Iraqi Journal of Physics, 2011 *Vol. 9, No.16, PP. 34-40*

Surface Modification of Ti-6Al-4V Alloy by Glow Discharge-Plasma Nitriding

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Abstract

Titanium alloy (Ti-6Al-4V) samples were nitrided in low pressure (*1.3, 3 mbar*) *dc*-glow discharge plasmas of nitrogen. The treating time was *5*, *10* and *15* hour and the temperatures range of the samples during the nitriding process was close to 800^oC. The obtained microstructures of the nitride layers were studied by x-ray diffraction and optical microscopy. The $\varepsilon –Ti_2N$, ζ-Ti_3N_{3-x} and η-Ti_3N_{2-x}.phases were formed and addition to the solid solution of nitrogen in titanium, $\alpha\ (Ti,N)$. Micro hardness measurements exhibit an increment for the Ti-alloy specimens which nitrided at 800^oC for *10* and *15h*.Corrosion measurements were obtained for the Ti-6Al-4V alloy in Ringer solution after plasma nitriding. The clear improving in the corrosion resistance was observed rather than for untreated specimens.

Key words
Plasma nitiding,
DC-glow discharge,
Titanium,Ti-6Al-4V

Article info
Received: Mar. 2010
Accepted: Apr.. 2010
Published: Dec. 2011

تحسين سطوح سبيكة Ti-6Al-4Vباستخدام النترتة لبلازما التفريغ التوهج

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** وزارة العلوم التكنولوجيا

الخلاصة

في هذا البحث تمت معاملة عينات من سبيكة Ti-6Al-4V ببلازما النايتروجين بضغوط (3,1.3) ملي بار بمبدأ التفريغ التوهجي للتيار المستمر . اجريت المعاملة للعينات بزمن (15,10,5) ساعة وبدرجة حرارة تقريبا ٨٠٠ درجة مئوية. التركيب البلوري لطبقات النترته فحصت وشخصت بأستخدام حيود الاشعة السينية والمجهر البصري . الاطوار المتشكلة هي ε-Ti_2N, ζ - Ti_3N_{3-X} , η - Ti_3N_2-X بالاضافة الى طور الصلب للنايتروجين في التيتانيوم $\alpha(TiN)$. فحوصات الصلادة المايكروية اظهرت زيادة في المقدار لسبائك التيتانيوم المعاملة ببلازما (لمدة ١٠، ١٥ ساعة بدرجة ٨٠٠ درجة مئوية). قياسات التأكل حصلت باستخدام محلول (Ringer) للعينات المعاملة بالبلازما واظهرت وجود تحسس واضح في مقاومة التأكل للعينات المعاملة بالبلازما مقارنة مع العينات غير المعاملة.

Introduction

Plasma treating in a partial pressure of nitrogen has been called glow discharge nitriding, ion nitriding and plasma nitriding. The term glow discharge is generally reserved for fundamental descriptions of the electrical process. Plasma nitriding permits between control over the final work surface composition, its structure, and its properties. It is accomplished without the formation of a mixed-phase, brittle, and compound zone. Plasma nitriding can be at temperature below those employed for conventional nitriding, retaining maximum core properties [1, 2].

Plasma nitriding is a surface harding process which involves diffusion of nitrogen atoms into the metal surface in presence of a plasma environment. This process makes the metal surface harder (more wear resistance) and improves corrosion resistance and fatigue strength. Because of these useful properties, it ha found applications in the industry, where it is used to treat parts such as cutting tools, gears, shafts, paper rollers, plungers, plastics moulds and dies, extrusion screws, surgical instruments (orthopedic prostheses), etc. to increase their service lives [2-5]. Basically, all plasma based diffusion processes are carried out, in a glow discharge reactor which consists of a vacuum vessel, an 800-1500Vd.c. (continuous or pulsed) power supply and a gas handling system.In plasma nitriding a N_2 or a mixture of N_2/H_2 and N_2/Ar gases are generally used. While nitrogen atoms are responsible at the final stage, hydrogen and argon gases are added for different reasons (several advantages) such as it removes the thin oxide layer at the surface by chemical sputtering thus helps in cleaning the surface. [6] The diffuse nitrogen atoms can react chemically with alloying elements and form stable compounds. Chemically aluminum nitride is the most stable compound while iron nitride is the least stable compound. In terms of stability nitrides may be ordered as follows; Fe < Mn < W ~ Mo ~ Cr < V < Ti < Al. Thus alloys containing high percentage of aluminum will provide maximum hardness after nitriding because of the presence of very stable AlN compounds at the surface [7]. Studies on the nitriding of Ti and Ti alloy show that the temperature is the dominant factor controlling the structure and properties of the diffusion layer [8].

