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Surface Modification of Titanium alloys by RF Magnetron Sputtering at Different Thin film TiO_2 Nano Thickness

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Abstract: *A new biocompatible coating was developed by alternately depositing Titanium oxide(TiO_2) ,with piratical size 22nm, purity 99,9 layers on CPTi and Ti6Al4V layers substrates using radio frequency magnetron-assisted sputter processing to improve the interface properties between the coating and the substrate .Thin film with thicknesses(200,300 and 500nm) of polycrystalline TiO_2 deposited on Ti alloys heated substrates at 100 C° using in argoon gas Ar with purity 99.8 under vacuum 7×10^{-3} Toor. For different power and time deposition depend on thickness of thin film. Field-emission scanning electron microscopy SEM was used to observe the surface morphologies, microscope. microstructure captures are also taken using an optical , the Vickers Micro Hardness tests performed on each specimen and corrosion test have been carried out to determine the optimum dose that can give good corrosion resistance in a simulated body fluid condition. The experimental results indicated that the hardness measurements exhibit an increment for the Ti-alloys specimens. Microscope , the value of hardness decreasing for increasing thickness of thin film also there is clear improving in the corrosion resistance was observed rather than for untreated specially specially for 300nm thickness thin film.*

Keyword: *- Titanium oxide thin film, RF sputtering technique , Vicar Micro hardness, corrosion teast.*

I. INTRODUCTION

Titanium was first discovered in England by W. Gregor in 1791 .The material has low density property relative to other structural metals and alloys, but it has an excellent corrosion resistance [1, 2, 3]. Nowadays, titanium is widely used in industry and medical field [4, 5, 6, 7]. Due to its biocompatibility, titanium is used in medical applications including surgical implement and implants, such as hip balls and sockets (hip joint replacement) that can last up to 20 years [8]. Titanium is also used in other several medical fields such as dental implant materials, bone fitting, replacement of the skull [9,10,11]. Because titanium is a non-ferromagnetic material, the implant to the patient is very safe with magnetic resonance imaging . High Titanium properties arise from, excellent chemical inertness ,corrosion resistance due to oxide film grows spontaneously on the surface upon exposure to air of 3–8 nm almost instantaneously forms on metallic titanium at ambient atmosphere, TiO_2 which is the main constituent of natural surface oxide films, thermodynamic ally very stable and the Gibbs free energy of formation is highly negative for a variety of oxidation media ,such as water or oxygen containing organic molecules [12] .but although a certain degree of short-range order in the nanometer scale is likely to occur, thin surface oxides on bulk titanium are essentially non-crystalline and very thin .The excellent tissue compatibility and better corrosion resistance ,the use of commercially pure titanium (CPTi) in implants, but the material was hindered by limited strength and very poor wear resistance. Interest in the use of Ti-6Al-4V for prostheses. It is seen from literature that cpTi α phase ,vanadium is added up to 4 wt.%, which is found to be sufficient to stabilize10% in volume of β phase at room temperature also add 6wt.% of aluminum in cpTi. Though at the outset α+ β alloy Ti-6Al-4V. In spite of the sound mechanical properties of the presently used surgical implants, deleterious corrosion process has been considered in certain clinical settings [13]. Corrosion of the implant by the reaction of the body fluid and tissues is found to change the physical properties of the material. Consequently, there may be isolation and rejection of this foreign body. Furthermore, the long-term effect of the corrosion products present in human system may be toxic, causing carcinogenic response [14]. Hence protection of an implant material from corrosion is highly indispensable. The corrosion stability of a material can be determined kinetically as a result of the ability of that material to form stable a oxide layer, affording protection from further corrosion. The anodic behavior of different alloys is caused by the different conduction mechanisms of the passive layers of the materials. The oxide layer of titanium is an n-type semiconductor, and under a typical redox potential of about 200 mVSCE in biosystems, such oxide layers will have only ionic conductivity and no electronic charge transfer is possible. This is responsible for the high corrosion resistance of titanium [15]. Though extensive work on titanium alloys has been made to develop the relationship between microstructure and mechanical properties . When wearing is one of parameters that mostly

