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Deposition of TaN Film on Commercial Pure Titanium Disk by Modified Reactive Plasma Sputtering Technique

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Abstract

Background: The new trend of implants is to find materials which accelerate bone formation at bone implant interface and improve Osseo integration to provide immediate or early loading after placement and eliminate waiting period which is uncomfortable and disturbs patients. Titanium as an implant material still need some improvement of surface properties physically and chemically. Tantalum which is gaining more attention as a new metallic biomaterial. Coating layer over implant is an important way for improvement of surface properties of titanium. Plasma used for surface modification, has several advantages such as changing surface topography, increasing surface roughness and in increasing the wettability of the surface.

Aim of study: To evaluate the effect of TaN coating by modified plasma sputtering technique of commercially pure titanium disk on wettability, surface roughness, surface chemical composition in comparison to non-coated surface.

Materials and method: Two groups were tested in this study which include non -coated commercial pure titanium disks and coated commercial pure titanium with TaN. Modified reactive plasma sputtering apparatus was used to coat CpTi with TaN at 4, 6 &8, h. Surface characterization by x-ray diffraction (XRD) analysis, scanning electron microscope (SEM), energy dispersive spectroscopy(EDS), contact angle measurement, were carried out for coated and uncoated disks.

Results: The result of coating specimen with TaN at times (4,6&8) h showed that 8 h coating time was the best time. And this was according to the results of X-ray diffraction analysis which show a new peak formation of Ta N coated CpTi disk which was not present in non- coated CpTi disk. The results of wettability test for CpTi disk coated with TaN disk was more than wettability of non- coated CpTi disk. Surface Roughness was more and better distributed in CpTi coated with TaN disk than non- coated one which appear clearly in electron microscope.

Keywords: *TaN film, pure titanium disk, modified reactive plasma sputtering technique*

Introduction

Engineering and surface modification of dental implant material become much advanced than it was earlier [1]. Titanium shows a favorable combination of intrinsic properties for the fabrication of dental implants such as low specific weight, high strength to weight ratio, low modulus of elasticity, very high corrosion resistance, easy surface coating and excellent general biocompatibility [2] enhancing the osseointegration of CpTi results in reducing the non-functional time period of the implant, increase its applicability in alveolar bone with low quality, cause minimum discomfort to patient, and minimize the failure rates. [3]. Surface coating was one of the methods used in accelerating the Osseointegration process and this by increasing roughness and change surface properties physically and chemically. Chemically and physically reactive plasma discharges are widely used to modify the surface properties of materials. [5.] The stable chemical element Tantalum (Ta) can exist in the surface layers of base materials. Ta is one of the promising materials used in medical and dental fields

[6]. The stable TAN protective film can provide better corrosion resistance and bioactive property than that of TiO film. [7.] The Ta components offer a low modulus of elasticity, high surface frictional characteristics, and excellent Osseo integration properties (i.e. Bioactivity and biocompatibility) [8.] Surface-coated implants are reported to have less failure and can support heavier and more dynamic forces [9] surface coating with TaN by using plasma sputtering techniques was applied in this study on Cp Ti disk. In dental field especially in dental implant, plasma coating constitutes a simple, dry technique, which does not harm the environment, of low cost and does not comprise the intrinsic properties of the biomaterial, affecting only its surface. Many types of gases can be used in such technique to modify surface properties physically and chemically. Aim of our study to coat CpTi with TAN by using coat plasma sputtering technique.

Material and Method

Sample preparation

Titanium disks were prepared (10×5mm) diameter and thickness respectively which were cut from Cp Ti rod by using Bench Nibbling machine (TAURUS 7000-W6 CNC, Italy). All specimens were abraded successively using Si C grinding paper with different grits started from 80 grit, and continued by 120, 230, 400, 600, 800 and 1000 grit to get flat and scratch free surface. These disks were polished until a smooth and mirror polished surface was obtained. After that all specimens cleaned by using ultrasonic cleaning device (الشركه with ethanol 99.8%.

