Journal of Engineering and Applied Sciences 13 (Special Issue 14): 10992-10997, 2018
ISSN: 1816-949X

Deposition Hydroxyapatite/Titania Composite on Ti-6Al-7Nb Alloy for Human Body Implants

Dunya Abdulsahib Hamdi
Department of Prosthetics and Othotics Engineering, Al-Nahrain University, Baghdad, Iraq

Abstract: The microstructural analysis and electrochemical measurements tests were used to investigate the behaviors of TiO_2 and (HAp)-coated Ti-6Al-7Nb alloy in the SBF solution. By using RF sputtering, a thin TiO_2 layer coated the substrate while a thick layer of HAp coated the outer side of surface. The generated middle layer consist of the composite of TiO_2 and HAp which is by AFM characterized as uniformly distributed coating system with nano size. The images of the Scan Electron Microscopy (SEM) shows that there is no any cracking observed in the outer layer of tested samples due to the use of thin film TiO_2 as mid lead to reduce the difference in the thermal expansion between the HAp material and Ti-6Al-7Nb substrate. The HAp upper layer significantly improve the bioactivity of the Ti-6Al-7Nb alloy. In this study, the bonding strength and the corrosion resistance was improved by using thin layer of TiO_2. From Electrochemical Impedance Spectroscopy (EIS) study Bod plot, the composite layer of TiO_2 and HAp was suggested by the capacitive act as barrier layer coated substrate and prevent the relays of the ion from metallic. The results shows the values of R_{ox}(309.2 kΩ cm^2) are greater than for R_{ct}(19.2 kΩ cm^2) by assumes the presence oxide film increases for coated substrate are greater than that of uncoated which is a result of the presence of coated film that improve the corrosion resistance of the sample.

Key words: Magnetron sputtering, hydroxyapatite, Ti-6Al-7Nb alloy, titania, biomaterials, electrochemical corrosion

INTRODUCTION

The metallic materials Titanium (Ti) alloys are widely used in manufacturing of implants material because their high toughness and strong strength (Sittig *et al*., 1999). The ability of Ti alloy to interact with body fluids might cause adverse effects to the surrounding tissues due to release of ions from metallic (Heakal and Awad, 2011). The hydroxyapatite ($Ca_{10}(PO_4)6(OH)_2$, HAp) used to modificate the metallic implant to improve the activity of the surface (Wu *et al*., 2008). The difference in thermal expansion coefficients between HAp (13.6×10^{-6}/K) and Ti alloy (8.6×10^{-6}/K) lead to mismatch between coated and substrate, so, other material like TiO_2 is used as thin mid layer between the substrate and HAp which have thermal expansion (7.249×10-6/K) approximately near the thermal expansion of substrate (Bolat *et al*., 2012; Mohan *et al*., 2012). From literatures review, there were many attempts have been made to form a thick TiO_2 layer on the Ti substrate because they found that the corrosion resistance of implants material is increases with increasing the thickness of the oxide layer on the surface. The improved biocompatibility and biological processes of implants using HAp coatings is belong to the biological and chemical similarity of HAp to biological types tissues and it's could direct bonding to the bones (Kim *et al*., 2004). Different methods are used for coating such as chemical and physical vapor deposition such as electrophoretic, laser beam, ion implant and sol-gel method (Roncevic *et al*., 2014; Wei *et al*., 2007; Kim *et al*., 2005). Plasma sputtering is currently the one of the beast method commercial process was used for deposited ceramic such as HAp and TiO_2 coatings on metallic implants. This belong to the film coated with good adhesion, high quality, full cover with low porous (Wei *et al*., 2007). The Ti-6Al-7Nb alloy was achieve due to, a dense and stable passive surface layer, high corrosion resistance good mechanical properties (Bolat *et al*., 2012). The aim of the present research is to enhance the properties of the bioactive of the Ti6-Al-7Nb alloy. The TiO_2 film coated the alloy as mid layer to enhance the adhesion between the HAp layer and Ti6-Al-7Nb substrate and hence increasing the corrosion resistance of the substrate. The HAp was used to improve the biocompatibility of surface. The materials used in this research are powder targets (4~5 μm TiO_2 and 2 μm HAp