The purpose of this work is to study the effects of process time in a plasma nitriding system on the microstructure characteristics of nitride titanium and its alloy. The nitriding was performed in non-equilibrium, low pressure dc-glow discharge plasma of N_2 and N_2-Ar mixtures.

Experimental Procedure

The specimens of Ti – 6Al – 4V alloy were used in plasma nitriding experiment with a ($3\times10\times10$) *mm* dimensions by using a diamond cutter (Struers, Denmark). The specimens' Ti – 6Al – 4V alloy was machined by grinding and mirror polishing respectively [100], using Struers-RotoPol-21 system, Denmark. The samples were ground by SiC paper in the flowing steps :(*120, 180, 240, 320, 500, 600, 800, 1000* and *1200μm* of grain size). The samples polished with a DP-suspension for (*15, 9, 6, 3,1μm*) and using the DP-cloth of the same company. The fine polishing of samples were done by using the same machine with (*0.5-1μm*) alumina powder and DP-Lubricant red. The polished specimens were degreased with acetone trichloroethylene and cleaned in the same solution. The degreased specimens were washed with deionized water, dried and kept in a dissector over a silica gel pad and used for plasma treatments, microstructure evolution and electrochemical investigation. The clean samples were kept on the sample holder and placed on the cathode plate for glow-discharge plasma nitriding. The system was pumped down to the base pressure ($\sim10^{-4}$ *mbar*) using a mechanical rotary pump and turbo pump. When the plasma chamber evacuated, the argon gas was introduced in the chamber. The *dc*-glow discharge of argon (argon plasma) was ignited and applied to each samples for one hour period. The sample was sputter cleaned until all micro arcs disappear and a uniform glow could be seeing throughout the sample. The treatment by plasma of only argon was used as a standard procedure to clean the surface of Ti alloy specimens. This process was performed only to ensure the exposure of the active surface of the samples for glow plasma, nitriding and removing the native oxide and contaminated layer. The nitriding gas (N_2) was introduced in the evacuated chamber and the flow rate was adjusted until the pressure was stabilized at the desired pressure. The high voltage *dc* power supply was turned on and the cathode voltage and the discharge current were increased and adjusted until the sample temperature established of the nitriding temperature. At the end of the glow plasma nitriding, the nitrided specimens were cooled in the same gas. The cooling in the same environment is mostly performed to inhibit the oxidation of the samples. The plasma treatment of Ti-6Al-4V samples was done under a N_2 (*1-3mbar*) pressure. The nitriding holding times were varied from *5-15 h*. The applied bias voltage was (*400-500 V*) with direct current density of (*0.5-1 mA/cm*^{2}). Table 1 summarized the nitriding conditions where the nitriding temperature in this study was adjusted between *700-800*^{o}*C*. Fig.1 illustrates the photograph of the main experimental set-up used in this work

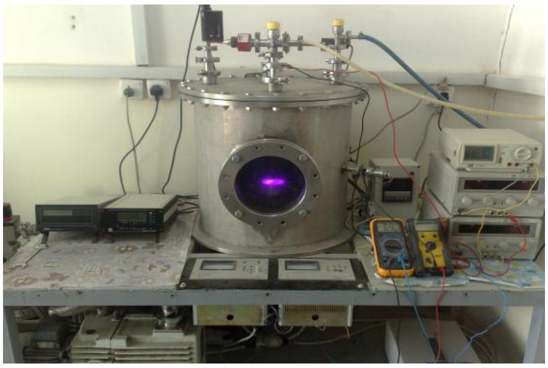

Fig.1: A photograph of the main experimental set-up

In order to identify the phases existing in the nitriding layer, all samples were analyzed with x-ray diffract meter (Shemadzu-XRD,Cu$K_\alpha$radiation 1.5A^o).

Table (1): Plasma nitriding conditions of Ti-6Al-4V alloy

Specimen	Gas	Pressure /mbar	Process time/hour	Cathode voltage/ volt	Discharge current/mA	Temperature /°C
Untreated Ti-6Al-4V	Ar	3.5×10-2	1	2500	10	
Ti-6Al-4V nitride	N2	3	15	426	45	800
Ti-6Al-4V nitride	N2	3	10	426	45	800
Ti-6Al-4V nitride	N2	1.3	5	510	20	770

