Facile Coating of HAP on Ti6Al4V for Osseointegration

Shafaq Asrar
Department of Metallurgical Engineering
NED University of Engineering and Technology
Karachi, Pakistan
shafaqfara@neduet.edu.pk

Muhammad Tufail
NED University of Engineering and Technology
Karachi, Pakistan
mtufail@neduet.edu.pk

Ali Dad Chandio
Department of Metallurgical Engineering
NED University of Engineering and Technology
Karachi, Pakistan
alidad@neduet.edu.pk

Abstract-Ti6Al4V alloy is a material with great strength, low-slung modulus, inferior density, and a virtuous blend of mechanical and exceptional corrosion resistance. However, it does not offer good osseointegration and bone development properties. Conversely, hydroxyapatite (HAP) is highly bioactive in nature to bind with the nearby bone tissues when implanted in the host body. In this work, we have extracted HAP from bovine bones by using the thermal decomposition method. This was followed by its deposition onto the Ti6Al4V alloy using the Electrophoretic Deposition (EPD) technique. TiO_2 is used as a bond coat layer to increase the adhesion between HAP and Ti6Al4V alloy substrates. The coated samples after sintering exhibited excellent adhesion. This was followed by characterization using Scanning Electron Microscopy (SEM) and Fourier Transformed Infrared Spectroscopy (FTIR). FTIR and SEM confirm the formation of HAP and its presence after the immersion in SBF. Vicker hardness tester confirms the increase in hardness value of coated samples up to 35%. Potentiostat tests were conducted to compare the corrosion rate of both samples. In addition, the particle sizes were also identified by a laser particle analyzer, whereas X-Ray Diffraction (XRD) technique was also used to determine the crystalline phases of alloy and HAP.

Keywords-corrosion; electrophoretic deposition; hydroxiapatite; simulated body fluid; Ti6Al4V alloy

I. INTRODUCTION

Materials having biotic nature or host tissue compatibility can be implanted into living organisms to augment or replace impaired parts. Generally, metals, ceramics, polymers, and composites are materials widely used in biomedical applications. Amongst them, titanium-based alloys are some of the most widely used as implant materials [1]. Titanium and its alloys bear enhanced properties like excellent strength [2], optimum elastic modulus [3], low density [4], blend of other mechanical properties [5], and excellent corrosion resistance [6-12], needed for various applications including orthopedic [13], dental [14], and surgical implants [15], artificial joints [15], etc. It should be noted that the elastic modulus of titanium-based alloys is considerably close to bones' [16, 17] which makes it ideal for long term applications [18]. However, titanium based alloys do not possess good osseointegration [19] thereby requiring additional surface treatment. This means that there is a poor bond between titanium and bones causing implant loosening which is highly undesirable. Therefore, surface modification plays a vital role in optimum osseointegration [15, 20]. There are several techniques used in this regard such as: sand blasting [21, 22], etching [23], electrochemical treatment [24], and thermal spray coatings [25]. Amongst them, bio-ceramic coatings using, the hydroxyapatite (HAP - $Ca_{10}(PO_4)_6(OH)_2$) [26-28] are very promising for the modification of implant surfaces since they create strong bonding with bones [29-31]. One of the great advantages of the HAP is its great lifespan [32, 33]. The calcium phosphate (CaP) ratio of HAP is 1.67 which is highly stable at a normal temperature and its pH ranges from 4 to 12. However, the properties and resultant applications of HAP depend on morphology, size, chemical composition and crystallinity [31]. In addition, it provides speedy and durable fixation to the host bones and possesses osseoconductive properties [34], protecting the metal surfaces from the environmental effects and thereby reducing the discharge of metallic ions from the implant surface to the host body. The main advantage of CaP is that it is already present in the bones and teeth of the vertebrates [35]. Moreover, there are several methods to produce HAP such as: dry methods, wet methods, microwave (MW)-assisted methods, ball-milling or ultrasound, etc. [36]. Additionally, numerous coating strategies are available to coat HAP on metallic alloys, for instance: plasma spraying [37, 38], sol gel [39, 40], Electrophoretic Deposition (EPD) [11, 41-43], etc. Amongst them the most economically viable technique is EPD [44], offering a controlled coating composition with the process being highly pure [45], fast [41]

Corresponding author: Ali Dad Chandio

that could be used to coat complex shaped substrates [45]. In this study, HAP was produced from bovine bones since they are an abundant and economical source. This was followed by the deposition of HAP on chemically treated Ti6Al4V alloy.

