International Journal of Engineering & Technology, 7 (3.17) (2018) 176-179

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Improvement of Surface Properties of Prosthetic Implants through TiO2 by Using Dip Coating Method

Wajdi Sadik Aboud[1*], **Dunya Abdulsahib Hamdi** [1,2]

[1]*Prosthetics & Orthotics Engineering Department,*
College of Engineering, Al-Nahrain University,
Baghdad, Iraq
[2]*Surface Analysis and Materials Engineering Research Group,*
School of Engineering and Information Technology,
Murdoch University, Murdoch, WA 6150, Australia
**Corresponding author E-mail:* wajdisadik@gmail.com

Abstract

In this research, the dip coating method is used to prepare the Ti-6Al-4V alloy by powder ceramic titania (TiO2 of 50 nm particle size) in order to improve the biocompatibility of the alloy surface for implant applications. Atomic Force Microscopy, Optical microscope, X-ray diffraction, and Scanning Electron Microscopic are performed to describe the phases and microstructure of alloy surface. Moreover, the In vitro test was performed to investigate the morphology of the alloy surface in simulated body fluid solution before and after the coating process. The experimental results of the Atomic Force Microscopy showed that the coated particles film is still with a nano-size of 90 nm. Furthermore, the X-ray diffraction outcomes showed that the TiO2 is within the retail phase, very visible, and fully coated with high intensity of plane (110). The optical microscope is clearly showed that the grain boundary is reduced with increasing the film thickness. The Scanning Electron Microscopic images are clarified that the alloy is completely coated by TiO2. Additionally, no crack appeared within the coated film and the aggregations are formed with a size of 300 nm. The results of the in vitro test for the coated samples are shown the following advantages; the values of corrosion potential (Ecorr) were shifted towards the positive direction of the potential, the values of corrosion current density (Icorr) were reduced to be more negative as well as the Corrosion Rate CR is also reduced accordingly.

Keywords: *corrosion, dip coating, polymer, titania, titanium alloy*

1. Introduction

The chemical, mechanical, and physical properties of Titanium alloys made it widely used for load-bearing applications such as dental and orthopaedic implants. Furthermore, the Titanium alloys are inert materials in which they can not make a bond with bone. Thus, these materials can cause clinical failures and interfacial displacements which led to detrimental effects on the patients. Therefore, different methods of bioactive coating are used to enhance the bone-bonding ability of Titanium alloy [1]. The inert and bioactive ceramic methods were used as coated to improve the bioactivity properties of implant materials. The TiO_2 has three phases or crystalline structures in atmospheric conditions: anatase, rutile, and brookite. Every structure has its specific applications which depend on its own properties [2]. Pure rutile is a desirable phase in medical applications due to the large single crystals that can be easily obtained high corrosion resistance of metallic implants, which usually stated to be the thermodynamically and high biocompatibility [3]. Moreover, different methods of TiO_2 coating on titanium alloy substrates have been carried out and the resulting layers are different from one method to another in thickness, adhesion purity, quality, breakage between the layers, and high crystallinity [4].

The dip coating is one kind of chemical methods and it is very simple which forms a thin layer quality depends on the concentration of the solution, the speed of withdrawal, and sintering process after coating [5]. The mixing of Si-HAp coated on titanium alloy substrate at three different concentrations of HAp by using dip coating method for medical applications [6]. Thin film calcium-doped silica and titanium dioxide deposited on two different metallic substrates; stainless steel (316L) and titanium alloy (Ti-6Al-4V) by using the sol-gel method, the coatings are shown that the surface properties and physicochemical are suitable for implant applications [7]. Spin and dip coating method was used as factors influencing thickness and uniformity of thin light-emitting polymer (LEP) solutions. The characteristics of film change with changing retraction speed as a primary variable for both spin and dip coating as well as the speed developed to include the solvent effect of solution viscosity change during evaporation. The crystallization process of mixing different concentration of Sr-TiO3 thin films was investigated by using a chemical method dip coating at a temperature of above 450 °C [8]. Ultimately, the goal of the present study is to study and investigate the physical properties, surface topography, and corrosion behaviour of TiO_2 film that deposited on Ti-6Al-4V alloy for implant metallic substrates using dip coating method.