Surface coating with TaN: -

The procedure of sputtering was performed by using modify Dc glow discharge reactive plasma sputtering system. The total number of samples were 10 disk which divided as 1 uncoated and 9 coated disk. These coated disks were divided into 3 groups according to the time of coating (4,6, &8) h. The procedure of sputtering started with placing the clean and polished disks on the center of anode base. Then evacuating process of chamber to high vacuum (≈1x10ˉ5mbar) by using high vacuum system which consist of rotary and turbo molecular vacuum pumps to ensure the complete removing of the heavy gases like hydrocarbons. After that Power supply negatively charged voltage of 3.5 kV applied. For sputtering process, the voltage was gradually applied using variac until the required energy achieved (applied voltage and current), The pressure was $2x10^{-2}$ to $7x10^{-2}$mbar and this pressure was achieved by feeding the bombardment and reactive gases. The appropriate voltage and amber were adjusted precisely by regulator until intended sputtering glow (purple color, which standardized for each gas) is achieved. One of the most important modification done to convert normal plasma system to sputtering plasma system include replacement of electrode position, so the cathode placed in upper part and anode electrode placed in lower part of chamber. A Target (cathode) and anode stainless disk. The cathode faced the anode with 7 cm distance between them, which provides electric field for the gas to be discharged. The electrical electrodes and the associated dc-power supply of 5kV.The bottom of the stainless steel disk cathode electrode are covered with tantalum sheet which regarded as target. The clean and polished samples were placed on the anode in the center of base which regarded as substrate. All the samples were cleaned by argon plasma sputtering for 15 min prior to the TaN coating process by applying a bios dc voltage of 100 Von the anode. Parameters used for reactive plasma sputtering procedure: argon was used as bombardment gas and nitrogen as reactive gas. The process was carried out at various sputtering times (namely 4, 6 and 8 hours). The reactive gas nitrogen was introduced into the evacuated chamber and the flow rate was adjusted until the pressure was stabilized to the required pressure (1×10ˉ2 mbar), then the argon gas introduced to the chamber until the sputtering pressure of 5×10ˉ2 mbar achieved. After the sputtering process completed, the samples were kept until ambient temperature in the vacuum chamber was reached. \

Phase Analysis by using X-Ray Diffraction

Surface analysis for Phase's distribution was performed for non-coated CpTi, and CpTi coated with TaN. It done by using X-ray Diffraction Facilities (SHIMADZu 6000, Japan) using Cu Kα radiation. XRD analysis were performed at room temperature in the 2θ range from 30°- 80° with a 0.05° step and counting time of 5 secs per step. The indexing of the data and the diffraction peaks were identified according to the powder diffraction files. (PDF), received from ICDD (Intimations' Center for Diffraction Data).

Wettability test

In this test, non-coated and coated disk (10×5) mm diameter and thickness respectively were used. An equal amounts of normal saline (0.25ml) from graduated container dropped on each disk. Then after 20 second from putting the drop on disk, surface measurement for the angle formed between titanium disk surface and drop of normal saline done by taking a picture obtained from a digital camera [10]

Scanning electron microscope examination

All tested group were examined by using SEM (JEOL-JSM-5600). Samples were prepared as cross section and then mounted in double face metal tape (electrically conductive) to make the sample holder electrically conductive before entering the samples into the SEM Chamber. VEGA3 TESCAN, SEM HV: 20 KV, SEM MAG:7.50kx, VIEW FIELD:27.7

Energy dispersive spectroscopy analysis

Chemical structures and relative concentrations for non-coated CpTi and coated CpTi with TAN discs were assessed via energy dispersive spectroscopy (EDS). EDS use of the X-ray spectrum radiate a solid sample with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle. Qualitative analysis involves the identification of the elements in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis determination of the concentrations of the elements.

Atomic force microscopy examination

Atomic force microscope able to detect both conductive and nonconductive surfaces on the atomic scale. The AFM relied on the scanning technique and provided a high-resolution 3D image from the surface of the sample. A sharp tip at the end of the cantilever is in contact with the surface of the development and the sample displaced with piezoelectric scanners. The force on the tip causes deflection to measure with tunneling capacitive or optical detectors such as interferometer laser in this technique, the standard pressure applied to the joint is zero (to prevent any surface deformation).

Result

Surface characterization by using X-Ray Diffraction.

A: Before Heat treatment:

XRD patterns of the non-coated Cp Ti specimen and TaN coated by modified reactive plasma sputtering after different sputtering time (namely 4, 6 and 8 hours) are demonstrated in Figure (1). and these data were indexed according to the Powder Diffraction Files (PDF) for the hexagonal αTi (JCPDS-ICDD file # 44-1294), TaN (JCPDS-ICDD file # 25-0922, 33-1391and 33-1390), and TaN (JCPDS-ICDD file # 34-0977). The diffraction peaks of the uncoated CpTi were found to be corresponding to (100), (002), (101), (102), (110), (200), (112) and (201) α-Ti at 2θ values 35.00°, 38.30°, 40.05°, 52.9°, 62.8° ,70.6°, 76.25°and 77.35° respectively. The patterns of the plasma sputtered specimen for 4 and 6 hours show wide peak in the range of 2θ 20-30^{o} which seems to be due to the formation of not fully crystalline TaN, whereas the pattern of the specimen sputtered for 8 hours show clear and prominent TaN peaks corresponding to the reflections (111) at 2Θ 35.14 and (200) at 2Θ 41.24^{o}.Also its very clear there are a shift in the 2θ position of the CpTi reflections towards the higher 2θ indicting the change in titanium crystal cell volume.

