

# Wear Behavior Evaluation In Simulated Body Fluid of A Modified Ti-6Al-4V Alloy by DC Glow Plasma Nitriding

Safa Hussain Ali<sup>1</sup>, Thair L. <sup>2</sup>

<sup>1</sup> Department of biomedical engineering, College of engineering , university of Thi-Qar, Thi-Qar, 64001,Iraq.

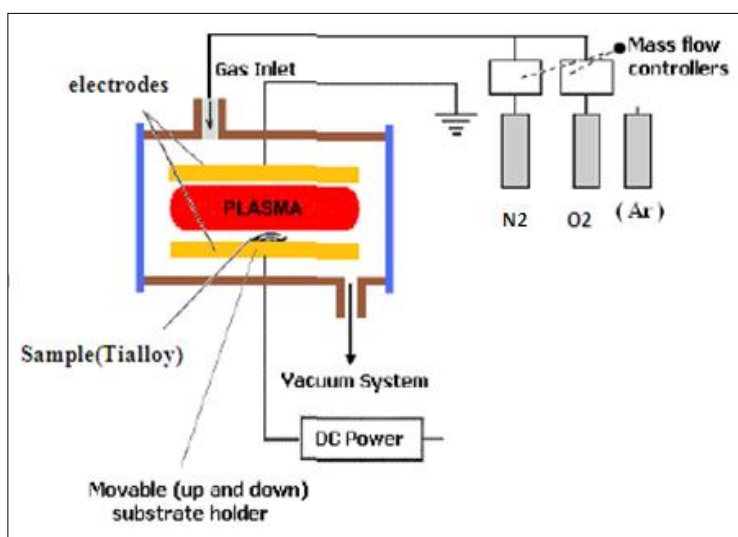
<sup>2</sup>Iraqi Atomic Energy Commission (IAEC), nuclear research centre, Iraq.

[Safa.hussain.ali@utq.edu.iq](mailto:Safa.hussain.ali@utq.edu.iq)

**Abstract:** As implant materials in biomedical application titanium and titanium alloys are used frequently in this field due to high strength to weight ratio, good corrosion resistance and good biocompatible when compared with other material used in biomedical application (such as stainless steel and cobalt base alloys). But this alloy when reacted with body fluid will release aluminum and vanadium then causes neurological disorders and toxicity in human system. "The glow discharge is just one of many forms of gaseous discharges, often called plasma". An electric discharge can be seen when two electrodes are inside a pipe and linked to a power supply the pipe can be filled with different gases or evacuated electrical current goes past between two special electrodes. The plasma nitriding process was performed at different nitriding times (5, 10, and 15 h), and the effect of plasma nitriding was examined on the chemical composition of Ti-6Al-4V alloy and the appearance of phases was studied by scanning electron microscopy, FESEM, X-ray diffraction (XRD) and pin on disk wear resistance. The results indicate that the formation of layers and phases Ti<sub>2</sub>N and Ti<sub>2</sub>N<sub>3-x</sub> on a surface of the alloy were achieved, which would improve the surface characteristics of wear resistance in simulated body fluid.

## Introduction

The direct current glow discharge consists of two electrodes, separated this electrodes space and vacuum vessel, in this vessel voltage at low pressures "between a few and a hundred Pascals". Hundreds to thousands of Volts requirement to the voltage inside the vessel to collapse the gas into a plasma. Four variables through which control the properties of plasma: different voltage, the kind of gas used, the space between the electrodes and the pressure inside. (shown in Figure 1 the schematic of DC glow discharge reactor) [1].



**Figure 1.** DC glow discharge plasma reactor [2]

For PVD coated metals a typical wear failure mechanism is cracking of the coating due to substrate deformation when high shear forces are applied. For plasma nitrided metals, on the other hand, the presence of a subsurface hardened zone increases the capability to withstand the high shear forces developed at the coating interface during sliding wear processes [3]. Titanium and titanium alloys are used frequently in this field due to high strength to weight ratio, good corrosion resistance and good biocompatible when compared with other material used in biomedical application (such as stainless steel and cobalt base alloys).  $\alpha+\beta$  Ti6Al4V is one of alloys can be used frequently in biomedical application where have required high strength [4]. The passive oxide films that formed on surface of titanium alloy assist to increase corrosion resistance. This passive oxide films dissolve when exposed to the oxygen from the air or from other medium. Drinks and foods when they are acidic, containing sodium chloride are corrosive materials. Saliva is a media of strong corrosive effect. As its pH factor decreases and as chloride concentration increases, the increase in corrosion potential of saliva is observed. The corrosion process occurs, as a result, metal ions directly loss into the solution or the passive oxide films dissolve [5].

