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Structural and Elemental Analysis of Plasma Nitrided Commercially Pure Titanium and Ti-6Al-7Nb alloy

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ABSTRACT

Titanium and Ti – 6Al – 7Nb alloy biomaterials have become relatively popular for surgical implants. Plasma nitriding are commonly used for orthopaedic devices which are subjected to articulation and wear, to increase the surface hardness, and reduce the generation of wear debris. This paper aims to demonstrate the structural and elemental analysis of plasma nitrided titanium and titanium alloy. A Commercially pure titanium Cp Ti and Ti – 6Al – 7Nb alloy were surface modified using plasma nitriding in order to study its microstructural changes. DC glow discharge plasma nitriding was performed for different period of time (namely 5, 10, 15, 20, 25 and 30 hours). The glow discharge was occurred by applying 650 V between the two parallel electrodes under 3 mbar nitrogen gas pressures. To characterize the nature of the modified layers produced and to correlate with the corrosion behavior of these medical materials, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) was employed on the modified surfaces. The effect of sputtering process that can occur during the nitriding process on the surface roughness was studied using Atomic Force Microscopy (AFM). The results shows that as the nitriding time processed the N^+ concentration increases comparing to the metal and alloy matrix elements. Also the SEM micrographs shows two effected zones of the nitriding in the modified surfaces and the thickness of each zone depend on the nitriding time. The AFM results show that the nitriding process leads to reduce the surface roughness.

Keywords: Commercially Pure Titanium Cpti, Ti-6Al-7Nb Alloy, Plasma Nitriding, Dc Glow Discharge.

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التحاليل التركيبية والعناصرية للتيتانيوم النقي تجاريا" وسبيكة Ti-6Al-7Nbالمنترده بالبلازما

الخلاصة

التيتانيوم وسبيكةTi-6Al-7Nbمن المواد الاحيائية شائعة الاستخدام لجراحة الغوارس .تعتبر النتردة بالبلازما من الوسائل التجبيرية شائعة الاستخدام لحل مشاكل الربط بالمفاصل , والبلى عن طريق زيادة صلادة السطح وتقليل تولد مخلفات البلى . يهدف البحث الى اظهار وبشكل واضح البنية التركيبية وتحليل العناصر للتيتانيوم النقي وسبيكته المنتردة بعد تعديل سطوحهما بالنتردة بالبلازما, تم تحوير سطح التيتانيوم النقي تجاريا وسبيكة Ti-6Al-7Nb باستخدام النتردة بالبلازما لغرض دراسة تغيراتهم التركيبية .استخدمت فترات زمنية مختلفة لبلازما التفريغ التوهجي هي(5, 15,30,25,20 ساعة) على الترتيب. وتم التفريغ التوهجي تحت فولتية 650 فولت بين قطبين متوازيين وضغط 3 ملي بار لغاز النتروجين النقي. تم استخدام تقنية الفحص بالمجهر الالكتروني الماسح (SEM) وتقنية مطيافية الطاقات المتشتتة (EDS) لوصف طبيعة سطح الطبقة المتولدة وعلاقتها بسلوك التاكل للمعادن الطبية . لقد استخدم مجهر القوى الذرية (AFM) لقياس وتحليل خشونة الطبقة المتولدة اثناء عملية النتردة وتاثير عملية الترذيذ التي تحدث ايضا اثناء النتردة. أظهرتالنتائج التي تم الحصول عليها الى زيادة تركيز النتروجين اثناء زيادة وقت النتردة مقارنة بالعنصر الاساس (التيتانيوم) والسبيكة قبل النتردة. اظهرت الصور المجهرية وجود منطقتان على السطح الاولى تسمى المتاثرة بالحرارة من جراء عملية النتردة وبسمك يعتمد على اختلاف زمن النتردة والثانية هي طبقة النتردة, كما ان قيمة خشونة السطح اخذت بالتناقص مع زيادة زمن النتردة من خلال الفحص بمجهر القوى الذرية.