considered, the Titanium alloy has a good wear resistance. But, there are some concerns about the toxicity of Al and V wear debris in the human body that might negative side effects to the human body ,also, the bone in growth properties and implant fixation behavior need to be improved in order to shorten the implant-tissue osseointegration time. Therefore, a great deal of research has been carried out to improve the physical and chemical properties of the surface structure of Ti [16]. The excellent biocompatibility of TiO2 ceramics and thin films has also been recognized, Among the different solutions which have been proposed, titania (TiO_2) coated on titanium alloys . Surface treatment has been used to increase the surface bioactivity of some materials, and the methods include chemical treatment [17], laser treatment [18], ion injection surface modification [19], and so on. Since Branemark first reported their application, titanium and titanium alloys have. been widely used as implant materials, and their bioactivities are believed to be linked to TiO2.The conventional sputtering methods, among others, are the most preferred technique owing to the reproducible deposition of the films accomplished quite easily compared to the other methods[20]. In the present work, the corrosion behavior of cpTi and Ti-6Al-4V alloys under different thickness of TiO2 thin film in simulated body fluid solution are compared.The TiO_2 film exhibits three distinct polymorphs: the rutile, anatase and brookite phase.. radio frequency (RF) magnetron sputtering have different crystalline structures that strongly depend on preparation conditions. Among thin film preparation methods, RF magnetron sputtering is one of the most easy to industrialize. It is suitable for medical coatings due to the high density, high adhesion, high hardness, and good thickness uniformity of the deposited layer over a large area. The structure and composition of TiO_2 thin films can be easily controlled by adjusting the deposition conditions.[21,22]. In this study, the influences of plasma sputtering to hardness of cpTi and Ti 6Al 4V surface are investigated. Hardness, one of mechanical property that important to consider, is a measure of a material's resistance to localized plastic deformation (e.g., a small dent or a scratch). Hardness is an indicator of wear resistance and ductility. The instrument used to measure the hardness is Micro Vickers. Micro Vickers is referred to as micro indentation-testing method on the basis of indenter size. It is well suited for measuring the hardness of small, selected specimen regions. Hardness test is very useful for materials evaluation, quality control of manufacturing processes, and development effort.

II. EXPERIMENTAL PROCEDURE

The specimens of cpTi and Ti – 6Al – 4V alloys were used in plasma sputtering experiment with a circular shape (2 cm diameter and a 1.8 mm thickness) dimensions. The specimens' alloys was machined by grinding ,using (Struers-RotoPol-21 system, Denmark by SiC paper and etching. Titanium disc (99.99% pure sigma -aldrich) with particle size (<20 nm) and dimension (5 cm diameter and 5 mm thickness) is used as sputtering target. The distance between the target and substrate is adjusted to be about 100 mm. The substrates was mounted to the plate holder ,which was rotating during the deposition in order to increase the film's uniformity also the plate heated at (100 °C) in a vacuum chamber evacuated to a pressure lower than 10^{-3}Toor for the film fabrication. All the samples sputtered in 98.8% pure argon (27.8 sscm for sputtering gas). Titanium dioxide films with different thickness(200,300 and 500nm) are deposited on CPTi and Ti – 6Al – 4V substrates by RF magnetron sputtering method as shown in Fig (1)(TORR .CRC-600 Sputtering System) degreased specimensThin film with thicknesses(200,300 and 500nm) of polycrystalline TiO_2 deposited on Ti alloys heated substrates at 100 C˚ using in argoon gas Ar with purity 99.8 under vacuum 7×10^{-3} Toor. For different power and time deposition depend on thickness of thin film as show in table (1). This hardness test follows (standard ASTM E 384). The micro-hardness measurement works with indenter force as light as 0.49 N, with indentation time in 15 sec.. This indenter and its diagonals of impression are illustrated in Fig. 2. Due to the morphology and structure SEM of TiO_2 Coatings on $cpTiO_2$ and Ti6Al4V for different thickness have been Characterized. Corrosion test(Wenking M Lab-200 Germany) made for $cpTiO_2$ and Ti6Al4V alloys by using electrochemical behavior will be evaluated as shown in fig(4).

Figure 1: RF magnetron sputtering system

Table 1 : Thin film with different thicknesses of TiO_2 deposited on Ti alloys.

N0	Targets	Substrate	Thickness of thin film (nm)	Time of run (min)	Heat of substrate (℃)	Pressure (Toor)	Power (w)
2	TiO2	1-CPTi 2-Ti6Al4V	200	118.06	100	7×10^{-3}	120
3	TiO2	1-CPTi 2-Ti6Al4V	300	210.83	100	7×10^{-3}	110
4	TiO2	1-CPTi 2-Ti6Al4V	500	88	100	7×10^{-3}	55