2. Used materials

The materials used in the current work were as follows; a) Titania dioxide (TiO_2) of particles size of about 50 nm. The used TiO_2 was of rutile phase with purity of 3N (98.5%) which provided from (Sky Spring Nanomaterials). b) Polyvinyl butyral Polymer (PVB), with the chemical formula ($n\text{-}C_8H_{14}O_2$) which also provided from (Sky Spring Nanomaterials). c) The substrate titanium alloys (Ti-6Al-4V) of GR2-ASTM-F136 that supplied by Baoji Jinsheng Metal Material Co. Ltd. The chemical compositions of the used alloy are shown in Table 1:

Table 1: Chemical composition Ti-6Al-4V alloy (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 work

The TiO_2 precursor powder was used in the preparation of dip-coating solution to coat the Ti-6Al-4V alloy. The film was prepared by using TiO_2 (25 g of particles size of 50 nm) as the precursor with 0.35 g/L of PVB polymer to prepare the appropriate solution of CH_2CH_3OH with a volume of 1000 ml with continuous stirring for 2 hr [9]. The specimens of Ti-6Al-4V alloys were used as substrates with a square shape of dimensions of 2.6 mm and 0.8 mm in thickness. The specimens 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. The polished alloys were ultrasonically cleaned and three strips of the Ti-6Al-4V substrate were vertically immersed in the chemical dip coating for dipping at a temperature of 35 °C.

The first sample is immersed for 1 min in the solution as one layer. The second sample is immersed for 2 min in the solution as a thick layer. The third sample is immersed for 3 min in the solution as a thicker layer, then withdrawal of the samples after coated. The dip coating method should be equal in stirring velocity and time of immersion and withdrawal. The deposited films were amorphous and to promote their crystallization, the samples were annealed in an oven for 1 hours at 400 °C. The potential dynamic polarization in a simulated body fluid (SBF) is suggested for the corrosion test at a pH of 7.4 and 37 °C using conventional three-electrode cell connected with a CHI-660A electrochemical system (An Ag/AgCl reference) [10].

4. Results and discussion

4.1 Thickness

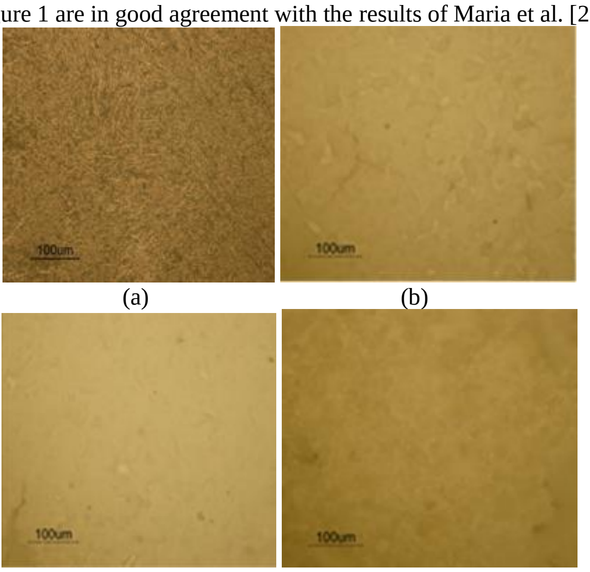
The thickness of the thin film was determined using the minutest device of a model of 3000. As shown in Table 2, the film thickness is increased with increasing the time of immersion in the coated solution.

Table 2 The values of the thickness of the thin film TiO_2 coated Ti-6Al-4V substrate

Time immersion (minutes)	Thickness of thin film (µm)
1	20
2	35
3	58

4.2 Optical microscopy

Figure 1 shows the optical microscopy of substrate Ti-6Al-4V alloy before and after the coated process of TiO_2 with a magnification of 100 µm. Figure 1.a illustrates that the grain boundary of the substrate is very clear before coating, which belongs to the Ti-6Al-4V alloy that has two phase α and β. Figures 1(b), (c), and (d) are clearly shown that the change in microscope images when the films of TiO_2 is coated with the substrate using a dip coating technique. In which, the grain boundary progressively disappeared with increasing the thickness of the coated film. Moreover, for an immersion time of 1 minute the grain boundary is cleared with a thin layer film coated and for 2 min of immersion, the grain boundary reduced with increasing the thickness of the coated film. For 3 min of immersion time, Figure 2.d shows the high thick of 58 µm with a uniform distribution of film coating which led to disappearing the grain boundary. The optical photos presented in Figure 1 are in good agreement with the results of Maria et al. [2].