II. EXPERIMENTAL PART

A. Materials

The materials utilized in this research are shown in Table I. All of them were of analytical grade and were used in as received condition.

TABLE I. MATERIALS/CHEMICALS USED

S.No.	Chemicals / materials	Purity (%)	Supplier
1	Ti-6Al-4V	99.0	Baoji North Hongsheng Industry & Trade Co., Ltd.
2	Sodium chloride	99.0	Sigma Aldrich
3	Sodium bicarbonate	99.0	Sigma Aldrich
4	Potassium chloride	99.0	Sigma Aldrich
5	Di sodium phosphate tri hydrate	99.0	Sigma Aldrich
6	Magnesium chloride hexa hydrate	99.0	Sigma Aldrich
7	Hydrochloric acid	99.0	Sigma Aldrich
8	Calcium chloride dehydrate	99.0	Sigma Aldrich
9	Di sodium sulphate	99.0	Sigma Aldrich
10	Cyano hydride tri methanol	99.0	Sigma Aldrich

B. Methods

1) Preparation of Hydroxyapatite

HAP was synthesized from bovine bones, purchased from the local market, by the thermal decomposition process. This was followed by their boiling in deionized water for about 3 hours to remove the unwanted fats. Additionally, second boiling was carried out for the deproteinization of bones. Thereafter, the bones were immersed in acetone for two hours in an ultrasonic bath for further cleaning. Subsequently, the bones were dried and cut into smaller sizes by mortar and pestle. The resultant powder was placed into a box furnace and heated at 1100°C at a heating rate of 5°C/min for 3 hours for the preparation of HAP. Later on, XRD and laser particle analysis were conducted to confirm the peaks and particle sizes of as-synthesized HAP powders respectively. The process details are shown in Figure 1.

2) Activation of Substrates

Titanium alloy Ti6Al4V was used as substrate in plate form, having a thickness of 2mm. The microstructure of the as-received Ti alloy was revealed by following the steps of grinding and polishing followed by etching for 20-25s in the Kroll's reagent (96ml distilled water + 6ml HNO3 + 2ml HF). A wet chemical etching process was carried out to enhance the surface available for coating at room temperature. Several chemicals were used to immerse the electrode into the solution for the desired time and then it was ready to be used as a substrate for coating. Next, we took an equal quantity of 5ml each for hydrochloric acid, nitric acid, hydrogen peroxide, sulfuric acid and introduced them into 30ml of distilled water followed by the immersion of substrates into the prepared solution for 3 hours. Then, titanium substrates were placed in 5 Molar NaOH solutions for 72 hours at room temperature. In the next step, the substrates were annealed in the air using a box furnace at 600°C followed by holding for 1 hour. This process was used to create the small nano-sized pits on the surface of the substrates used for the coating purpose. The samples were then considered ready for the EPD process.

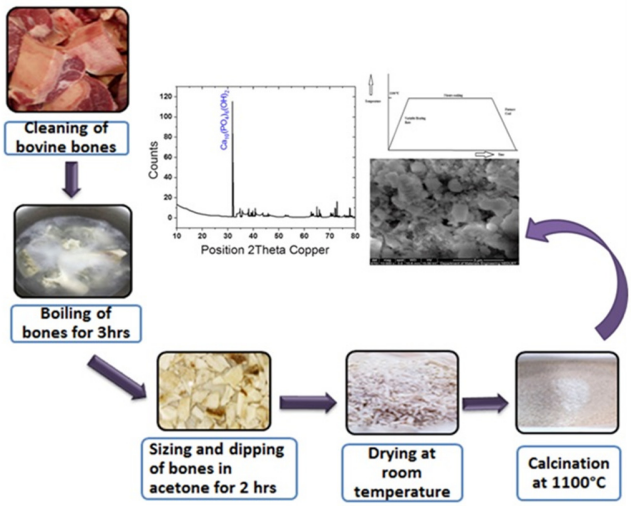

Fig. 1. Steps of producing HAP from bovine bones, calcination cycle, and XRD pattern of successfully produced HAP.