Hardness

Prior to hardness testing, This hardness test follows the standard Fig .3.ASTM E 384. The micro-hardness measurement works with indenter force as light as 0.49 N, with indentation time in 15 sec. After force removal, the impression diagonals are with a light microscope Hardness testing is conducted at 3 locations on the surface of the specimen, namely the location d_1, d_2 andd_3. Figure 4 shows these locations. It is assumed that the indentation does not undergo elastic recovery after force removal. The Vickers hardness number can be determined by the following equation[23]:

HV=1,854 p/d^2 (1)

where, P : The applied force (Kg)
d :Mean diagonal of impression (mm) Digital Micro Vickers hardness Tester TH714 is used for measuring the hardness of the specimen. This micro hardness tester can b

Fig ure 2: Digital Micro Vickers hardness

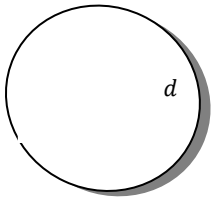

Figure3:Hardness testing locations

III. CORROSION

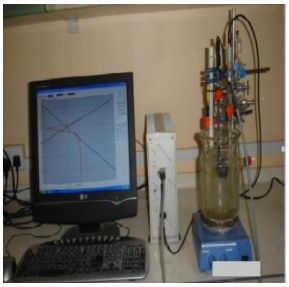

Figure4 :Corrosion system

The typical potentiodynamic polarization curves for the uncoated and coated .It can be seen that TiO_2 coated on Ti alloys indicated a passive region more than that uncoated .A simulated body fluid (SBF) suggested by Kokubo[24] was used for all corrosion tests to pH 7.4 with (polarization test in aerated SBF at 37℃).using a conventional three-electrode cell connected with a CHI 660A electrochemical system. An Ag/AgCl reference electrode , a platinum counter electrode and working electrode were employed. For corrosion rate in millimeter per year, were calculated for two alloys for different thickness by using the following equation[25] :

$$r = 0.00327 \frac{i_0 a}{zD} \ (in \ \frac{mm}{yr}) \text{ ------(2)}$$

where i_o defined as current density (I/A). This equation shows proportionality between mass loss per unit area per unit time (e.g., mg/cm^2/day) and current density (e.g., µA/cm^2). Units of penetration per unit time.

IV. RESULTS AND DISCUSSION

The results are analyzed and plotted to see the effect of the time sputtering and thickness of thin film to the material hardness and corrosion .After hardness testing, the mean diagonal of impression is obtained and then it is used to calculate the vickers hardness. The result can be seen in Table 2 and 3. Also for same thickness the log I_{corr} E_{corr}, and corrosion rate calculated as shown in Table 4 and 5.In biomechanical applications it is intended that the surface treatment to reduce the surface hardness

Table 2 :CPTi Process hardness

	Thickness(nm)	d1 mm	d2 mm	d3mm	HV $_{average}$
1	Without coating	0.0798	0.0799	0.078	145
2	200	0.0833	0.0843	0.0843	130
3	300	.090	.0937	.09007	114
4	500	0.08779	0.0879	0.08	120

Table 3: Ti6Al4V Process hardness

	Thickness(nm)	d1mm	d2mm	d3 mm	HV $_{average}$
1	Without coating	0.05	0.048	0.04966	375
2	200	0.0514	0.0515	0.051	350
3	300	0.053	0.0533	0.0529	330
4	500	0.0522	0.0520	0.0525	339

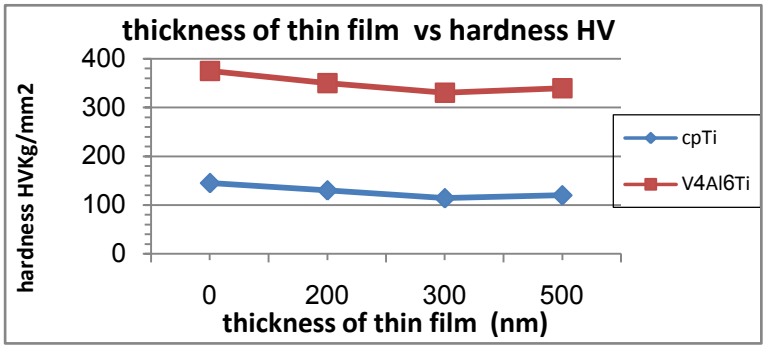

Figure5 :Micro hardness fotCPTi andTi6Al4V with thickness

Table 4:cpTi alloy

No	Thickness (nm)	log I_{corr} (A/cm^2)	E_{corr} (mV)	Corrosion ratio (mm/y)
1	uncoated		-370.4	
2	200 nm		-239.8	
3	300 nm		-288	
4	500 nm		zero	

