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CORROSION CHARACTERSTICS OF HYDROXYAPATITE COATED TITANIUM SUBSTRATE FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

In this paper, the discussion has been made on corrosion behavior of the hydroxyapatite coatings over Titanium substrate using electro deposition method. Hydroxyapatite [Ca $(NO_3)_2$ + $(NH_4)2HPO_4$] has been synthesized at room temperature by the mixture of calcium nitrate and diammonium hydrogen phosphate and deposited over titanium substrates. The corrosion behavior of the coatings has been examined by treating the samples with Simulated Body Fluid solution. It was observed that the coated samples of HAP exhibits excellent corrosion resistance at the rate of 0.296×10^{-3} mm yr^{-1} when compared to the uncoated samples of titanium with 2.001×10^{-3} mm yr^{-1}. Also the surface roughness of the coatings were evaluated using AFM analysis with an average roughness of 6.67235 nm.

Key words: Calcium nitrate, Diammonium hydrogen phosphate, Hydroxyapatite, Titanium, Simulated body fluid.

Nomenclature: HAP – Hydroxyapatite; Ti – Titanium; Ca $(No_3)_2$ – Calcium nitrate; $(NH_4)2HPO_4$ – Diammonium hydrogen phosphate; AFM – Atomic force microscope; SBF – Simulated body fluid.

INTRODUCTION

Hap coatings, with both porous and actinomorphic-assembled lamellar structures, on Ti substrates can be conveniently fabricated through an electrochemical deposition route with the increasing voltage[1]. The surface morphology of the HAp coatings has significantly changed after immersion for several days in SBF solution as observed by FESEM. It can be concluded that the prepared HAp is bioactive by forming new apatite crystals when immersed in SBF solution[2]. The electrochemical results revealed that the M-HAP coating on 700 keV HELCDEB-treated Ti showed higher corrosion protection compared with the untreated Ti and the other coatings. The results showed that no large-scale dissolution

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occurred from the M-Hap coating in the SBF environment for 7 days, which proved the stability of the coating[3-5]. The Electro depositions of HAP over Ti plates were achieved with uniform coating thickness. In general HAP material is exhibits poor mechanical properties when compared to other biomaterials. Whereas during the deposition over Ti plates improves the stability of the implant, also this HAP act as an bioactive material and helps in formation of strong bonding between the implant and the surrounding tissue.[6-9] The chemical composition of the Ti substrates is listed in Table 1.

Table 1: Chemical composition of Ti substrates

Metals	Ti	C	N	O_2	Fe	H
%	98.60	0.8	0.03	0.25	0.30	0.015

EXPERIMENTAL

Synthesis of HAP powder

The HAP powder has been synthesized using the combination of calcium nitrate and diammonium phosphate. Initially both the salts are taken with the measurements and molar concentrations discussed in Table 2. Both the salts were mixed with distilled water separately. Each solution is stirred continuously using magnetic stirrer at 350 RPM for 30 minutes, to ensure complete dissolution of salts. For titration process, calcium nitrate is kept in the beaker and the di-ammonium phosphate solution is transferred to burette.

Table 2: Molar concentration and weight of salts before titration

Molar concentration	Salt	Vol. of liquid in mL	Weight of salt in g
0.1	Calcium nitrate	500	32.818
0.239	Di-ammonium hydrogen phosphate	500	5.781

The solution containing calcium is kept in a magnetic stirrer stirred continuously at the rate of 350 RPM and the phosphate solution is added drop wise at the rate of 3 mL/min as shown in Fig 1(a). During the process the solution in the beaker turns milky white this precipitate was aged overnight and then washed with double distilled water to ensure complete removal of impurities. The washed solution is then centrifuged in a cooling centrifuge at 2500 RPM for 15 minutes maintained at 4°C so as to obtain a sol gel state. The sol gel sample is then dried in a hot air oven maintained at 80°C. After drying, the solid sample is crushed using mortar and pestle to obtain powder form as shown in Fig. 1 (b).

