an electrode. The value will then determines the solvent electrochemical stability.

3.3 Scanning Electron Microscopy (SEM)

A method which was a focused electron beam scans on the surface of sample and then produced image from the upper most layer of the materials. The method yielded a microstructure image. Areas on the surface emitted a small amount of electrons, such as cracks or holes, appear dark. Areas that emitted a large amount of electrons, such as a flat surface or a peak would appear bright.

3.4 Surface Roughness Tester

The machine was used to measure and determined the surface roughness of a material. This machine measured Ra which was the mean surface roughness value calculated in unit nm.

3.5 Experiment Methodology

Figure 3.2 shows the experiment methodology the project starting from the setup of the experiment until the analysis of the experiment.

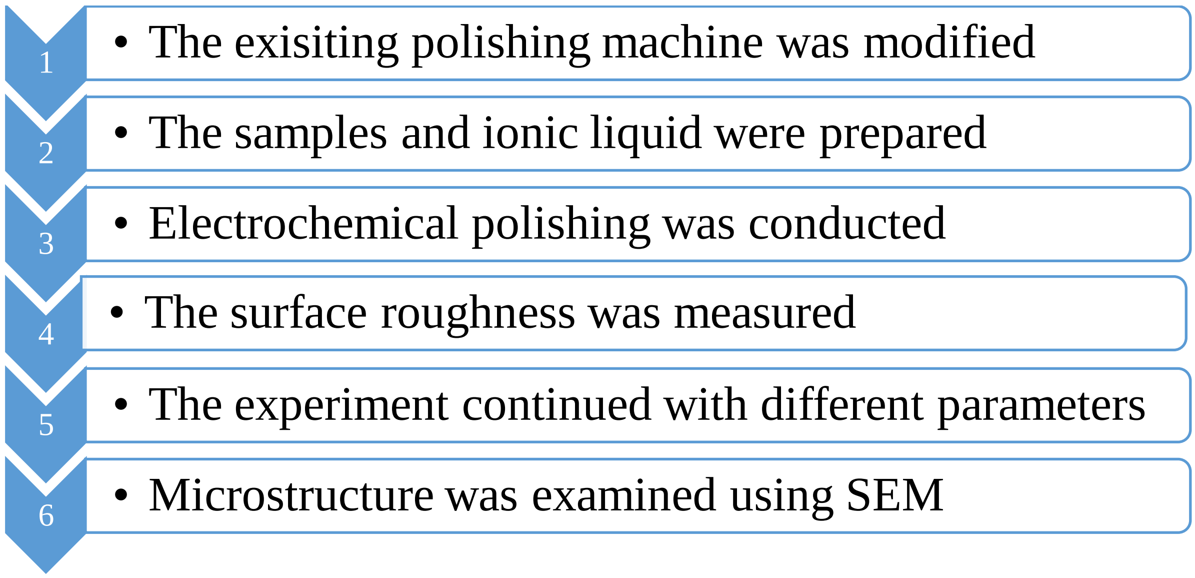

Figure 3.2 : Experiment Methodology

3.6 Calculation of Ionic Liquid Solution

The ionic liquid received was in solid state. Therefore, it was necessary to mix the solid with a solvent to form a solution. Formula for mixing solution from solid state was shown in Table 3.1 [10].