Corresponding Author: Dunya Abdulsahib Hamdi, Surface Analysis and Materials Engineering Research Group, School of Engineering and Information Technology, Murdoch University, WA 6150 Murdoch, Australia

particles) with purity is (98.999%) and (95.999%), respectively provided from VTFM (Vacuum Thin Film Materials). The substrate used was titanium alloys (Ti-6Al-7Nb) (Baoji Jinsheng Metal Material Co. Ltd.).

MATERIALS AND METHODS

Experimental procedure: The substrate Ti-6Al-7Nb alloy was grinded, polished and cleaned ultrasonically in ethanol and deionized water for 20 min at 25°C temperature. The RF magnetron sputtering device with frequency of 13.65 MHz was situated in a vacuum chamber 1×10^{-6} Torr, Ar gas (purity 99.9) atmosphere was used as sputtering gas with working pressure 5.5×10^{-3} Torr and the distance between target and substrate equal to 5 cm. Deposition time was controlled to 10 h (2 h for deposit TiO_2 and 8 h for deposit HAp) to obtain a uniform film thickness. The thickness of TiO_2+HAp films equal to 2 μm determined using minutest (3000 of a model) device. The samples was annealed by using furnace at 600°C for 1 h in still air. The Atomic Force Microscope (AFM) were used to investigate the particle size and topography surface of HAp and TiO_2 layer coated with Ti-6Al-7Nb alloys. The Scanning-Electron Microscopy (SEM) used to investigate the properties of surface after and before corrosion test. The driving force for formation of oxide layer on the mate under open circuit conditions. The results from EIS bode plot behavior under conditions of open circuit in Simulated Body Fluids (SBF) solution seem to give more information for the extent reactivity surface of alloy “Ti-6Al-7Nb”. The low capability of frequency (100 MHz) made the EIS probe the relaxation phenomena readily detected including surface intermediates and thus, studying the mechanisms of passivation and electrochemical corrosion (De Souz *et al*., 2006). The used SBF containing concentrations of ion which is similar to those in human body. The solution of Simulated Body Fluids (SBF) which is suggested by Kokubo (Ding, 2003) 0.305 g $MgCl_2$ $6H_2O$, 0.2775 g $CaCl_2$, 0.071 g Na_2SO_4, 7.9949 g NaCl, 0.3528 g $NaHCO_3$, 0.2235 g KCl, 0.147 g K_2HPO_4 in 1000 mL distilled water and pH adjusted to 7.4 at temperature of 37°C, the samples were soaked in SBF at test of electrochemical measurements.

RESULTS AND DISCUSSION

Atomic Force Microscopy (AFM): Figure 1a shows AFM as evidence by the scanning process for an area with dimensions pixels (48*49) for films HAp prepared by RF sputtering coated Ti-6Al-7Nb alloy and annealing at 600°C. Have semispherical peaks which is useful for medical application. The image shows the particle with micro size, although, the scale of particle with nano size, these belong to aggregation of particles. Figure 1b have range of particles with nano size (50,00-120,00 nm) and the largest number of particle size HAp through 90,00 nm. That is mean the coating RF sputtering process research to convert the particle size of target from micro to nan size.