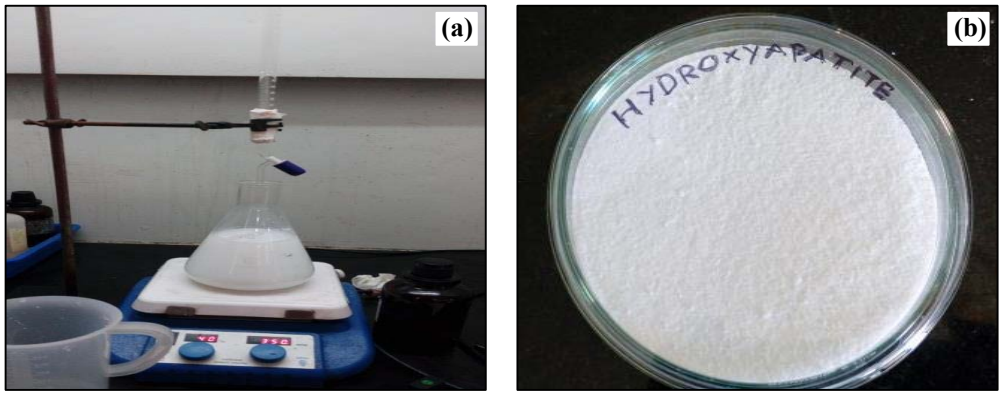

Fig. 1: (a) Titration of calcium nitrate and Di-ammonium phosphate (b) Final HAP powder

Electro deposition of HAP over Ti substrate

Initially the Ti substrates were cleaned mechanically and etched with 12 M of HCl at 80°C for 1 hour. After the etching process, the substrate is washed with distilled water and dried. The electro deposition was carried out in an electro chemical cell making Ti substrate as cathode and Pt as Anode. The electrodes are maintained with the distance of 40 mm. The electrolytic solution contains 0.4 M of calcium nitrate [Ca $(NO_3)_2$] and 0.239 M of diammonium hydrogen phosphate [$(NH_4)2HPO_4$] with Ca/P ratio 1.67. The salts were dissolved in 60 mL of distilled water each. The dissolved salts were then mixed into a 200 mL beaker. 0.1 M dil. HCl was added to make a clear solution and the pH was maintained at 3.5. The temperature was maintained at 80°C for 1 hr under constant applied potential (voltage) of 5V during the process. The process parameters of the deposition were discussed in Table 3.

Table 3: Process parameters of electro deposition

S. No.	Components	Levels
1	Voltage (V)	5
2	Temperature (^{0}C)	80
3	Distance (mm)	40
4	Deposition duration (min)	60
5	Cathode	Ti Electrode
6	Anode	Pt Electrode

During the electrolysis process the following reactions are observed. (1) Initially the electrolyte undergoes equilibrium condition.

$$H_2PO_4 \longleftrightarrow HPO_4^{2-} + H^+ \quad \ldots(1)$$

$$2H_2O + 2e \longrightarrow H_2 + 2OH- \quad \ldots(2)$$

$$Ca^{2+} + HPO_4^{2-} + 2H_2O \longrightarrow CaHPO_4.2H_2O \quad \ldots(3)$$

$$10CaHPO_4 + 2OH- \longrightarrow Ca10\ (PO_4)_6(OH)_2 + 4PO_4^{3-} + 10H^+ \quad \ldots(4)$$

(2) The solution in the cathode side has decomposed into hydrogen gas and hydroxide ions. (3)

HPO_4^{2-} combines with Ca^{2+} to produce $CaHPO_4.2H_2O$ precipitation and deposits on the surface of the substrate. (4) Finally the OH- in the solution causes the following reaction to take place. The coated substrate was rinsed with distilled water and dried in hot air oven maintained at 80°C.

Simulated body fluid

The SBF solution has prepared for the corrosion test. The SBF solution contains 7.996 g of NaCl, 0.350 g of $NaHCO_3$, 0.224 g of KCl, 0.228 g of $K_2HPO_4.3H_2O$, 0.305 g of $MgCl_2.6H_2O$ and 40 mL of 1 M HCl Per liter of solution. The electrolyte was maintained at the pH of 7.4.

RESULTS AND DISCUSSION

The coated samples were undergone various tests for the identification of surface morphological characteristics of the samples and to understand the corrosion behavior of the coatings.

X-ray diffraction

The X-Ray diffraction pattern of synthesized HAP powder and HAP thin film. The XRD pattern thus obtained shows the presence of pure HAp phase. It is identified that the crystal structure of HAP coated Ti substrates are Hexagonal in nature and angle of incidence is about 20-90 degrees. Also the peak obtained at 38^0.4". The Fig. 2 shows the peak obtained for the coated sample.

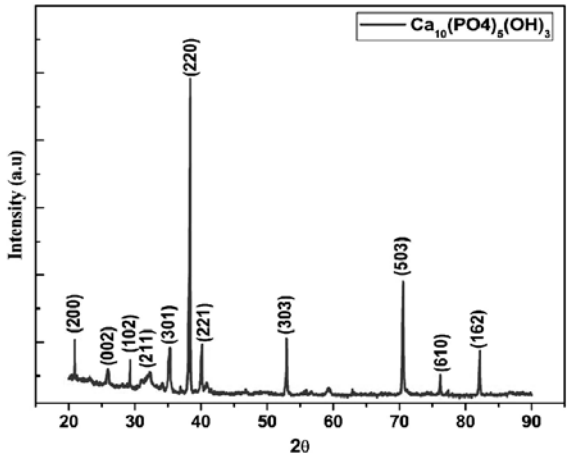

Fig. 2: XRD of HAP coated Ti substrates

Atomic force microscope

The AFM analysis was carried out for the coated samples. This results are shown in Fig. 3 (a). The peaks denote the roughness of the surface. The average surface roughness is found to be 6.67235 nm. From Fig. 3 (b), we can depict that the grain size of HAP, is found to be between 17 – 36 nm.

