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Investigate the surface properties of Ti6Al4V alloy for prosthetic implants through coating by Tio$_2$ using dip coating technique

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Abstract

Physicochemical properties, surface topography and mechanical test of thin film TiO$_2$ deposited on Ti-6Al-4V alloy substrates using dip coating were examined. The results obtained provided complete information on the structure of the produced materials. Thickness of double layer (59µm) used to examine. Optical microscopy for double layer shows the grain boundary reduced with increasing thickness of film and uniform distribution. X-ray diffraction proved that the film TiO$_2$ crystalline form with major Rutile phase high intensity peaks (110,101 and 211) at $2\theta^{o}$ (27.4, 35.5 and 54.5) respectively. Scanning Electron Microscopic confirms the particle size in the range of nano-meter ~ (184-280 nm), and the gaps smaller than (600nm) on the surface will readily help to absorbs the proteins which constitute an origin of bone tissue. Using polymer PVB help to increasing addition between coated, substrate and create porous on the surface coated which is necessary for the interface growth between coated and bone tissue for implant in a human body. Energy Dispersive X-ray spectroscopy, shows the presence of TiO$_2$ from chemical concentration, the increasing in value of Ti and O belong to coated TiO$_2$ layer lead to increasing these weight concentration and intensity. Vicker's Micro Hardness test used to study mechanical structure, titania coating hardness various parabolic with change in thickness of film which increasing at increasing it. The growth of thicker films could improve mechanical resistance by increasing the amount of material available to hold the loads. TiO$_2$ gives better results that is suitable for orthopaedic implants.

Keywords: Titania, polymer, Ti-6Al-4Valloy, Dip coating, Immersion and withdrawal.

1. Introduction

The biomaterials play an important role for the human beings born and dental with some disorders and disabilities for the aged people and like congenital heart disease who require medical transplants or surgical to extend their life expectancy. Metals, ceramics, polymers, and composites are the four main categories of biomaterials. Titanium ally are widely used as implant material for medical application due to good mechanical properties and biocompatibility. Ruggero Bosco *et al* [1] was investigate the requirements for bone implants and the approaches that are currently investigated to increase their performance by means of surface modifications with different methods. To increasing the Osseo integration, bioactivity and to reduce the corrosion ratio, inert and bioactive ceramic are used to coated implant material [2]. The Ag nanoparticles enhance the antibacterial activity of TiO_2 by increasing UV ray absorption rather than through Ag ion elution. Given the potentially harmful effects associated with UV light exposure, other groups have modified TiO_2 with carbon (C) [3]. Titania (TiO_2) has three or crystalline structures: brookite, anatase and rutile. Every structure have special applications depend on its properties [4]. Rutile phase is widely used in medical applications belong to the large single crystals can be easily obtained, high corrosion resistance of metallic implants, usually stated to be the thermodynamically and high biocompatibility [5]. Different methods of TiO_2 coating on titanium alloy substrates has been carried out and the resulting layer is different from one method to anther in thickness, adhesion, purity and quality, breakage between the layers and high crystallinity. E. Mohseni *et al* [6] was study the HA coating on Ti–6Al–4V implants using dip coated method and investigated improve its adhesion strength of ceramics film to the metal alloy and its long-term reliability. The advantages of dip coating is that the small amounts of material required, the costs of precursors are relatively low the film deposition homogeneity, stoichiometry control, purity, Ease of possessing, lower temperatures and controlling the composition, and useable to coating an extensive and uniform area substrate. Titanium dioxide (TiO_2) is wide use in medical applications. María Laura Vera *et al* was study process parameters in producing thin TiO_2 films coated Ti alloy by using sol-gel dip-coating and anodic oxidation, both techniques produce thin films with smooth surfaces which at most reproduce the roughness of the polished Substrate. AlsoTiO_2-coated Ti alloys are more resistant to dilution in simulated body fluids than noncoated ones [7]. The aim of study to enhance the surface properties Ti alloy coating by using TiO_2 nano partical, & interface between the coating and substrate with polymer PVB type using dip coating method.