3) EPD of HAP

For the enhancement of adhesion properties of hydroxyapatite, Titania (TiO_2) was used as an intermediate layer between HAP and Titanium alloy substrate. The process flow chart is shown in Figure 2. In this process, an electrolytic solution containing 0.5g TiO_2 and 0.5g HAP was dissolved in 100ml ethanol solution followed by sonication for 15 minutes and was ultrasonically shook for 30 minutes. It was then left for settling for 20 minutes and was stirred again for 25 minutes at 40°C. The EPD process was done at 20V for 5 minutes while keeping the distance between electrodes at 2cm. The resultant coating was sintered in the tube furnace at 800°C. Finally, the samples were ready for characterization to further evaluate the properties of Ti-6Al-4V alloy coated with hydroxyapatite.

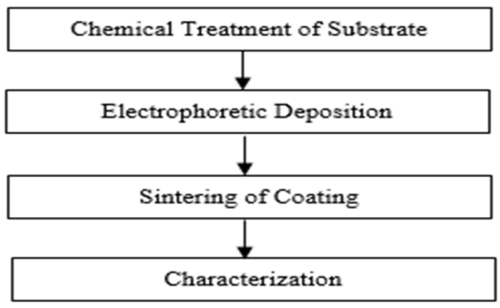

Fig. 2. Process flowchart of coating HAP on Ti-6Al-4V substrate.

III. RESULTS AND DISCUSSION

A. Particle Size Analysis

We used the BT-9300H laser particle analyzer for the determination of particle size of HAP powder. The results are shown in Figure 3. The average obtained particle size was 25.73 microns with respect to cumulative percentage.

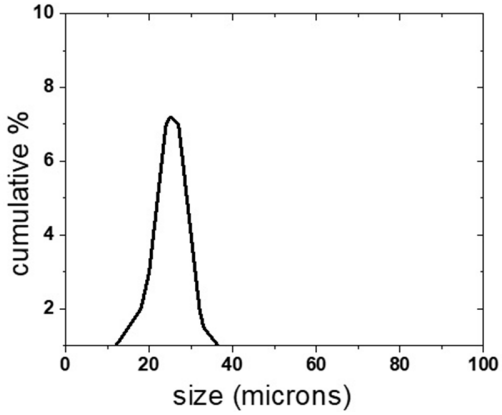

Fig. 3. Average particle size of HAP powder synthesized by bovine bones.

B. XRD Analysis

The X-pert Pro XRD DY3313 XRD machine operating at 40kV and 30mA using Cukα radiation was used to analyze the phase of the HAP. The diffraction pattern was recorded over 2θ at the scanning rate of 0.1 and was performed over the angular range from 10° to 79°. Figure 4 reveals the XRD spectra of bovine bones calcinated at 1100°C which is in good agreement with the standard HAP pattern [46, 47]. The calcinated sample peak at 31.8 confirms the formation of hydroxyapatite powder. Moreover, the XRD spectra of the chemically treated Ti alloy surface show the presence of TiO_2 and coated alloy confirming the presence of the HAP layer on the chemically treated Ti6Al4V.