INTRODUCTION

Titanium has many desirable features such as good high temperature properties, excellent strength-to-weight ratio, wear-corrosion failure can occur in the field. Plasma surface treatment has been applied to substantially improve the hardness and wear resistance of titanium and its alloys. Many kinds of plasma nitriding, such as pulsed plasma nitriding[3,4], and radio frequency (RF) nitriding [5,6] have been developed as primary surface hardening treatment. RF plasma nitriding presents the following advantages: (a) reduced process duration (b) electric power saving (c) higher nitriding rate can be achieved (d) overcoming the complex geometry. However, these advantages are achieved by a rigorous control of suitable input plasma processing powers. The principle objective of this study is to understand the microstructure changes on the surface of two materials after plasma nitriding process. In a DC glow discharge plasma nitriding process, nitrogen plasma is an effective means to improve the wear and corrosion resistance of titanium and titanium alloys by forming TiN, Ti2N, and Ti (N) superhard phases through the surface [7, 8]. The aim of the present investigation is to study the structure of the Cp Ti tanium and Ti – 6Al – 7Nb alloy aftersurface modification by DC glow discharge plasma nitriding in comparison with untreated samples.

EXPERIMENTAL WORK

Ti-6Al-7Nb Specimens and CpTiused in this workare received from DMRL (Defense Metallurgical Research Laboratories, Hyderabad, India), Table (1a, b) show the elemental composition of two materials. Commercially pure titanium (CpTi) and Ti – 6Al – 7Nb alloy were used as a substrate for nitriding.The samples were cut from the sheet in rectangular shape of 20 mm x 20 mm x 2 mm size. The specimens were grinding using silicon carbide papers started from 400 to 1200 grit to bring the sample to uniform surface condition using grinding machine. The specimens then were polished with diamond suspension of 6µm, 3 µm, and 1 µm until a mirror-polished surface was obtained. The specimens were degreased with trichloroethylene followed by ultrasonic cleaning with distilled water. Glow discharge plasma nitriding was performed on the polished surface using a pure nitrogen gas under a total pressure of 3 mbar with applied voltage of 650 V for different times (namely 5,10,15,20,25 and 30 hours), Figure (1) display the evacuated chamber of glow discharge plasma unit. Surface Characterization was done using X-ray Diffraction (XRD) Shimadzu LabX XRD-6000 Powder X-ray diffraction with Cu Kα radiation. The 2θ angles were swept from 30- 80° in step of one degree. Roughness of the nitrided samples was measured using atomic force spectroscopy AFM. Scaning electron microscopy (SEM) examinations were performed with a JEOL-JSM-5600, Scaning Electron Microscope (JEOL, USA) equipped with an energy dispersive spectrometer (EDS) PRISMS^{IG} PGT (PRINCETON GAMMA-TECH, USA).

RESULTS AND DISCUSSION

X-ray Diffraction

XRD studies have been carried out on the Ti-6Al-7Nb plasma nitrided specimen for 30 hours in comparison to untreated specimen to understand the phases formed during the nitride process. The diffraction patterns of the specimens are shown in Figure (2).

According to the Figure, new patterns were created which means that the plasma nitridinghad destroyed most of the crystallinity of the alloy near the surface. The lattice of α-Ti phase is expanded in the treaded region and at greater depth (bulk region); the peak positions are shifted to higher Bragg angles. The pattern shows a systematic shifting of the peaks at the 2θ values of α-Ti towards upper 2θ side. An increase in the Full Width Half Maximum (FWHM) of these peaks leads to formation of (104), (015), (114) and (205) η-Ti_3N_{2-x} at 2θ values of 38.8, 40.7, 71.2 and 77.1 respectively and (220) and (224) ε-Ti_2N at 2θ values of 63.9 and 78.5. Fernandez et al [9] found that nitridation leads to form Ti_2N layer on Ti-6Al-4V alloy (almost without Al and V). The presence of those phases is well correlated with the chemical analysis.