2. Materials

Titania dioxide (TiO_2), has particle size less than 200nm, rutile phase, with purity is 3N (98.5%)) provided from (SkySpring Nanomaterials). Polymer PVB (Polvinyl butyral) $(C_8H_{14}O_2)_n$. The substrate was used titanium alloys (Ti-6Al-4V) GR2 ASTM F136 (Baoji Jinsheng Metal Material Co. Ltd). According to the manufacturer, have a chemical composition show in Table 1.

Table 1. Chemical composition (WT %).

Ti	Al	V	Fe	C	N	O	H
89.2	5.5-6.5	3.5-4.5	0.40	0.1	0.05	0.20	0.0125

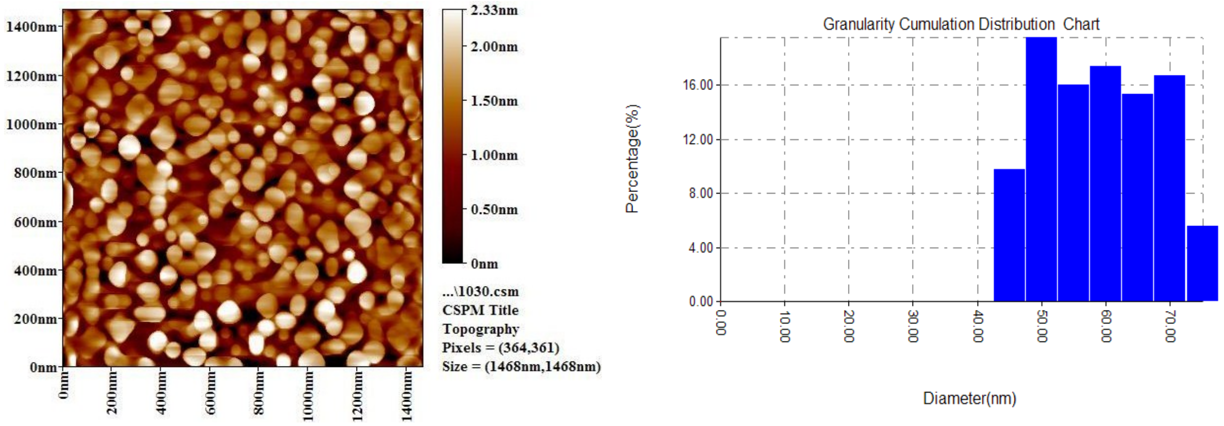
3. Experimental works

TiO_2 precursor powders was use in the preparation of dip-coating solution for coated the Ti-6Al-4V alloy. The specimens of Ti-6Al-4V alloys were used as substrates with a square shape of dimensions of 2.6 mm and 0.8mm thickness. The specimen alloys were grained with various grades of SiC paper such as 180, 240, 320, 500, 600, 800, 1000, 1200, 1800 and 2000 µm of grain size and polished using Struers-DAP-U system, Denmark. The polished alloys were ultrasonically cleaned. Thin film were prepared by using TiO_2 (25 g) as the precursor with PVB polymer ($C_8H_{14}O_2$) (0.35 g/L) (based on the zhitomirsky) to prepare the appropriate solution, 1000ml of CH_2CH_3OH with continuous stirring for 2hrs [8]. The three strips of Ti-6Al-4V substrate immersed vertically in the chemical dip coating for dipping, first sample immerse 1 min in the solution mentioned above as one layer shown in Figure (1-b). The second sample is immersed twice in the solution (first immersion within 1 min then let it to dry then immerse it again for 1min) as two layer. The third sample is immersed three times in the solution as three layer, then withdrawal sample after coated. The dip coating method must be equal in time and velocity at each time of immersion and withdrawal. The as-deposited film coatings were amorphous, to promote their crystallization, the samples were annealed in an oven for 1 hours at 400°C.

4. Results and discussion

4.1 Atomic Force Microscopy (AFM)

AFM shows in Figure 1a, as evidence by the scanning process for an area with dimensions (1467.64 ×1467.88) nm^2 for TiO_2 powder use for coated nano size particle. The range of particle size (45,000nm_75,000nm) and the largest number of TiO_2 with particle size 50nm as shown in chat Figure 1b.