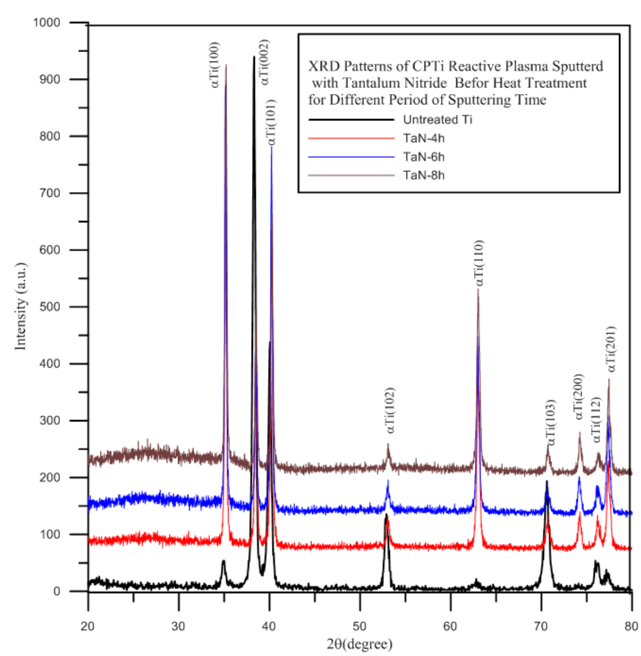


Fig (1): XRD patterns for uncoated CpTi and coated specimen with TAN at (4, 6, and 8 hr.)

B: After Heat treatment:

The CpTi specimen's coated with TaN for sputtering time 8 hours before and after heat treatment are shown in Figures (2). The pattern of the heat treated specimen show prominent new peaks of 111 TaN at 2θo 36.00 and developed one assigned as 200 TaN at 2θo 41.24. also The XRD pattern of the heat treated specimen shows the formation of 110 of tantalum peak TaN at 2θ° 27.23.

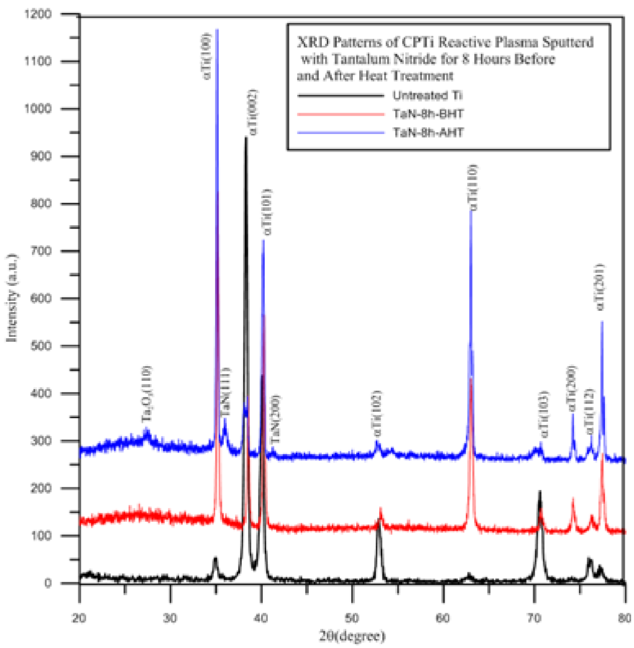


Figure (2): XRD patterns of uncoated Cp Ti and coated with TAN for 8 hours before and after heat treatment.

Surface characterization using Wettability test

From the result of wettability test, 8 hr. coated disk with TaN give more hydrophilic surface feature with contact angle formed less than non-coated disk as shownin Figure (3) .