## Experimental

### 1. Materials and Methods

The ( $\alpha + \beta$ ) Ti-6Al-4V alloy (provided by MC MASTER USA) is cut by Knuth smart DEM cutting machine made in Germany, into dimensions of 15.8 mm in diameter and 4 mm in thickness. The chemical composition of the Ti-6Al-4V alloy is given in Table 1. The first step involved the grinding of samples by silicon carbide papers (120, 220, 320, 500, 600, 1000, and 1200)  $\mu\text{m}$  grit, after which these samples were rinsed

by distilled water, then polished using a polishing cloth with diamond suspension of (9, 6, 3, 1)  $\mu\text{m}$  to get a bright mirror finish. After polishing the samples, they were ultrasonically cleaned with an ethanol medium for 5 min to remove any impurities from the surface, and then dried the sample by hot air. The most common chemical etchant for Ti-6Al-4V alloy is Kroll's reagent according to ASTM E407 [6]. The solution for etching was prepared by adding 1 ml of hydrofluoric acid (HF), 3 ml of nitric acid ( $\text{HNO}_3$ ), and 6 ml of water ( $\text{H}_2\text{O}$ ). After 5 s of the etching process (immersion time), the sample was washed in water and allowed to air dry.

## 2. Surface Modification by Plasma Nitriding

The nitriding procedure was performed on mirror polished finished Ti-6Al-4V specimen for different nitriding times (5, 10, and 15 h) in DC glow discharge plasma system. This is a low-pressure gas discharge unit consisting of a vacuum chamber with two parallel electrodes. The plasma chamber contains a Target (cathode) and anode disk of stainless steel. The cathode faces the anode, which provides an electric field for the gas to be discharged. The bottom shaft of the cathode electrode is shielded by insulator disk (ceramic). The top of cathode is shielded by cathode space assembly which includes ceramics insulator and stainless-steel holder. The diameter of the top electrode is 14.5 cm while the target electrode (effective area of cathode dark space) is 7.5 cm and the gap distance between them can be varied from 4 to 6 cm and in the current study a 4 cm distance is used. The feeding of N gas was done after evacuating the process chamber to high vacuum ( $\approx 1 \times 10^{-5}$  mbar) using high vacuum system consisting of rotary and turbomolecular vacuum pumps to ensure the complete removal of the heavy gases like hydrocarbons. A 4 kV DC voltage-power supply is used to ensure the necessary voltage for nitriding and the discharge voltage for nitriding was 650 V. The nitriding process was performed in 2 mbar pressure of nitrogen.

## 3. Metallographic Characterization of Ti-6Al-4V Alloy

The main aim of using FESEM, ZEISS-type microscopes were used to observe the surface morphology at the different conditions, determination of affected depth, and thickness of the diffusion zone as well as the average grain size related to the nitriding process. X-ray diffraction (XRD) (The Shimadzu Lab X XRD6000, Japan) was used in this study to determine phase formation during plasma nitriding. The test was accomplished by using a copper target ( $K\alpha$  radiation = 0.15418 nm) with a nickel filter. The scanning speed of the diffractometer was adjusted to 5 deg per minute with the range of the diffraction angle  $2\theta^\circ$  was  $20^\circ$ – $80^\circ$ .