(a) AFM scan proses. (b) The range of practical size.

Figure 1. AFM images for TiO_2 powder with nano size particle.

4.2 Thickness of TiO_2 film

Minutest 3000 system was used to determine the thickness of TiO_2 films dip coating thickness monitor was used and are demonstrated in Table 1. The thickness increasing from 36 µm to 78 µm, it is clear from data the value of thickness increasing with increasing the number of layer that is mean the dip coating is successfully method used for coated Ti alloy, as shown in Table 2.

Table 2. Thickness of TiO_2 film coated on substrate.

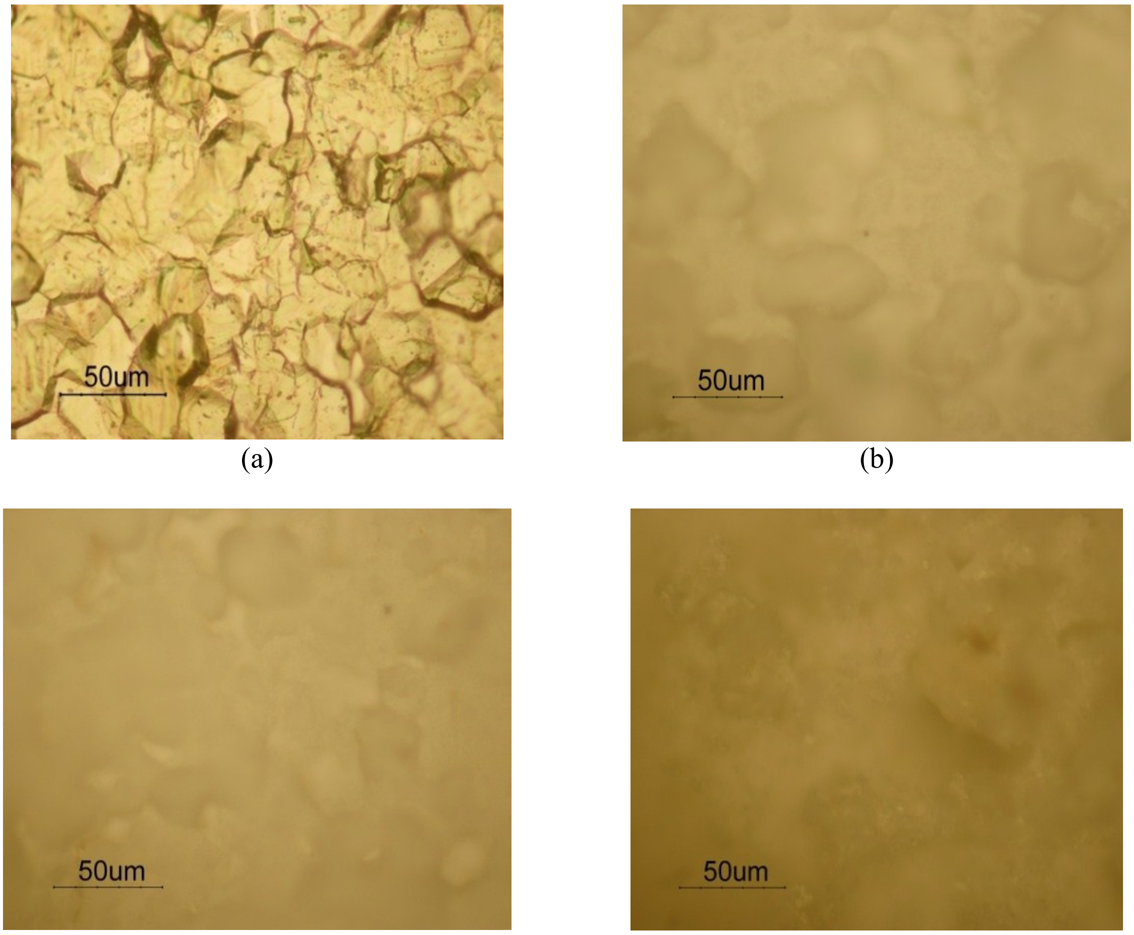
Thickness of thin TiO_2film	Value
Thickness of single layer	36 µm
Thickness of double layer	59 µm
Thickness of triple layer	78 µm