Scanning Electron Microscope (SEM) before corrosion: The morphologies surface of coated specimens are shown in Fig. 2. In general, the observation of the image of SEM shows that the coated layer is smooth and fully coated substrate. Also, there are some few gaps and pores due

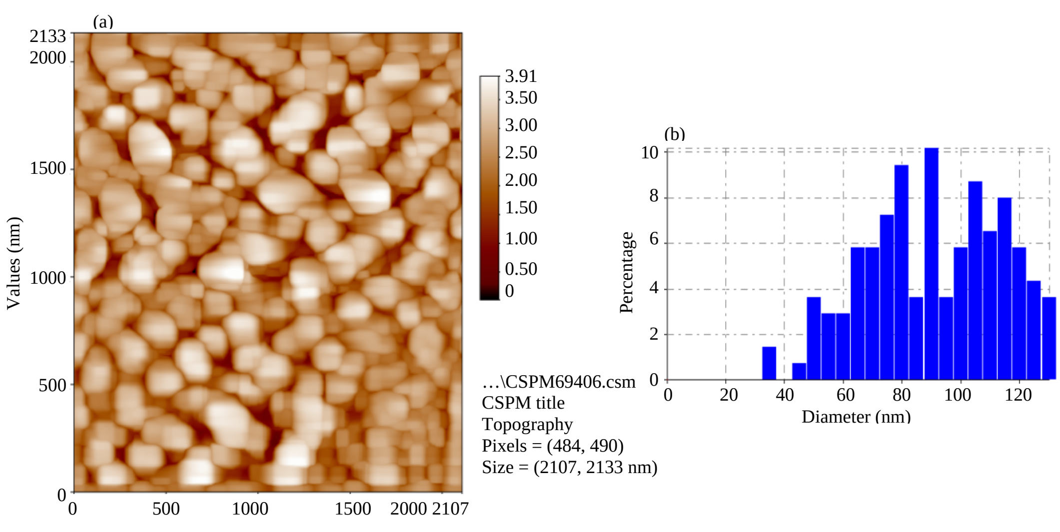

Fig. 1: Top view scan process and range of particle size for ceramic HAp in nano size coated Ti-6Al-7Nb alloy: a) AFM scan proses and b) The range of particle size and distribution (Granularity cumulation distribution chart)