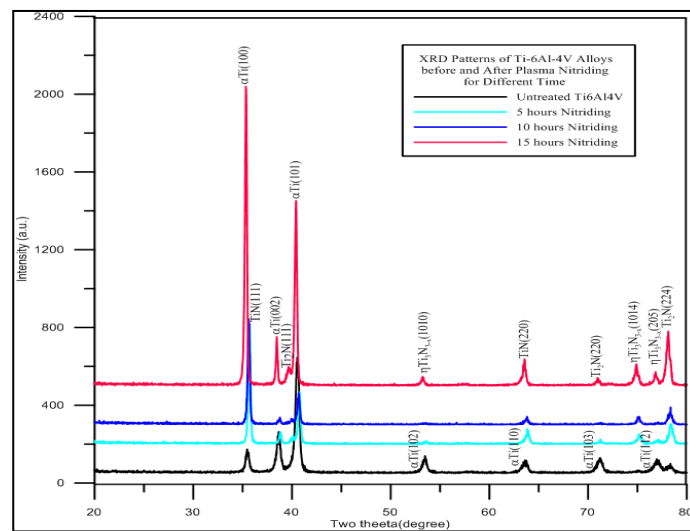
#### 4. Pin on Desk wear test

The wear tests were carried out on pin-on-disc tester (MICROTEST, S.A. Spain), the pin on disk wear tester using a 16mm diameter SiC ball as the pin. lubricated wear tests with simulated body fluid (Ringer solution), a sliding distance of 99 m were carried out at room temperature (25 °C), a sliding speed of 0.2 ms<sup>-1</sup>(200rpm), normal loads of 10 and 15N. To calculate the weight loss before and after wear test and coefficient of friction .According to the American Society for Testing and Materials (ASTM G99-04) [7].

### Results

#### 1. Phases Identification

Identification of phases after plasma nitriding by x-ray diffraction analysis. Figure 2 represented diffraction patterns of samples untreated and treated at 5h, 10h and 15h times ,untreated samples consist of  $\alpha$ Ti and  $\beta$ Ti phases ,after nitriding a compound layer on the material surface consist of  $\delta$ TiN,  $\epsilon$ Ti<sub>2</sub>N and  $\eta$ Ti<sub>3</sub>N<sub>3-x</sub> phases depend on the time of plasma nitriding.

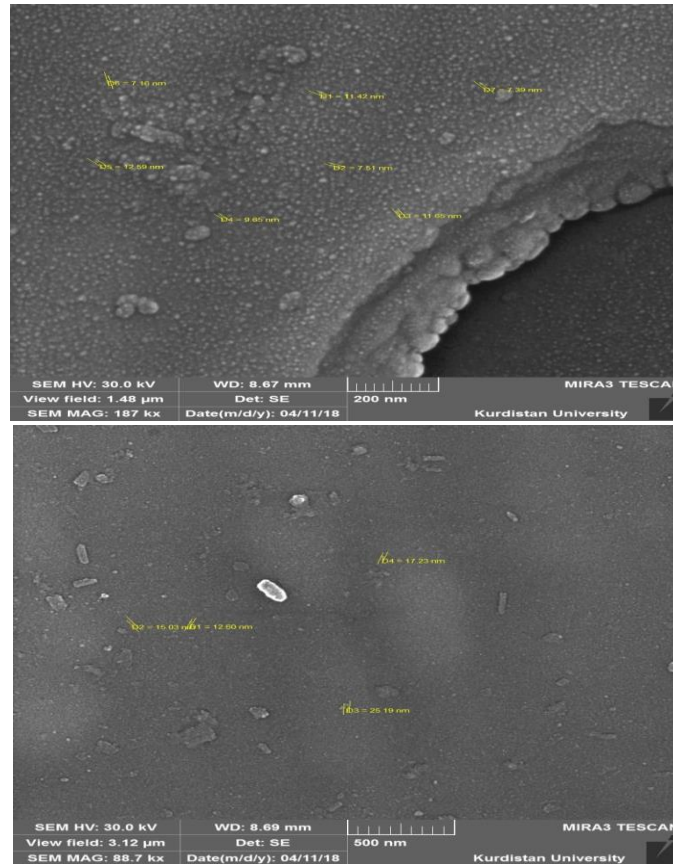


**Figure 2.** XRD Patterns of Ti-6Al-4V alloy before and after plasma nitriding at different times

#### 2. Morphology observation

The surface morphology of Ti-6Al-4V alloy plasma nitriding , as-received having the particle size on the surface deferent when comparable one another due to the diffusion of nitrogen atoms on the surface lead to large grain size large than original size for Ti-6Al-4V alloy. The nitrided layer is formed by diffusion of nitrogen in the substrate

bulk.