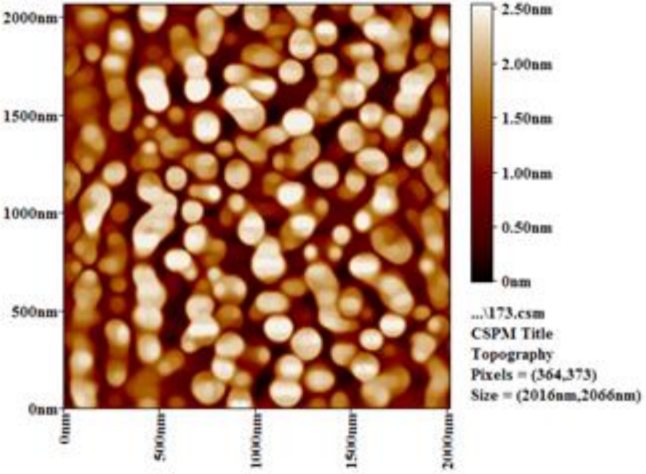
(a) (b)

(c) (d)

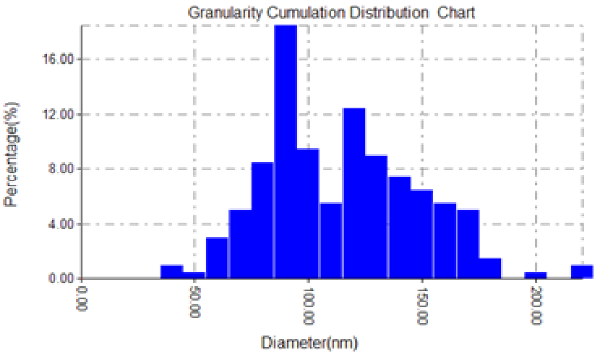
Fig 1: Optical microscopy for Ti-6Al-4Vally (a) uncoated & (b, c, and d) coated with TiO_2 for different thicknesses.

4.3 Atomic force microscopy (AFM)

Depends on the optical microscope (AFM) results, the AFM as an evidence of the scanning process for an area with dimensions of (36 × 37 pixel) for films of TiO_2 which prepared using dip coating for 3 min of a thickness of 58 µm and annealed at 400 °C clearly illustrated a surface morphology with nano-size particle and circular shape as shown in Figure 2.a. The range of particles size is 50,000 nm-200,000 nm and the largest number of particles size are of 90,000 nm as shown in Figure 2.b. The growth of large grain size of the film is due to the aggregation which increased with the increase in the film thickness, this means that the dip coating method is successfully implemented when coated with nano-sized particles.



(a) AFM scan process



(b) The range of particle size

Fig 2: Atomic Force Microscopy for titania TiO_2 (thickness 58 μm) coated Ti-6Al-4V alloy.

4.4 X-ray diffraction

Figure 3 shows the X-ray diffraction of the TiO_2 which fully covered the substrate surface of the Ti-6Al-4V alloy (thickness 58 μm). The peaks at angles ranging from 20° to 80° which represents the presence of TiO_2 particles. There are more than one peaks of (110,101, and 211) phase rutile of TiO_2 at 2θ° (27.44, 36.08 and 54.3) was stronger compared to the other phase titania crystals structures anatase there are peaks of (112 and 116) at 2θ° (38.5 and 68.7). The secondary peaks for Rutile with low intensity are (210, 220, 002 and 112) at 2θ° (44.0, 56.6, 62.7 and 69.7) respectively. These results are in good agreement with the review study done by [11]. The peaks of titania have a stronger intensity than that of substrate Ti of (101 and (110) at 2θ° (40.1 and 62.9) alloy because the coating is fully covered the substrate surface. The rutile phase of TiO_2 is more important than other types of titania for medical application due to more stable and crystal structure. The sharp peaks confirmed that the particles of the coated film are crystal with nano size. The grain size growth, narrow-scan spectra of the (110), from 26.5° to 27.5° peak have been recorded and the particles size are calculated using Scherer equation (Equation 1) in which the values of λ, β, and θ of the (110) peak are estimated at full-width-at-half-maximum (FWHM) [12]. The TiO_2 crystal size was found to be of 85 nm. It is worthy to note that these results are agreed with the above result of AFM as shown in Figure 2.