Table 3.1 : Solution Requirements

Grams of solute, g	20 g
Volume, V	0.5 L
Molecular Weight, MW	174.67 grams/mole

$g = M \, x \, V \, x \, MW$ where M is the Molarity in moles/liter

Modified equation,

$$M = \frac{g}{V \times MW}$$

$$M = \frac{20}{0.5 \times 174.67}$$

$$Therefore\ M = 0.229\ moles/liter$$

3.7 Assembly of Polishing Machine

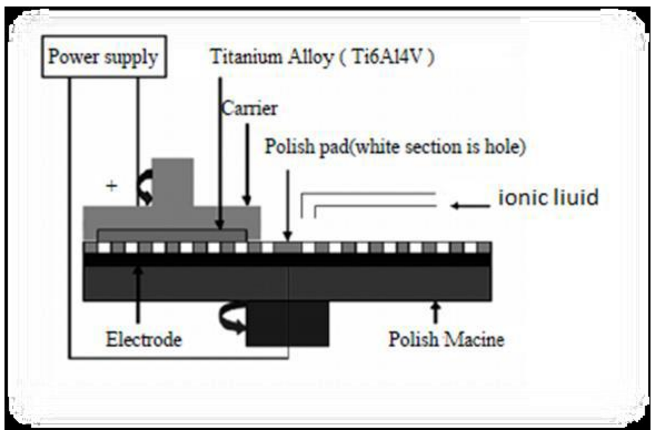

Figure 3.3 : Electrochemical Polishing Modified Machine

There were two processes that started concurrently which were polishing and chemical dissolution process. The existing polishing was modified as shown in the Figure 3.3 above.

The sample was put inside the carrier and connected with the positive terminal from the power supply. The negative terminal was connected to the polishing machine. Ionic liquid was supplied continuously from the feeder machine. The polishing disk and the sample had a gap about 200 – 500 nm.

The parameters varied in the experiment were stated in Table 3.2.

Table 3.2 : Experiment Parameters

Sample	Voltage (V)	Speed (rpm)
1	15	50
2	15	200
3	30	50
4	30	200
5	45	50
6	45	200
7	60	50
8	60	200

3.8 Gantt Chart

No.	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
FYP 1															
1	Purchasing Titanium (Ti-6Al-4V)										△				
2	Sample preparation														△
3	Ionic Liquid obtained														
FYP 2															
4	Experiment setup														
5	Start of experiment														
6	Surface roughness analysis										△				
6	SEM images obtained														
7	SEM images analysis														△

△ = Key milestone

CHAPTER 4

RESULT AND DISCUSSION

4.1 Surface Roughness

Table 4.1 shows the parameters varied in the experiments which were voltage, rotation speed and polishing time. Figure 4.1 shows the graph of mean surface roughness vs polishing time.

Table 4.1 : Experiment Result

Sample	Voltage, V	Rotation Speed, rpm	Polishing Time, min				
			0	2	4	6	8
			Mean Surface Roughness, nm				
1	15	50	0.403	0.455	0.528	0.591	0.653
2	15	200	0.499	0.461	0.444	0.416	0.388
3	30	50	0.549	0.755	0.941	1.137	1.333
4	30	200	0.682	0.576	0.491	0.396	0.311
5	45	50	0.295	0.86	0.498	0.599	0.701
6	45	200	0.764	0.803	0.863	0.912	0.962
7	60	50	0.783	1.464	2.145	2.826	3.527
8	60	200	0.494	0.450	0.426	0.392	0.358