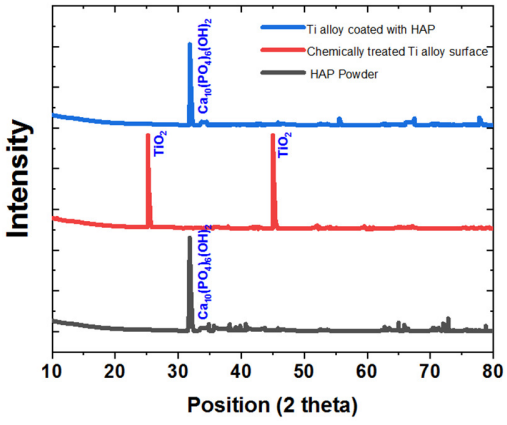

Fig. 4. XRD pattern of synthesised HAP, chemically treated surface and Titanium alloy coated with HAP powder after sintering.

C. Chemical Composition

The chemical composition of titanium alloy is found by using an X-ray fluorescence spectroscope (INNOV-X SYSTEMS) which is comparable to ASTM F136 standard [48]. The results are presented in Table II.

TABLE II. CHEMICAL COMPOSITION USING XRF ANALYSIS

Alloy	Titanium	Vanadium	Aluminum
ASTMF136	Balance	3.5-4.5	5.5-6.75
Ti6Al4V	Balance	4.17	6.12

D. Microstructures

The polarized light microscope OLYMPUS GX51 was used to reveal the microstructure of the as-received samples. It was found that the titanium alloy consists of two different phases: equiaxed Alpha and transformed Beta phase [49] which are shown in Figure 5(a). Figure 5(b) shows the SEM image of the HAP powder. The powder comprises of agglomerated fine particles while the shape of the particles is angular and non-spherical [50]. Figure 5(c) shows Ti6Al4V alloy coated with HAP after sintering which revealed that there was an enhanced linkage and the interconnection of HAP powders that exist on the coated surface morphology [51]. Figure 5(d) shows the HAP coated on Ti6Al4V after the immersion in SBF [52].

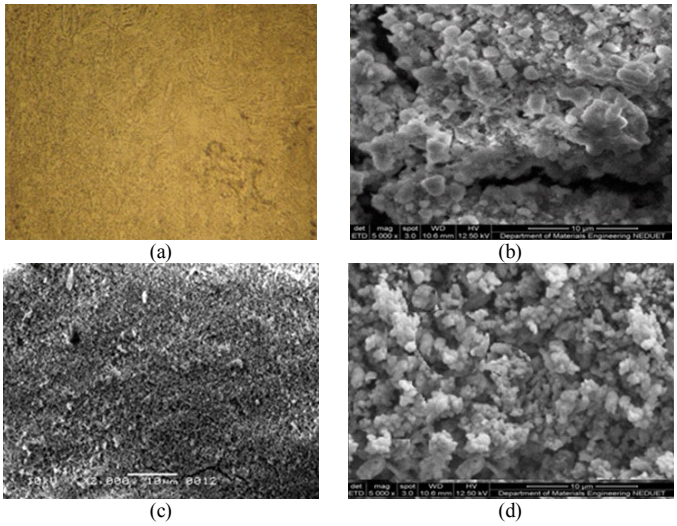

Fig. 5. (a) Optical structure of as received sample. (b) SEM image of the produced HAP powder. (c) Ti6Al4V coated with HAP and sintered at 800°C. (d) After immersion in SBF solution.

E. Hardness

Micro Vickers hardness tester (DIN EN 6507) was used to examine the hardness of bare and coated Ti6Al4V alloy by applying a load of 500g with a dwell time of 10s. The results are shown in Table III. A significant increase in hardness value of 468HV was obtained for a coated sample as compared to the pristine sample with a hardness value of 340HV. The Ti-based alloy produced a high hardness value which is a major requirement in being compatible with the body environment.

TABLE III. HARDNESS RESULTS

Alloy	Hardness (HV)
Ti6Al4V (before coating)	340
Ti6Al4V (after coating)	468

F. Corrosion Behavior

1) Immersion Test of Coated Samples in SBF

The coated samples of the HAP were immersed in Simulated Body Fluid (SBF) solution which was prepared according the procedure defined in [40]. The chemical composition of the SBF solution is shown in Table IV. The characterization was based upon the pH scale. For comparative analysis, the pH of the solution was measured before immersion and was found to be 7.4. The sample was then immersed in the solution enclosed in a glass beaker at 37°C for 7 days. Agitations and vibrations were provided to the beaker to create an artificial environment of fluid movement around the coating. After a passage of the prescribed time, the sample was removed from the solution. The solution pH was measured after the immersion and was found to be the same as before, i.e. 7.4. Therefore it was confirmed that no exchange of ions took place between the sample and SBF.