Scherrer's relation: $$a = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

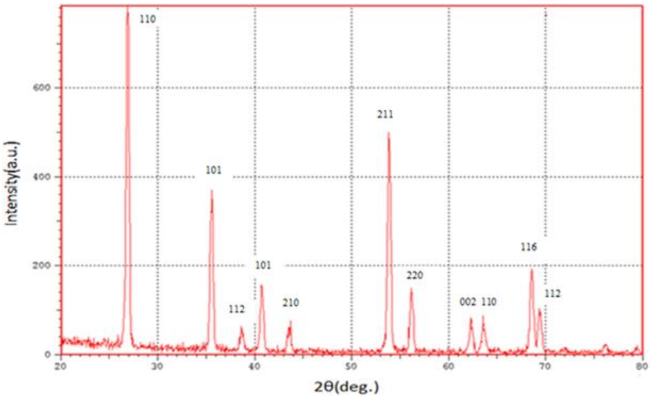
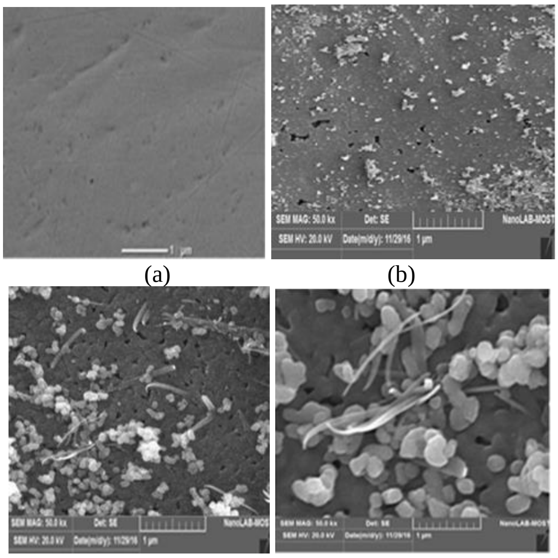


Fig 3: X-ray diffraction for titania TiO_2 (thickness 58 μm) coated Ti-6Al-4V alloy.

4.5 The scanning electron microscopy (SEM)

Figure 4 shows the morphology Ti-6Al-4V alloy (a) uncoated, (b) coated with TiO_2 (thickness 20 μm), (c) coated with TiO_2 (thickness 35 μm), (d) coated with TiO_2 (thickness 58 μm). It is clearly shown that the morphology of the coated surface is improved with increasing the thickness of the coated film, in which the coated process reduced the pores and made the distribution of the coated film more uniformly. Figure 4.b shows that TiO_2 is fully covered the surface with no crack, exhibit an apparent interface with the titanium substrates which has pores and nano crystallized. The Ti presented in Ti-6Al-4V alloy substrate tends to oxidize the alloy. The oxidation can be increased with temperature (during the annealing process), therefore the substrate can easily absorb the oxygen from the TiO_2 coating, as a result, the pores and oxygen vacancies in the coating layer can be developed. However, it can be reduced by increasing the thickness of the coating film [7]. The vacancies and the pores of size ranging from 250 nm to 500 nm which are located on the implant surface may have a positive effect on implant and tissue biointegration. In which, the osteoblasts (bone forming cells) do not notice the gaps that smaller than 600 nm [13]. The other particles appear as planer shape with aggregation which have an average particles size of 300 nm, the nano size has a strong surface charge that led to forming the aggregations on the surface.


(a) (b)

(c) (d)

Fig 4: Top view of the SEM of Ti-6Al-4V alloy (a) uncoated, (b) coated with TiO_2 (thickness 20 μm), (c) coated with TiO_2 (thickness 35 μm), (d) coated with TiO_2 (thickness 58 μm).