ROUGHNESS MEASUREMENTS

AFM micrographs in Figure (3) show the surface topography of the untreated CpTi and plasma nitride specimens for three different periods 5, 10 and 15 hours of N^+ plasma processing. And in Table (2) lists the roughness (Ra) value of Cp Ti tanium untreated and nitriding samples for different period (5, 10, 15 hours) measured by

AFM.The surface roughness of the treated specimens decreases as the plasma nitriding time increases, Subsequently, the reduction in the surface roughness may be due to the sputtering process which occurs during the N^+ ions collision with surface, and it can be seen from Figure (4) that there is a significant decrease in the roughness value of the specimen nitride for 15 hours in comparison to the untreated one (30.184 nmand 40. 811.Nmrespectively).

SEM and EDS Microstructral and Elemental Evaluation

The cross-section of the surface layer produced on the Ti-6Al-Nb alloy by DC glow discharge plasma nitriding is shown in the SEM micrograph Figure (5a-b), the microstructure of the untreated alloy is shown in Figure (5c) which represents the typical equiaxed structure of β grains in matrix of α phase. In the colony structure. The nitriding process produced η Ti_3N_{2-x} and ε Ti_2N compounds (brighter portion) followed by an heat effected zone and then α -Ti layer consisting of excess nitrogen in solid solution, and a compound layer with an average thickness 100μm was noticed for the specimen plasma nitride for 20 hours Figure (5b) comparing to the nitride layer formed on the specimen plasma nitride for 10 hours (20 μm). Rie and Lampe [10] reported that a layer of 120 μm in 10 hours pulse plasma nitriding of pure titanium.The visual inspection of the nitrided layer showed a thick coating on the surface of the nitride specimens after 30 hours processing. The Energy dispersive Spectroscopy (EDS)shows that the nitride layer formed on Ti-6Al-7Nb alloy after 20 hours nitriding time is 12.545 wt% comparing to that for 10 hours nitriding time 6.390 wt% Figure (6) whereas the N concentration of the layer formed on CpTi specimens Figure (7) show systematic increase as the nitriding time increases.

CONCLUSIONS

A systematic study of DC glow discharge plasma surface treatment of commercially pure titanium and Ti-6Al-7Nb alloy has been carried out. The results obtained from the study are summarized here:-

1-The structural analysis (XRD) show that the nitride layer built up on the surface as the nitridingtime progressed and the layer composed of η -Ti_3N_{2-x} and ε-Ti_2N compound .

2-This layer was clearly seen from the SEM cross-sectional micrographs. Nitrogen concentration was found to be high on the subsurface layer and maximum layerthickness for the specimens treated for 20 hours.

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Table (1a) Chemical Composition (wt %) of the as received Ti-6Al-7Nb alloy (Thair 2002).

Elements	Al	Nb	Ta	Fe	Mo	Ti
Wt%	6.0	7.2	0.46	0.22	0.005	Balance

Table (1b) Chemical Composition (wt %) of the CpTitanium, ASTM grade 2.

Elements	C	Fe	H	N	O	Ti
Wt%	Max 0.1	Max 0.3	Max 0.015	Max 0.03	Max 0.25	99.2

Table (2) The Roughness (Ra) value of Cp Ti tanium untreated and plasma nitriding for different period (5, 10 and 15 hours).

	uncoatd	5 hours	10 hours	15 hours
1st trial	39.387	37.287	35.197	28.778
2nd trial	40.365	41.826	33.067	31.672
3rd trial	44.866	34.193	34.058	32.249
4th trial	42.097	41.23	33.79	28.463
5th trial	37.342	29.301	37.502	29.759
Ra av	40.8114	36.7674	34.722	30.1842