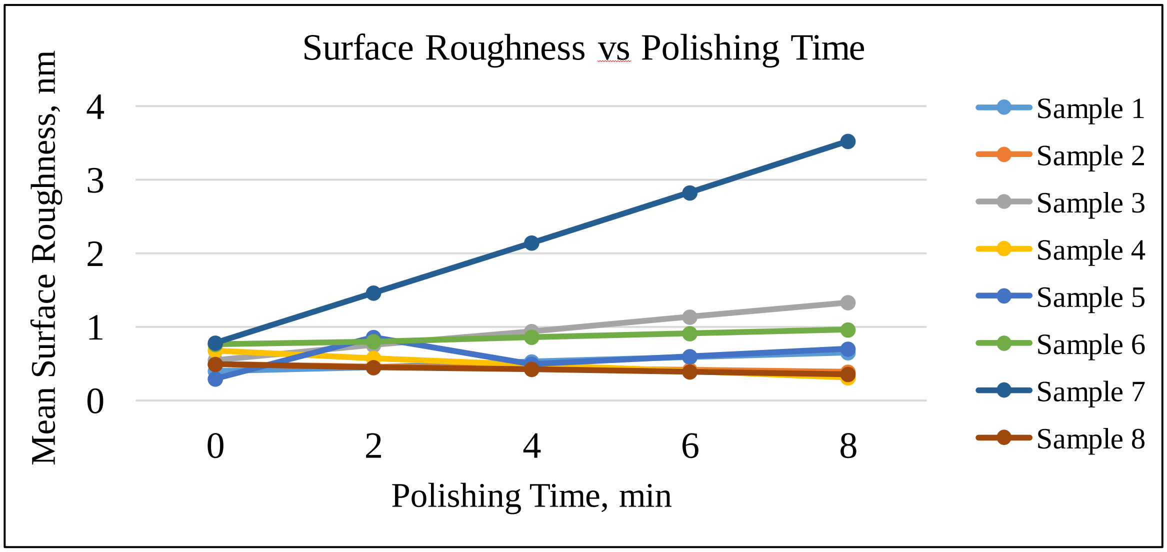

Figure 4.1 : Graph of Mean Surface Roughness vs Polishing Time

From the graph plotted, samples 2, 4 and 8 show good results. The surface roughness of these samples decreased from their initial surface roughness. However, for samples 1, 3, 5, 6 and 7 show bad results as their surface roughness increased from their initial surface roughness.

Based on the result obtained, as the voltage increases, the surface roughness decreases. As the polishing time increases, the surface roughness decreases. However, this statement was only true when the rotation speed is 200 rpm. The best result could be seen in sample 4 with the decreased of 54.4% of surface roughness from the initial surface roughness.

Surface roughness of samples 1, 3, 5, 6 and 7 increased due to passivation film on the surface were not able to protect the titanium alloy from anodic oxidation. Therefore, after a few minutes the surface got rougher. Rotation speed of 50 rpm proved to be favorable for the formation of the oxide layer.

4.2 Scanning Electron Microscopy

Figure 4.2 shows the SEM image of the sample before electrochemical polishing. Figure 4.3, 4.4 and 4.5 show the SEM images of sample after polishing.