4.6 In vitro tests coating morphology of film TiO_2

In vitro Tests coating morphology of Film TiO2 Figure 5 shows the In vitro corrosion test for of Ti-6Al-4V alloy (a) uncoated, (b) coated with TiO2 (thickness 20 μm), (c) coated with TiO2 (thickness 35 μm), (d) coated with TiO2 (thickness 58 μm) were performed using (SBF). In general, a stable of the oxide film of all the samples has been achieved. Table 3 represents the corrosion parameters that extrapolated from Figure 5. There is a clear improvement in the polarization behaviour of a Ti-6Al-4V alloy, in which the potential has been increased with increasing the thickness of coated film with TiO2.

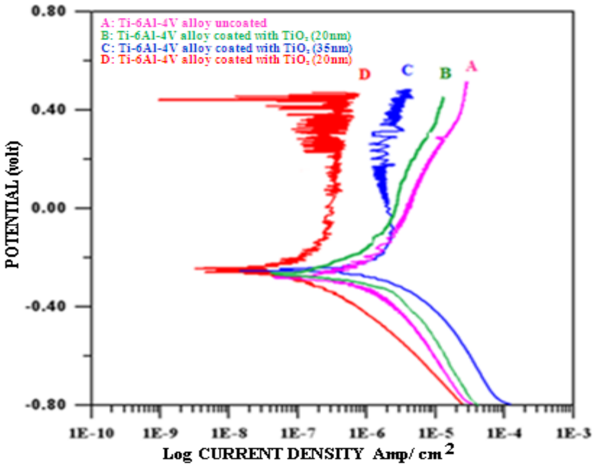


Fig 5: The LCV behaviour of the of Ti-6Al-4V alloy (a) uncoated, (b) coated with TiO_2 (thickness 20 µm), (c) coated with TiO_2 (thickness 35 µm), (d) coated with TiO_2 (thickness 58 µm).

The values of corrosion potential (E_{corr}), Corrosion current density (I_{corr}), Corrosion ratio (C_R) and passivation current of the uncoated and coated samples with TiO_2 are presented in Table 3. The value of E_{corr} shifted towards the positive direction of potential, the value of I_{corr} reduced and moved to be more negative. C_R is also reduced, which mean that the increase in the resistance corrosion has occurred. The coated Ti-6Al-4V alloy with TiO_2 is showed higher passive current density than the uncoated specimen. The lowest passive current density value is recorded for the uncoated Ti–6Al–4V, the improvement in the passivity of the coated specimen may be attributed to the film layer formed on the surface (thick TiO_2 film). The natural oxide layer with a coated film of TiO_2 which varying in thickness was formed on the surface and creates a protective layer which preventing titanium from being exposed to the reactive ions of the solution. The presence of pores in the deposited on the Ti-6Al-4V alloy that shown in the micrograph of SEM (Figure 4) was not preventing the improvement in corrosion resistance of Ti-6Al-4Valloy. Moreover, from Figure 5 and the data in Table 3, it is clearly shown that the alloy with coated film gives a better improvement in corrosion resistance which increased with increasing the TiO_2 deposition.

Table 3: Represent the corrosion parameters that extrapolated from Fig. 5, the corrosion test Ti-6Al-4V of uncoated and coated samples with TiO_2

Item	Description	Corrosion Rate C_R (mm/year)	E COR. volt	I COR. Amp µ	Passivation log Current density (Amp/cm^2)
a	Ti-6Al-4V alloy uncoated	2.89×10^{-3}	-0.28	0.732	2.8×10^{-5}
b	Ti-6Al-4V alloy coated with TiO_2 (thickness 20 µm)	3.35×10^{-3}	-0.244	0.551	5.45×10^{-5}
c	Ti-6Al-4V alloy coated with TiO2 (thickness 35 µm)	6.33×10^{-3}	-0.244	0.331	4.45×10^{-6}
d	Ti-6Al-4V alloy coated with TiO2 (thickness 58 µm)	5.56×10^{-4}	-0.245	0.0639	7.66×10^{-7}

5. Conclusions

The dip coating methodology of a TiO2 film on Ti-6Al-4V alloy is studied in order to qualify the biocompatibility of the alloy surface for implant applications. The dip coating method is implemented at different operating conditions of immersion times. The uncoated and coated samples are tested to check their physical properties, morphology, and corrosion resistance using several experimental techniques of Atomic Force Microscopy, Optical microscope, X-ray diffraction, Scanning Electron Microscopic, and in vitro test. The results of the experimental tests are shown the following:

1- The dip coating method is successfully implemented for coating the Ti-6Al-4V alloy by TiO_2 with nanostructure particles that enhanced the surface morphology and corrosion resistance.