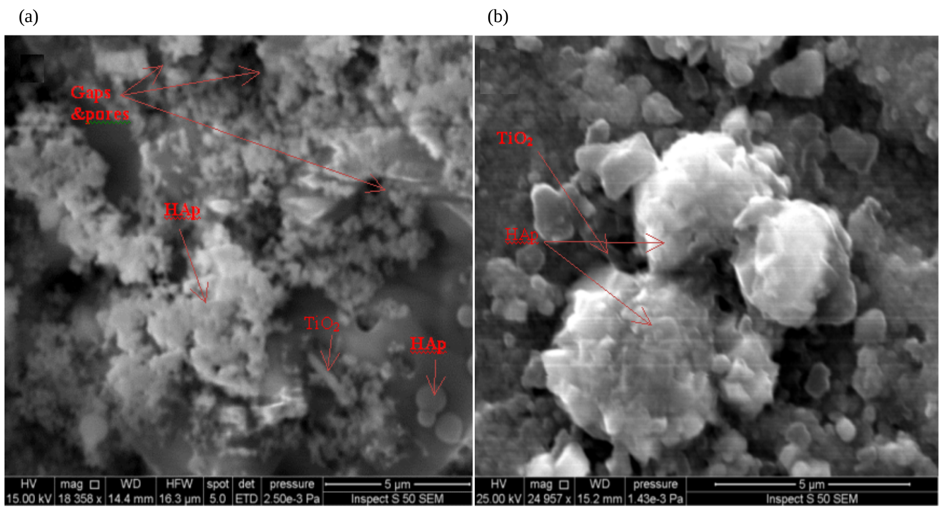

Fig. 2a, b): Morphology of TiO_2 and HAp coating Ti-6Al-7Nb alloy

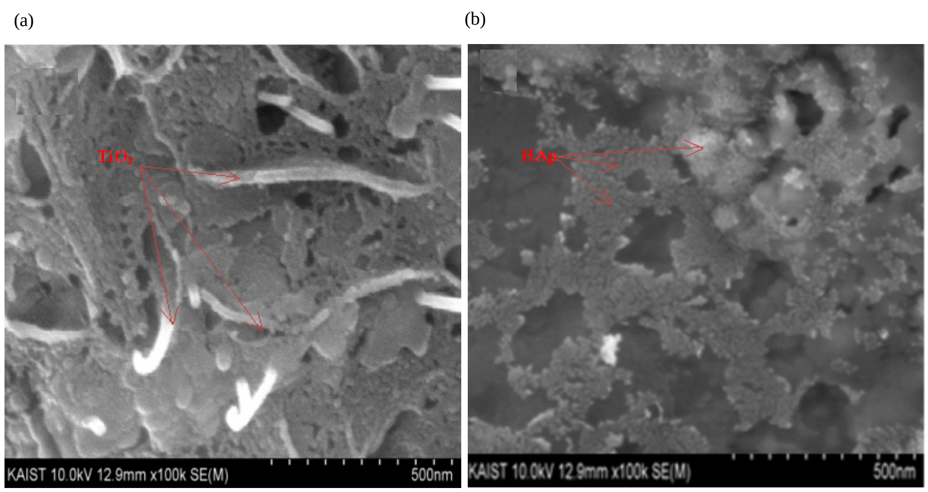

Fig. 3a, b): Morphology of TiO_2 and HAp coating Ti- 6Al-7Nb alloy after corrosion

to the heat treatment, these pores are important to connect the tissue and the used material through the implant process in the human body. It is worthy to noting that these pores work as a channels to increase the bond between the tissue and implant part. There is no any cracking observed in the outer layer of coating film belong to use thin film TiO_2.

Figure 2a, b shows the needle shape belong to growth TiO_2, the circular and lumbar were belong to growth HAp. The grain growth is associated with volume expansion due to heat treatment and it having the thermal expansion mid value between Ti alloy and HAp lead to reduce the difference in the thermal expansion between the HAp material and substrate during heating and cooling. Oxidation reaction which is similar to result obtained from composite TiO_2 and HAp coated Ti alloy using electrophoretic deposition (Mohan *et al*., 2012). Figure 2b clearly shows the aggregation for HAp nano size particles on the surface of sample with big flowers, this belongs to the (HAp and TiO_2) with nano size particles having strong surface charge which lead to aggregation.

Electrochemical corrosion

Scanning Electron Microscope (SEM) after corrosion: Figure 3a, b shown the effect of corrosion test on surface samples. The surface become more smooth due to chemical interaction between surface and ions composite of SBF with reaming small size of HAp. Thin layer TiO_2 coatings growth through gaps and porous with needle shape. The needle crystals shape of the TiO_2 coating provides the biologically compatible coating for medical application (Fomin *et al*., 2013).