**Figure 3.** SEM morphology of Grain size at a) 200 nm b) 500nm.

### 3. Wear behavior for Ti-6Al-4V alloy

Tribological characterization in terms of friction coefficient and wear rate is important for the durability of surgical implant, especially for hard tissue replacements like hip and knee joints consisting of mating component. From the wear test against WC-Co ball, Figure 4, 5, 6 and 7 shows the result of wear test and friction coefficient for nitriding at different condition at constant time and distance but different in load and comparison with untreated sample. shown in table 3.1, but for 15hours nitriding have large wear rate and coefficient friction because the different the film composition and increase roughness the surface when increase the power process and this decrease from the hardness.

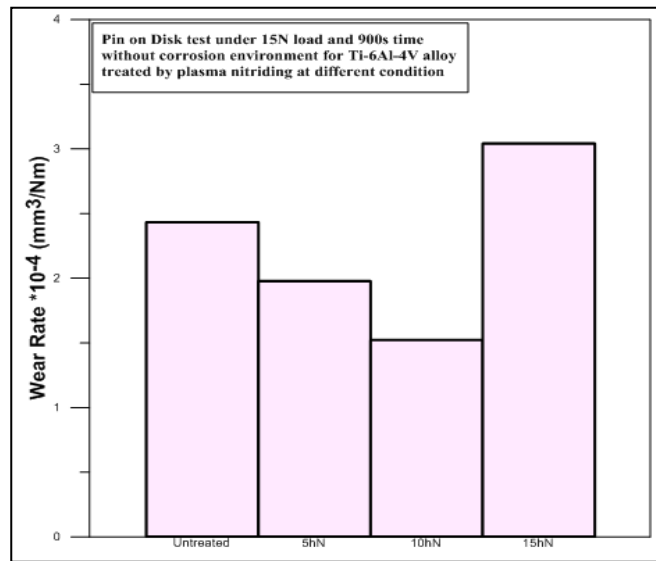


Figure 4. Wear characteristic curves of plasma nitrided Ti 6Al 4V alloy at different and 10N load obtained in Ringer solution at room temperature.

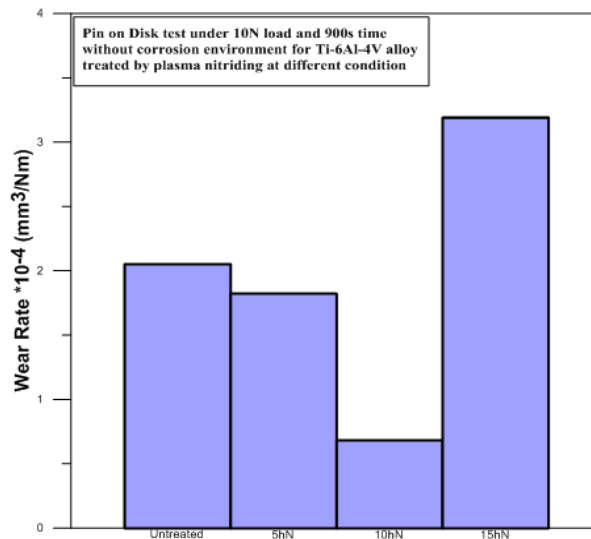


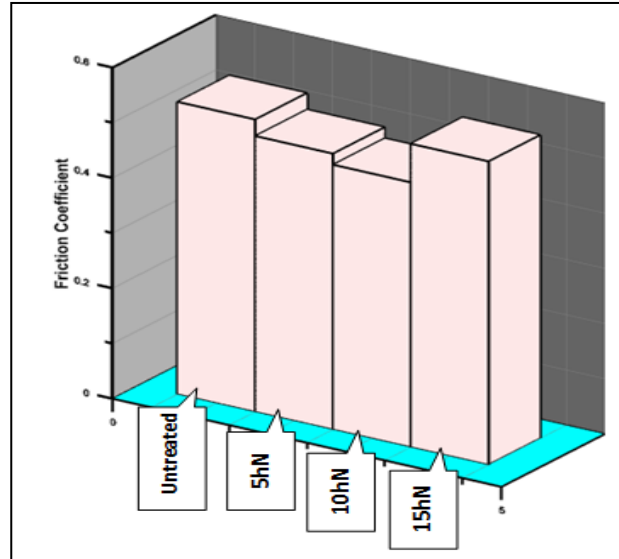
Figure 5. Wear characteristic curves of plasma nitrided Ti 6Al 4V alloy at different condition and 15N load obtained in Ringer solution at room temperature.