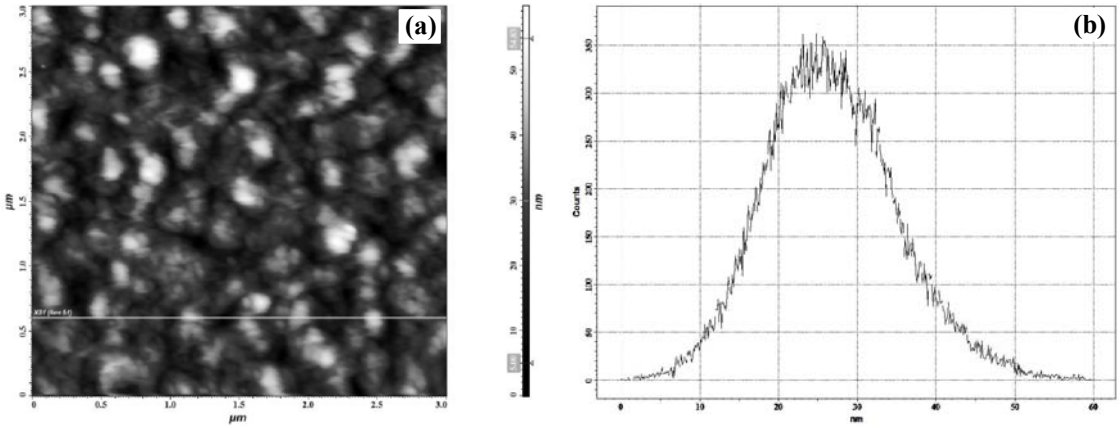

Fig. 3: (a) AFM of HAP coated Ti (b) Histogram analysis of coated samples

Corrosion behavior

The corrosion behavior of the coated samples is list in the Table 4. Also the graph Fig. 4 as been plotted between the corrosion resistance between uncoated Ti substrates and

HAP coated Ti substrates. It is observed that the corrosion rate of uncoated Ti substrate is 2.001×10^{-3} mm yr^{-1} whereas the HAP coated Ti substrates exhibits 0.296 x 10-3 mm yr^{-1}.

Table 4: Corrosion behavior of the coated and uncoated samples

Samples	Ecorr (V)	Icorr (nA cm^{-2})	Corrosion rate ($\times 10^{-3}$ mm yr-1)	Rct (kΩ cm^2)	Cdl (nF cm^{-2})
Ti Substrate	-0.77	180.0	2.001	4.2	15.45
Hydroxyapatite Coated Ti Substrate	-0.5	52.3	0.296	46.36	0.18

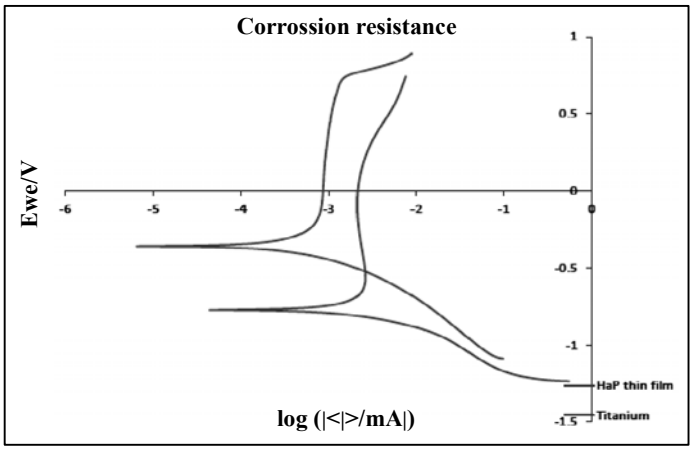

Fig. 4: Corrosion characteristics for coated Vs uncoated

CONCLUSION

The HAP deposited Ti substrates were examined for the corrosion resistance characteristics. It is observed that the coated samples exhibit excellent corrosion resistance (0.296 x 10^{-3} mm yr^{-1}) property when compared to the uncoated samples (2.001×10^{-3} mm yr^{-1}) as the result of corrosion test. Also the presence of HAP phase has been identified in XRD analysis for the chemically synthesized HAP powder. The average surface roughness is found to be 6.67235 nm through AFM analysis of the coated samples.

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