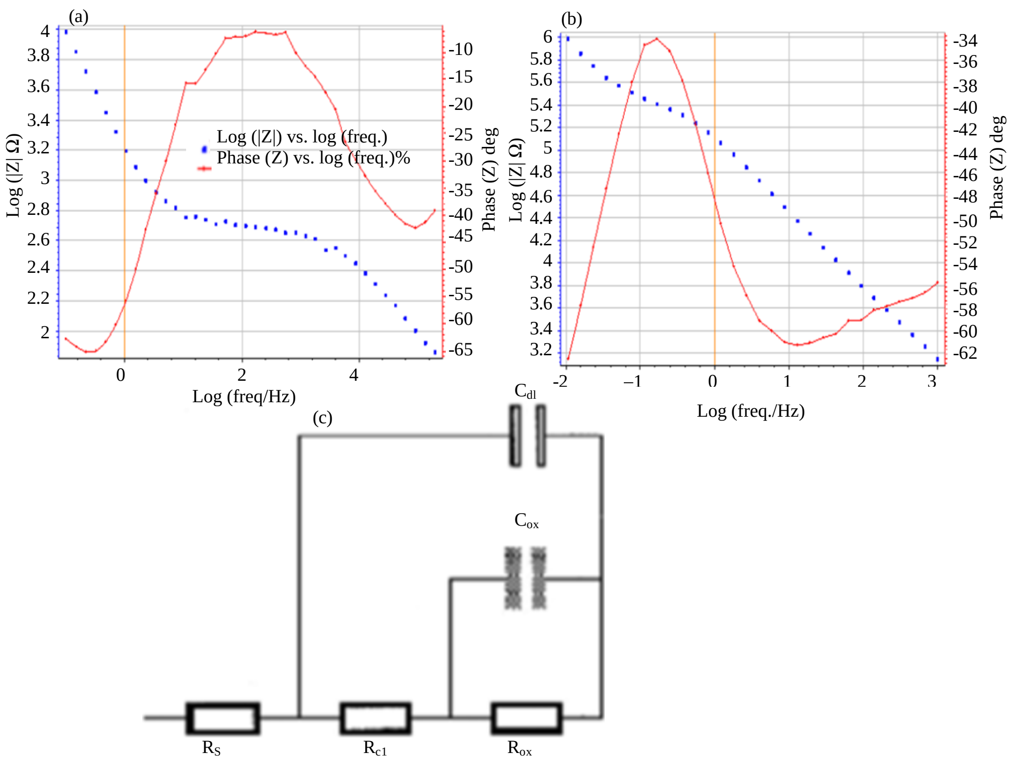

Fig. 4: Corrosion bode plots of: a) Uncoated Ti-6Al-7Nb substrate; b) Coated Ti-6Al-7Nb substrate with ($HAp+TiO_2$) and c) Equivalent circuit of the electrical using for analysis the illustrated experimental electrochemical impedance spectroscopy data

Electro chemical corrosion bode plots: Figure 4a, b showing two segments lines, theses lines corroborating to form passive layer represent corrosion bode plots of uncoated and coated Ti-6Al-7Nb substrate with ($HAp\&TiO_2$). The first line (log (Ð ZÐ) vs. log (freq.)) is representing the formation of a thin barrier of layer of oxide while the second line (phase (Z) vs. log (freq)) is related to thick outer film layer formation. The thickening rates form of the outer ($HAp\&TiO_2$) and inner oxide form.

This behaviour suggests that medium of SBF is favours self-passivation of Ti-6Al-7Nb (coated and uncoated) alloys while the highest efficacy a chive in the direction of passive film formation was notice. The results shows that the addition of TiO_2 and HAp as layers to Ti-6Al-7Nb mechanical traits improves by increasing the ability of the passive layers on the chemical dissolution to material of surface in (SBF) medium which is similar to result obtained from Wua. C and Ramaswamy (Wu *et al*., 2008). The passive layer enhancement by addition of (TiO_2 and HAp) as layers to Ti-6Al-7Nb by increasing the resistance of passive layer for chemical reaction in SBF. It can be notes from inner and outer values of the substrate in comparison to uncoated alloy at SBF. (For uncoated, the solution goes inside lattice of passive film rend it high defective and hence, the film becomes low stable. Impedance scan to EIS-bode plot prior the spa cement left immerse in solution until a steady state was achieve open circuit. At frequency domain 100 kHz-100 mHz, the measurement was carried out and the results are shown as bode plots of electrodes as represented in Fig. 4a, b.The electrochemical impedance spectroscopy result are shows equally and phase angle is a sensitive index to phenomena of surface occurred at electrolyte/electrode interface (Wu *et al*., 2008; Podhorodecki *et al*., 2009). As it is represent, the spectra in Fig 4b shows high capacitive worthy belong to typical of passive materials as represented with angle phase a remain for wide range close to 90° from medium to low frequencies.