The microstructure of the plasma treated samples was examined by optical microscopic techniques by using Nikon type 120-Japan optical microscope with digital camera *DXM1200F*, and the images were analyzed with Act-Version *2,62,2000* program. Microhardness measurements were preformed on untreated and nitrides surface with a made Vickers Microhardness tester (HV-100, Japan) using different values of load and three readings were taken to determine the average value. The microhardener has a function of process time and the depth profile was determined from the edge to the core over the cross section of the samples. The load was applied smoothly onto the specimens using a diamond indenter under specific conditions of load for affixed time. The indenter is of rhombohedral- shape that is said to restrict the elastic and the recovery to minimum. The long diameter of the rhombus shaped indent thus obtained was measured; the Vickers hardness was calculated using the formula [9]:

$$VH = 1.85444\frac{P}{L^2} \qquad \ldots\ldots\ldots\ldots \qquad (1)$$

where L is the length of the long diagonal of the indent in µm and P is the load. Multiple attends were carried out different loads (*0.10 N, 0.245 N, 0.49N &*

1N) at least three indentations were performed at each loading level.

Plasma Nitriding Results and Discussion

The nitriding process of glow-discharge plasma allows treated specimens to obtain a modified surface layer which can examine by X-RAY diffraction analysis. Figure 2 shows the x-ray diffraction patterns obtained before and after the plasma nitriding (pure N_2 plasma) of Ti-6Al-4V alloy samples. Additional peaks (marked with arrows) are observed in the nitrided sample compared with the untreated sample. Nitrided Ti-6Al-4V alloy exhibits two distinct surface layers resulting from the nitrogen concentration profile created and a diffusion layer consisting of solid solution on nitrogen in α-titanium. Analysis of the peaks shows that the nitrided layer consists of three phases, namely (a) α-(Ti, N),(b) ε –Ti_2N and(c) ζ-Ti_3N_{3-x} and η-Ti_3N_{2-x}.Our measurements show an agreement with XRD pattern of N1997 JCPDS-International Center for Diffraction Data for as-received material and the plasma nitrided Ti-6Al-4V alloy [10].Also X-ray analyses showed that the surface layer consists essentially of TiO_2 (rutile) and of TiN_xO_y (fcc). Oxidation of titanium specimens produces oxide layer with low friction coefficient and the solid solution of oxygen in α-Ti causes a significant strengthening of the material [11, 12]. The presence of oxynitride TiNxOy can be inferred from the fact that its x-ray diffraction peaks occupy intermediate position between those of TiN and TiO.

Microscopy Results

Optical microscopy for the compound layer of our nitrided specimens has gold like appearance (fig.3b) and consists of composed the TiN (fcc) and Ti_2N (tetragonal) nitrides. This sample nitrided at treatment temperature of *720°C* and *800°C* at pressure of *1.3* and *3mbar* for *5h* and *10h* respectively. Furthermore increasing of the nitiding time to *15h* exhibits a bluish compound layer consisting of TiO_2, Ti_2N and TiN_xO_y (Fig.3c). Moreover it should be noted that specimens treated at high temperature shows a bluish-grayish compound layer that is highly adherent to the substrate [11, 12]

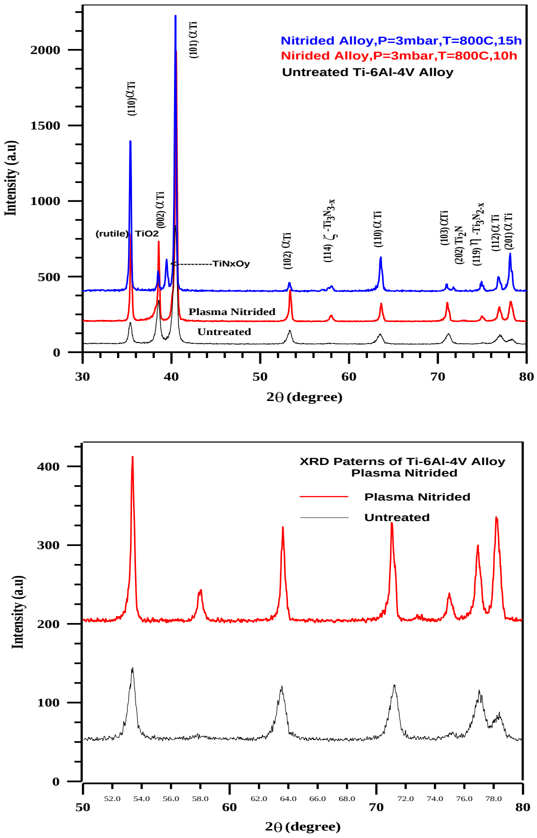

Fig.2: XRD diffraction pattern of specimen of plasma nitrided at N_2, working pressure of *3 mbar*, *T=800°C*, for *10* and *15h*.