4.3 Optical microscopy

Figure 2 shown the optical microscopy of substrate Ti-6Al-4V alloy after and before coated by TiO_2 with magnification 50 µm. The grain boundary of substrate is very clear in Figure 2a before coated using dip coating technique belong to the Ti-6Al-4V alloy have two phase α and β. Figure 2b, c and d shows the change in the microscope image when the films TiO_2 was coated the substrate and annealing, the brightness of the sample are gradually change and observed as single, double and triple layer respectively. The grain boundary disappear progressively with increasing the thickness of film coated. The Dip coating produce thin films with smooth surfaces [7]. For single layer the grain boundary clear with thin layer film coated, for double layer the grain boundary reduced with increasing thickness of film and uniform distribution. Figure 2d triple layer show high thick, homogenous distribution of film coating lead to disappearing the grain boundary. The photos optical agreement with results [4].

4.4 XRD phase analysis of TiO_2 double layer

Depends on the results of optical microscopy as show in Figure 3, the X-ray diffraction was used to study the Physicochemical properties and structure of film TiO_2 double layer coated Ti -6Al-4V specimen with thickness film (59µm). XRD pattern which represents the presence of TiO_2, the sharp peaks means have crystal structure with nano size and small grain size [5, 9]. The major phase is Rutile with high intensity peaks (110,101 and 211) at $2\theta^o$ (27.4, 35.5 and 54.5) respectively. Anatase phase appear as miner weak sign, the peaks (204and 301) at $2\theta^o$ (62.6 and76.0). Secondary peaks for Rutile with low intensity (200, 111, 220, 310and112) at$2\theta^o$ (39.1, 41.2, 56.6 69.0 and 69.6). Rutile titanium dioxide (TiO_2), which is having greater biocompatibility and provides better osseointegration surface coated for orthopedic application [9].



(a) (b)

(c) (d)

Figure 2. Top view of microstructure of Ti-6Al-4V alloy (a) uncoated alloy (b) coated of the single layer (c) coated of the double layers (d) coated of the triple layers.