TABLE IV. CHEMICAL COMPOSITION OF THE SBF SOLUTION

S.No.	Chemicals	Amount
1	Sodium chloride	6.559g
2	Sodium bicarbonate	2.26g
3	Potassium chloride	0.3773g
4	Di potassium phosphate tri hydrate	0.1496g
5	Magnesium chloride hexa hydrate	0.3411g
6	Hydrochloric acid	10ml
7	Calcium chloride dehydrate	0.3635g
8	Di sodium sulphate	0.0731g
9	Cyano hydride tri methanol	6.0662g

2) FTIR

FTIR (Perkin Elmer spectrum one system) was used to identify the functional groups of HAP coated samples in the area of 400-4000cm^{-1}. The FTIR spectra before and after the immersion in SBF solution is shown in Figures 6 and 7. The PO_4^{3-} group displays peaks at 560 and 600cm^{-1} and at 1000–1100cm^{-1}. The peak at about 2600–3600cm^{-1} links to the hydrated OH^- ion of HA [53]. The peak from 2000 to 2200cm^{-1} shows the stretching of P-O-H [54]. The peak at 1490cm^{-1} matches CO_3^{2-} which specifies that HAP is a carbonated-apatite (HCA) [55]. The representative peaks of PO_4^{3-} appear at 1090, 1014, and 590cm^{-1}. The peak at 1650cm^{-1} shows the presence of H_2O [54].

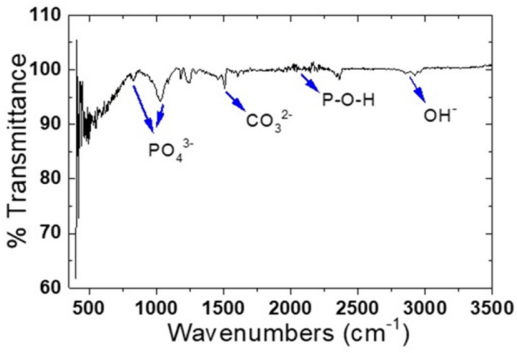

Fig. 6. FTIR spectra of Titanium alloy coated with HAP powder after the immersion in SBF solution.

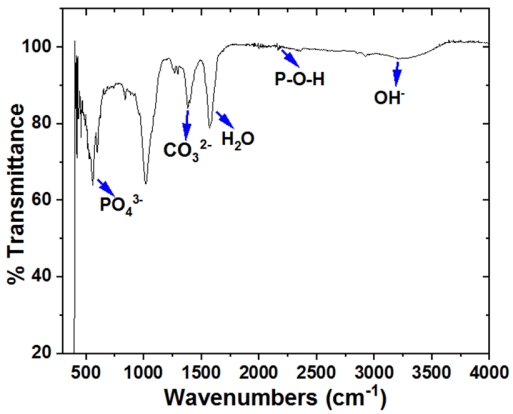

Fig. 7. FTIR spectra of the Titanium alloy coated with HAP powder before the immersion in SBF solution.