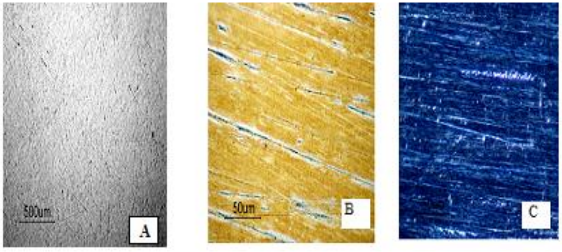

Fig.3: Micrographs showing typical surfaces colors of (a) untreated, plasma nitrided samples at *800°C* for (b) *10h* and (c) *15 h* respectively

Figures 4(a to f) show the optical micrographics of metallographic cross-section of Ti-6Al-4V samples nitrided at treatment temperature of *700C* and *800°C* with pressure of *1.3* and *3mbar* for *10* and *15h* respectively. The modified surface layer of the treated specimens is constituted by an outer compound layer and an inner diffusion layer. It is to be noted from these figures that plasma nitriding produces a very thin "white layer". The layers are about $10\text{-}100\mu m$ thick and found to consist of different titanium nitride phases as shown in previous XRD results. The characteristics of these layers depend on experimental conditions and especially on temperature (discharge current) and process time at nitriding temperature [11]. The compound layer thickness increases as treatment time increases, ranging from about $10\mu m$ *at 5h* (Fig.4a,b) to about $100\mu m$ for *15 hour*.

In present work, the stratified structure of the compound layer can be a scribed to the high content of TiN and TiO_2 in the layer, as observed by previous studies [11, 13]. The creation of outer most compound layer could have the following explanation. The sputtering and redeposition of the already existing titanium nitride, and spectroscopic observation [14] of the titanium peak in the plasma layer suggests the formation of TiN in the plasma layer (homogeneous reaction) and its deposition on the surface.

Table 2 shows the microhardness variation of Ti-6Al-4V specimen with processing temperature and working pressure of plasma nitriding for *5, 10* and, *15h.*It can be seen that the value of microhardness at load of *0.24N* increased from about *318VH* for a untreated Ti-6Al-4V sample up to about *720VH* for a plasma nitrided sample. As the temperature increases the nitrogen penetrates deeper into the surface of the sample and form a thicker modified layer. Plasma nitriding for various times produced very similar micro structures i.e. a compound layer (nitride film) on the surface and a diffusion zone beneath. The Microhardness of plasma nitrided of Ti-6Al-4V at *720* and *800°C* as function of process time has been obtained.

The microhardness profiles measured on loading of *0.24N* and timing of *20 second*. The samples which were nitrided for *15 hours* exhibit higher microhardness values than samples nitrided for other process time. This is probably due to higher concentration of nitrogen and by the formation of the δ-phase in the compound layer of samples surface. These values (Table 2) are of the same order with those obtained in different nitrided Ti-alloys by other researchers [14, 15, 16].

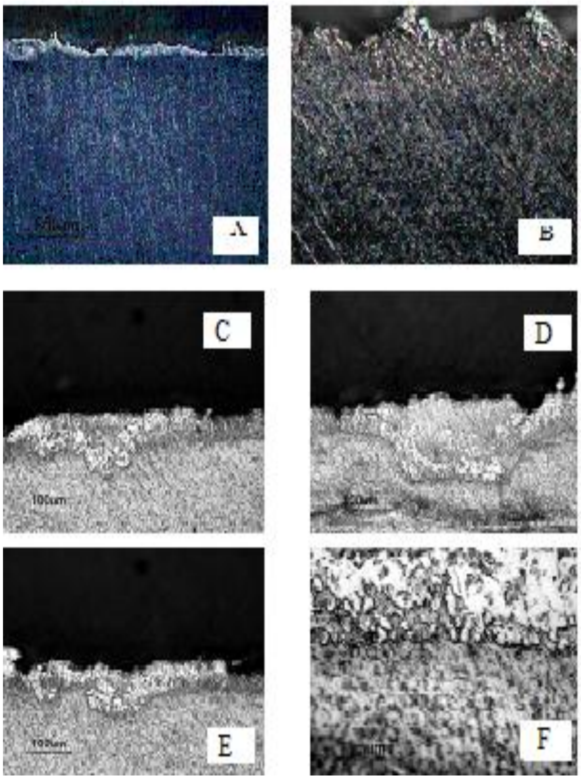

Fig.4:Cross-sectional microstructure of Ti-6Al-4°V samples, a,b: as plasma nitride (*720°C,5h*) and c(*800°C,15h*) ,d, e , f (*800C,10h*): after etching

Figure 5A shows the results of sample microhardness versus layer depth for Ti-6Al-4V plasma nitrided at 800°C.This figure shows the typical metallographic cross section of the surface and hardness profile through the nitrided case for this alloy. Fig.5B shows that hardness decreases gradually as a function of distance from surface producing a diffused interface between layer and core of the plasma nitrided Ti alloy.