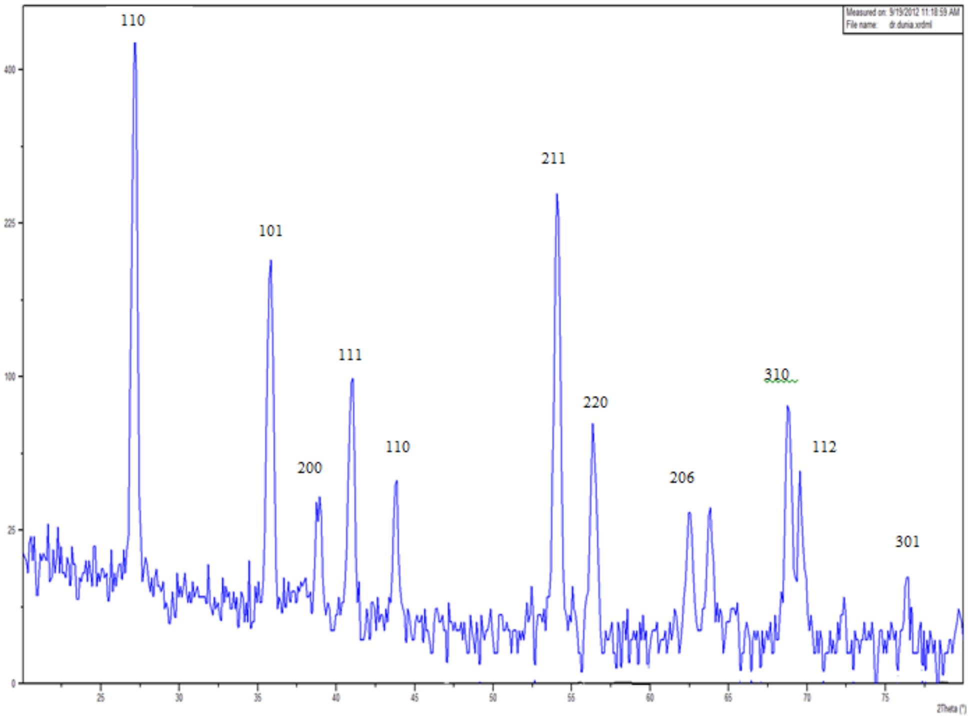
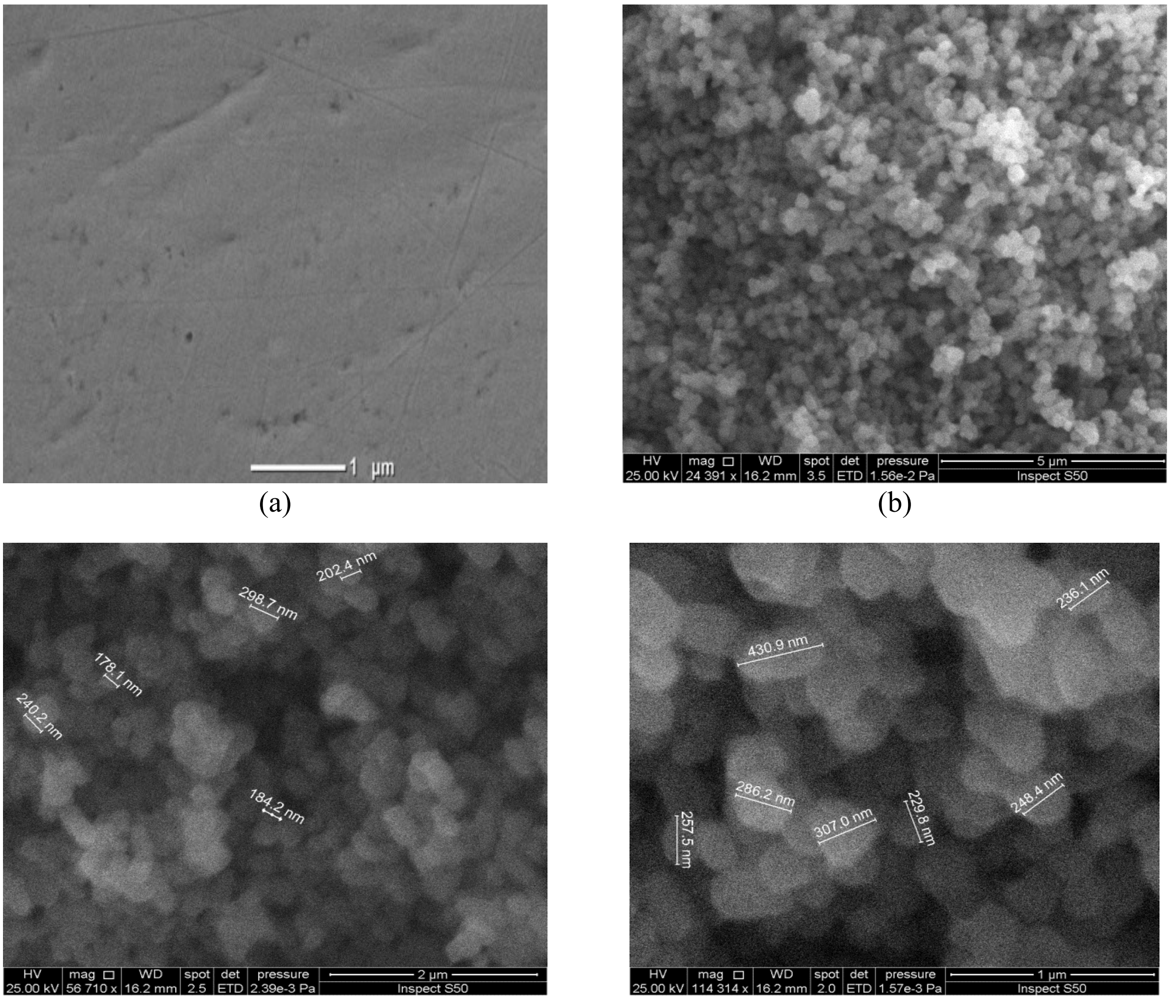


Figure 3. Xray diffraction for titania coated Ti-6Al-4V alloy as double layer.