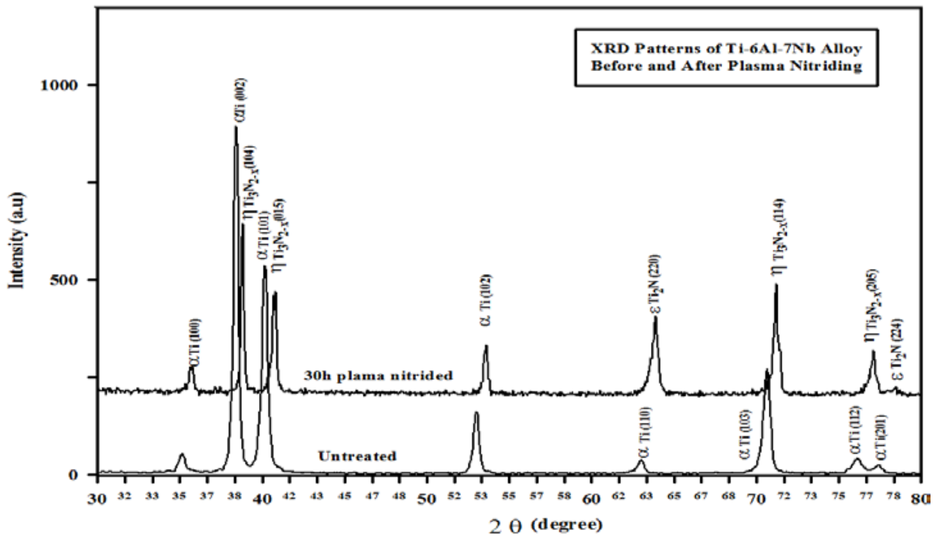

Figure (2) XRD patterns of Ti-6Al-7Nb alloy before and After plasma nitriding.

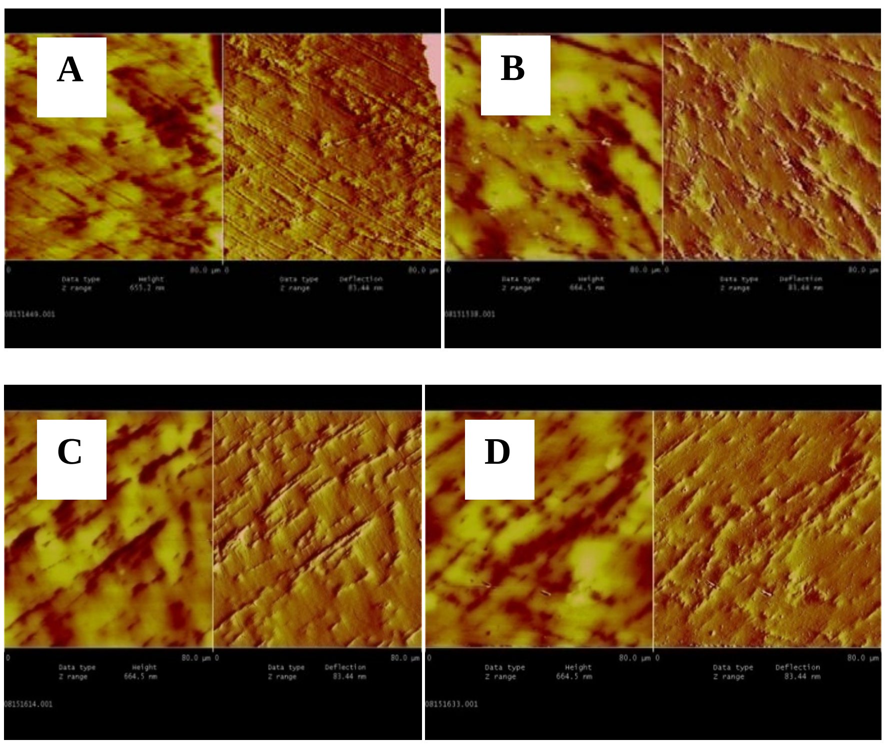

Figure (3) AFM micrographs of A: untreated CpTi; B: Plasma nitride for 5 hours; C: Plasma nitride for 10 hours; D: Plasma nitride for 15.