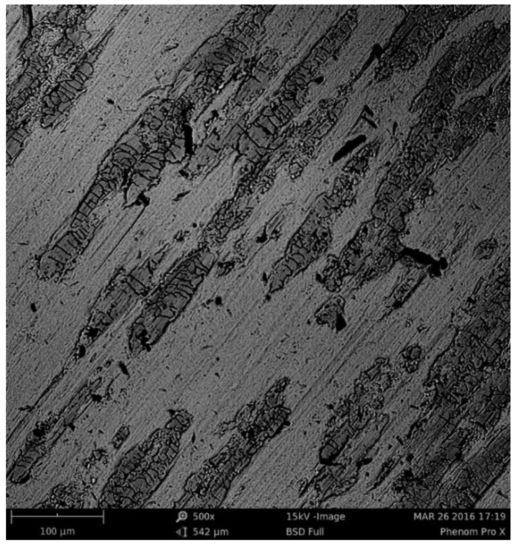

Figure 4.2 : SEM image before electrochemical polishing

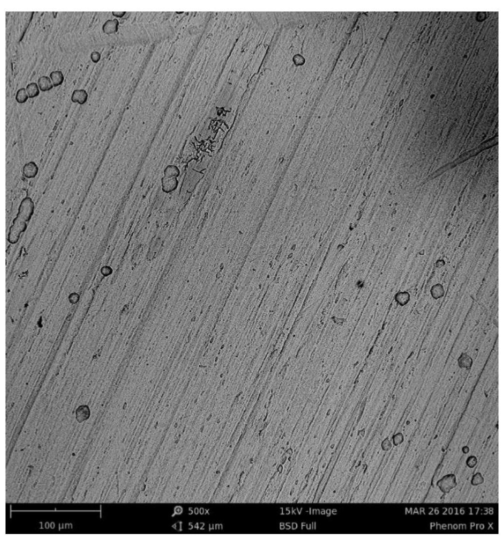

Figure 4.3 : SEM image for sample 2

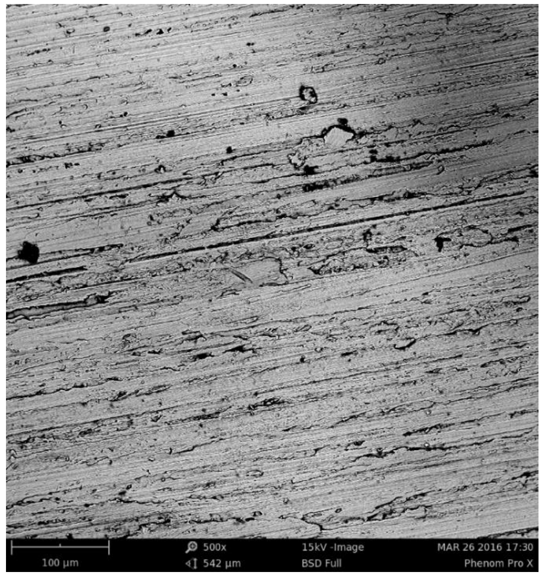

Figure 4.4 : SEM image for sample 4

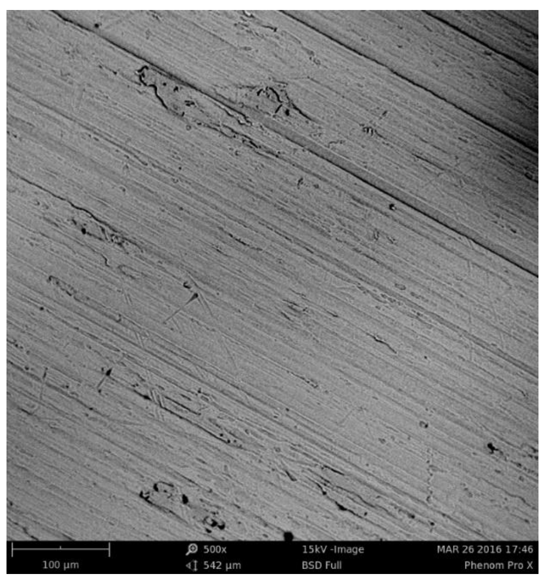

Figure 4.5 : SEM image for sample 8

The magnification for each sample was 500. There were significant changes between Figure 4.2 and Figure 4.3, 4.4, 4.5. Figure 4.2 shows the surface to be rough and uneven surface. SEM images after electrochemical polishing which are displayed in Figure 4.3, 4.4, 4.5 have better and finer surface.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Through the electrochemical polishing, nano polishing surface on titanium alloy using ionic could be achieved. The surface roughness which was measured in unit nm. Sample 2, 4, and 8 show decrease in surface roughness. The surface roughness of sample 4 was 3 times better than sample 2. Meanwhile, the surface roughness of sample 4 was 2 times better than sample 8. The effect of machining input parameters variation on the surface roughness on electrochemical polishing of Ti-6Al-4V using ionic liquid was obtained. The research work reveals the best parameters, using a low voltage and also a high rotation speed to achieve the finest surface finished. As the process is cost effective and environmental friendly, it is highly favorable to be applied in the industry.

5.2 Recommendation

In order to achieve an evenly contact between the samples and ionic liquid, it is recommended to provide a continuous amount of ionic liquid and in a large quantity from the feeder. Furthermore, the samples could be prepared using a better method such as waterjet cutting or plasma cutting to save time on sample preparation. Moreover, Atomic Force Microscopy (AFM) is preferably to be conducted to show the three dimensional surface representation.

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