

# **Electrophoretic Deposition of Hydroxyapatite on Ti6Al4V**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT  
OF THE REQUIREMENT FOR THE DEGREE OF

**BACHELOR OF TECHNOLOGY  
IN  
BIO-MEDICAL ENGINEERING**

By

**RAJAN ANAND  
(Roll No- 108BM018)**



**DEPARTMENT OF BIOTECHNOLOGY & MEDICAL ENGINEERING  
NATIONAL INSTITUTE OF TECHNOLOGY**

**ROURKELA**

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*Under the guidance of*  
**Dr. Amit Biswas**



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**NATIONAL INSTITUTE OF TECHNOLOGY**

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**NATIONAL INSTITUTE OF TECHNOLOGY  
ROURKELA**

**CERTIFICATE**

This is to certify that the project titled “Electrophoretic deposition of hydroxy-apatite on Ti6Al4V” submitted by **Mr. Rajan Anand (108BM018)** in the partial fulfillment of the requirements for the award of Bachelor of Technology in Bio-Medical Engineering during session 2008-2012 at National Institute of Technology, Rourkela and is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge the matter embodied in the thesis has not been submitted to any other University/Institute for award of any Degree/Diploma.

Date:

**Dr. Amit Biswas**  
**Assistant Professor**  
Department of Bio-Technology and Medical Engineering  
National Institute of Technology  
Rourkela-769008

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**Rajan Anand**

**Roll no. – 108bm018**

**B.Tech( Bio-medical Engineering)**

## Abbreviations:

<b>Ti6Al4V</b>	:	<b>Titanium-6Aluminium-4Vanadium</b>
<b>HAp</b>	:	<b>Hydroxyapatite</b>
<b>EPD</b>	:	<b>Electrophoretic deposition</b>
<b>Ca (NO<sub>3</sub>)<sub>2</sub>·4 H<sub>2</sub>O</b>	:	<b>Calcium nitrate tetra hydrate</b>
<b>(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub></b>	:	<b>Di-ammonium hydrogen phosphate</b>
<b>NH<sub>4</sub>OH</b>	:	<b>Ammonium solution</b>
<b>SEM</b>	:	<b>Scanning electron microscope</b>
<b>XRD</b>	:	<b>X-ray diffraction</b>
<b>V</b>	:	<b>Voltage</b>
<b>C</b>	:	<b>Centigrade</b>
<b>EDS</b>	:	<b>Energy dispersive spectroscopy</b>

## List of figures:

Figure number:	Figure description:	Page number:
<b>Figure 3.1</b>	<i>Flowchart of methodology</i>	12
<b>Figure 3.2</b>	<i>Flowchart of preparation of sintered and non-sintered hydroxyapatite(HAp)</i>	15
<b>Figure 4.1</b>	<i>Scanning electron micrograph of non-sintered HAp coating for 5 minutes at different magnification (A) 500X (B) 12000X.</i>	20
<b>Figure 4.2</b>	<i>Scanning electron micrograph of non-sintered HAp coating for 10 minutes</i>	21
<b>Figure 4.3</b>	<i>Scanning electron micrograph deposited non-sintered HAp coating for 15 minutes.</i>	21
<b>Figure 4.4</b>	<i>Scanning electron micrograph non-sintered HAp coating for 5 minutes</i>	22
<b>Figure 4.5</b>	<i>Scanning electron micrograph of non-sintered HAp coating at 10000X magnification for varying deposition time (A) 10 minutes, (B) 15 minutes</i>	22
<b>Figure 4.6</b>	<i>Scanning electron micrograph of surface Coated from (A) non-sintered HAp, (B) sintered HAp for 5 minutes</i>	23
<b>Figure 4.7</b>	<i>Energy dispersive spectra of non-sintered HAp coated surface</i>	24
<b>Figure 4.8</b>	<i>Energy dispersive spectra of sintered HAp coated surface</i>	25
<b>Figure 4.9</b>	<i>X-ray diffraction plot of sintered HAp</i>	26
<b>Figure 4.10</b>	<i>X-ray diffraction plot of non-sintered HAp</i>	27
<b>Figure 4.11</b>	<i>X-ray diffraction plot of Non-sintered hydroxyapatite for (A) 10 minutes, (B)15 minutes at 3.5 pH</i>	28

## List of table

<b>Table number</b>	<b>Table description</b>	<b>Page number</b>
<b>3.1</b>	<i>Samples prepared from non-sintered HAp at different time and temperature.</i>	16
<b>3.2</b>	<i>Samples prepared from sintered HAp at different time and temperature.</i>	16

## Table of content

Contents	Page number
Abbreviations	v
List of figures	vi
List of table	vii
Abstract	x
<b>Chapter 1: Introduction</b>	1`
1.1. Introduction	2
<b>Chapter 2: Literature review</b>	4
2.1 Bio-materials	5
2.1.1 Ti alloy (Ti 6Al 4V)	6
2.2 Surface modification	6
2.2.1 Hydroxyapatite	7
2.2.2 Surface modification technique for Ti6Al4V	9
2.2.2.1 Electrophoretic deposition (EPD):	9
2.3 Objectives	10
<b>Chapter 3: Materials and Methods</b>	11
3.1 work methodology	12
3.2 Preparation of titanium sample	13
3.2.1 Cutting	13
3.2.2 Grinding	13
3.2.3 Paper polishing	13
3.2.4 Cloth polishing	13
3.2.5 Diamond polishing	13
3.3 Preparation of hydroxyapatite	14
3.4 Preparation of HAp solution for electrophoretic deposition:	14
3.5 Parameters used for sample preparation	16

