**Shiraz University**
**Faculty of Engineering**

Ph.D.Thesis
In Materials Engineering

# Plasma electrolytic oxidation of Ti-6Al-4V alloy to improve tribological and mechanical properties

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September 2011

**IN THE NAME OF GOD**

# PLASMA ELECTROLYTIC OXIDATION OF Ti-6Al-4V ALLOY TO IMPROVE TRIBOLOGICAL AND MECHANICAL PROPERTIES

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**THESIS**

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (PhD)

**IN**

MATERIALS SCIENCE AND ENGINEERING

SHIRAZ UNIVERSITY

SHIRAZ

ISLAMIC REPUBLIC OF IRAN

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**SEPTEMBER 2011**

## Abstract

**Plasma electrolytic oxidation of Ti-6Al-4V alloy to improve tribological and mechanical properties**

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In the present work, plasma electrolytic oxidation of Ti-6Al-4V is investigated. The process was studied previously. In this study, the author tried to study some new aspects of the process. To do it, an electrolyte similar to that of used in other studies was selected. The constituents of the electrolyte were: sodium chloride, sodium hydroxide, sodium silicate, and hydrogen peroxide. These materials were used in electrolytes previously. In the present study, all of these constituents are used together to use the advantages of all materials. The application of all these materials together increases the growth rate and modifies the wear resistance of the coatings. Besides these constituents, starch was added. The primary objective of starch addition was to increase the viscosity and stability of the electrolyte against boiling and splashing out, but during the study it was clear that starch is effective in composition and wear resistance of the coating. The optimum concentrations of each of the electrolyte constituents were obtained by design of experiments via Taguchi method. One of the objectives of the present study was producing coatings comparable to the coatings of other researches while using very simple equipment and conditions. All materials used in the electrolyte were completely available and inexpensive and no expensive or complex were used. Tribological examination of the specimens coated in the optimized electrolyte showed that plasma electrolytic oxidation increased the wear resistance (reduction of friction coefficient and weight loss) of the alloy.

**Table of Contents**

**Title** **Page**

| Title | Page |
|---|---|

| Title | Page |
|---|---|

| **Title** | **Page** |
|---|---|

**List of Tables**

**List of Figures**

| **Title** | **Page** |
|---|---|

| Title | Page |
|---|---|

| Title | Page |
|---|---|

| **Title** | **Page** |
|---|---|
|  |

**List of Abbreviations**

| Title | | Page |
|---|---|---|
| AC | Alternative current | |
| Adj MS | Adjusted mean of squares | |
| Adj SS | Adjusted sum of squares | |
| ANOVA | Analysis of variance | |
| Bcc | Body centered cubic | |
| CAE | Cathode arc evaporation | |
| CVD | Chemical vapor deposition | |
| DC | Direct current | |
| DF | Degree of freedom | |
| DOE | Design of experiments | |
| EPT | Electrolytic plasma technology | |
| Hcp | Hexagonal close packed | |
| MAO | Micro-arc oxidation | |
| Min | Minute | |
| MSD | Mean squared deviation | |
| PED | Plasma | |
| PEO | Plasma electrolytic oxidation | |
| PES | Plasma electrolytic saturation | |
| PET | Plasma electrolytic twins | |
| PVD | Physical vapor deposition | |
| QC | Quality characteristics | |
| Rpm | Revolution per minute | |
| S/N ratio | Signal to noise ratio | |
| SBF | Simulated body fluid | |
| SEM | Scanning electron microscopy | |
| Seq. SS | Sequential sum of squares | |

| Title | Page |
|---|---|
| S-N curve | Stress versus number of cycles curve |
| SS | Sum of squares |
| XRD | X-ray diffraction |

Introduction

Ti-6Al-4V is a well-known alloy for many applications such as aerospace, automotive, and biomedical industries. Many studies has been carried out on improving the tribological behavior of the alloy via a variety of techniques such as physical vapor deposition [Ref1,Ref75, Ref119], ion implantation [Ref115], laser alloying [Ref116, Ref124], thermal oxidation [Ref140], sol-gel [Ref147] etc. one of the recently developed methods of improving tribological performance of this alloy is plasma electrolytic oxidation which has been developed rapidly in recent years. The process is a new generation of conventional anodizing which differs from the latter in applying high potentials [Ref13]. The high voltage leads to formation of a plasma envelope which appears as luminescent sparks on the surface of the anode [Ref]. The formation of plasma enhances the tribological properties of the coatings [Ref13].
Many research works studied the tribology of PEO coatings on Ti-6Al-4V and investigated the effect of porosity [Ref52], electrolyte composition [Ref105], current mode [Ref6, Ref58], sparking voltage [Ref126] and other factors on the microstructure, chemical composition, tribology and mechanical properties of PEO coatings.
The main objectives of the present work were:

- ☐ Lowering applied voltage
- ☐ Simplifying the process
- ☐ High wear resistance

Simplifying of the process was carried out by using simple equipment and familiar, available, and inexpensive materials. All materials were abundant and the process of making the electrolytes was easy. The power source used for PEO was a simple DC source with no extra attachments.

For lowering of the applied voltage, a combination of sodium chloride and sodium hydroxide was used and sodium silicate was added to the electrolyte for increasing the growth rate of the coatings.

To obtain high wear resistance, starch was added to the electrolyte and an optimum composition of the electrolyte was calculated using a statistical analysis by Taguchi method.

To evaluate the wear properties of the coatings wear tests were carried out by a pin-on-disk apparatus. Since one of the important applications of Ti-6Al-4V is production of biomedical implants, some wear tests were carried out in the presence of ringer's solution as the simulated body fluid. Results showed a better wear resistance for PEO coated alloy under dry conditions. In the presence of ringer's solution, however the uncoated alloy showed a better performance than the PEO coated alloy.

Fatigue tests showed that PEO is not a suitable method to enhance the wear properties of the alloy because of the brittle nature of the coatings and increasing the probability of fatigue crack initiation and propagation.

# Section One
# Theory

# 1. Titanium and its alloys

## 1.1. History of Titanium

Titanium is present in the earth's crust at a level of about 0.6% and is therefore the fourth most abundant structural metal after aluminum, iron, and magnesium. The most important mineral sources of titanium are ilmenite ($FeTiO_3$) and rutile ($TiO_2$). The first suspicion of a new, unknown element presents in a dark, magnetic iron sand (ilmenite) in Cornwall (UK) was expressed in 1791 by Gregor, a clergyman and amateur mineralogist. In 1795, Klaproth, a German chemist, analyzed rutile from Hungary and identified an oxide of an unknown element, the same as the one reported by Gregor. Klaproth named the element titanium after the Titans, the powerful sons of the earth in Greek mythology [1,2].
Wilhelm Justin Kroll from Luxembourg is recognized as the father of titanium industry. In 1932, he obtained significant quantities of titanium by combining $TiCl_4$ with calcium. He demonstrated that titanium could be extracted commercially by reducing $TiCl_4$ by changing the reducing agent from calcium to magnesium at the U.S. Bureau of Mines. Today this is still the most widely used method and is known as the “Kroll process”. After the Second World War, titanium-based alloys were soon categorized as main materials for