Table 5: Ti4AI6V alloy

No	Thickness (nm)	log I_{corr} (A/cm^2)	E_{corr} (mV)	Corrosion ratio (mm/y)
1	uncoated		-181.4	
2	200 nm		-317	
3	300 nm		-374.9	
4	500 nm		-179.7	

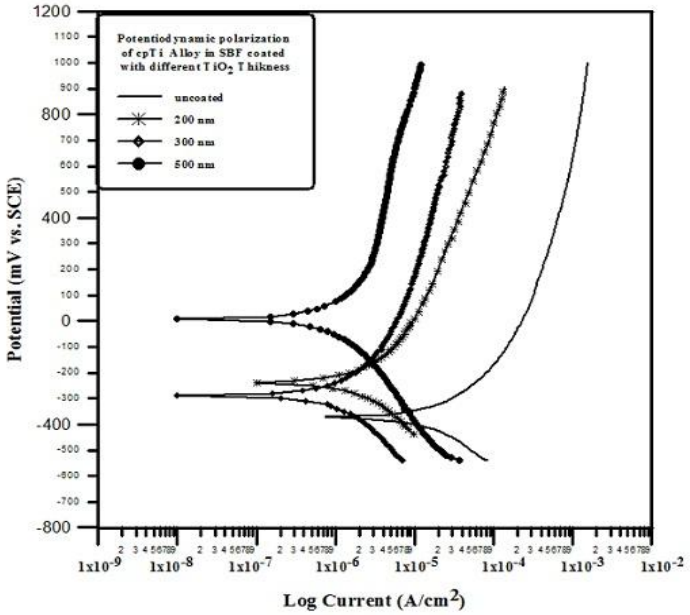

Figure 6 :Cyclic polarization behavior for the cpTi in SBF solution for different thickness of thin filmTiO_2

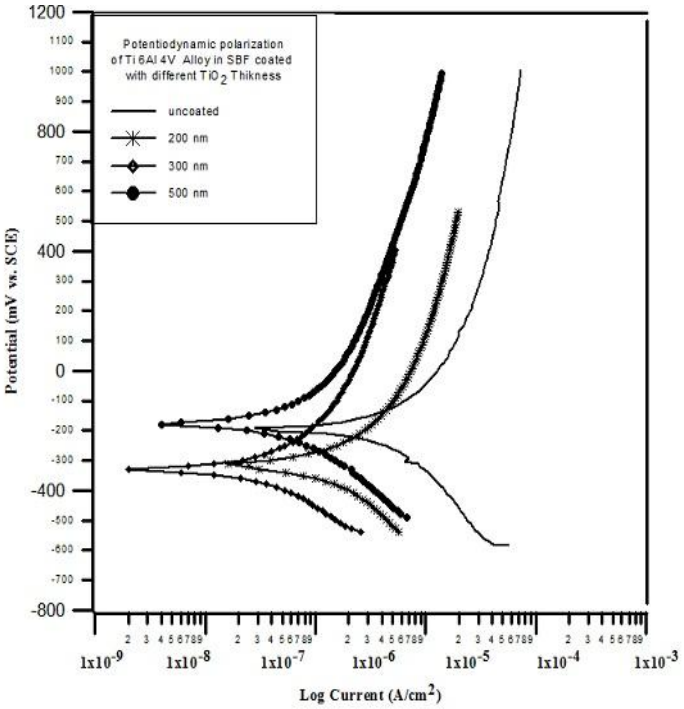

Figure7 :Cyclic polarization behavior for the Ti6Al4Vin SBF solution for different thickness of thin film TiO_2

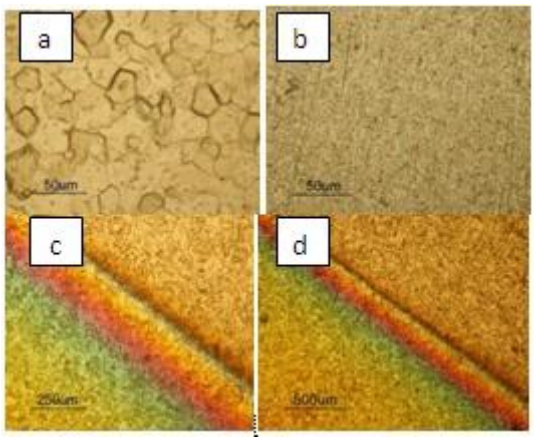

Figure8.:Microscop (a) and (b) for cpTi and Ti6Al4V uncoated respectively
(c) and (d) for cpTi and Ti6Al4V coated with 500 nm