This behaviour is more accentuated for pure Ti-6Al-7Nb alloy and more stable film suggested to form (TiO_2+HAp)-coated Ti-6Al-7Nb alloy. Is observed both samples that, although, it was calculated the electrochemical impedance at low frequency of 100 mHz, over this range there is no horizontal impedance plateau which can discerned in aspect, (log |z|-log freq.) high region relation become saturated with a phase angle drops to zero degree (Wu *et al*., 2008). The large phase of broad peak of angle peak show is interaction of two time constant, reflect the nature of bi-layer of passive film (TiO_2+HAp) coated and Ti-6Al-7Nb alloy. Ti-6Al-7Nb alloy comparing barrier porous outer and inner layer (Tamilselvi *et al*., 2006; Heakal *et al*., 1987, 2007). According to these facts the EIS data were examined according to the Equivalent Circuit (EC) which is show in Fig. 4c, the simulate solution/oxide/metal interface for Ti-6Al-7Nb alloy and oxid layer TiO_2 (Heakal *et al*., 2007). EC Model contain from circuit of the a simple Randles represent charge resistance transfer and layer of double capacitance (Rct and Cdl) in parallel branched arrangement with capacitance, resistance of passive film of oxide (Cox and Rox) and solution resistance (Rs) connected with whole are series. The CPE belong to apportionment times of relaxation this belong to the different surface degrees in roughness, random, influence and differences in surface layers ingredients impedance (ZCPE) represent Eq. 1 by Schutz (1993):

$$ZCPE = 1/Q_o(j\omega) \quad (1)$$

Where:

Q_o = Amount of Ω^{-1} cm^{-2} s^{-x} of CPE which is belong to the idealized capacitance (Cox) at ω =1

ω = Angular frequency ($\omega = 2\pi f$ rad s^{-1}) and $j = (-1)^{1/2}$

The magnitude of x can be between 1and -1 for a perfect inductor 1 for a perfect capacitor Ti-6Al-7Nb alloy. Fitting procedures by using in Eq. 2 transfer function (Ding, 1994) for proposed EC Model Fig. 4c adequately which represent the measured data error of 4% and the calculated EC parameters are in Table 1:

$$ZEC = R_S + \cfrac{1}{j\omega C_{di} + \cfrac{1}{R_{ct} + \cfrac{1}{(j\omega C_{ox})^x + \cfrac{1}{R_{ox}}}}} \quad (2)$$

The results shows the values of R_{ox} are greater than for R_{ct} by assumes the presence oxide film increases for coated substrate, the corrosion resistance to the sample and the EIS data commanded by passive film characteristics.

Table 1: Equivalent circuit parameters for formed passive film on Ti-6Al-7Nb alloy; Ti-6Al-7Nb coated (TiO_2+HAp) constant concentration

R_{ox}	kΩ (cm²)	Cox µF (cm⁻²)	x	R_{ct} Ω (cm²)	Cdl µF (cm⁻²)	Rs (Ω)
A	123.3	4.26	0.87	07.29	06.56	11.39
B	309.2	2.68	0.84	19.29	12.13	02.83

CONCLUSION

The RF magnetron sputtering was successful to convert the particle size of ceramic coated from micro to nano size through the sputtering. Use thin layer of TiO_2 is to enhance the capability of bonding of HAp layer with Ti-6Al-7Nb substrate and use HAp as up layer is to improved biocompatibility of implants. The corrosion resistance of Ti-6Al-7Nb alloy was enhancement by the TiO_2 coating the alloy as confirmed by potential dynamic polarization test with time OCP increasing positively, thus, indicate self-passivation for both the samples, the two layer (TiO_2+HAp) thicken rate comprising the oxide formed film is maximum. The results shown the mount of R_{ox} are more than those for R_{ct}, 309.2 kΩ cm^2 and 19.29 Ω cm^2 for Ti6-Al-7Nb coated with (TiO_2+HAp) and 123.3 kΩ cm^2 and 7.29 Ω cm^2 for Ti6-Al-7Nb uncoated, respectively which belong to oxide layer coated lead to increasing the corrosion resistance of the Ti6-Al-7Nb alloy.

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