Table 1. the wear rate and friction coefficient at different parameter obtained in Ringer solution at room temperature

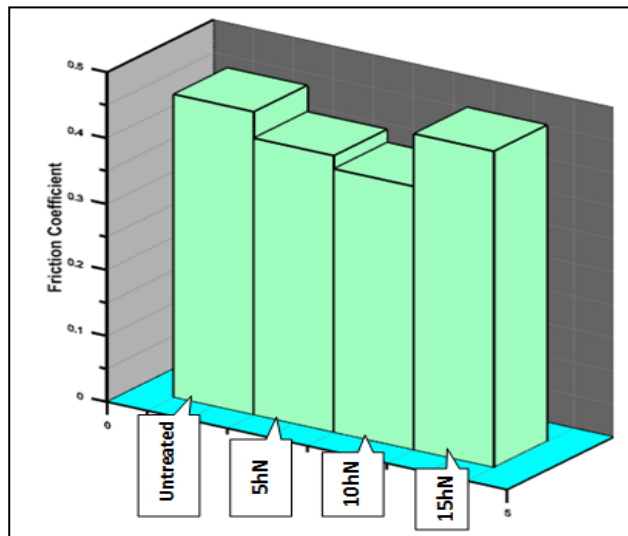
Samples conditions	Wear rate $10^{-4}$ (mm <sup>3</sup> /Nm)	Friction coefficient	Load (N)	Time (s)	Sliding speed (rpm)
Untreated	2.053	0.46	10	900	200
5hN	1.824	0.42			
10hN	0.684	0.40			
15hN	3.192	0.48			
Untreated	2.432	0.42	15		



5hN	1.976	0.38			
10hN	1.520	0.32			
15hN	3.040	0.45			



**Figure 6.** Coefficient of Friction plasma nitriding for Ti-6Al-4V alloy at different condition and 10N load compared with untreated substrate material obtained in Ringer solution.



**Figure 7.** Coefficient of Friction plasma nitriding for Ti-6Al-4V alloy at different condition and 15N load compared with untreated substrate material obtained in Ringer solution.

## Discussion

### 1. Influence of Plasma Nitriding on Phases Identification

It shows the XRD patterns of untreated and topography Plasma nitrided Ti-6Al-4V alloy samples by used standard Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICDD file #44-1294 and #44-1288). For the untreated sample, detected the diffraction peaks are corresponding to the  $\alpha$ Ti. (100), (002), (101) and (110)  $\alpha$ Ti at  $35.3^\circ$ ,  $38.09^\circ$ ,  $40.5^\circ$  and  $63^\circ$ . The lattice of  $\alpha$ -Ti phase is expanded in the treated region and at greater depth (bulk region), the peak positions are shifted to higher Bragg angles ( $2\theta$ ). The pattern shows a systematic shifting of the peaks at the  $2\theta$  values of  $\alpha$ -Ti toward upper  $2\theta$  side. It can be seen that after the nitriding treatment for 5, 10 and 15 hours, changes in diffraction peaks are observed and an increase in the Full Width Half Maximum (FWHM) of these peaks leads to formation TiN,  $\epsilon$ Ti<sub>2</sub>N and  $\eta$ Ti<sub>3</sub>N<sub>3-x</sub> phases corresponding to  $\epsilon$ Ti<sub>2</sub>N as per cubic TiN (JCPDS-ICDD file # 38-1420), (JCPDS-ICDD file #017-0386 and (JCPDS-ICDD file # 023-1455. When the time nitriding become 5h will appear the  $\eta$ Ti<sub>3</sub>N<sub>3-x</sub> (102) and (1014) at  $2\theta$  35.83 and 77.50 respectively and  $\eta$ Ti<sub>3</sub>N<sub>2-x</sub>(015) at  $2\theta$  and  $\epsilon$ Ti<sub>2</sub>N (224) at  $2\theta$  78.30. When increase in time nitriding at 10h will leads to the formation  $\delta$ TiN (111), (220) at  $2\theta$  36.66 and 63.50 respectively and  $\epsilon$ Ti<sub>2</sub>N (224) at  $2\theta$  78.30 and  $\eta$ Ti<sub>3</sub>N<sub>2-x</sub>(015) at  $2\theta$  and  $\eta$ Ti<sub>3</sub>N<sub>3-x</sub> (1014) at  $2\theta$  75.50. When increase the time nitriding process to 15h will leads to formation  $\delta$ TiN (220) at  $2\theta$  63.50 and  $\epsilon$ Ti<sub>2</sub>N(111), (220) and (224) at  $2\theta$  39.28, and 78.30 and  $\eta$ Ti<sub>3</sub>N<sub>3-x</sub> (1010), (1014) and (205) at  $2\theta$  53.10, 75.30 and 77.50. also this result is in agreement with other researchers [8].