4.5 SEM morphology Analysis of TiO_2 double layer

Figure 4a represent the SEM images for Ti6Al4V alloy uncoated. Figure 4b, c & d shown Ti6Al4V alloy coated with TiO_2 spherical TiO_2 nano particle size as double layer with different magnifications. The SEM image of dip coating derived nanoparticles show the high degree of crystallinity of the TiO_2 nanoparticles, this agreement with work of other group[9,10]. Figure 4c and d shows Clear nanostructures can be seen having particles size range ~ (184-280 nm), the aggregation nanoparticles (236-448 nm). The nano size particle of TiO_2film agreement with result of X-ray diffraction Figure 3. From Figure 4d it can be assumed that the presence of such gaps on the implant surface (640nm) may have a positive effect on implant and tissue biointergation. Such as, osteoblasts (bone forming cells) the gaps smaller than (600nm)which means that on the surface with numerous gaps wider than 0.6 µm, osteoblasts will readily settle down, proliferate, and synthesise proteins which constitute an origin of bone tissue. This gab belong to use PVB polymer [11, 12].



(a) (b)

(c) (d)

Figure 4. Top view SEM of Ti-6Al-4V alloy as: (a) uncoated, (b, c & d) coated with TiO_2 double layer spherical TiO_2 nano particle size with different magnifications.

4.6 EDS energy dispersive X-Ray spectroscopy

In addition to SEM, chemical propertise or elemental analysis energy dispersive X-Ray spectroscopy (EDS) is carried out. In order to investigate the chemical composition of the Ti-6Al-4V alloy after coated to characterized composion. Figure 5 and Table 3 shows the EDS patterns of the as resived Ti-6Al-4V alloy. The patterns shows transition energies 4.508KeV which belong to Ti Kα. The energy transitions elements O Kα are 0.5 KeV. Another energy transition that represents in 4.946 KeV blong to V $K\alpha$.The Al$K\alpha$ appears at energy of 1.48 KeV. The resoults whight concentration for EDS Ti-6Al-4V alloy coated with TiO_2. From Figure 5 and Table 3, the value of Ti and O increasing compared with value of it in Table 1 (whight of elements alloy without coated) this blong to coated TiO_2 layer lead to increasing these whight concentration and intensity. The element Au Mα appears at energy of 2.12KeV due to coated with gould for high resoulution SEM analysis.

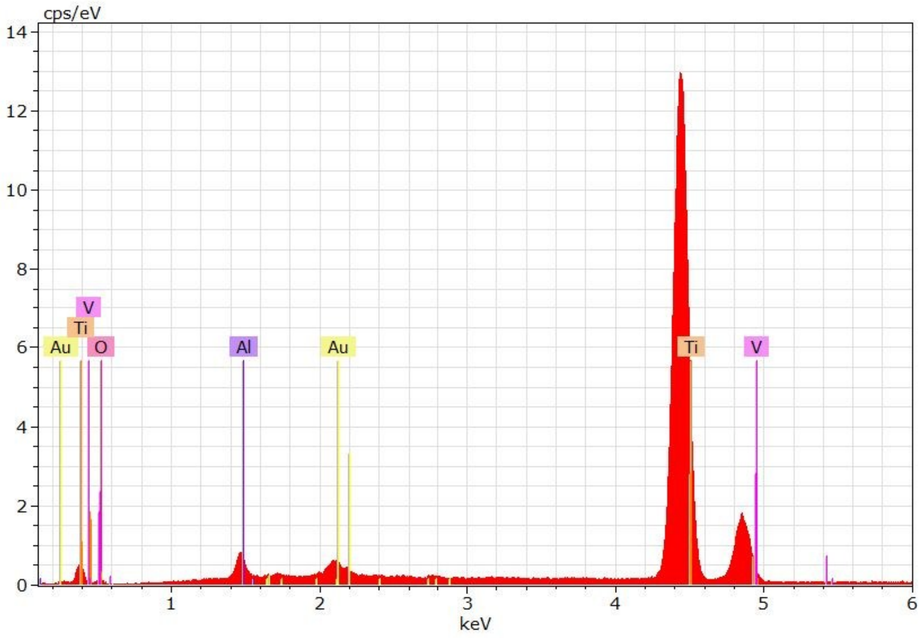


Figure 5. EDS spectra for Ti-6Al-4V alloy un coated.