The surface microhardness of all plasma nitrided samples is increased as shown in table 2 and, the maximum microhardness for each sample is obtained at constant load of 0.24N.

Table 2: Microhardness of untreated and nitrided samples

Specimen	Plasma chamber Pressure (N2,mbar)	Temperature treatment C°	Process time (h)	Vickers Hardness (VH)	Color scheme
Untreated Ti-6AL-4V				318	Silver
Nitride Ti-6Al-4V	1.3	720	5	382	Golden
Nitride Ti-6Al-4V	3	800	10	460	Golden-Bluish
Nitride Ti-6Al-4V	3	800	15	720	Bluish

The variation of microhardness with layer depth is shown in figure 5(a)s.The higher increasing of microhardness values in the first layer(compound layer)for plasma nitrided Ti-6Al-4V alloy than the microhardness in the second layer, which represented diffusion layer is probably due to a difference between the microstructures of the two layers. The change of lattice parameter of $\varepsilon -Ti_2N$ and δ-TiN phases for various nitride films or compound layer is related to changes in the nitrogen concentration in the films [15].

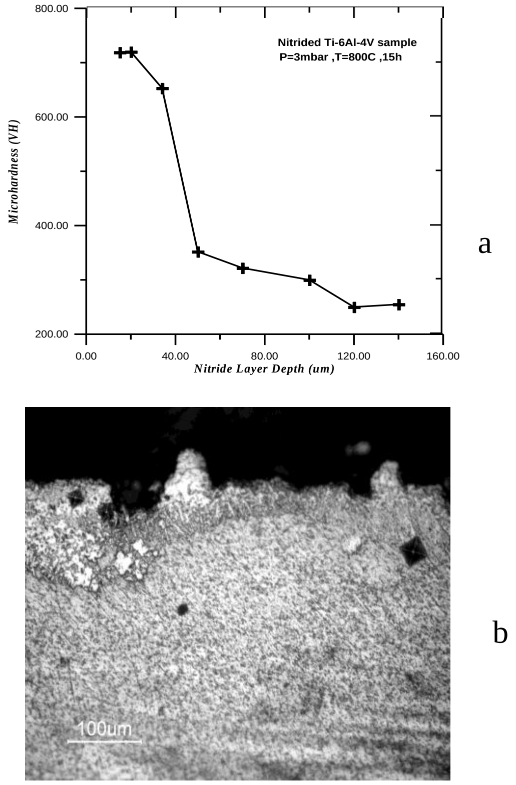

Fig.5: Microhardness profile curve of nitrided Ti-6Al-4V alloy as function of nitride layer depth

It was found that the maximum microhardness increasing with increasing of lattice parameter [16]. Figure 6 shows that the microhardness of sample nitrided in *3mbar* of N_2 plasma measured normal to the surface as function of applied load. With load increasing, the measured microhardness values were decreased .Fig. 6 shows the microhardness is a constant for loads below *0.24N*, while above a load of *0.24N*, a decrease in the microhardness is observed. This can be understood from the contribution of the relative concentration of δ-TiN and ε-TiN phases in the nitride films of samples surface. The load of *0.24N* is best for typical micro hardness values of the outer most layers (δ-*phase*).The decrease in the micro hardness at load higher than *0.24N* attributed to this influence of the substrate [10].

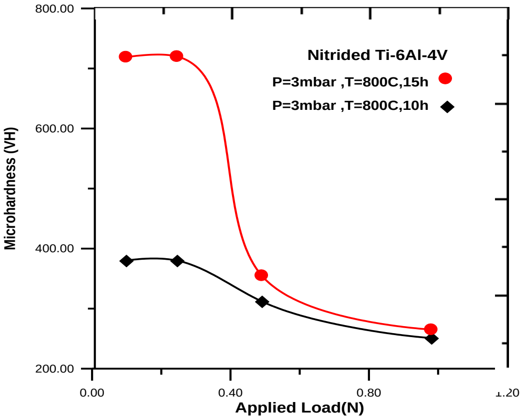

Fig.6: Variation in hardness of plasma nitrided Ti-6Al-4V as function of applied load.

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