TiO_2 respectively

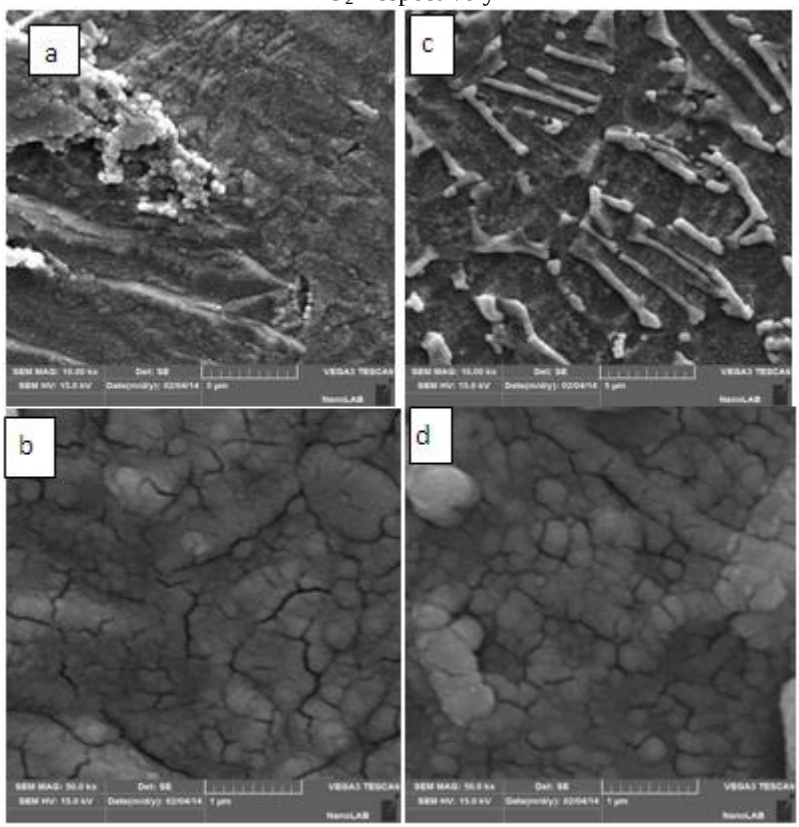

Figure 9: (a,b) for cpTi and (c,d)Ti6Al4V coated with 500 nm
TiO_2 respectively

V. CONCLUSIONS

From figure (8) ,we can see the thickness of thin film from compared between uncoated an coated fo two alloys by TiO_2

For hardness

In this research, the surface hardness of cp Ti and Ti 6Al4V is modified and improved by using plasma sputtering. The effects of such processes to hardness value can be concluded as the followings:

1-The hardness value of titanium alloys can be decreasing by extending the time during the plasma sputtering process. The degreasing hardness rate however does not show a linear behavior as shown in fig 5.

2-The hardness value resulted from the Ti 6Al4V alloy at same thickness thin film is higher compared with CPTi alloy. This belong to that Ti 6Al4V alloy has $\alpha+\beta$ –phase with mechanical properties stable more than CPTi α–phase.
3-The surface hardness value of CPTi and Ti 6Al4V alloys specimen which is. However, at 500nm there is no significant decreasing increasing of hardness .this due to brittle and crack in surface thin film as shown in fig: 9 .

For corrosion

1-cpTi alloy

From fig.(6),the passive region were similar to those of(200 and 300)nm thin film TiO_2 curves presented somewhat different corrosion potential started : -150mV (vs. Ag/AgCl) and (500)nm thin film TiO_2gives:-80mV.From table(4),I_{croo} decreasing for increasing the thickness of thin film compared with uncoated alloy also E_{croo} decreasing and moving towards the noble material .

2-Ti6Al4V alloy

From fig.(7),the passive region for (200)nm thin film TiO_2 started from -150mV(vs. pb/KCl) and -80mVfor (300 and 500)nm thin film TiO_2 .From table (4) table(5),I_{croo} decreasing for increasing the thickness of thin film compared with uncoated alloy also E_{croo} decreasing and moving towards the noble material .
In general The results confirmed that coatings alloys with TiO_2 exhibited a better electrochemical behavior than un coatings alloys possibly due to the better cohesion degree of the coating . The Ti 6Al4V alloy coated had the highest corrosion potential cpTi alloy coated gave the lowest corrosion potential (vs. Ag/AgCl).Hence, all coatings on Ti alloy did exhibit significantly improved corrosion resistance compared to uncoated Ti alloys.

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