### 2. Influence of Plasma Nitriding on Chemical Composition Distribution of Phases

The surface morphology of Ti-6Al-4V alloy plasma nitriding, as-received having the particle size on the surface different when comparable one another due to the diffusion of nitrogen atoms on the surface lead to large grain size large than original size for Ti-6Al-4V alloy. The nitrided layer is formed by diffusion of nitrogen in the substrate bulk. The mechanism of out flow of bubbles resulted from plasma nitriding to the upward direction to the surface, formation the cavitations on the surface due to the different environment and condition process. The origin of bubbles can be associated with the Ar atoms trapped in the films during sputtering. Since rare gas/solid systems have essentially zero solubility the injected Ar atoms may rapidly supersaturate the solid. The presence of Ar inclusions should decrease by deposition at a higher temperature or at lower Ar partial pressure [9].



### 3. Influence of Plasma Nitriding on wear Behavior

The wear rate is decrease with increase time nitriding and increase hardness and wear rate increase when increase the roughness. Wear rate at 10 hours nitriding is the best result investigated in this study  $0.684 \times 10^{-4} \text{ mm}^3/\text{Nm}$  and for untreated samples is  $2.053 \times 10^{-4} \text{ mm}^3/\text{Nm}$  and friction coefficient 0.40 at 10N as shown in table 3.1 and Figure 5 and 6, but for 15 hours nitriding have large wear rate and coefficient friction because the different the film composition and increase roughness the surface when increase the power process and this decrease from the hardness.

Different friction behaviour was observed when the normal load increased to 15 N , the coefficient of friction for samples nitriding maintains a relatively low value of about 0.32 when compare with untreated samples 0.42. However, the coefficient of friction for 15 hours nitriding increases abruptly to a high value of 0.45 , the wear rate increases with increasing load. The wear rate of plasma nitriding system remains a lower wear rate under different normal loads indicating better wear resistance. friction because the different the film composition and increase roughness the surface when increase the power process and this decrease from the hardness [10].

### Conclusion

- 1- XRD studies showed formation TiN,  $\epsilon\text{Ti}_2\text{N}$  and  $\eta\text{Ti}_3\text{N}_{3-x}$  phases, after plasma nitriding for Ti-6Al-4V alloy. When increasing the nitriding time at 10h that will leads to the formation  $\delta\text{TiN}$  (111) , (220) at  $2\theta$  36.660 and 63.50 respectively and  $\epsilon\text{Ti}_2\text{N}$  (224) at  $2\theta$  78.30 and  $\eta\text{Ti}_3\text{N}_{2-x}$ (015) at  $2\theta$  and  $\eta\text{Ti}_3\text{N}_{3-x}$  (1014) at  $2\theta$  75.50.
- 2- Surface analysis by SEM show the particle size on the surface deferent when comparable one another due to the diffusion of nitrogen atoms on the surface lead to large grain size large than original size for Ti-6Al-4V alloy.
- 3- The results obtain from pin on disk wear test indicated that wear resistance is improved after plasma nitriding of Ti-6Al-4V alloy, the change of microstructure and chemical composition of nitrided surface have high effect on decreasing the wear rate and coefficient of fraction, at 15h hours nitriding have large wear rate and coefficient of friction because of the different film composition and the increase of the surface roughness when the time process is increased.

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