Materail/Time	Cp Ti	TAN
A:Non coated	60◦	
B:4h coatment		75◦
C:6h coatment		65◦
D:8h coatment		55◦

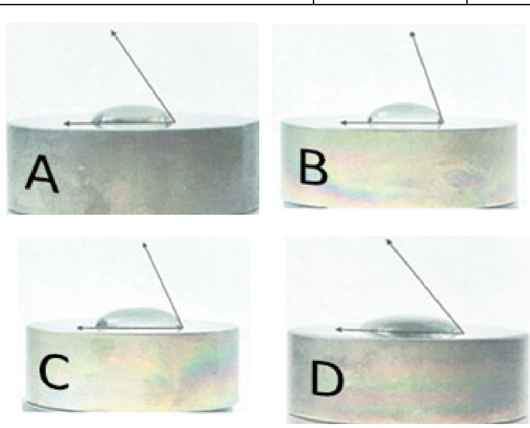
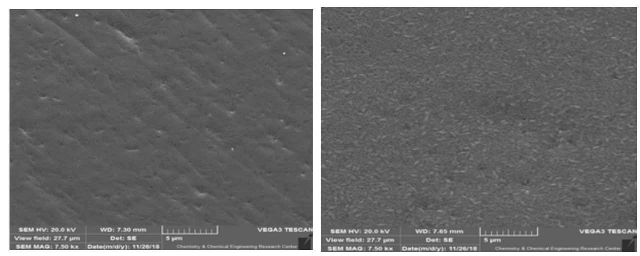


Fig (3) Wettability test for CpTi and experimental groups at 4,6 and 8hr

Surface characterization using SEM 3.3

A: Topographic

The scanning electron microscopy images of CpTi disk before coating in (figure 4a) revealed a relatively flat and smooth surface. While the surface morphology of CpTi plasma sputtering samples with TaN for 8 h showed a fully arranged nanochips and uniformly distributed in (figure 4b).



A: CpTi disk B: CpTi disk coated with TaN

Figure (4): SEM.A/CpTi disk without coating B/CpTi disk coated with TaN for 8 hr.

B: chemical composition by EDS

Regarding the analysis of the chemical structure of CpTi figure (5, A) show two titanium peaks with these values (kα 4.512 and lα 0.452), these values represent alpha phase of titanium. For coated disk with TaN, there were five peaks, two peaks for titanium which represent alpha phase, two tantalum peaks and one peak of nitrogen with following values percentage (kα 4.512 and la 0.452) (lα 8.146 and ma 1.712) (kα 0.392) respectively as shown in figure (5, b). Elemental composition of tested group as follow in (fig a) titanium was 100%, and in (fig b) percentage of titanium was 3%, tantalum was 22% and nitrogen was 75%.

A: CpTi disk B: CpTi disk coated with TaN

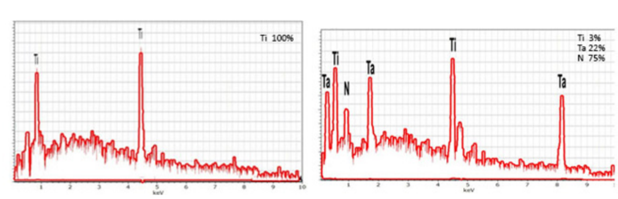


Fig (5): EDS.A/ CpTi disk without coating B/CpTi disk coated with TAN for 8 hr.

Discussion

The new trend in implant research is to increase and accelerate the osseointegration of Cp Ti [11] One of the methods used in accelerating the osseointegration process is to modify the surface properties of the implant [12]. Chemically and physically reactive plasma is widely used to modify the surface properties of materials. [13] in this research, tantalum is a material with specific properties which is used as a coat material with nitrogen gas to develop TaN surface on CpTi disk byusing modified plasma sputtering technique which has several advantages such as changing surface topography, increasing surface roughness, wettability of the surface. [14]. Reactive plasma coating constitutes a simple, dry technique, which does not harm the environment, does not comprise the intrinsic properties of the biomaterial.[15]

The results of X-ray diffraction analysis revealed a new peaks formation towards the 2θ direction in coated disk as a result of deposition of TaN material on the surface of CpTi, these new peaks were more prominent after heat treatment in coated disk as evidence to the more crystallinity of TaN. Surface properties and roughness of uncoated CpTi and TaN coated disk for 8 h were examined by Scanning electron microscope, showed fully arranged nanochips with uniform shape in coated layers, this might be due to difference of chemical composition of coated layer of non -coated and TaN disk, this shape of nanochips due to the deposition of TaN on the surface of CpTi. Contact angle of fluid drop in 8 hr. CpTi coated disk with TaN less than non-coated CpTi disk, which mean the coated disk more hydrophilic than non-coated disk. This may be due to more affinity of tantalum and nitrogen to fluid.

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Conflict of Interest: None to declare.

Ethical Clearance: All experimental protocols were approved under the College of dentistry. University of Karbala and all experiments were carried out in accordance with approved guidelines.

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