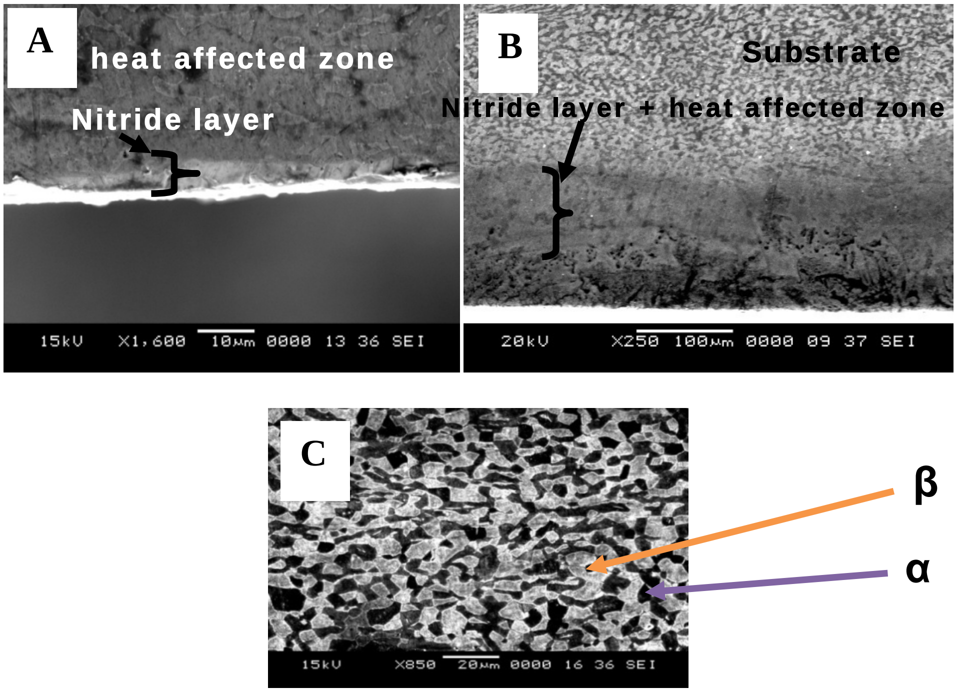

Figure (5) SEM micrographs of a cross section made on Ti-6Al-7Nb Alloy plasma nitrided for a) 10 hours, b) 20 hours c) untreated.

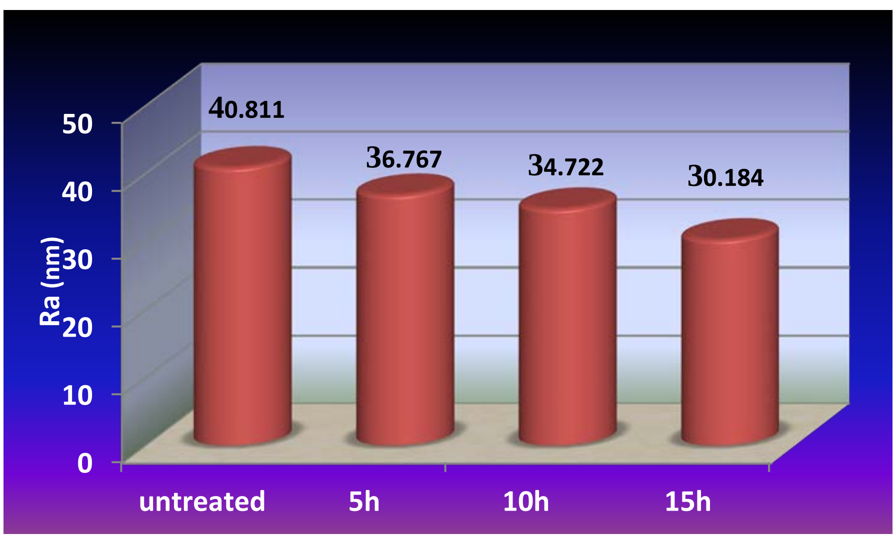

Figure (4) Roughness (Ra) of CpTi specimens after different period of nitriding time.