3) Potentiostat Test

Corrosion tests were conducted to find out the corrosion rate of the coated samples. The tests were conducted with a GAMRY potentiostat having a counter electrode (graphite) and a reference electrode (hydrogen) using Tafel. The corrosion rate was determined in an artificially created human body environment called SBF. The Tafel curve of the bare and coated sample is shown in Figure 8. The samples (i.e. the working electrode) were prepared according to the standard ASTM G108-94 analyzed at 37^{o}C using voltage ranges between -0.3 and 0.3V. Tafel curves were plotted at a rate of 1mv/sec to find the current density and potential. Figure 8 also shows the potentiodynamic curve for bare Ti6Al4V alloy having a current potential of -240V and current density of 1.63×10^{-4}μA/cm^2. Hence, the corrosion current density (I_{corr}) in the passive zone shifted down from 252nA to 701nA and the corrosion potential (E_{corr}) from -0.24V to 0.25V. The corrosion rate for HAP coated substrate was decreased as 11.95×10^{-3}mpy from 33.53×10^{-3}mpy for the bare Ti6Al4V alloy. The HAP coating consequence on Ti6Al4V alloy infers that the coating shows minimum release of metallic ions in SBF solution [14].

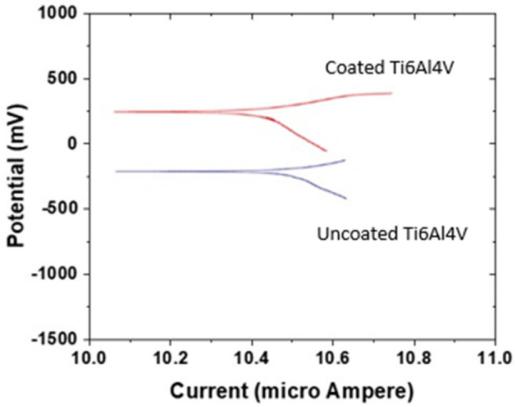

Fig. 8. Tafel curve of coated and uncoated Titanium alloy.

G. Adhesion

For evaluating the adhesion of the coated samples we used the scratch tester machine M-TGN80 having diamond intender

landed on the coated substrate producing an indent on the substrate surface up to a maximum load of 60N as shown in Figure 9. The result shows an excellent strength for the coating [56]. The morphological measurements were taken in the stereo microscope under low magnifications (5X) which reveal the distances of the crack from various aspects.

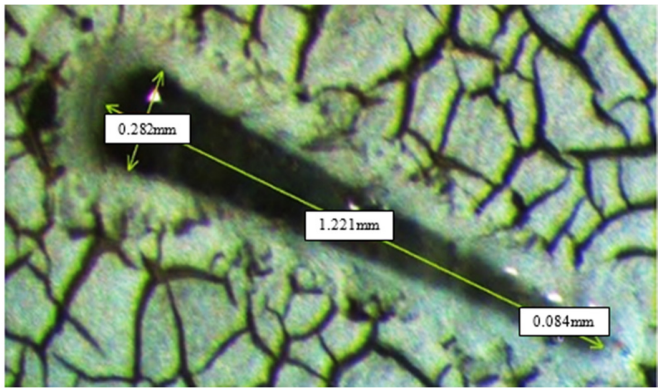

Fig. 9. Magnified scratch marked with the Adhesion tester.

IV. CONCLUSION

Hydroxyapatite is the furthermost noticeable inorganic substance for biomedical applications. Research showed that natural HAP from bovine bones can be synthesized by using the thermal decomposition method. From this study, no significant difference was observed between bovine bone-derived HAP and naturally occurring HAP. HAP powder electrophoretically deposited on Ti-6Al-4V alloy was used as substrate. The characterization of the coated sample confirmed that the coating enhanced the osseointegration properties of the implant. Moreover, the hardness of the coated samples was observed to be increased up to 35% as compared to the pristine samples. The corrosion rate for coated samples was found to be decreasing from 33.53×10^{-3}mpy to 11.95×10^{-3}mpy. Therefore, the resultant structures show that our produced samples can be used for a wide variety of medical applications with minimal expenses.

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AUTHORS PROFILE

Shafaq Asrar is currently serving as a Lecturer, and a Ph.D scholar in the department of Metallurgy Engineering, NED University.

Muhammad Tufail is currently serving as a Pro-Vice Chancellor of NED University. He has acquired his Ph.D from the University of Nottingham, UK

Ali Dad Chandio is currently serving as a Chairman of the Metallurgical Engineering Department, NED University. He has acquired his Ph.D from the University of Manchester, UK