Table 3. EDS whight concentration for Ti-6Al-4V alloy coated with TiO_2.

Element	AN	Series	[wt.%]	[norm.] wt.%	[norm.] at.%	(1 Sigma) wt.%
Tetanium	56	L-series	174.0144	90.11352	52.40666	4.732923
Nitrogen	7	K-series	13.05446	6.760263	38.54692	2.379877
Aluminium	13	K-series	2.269599	1.175314	3.478957	0.153302
Oxygen	8	K-series	2.011088	1.041444	5.198692	0.536871
Gold	79	L-series	1.75622	0.90946	0.368768	0.124714
		Sum:	193.1058	100	100	

4.7 mechanical properties Vickers micro hardness test (Hv)

Figure 6 and Table 4 shown Vickers hardness results, titania coating Ti-6Al-4Valloy hardness varius with change in thickness of film which increasing at increasing it,wichagrement with resoults EDSin Table 3. That is mean the bonding strength TiO_2 of the coated Ti-6Al-4Valloy is greater than the uncoated alloy. The increases in thickness of TiO_2 are able to improve the interfacial bonding strength of coated material and between the coated material with substrate [9, 12, 13]. The growth of thicker films could improve mechanical resistance by increasing the amount of material available to hold the loads [7]. Also increasing in value of hardness belong to crystal structure modification (phase α-Ti in alloy) as observed in the double layers X-ray Figure 3.

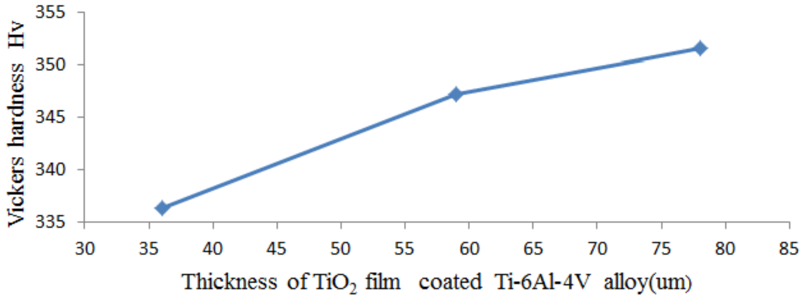


Figure 6. Vickers hardness for TiO_2 film coated Ti-6Al-4V alloy with different thickness.

Table 4. Vickers micro hardness test for uncoated and coated Ti6Al4V alloy.

Name of sample	Load (kg)	Diameter(mm)	Vickers hardness Hv
Un coating Ti6Al4V alloy	0.5	d1=0.053199 d2=0.053199	327.61
TiO_2 coating Ti6Al4V alloy single layer	0.5	d1=0.0525 d2=0.0525	336.32
TiO_2 coating Ti6Al4V alloy double layer	0.5	d1=0.051668 d2=0.051668	347.24
TiO_2 coating Ti6Al4V alloy triple layer	0.5	d1=0.056441 d2=0.056441	351.6

5. Conclusions

1. Polymer PVB use to help to increasing adhesion between coated and substrate and create porous on the surface coated which is necessary for the interface growth between coated and bone tissue for implant in a human body.
2. XRD and EDS results provides the information that TiO_2 coated on the alloy.
3. SEM results shows the coating with nano size, the presence of such gaps on the implant surface may have a positive effect on implant and tissue biointergation.
4. The increasing in hardness value come the growth of thicker films could improve mechanical resistance by increasing the amount of material available to hold the loads.
5. Dip coating method was successful for coated Ti-6Al-4Valloy by TiO_2 keep coating with nano size particle, good mechanical and provides adhesion strength, so it is recommended for orthopedic application in a human body.

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