2- The natural oxide layer with a coated film of TiO_2 (which varies in thickness) is formed on the alloy surface and created a protective layer which prevents the titanium metal from being exposed to the reactive ions of the SBF solution.

3- The addition of PVB polymer in the coating solution increased the adhesion between the coating film and the alloy substrate. Moreover, pores are created on the surface coating layers which is necessary for the interface growth between coated alloy and bone tissue when implant in the human body.

References

[1] Z. Zumrut, B. D.Polat, I. Akin, O. Keles and G. Goller “Bioactivity Characterization and a Full Factorial Design on the Adhesive Strength of Air Plasma Sprayed HA-TiO2 Coated Ti, ” Journal of The Australian Ceramic Society 49(2): 95 – 103 (2013).
[2] C. Maria, G. Firoz, C. Rigoberto, T. E. Ada, E. J. Lemons and L S. Bellis “Osteoblast adhesion and matrix mineralization on sol-gel-derived titanium oxide, ” Journal of Biomaterials 27: 2201-2212 (2006).
[3] J. Pawlowski, “Thick Laser Coatings,” Journal of Thermal Spray Technology.8(2):279-295 (1999).
[4] A Minatun, R. Apsari, Y. Yusuf and B. Suhariningsih, “Synthesis and Characterization of Hydroxyapatite Layer on Cobalt Alloys Through DIP Coating Method as A Prosthetic Bone Implant Candidate, ” Journal of Optoelectronics and Biomedical Materials. 7(1): 11 – 18 (2016).
[5] H. Raghu, S. Bose and P.A. Mahanwar, “Effect of Particle Size of Filler on Coloration and Properties of High-Density Polyethylene,” Journal of Mineral and Materials characteristics and Engineering (5), 87-100 (2006).
[6] N. Hijon., M. V. Cabanas., J. Pena. and M. V. Regi., “ Dip Coated Silicon Substituted Hydroxyapatite Films, ” ActaBiomaterialia 2, 567 (2006).
[7] V. Khalili, K. AllafiJ. And M. Ghaleh, “Titanium Oxide (TiO2) Coatings on NiTi Shape Memory Substrate Using Electrophoretic Deposition, ” Process. IJE TRANSACTIONS A: Basics. 26(7):707-712.Prepared by Dip CoatingMaterials Research2(2):93-97 (2013).
[8] R. L. Edson, R. V. Mastelaro, S. M. Zanetti, E. Longo, “Crystallization study of SrTiO3 thin films prepared by dip coating, ” Materials Research. (2), 93-97 (1999).
[9] I. Deen and I. Zhitomirsky, “deposition of composite halloysite nanotube-hydroxyapatite-hyaluronic acid film.” journal of Alloya and Compounds.586.S531-S534 (2014).
[10] T. Kokubo T., “ Surface chemistry of bioactive glass–ceramics,” Journal of Non-Crystalline Solids 120:138–51(1999).
[11] L. Miao, P. Jin, K. Kaneko and S. Tanemura, “Sputter deposition of polycrystalline and epitaxial TiO_2 films with anatase and rutile structures,” 8th International Conference on Electronic Materials (IUMRS-ICEM 2002, Xi’an, China, 10–14 June 2002)
[12] Y. Liu, B. Huang., J. Ruand.and Yuehui , “Behaviour of composition Ca/P bioceramics in a simulated body fluid,” Journal of Mater Sci. Technol. 14:533-537 (1998).
[13] K. Justyna., F. Jaroslaw, P. Celina and B. Agnieska, “The effect of substrate roughness on the surface structure of TiO2, SiO2, and doped thin films prepared by the sol-gel method,” Acta of Bioengineering and Biomechanics Original paper. 11(2);21-29 (2009).