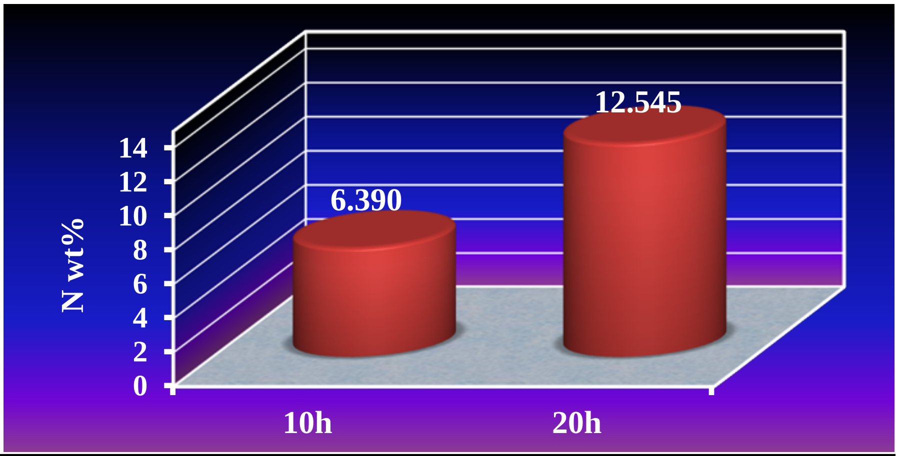

Figure (6) Nitrogen concentration accumulated on Ti-6Al-7Nb alloy after different period of nitriding time revealed from ED's measurement (6.39%for 10h, 12545 for 20h).

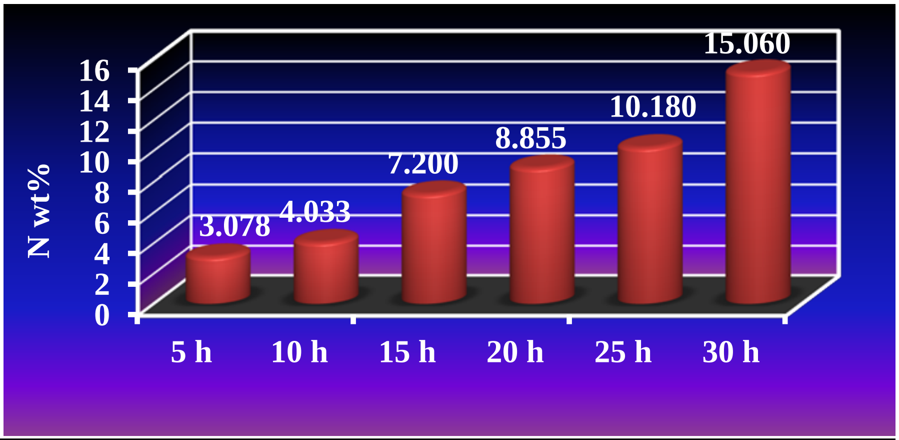

Figure (7) Nitrogen concentration accumulated on CpTi after Different period of nitriding time from EDS.

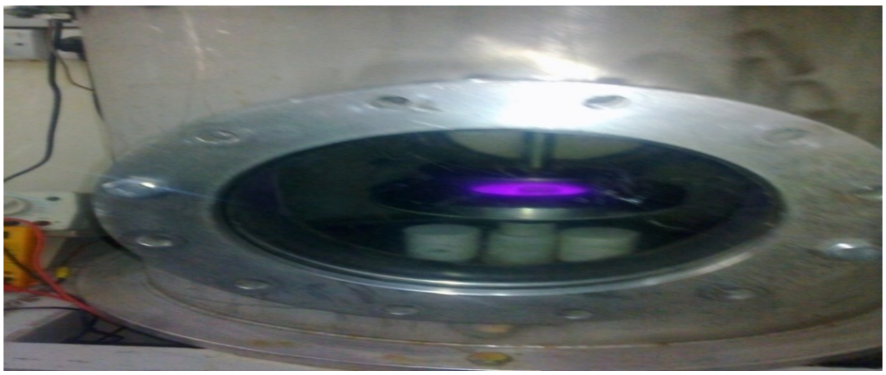

Figure (1) Evacuated chamber of glow Discharge plasma unit.