3.6 Characterization of the HAp and the coated surface of the Ti6Al4V	17
3.6.1 X- ray diffraction (XRD)	17
3.6.2 Scanning electron microscope (SEM)	18
3.6.3 Energy dispersive spectroscopy (EDS)	18
<b>Chapter 4: Results and discussions</b>	19
4.1 Morphological characterization	20
4.1.1 Difference between sintered and non-sintered HAp coating	22
4.1.1.1 Non-sintered HAp coating at same pH for different coating time	22
4.1.1.2 Difference between deposition of sintered and non-sintered HAp at pH 1.5 for 5 minutes	23
4.2 Energy dispersive Spectroscopy	24
4.3 Phase identification	26
<b>Chapter 5: Conclusions</b>	29
<b>REFERENCES</b>	31

## Abstract

In the present study, electrophoretic deposition of sintered and non sintered hydroxyapatite on Ti6Al4V has been carried out at a constant voltage of 30V for 5, 10 and 15 minute duration at different pH values of 1.5, 2.5 and 3.5 respectively for improving the property of coated layer. An uniform coating of hydroxyapatite (HAp) will results in a better cellular activity. As-received Ti-6Al-4V samples are polished by following the standard metallographic technique to prepare a scratch free surface. After coating under different processing conditions the surface are characterized by scanning electron microscopy (SEM) for morphological studies and x-ray diffraction technique for phase analysis. SEM images show that at lower pH value 1.5 and constant voltage 30V crack were not present at coating surface. Comparison between sintered (900° for 2 hrs) and non-sintered hydroxyapatite deposition and phase characterization analysis was done by XRD analysis. XRD analysis indicated that before sintering, some other compounds were present in HAp powder but after sintering they were not oxidized. The presence of chemical elements on the deposited surface was assessed by EDS.

**(Keywords:** Ti6Al4V, Electrophoretic deposition, Hydroxyapatite, XRD, SEM, EDS )

# *CHAPTER 1*

## **INTRODUCTION**

## 1.1. Introduction

The electrophoresis phenomenon has come in to existence from the beginning of the 19<sup>th</sup> century [1]. In 1917, Davey and General electric was awarded for his patent for electrophoretic painting. From the past 40 years it has been seen that electrophoretic deposition method has been vastly used in ceramic technology.

Titanium and its alloy (e.g. Ti 6Al 4 V) are generally used for the orthopedic application because of its high toughness, high corrosion resistance, biocompatibility and high strength [2, 6]. It has been seen that Ti alloy are increasingly used in the field of medical implant application for the two decades due oxide (TiO<sub>2</sub>) formation of titanium on to the surface of the implant. Due to formation of the oxide the titanium implant become more corrosion resistance and biocompatible [2-4]. Metallic materials are very sensitive to corrosion attack by the body fluids, with the subsequent release of metallic ion which might be cause adverse affect to the surrounding tissue. Adhering properties of the cells and proteins of the body is depend on the surface properties of the biomaterial [4]. Many number of coating methods are presents i.e. chemical treatment, physical vapor deposition, electrophoretic deposition, electrochemical treatment, plasma spray deposition, ion implantation, thermal oxidation [4-6]. Titanium implant is generally coated with hydroxyapatite that is a bio-ceramic which has similar constituents as human bone and teeth [2, 7, 8].

Chemical formulae of hydroxyapatite is  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \cdot 10\text{H}_2\text{O}$ . In hydroxyapatite the ratio of calcium and phosphate is 1.67[2, 4]. Hydroxyapatite coating decreases the release of metallic ions by acting like a barrier and also during coating the bioactivity of the plants increase [9]. Generally sintering temperature of the hydroxyapatite is kept below 850°C because above 850°C temperature, decomposition of the hydroxyapatite may possible [10]. EPD has capability to be used with different- different type of material and the combination of the material [11]. Electrophoretic deposition is one of the wet deposition method that is used for the film formation [12]. Electrophoresis and di-electrophoresis are method those are highly applicable in biology, pharmaceutical sciences, biochemistry, materials science, biotechnology and chemistry for evaluation of biological materials, e.g. enzymes, proteins, cells, as well as colloids, polymers and solid inorganic particles. Due to requirement of simple

processing equipment and infrastructure this EPD method is cost effective method [9-13]. Actually EPD is a colloidal processing technique that is used for the electrophoresis mechanism for the movement of the charge particle under the electric field [7]. EPD is applied to assemble spherical colloid into highly ordered colloidal crystal [6, 7, 13]. EPD is widely used in the lab because of efficiency, flexibility and control of thickness [14-16]. EPD has now become one of the most applied technique for the formation of thin and thick layer for both experimental and industrial process [17]. In EPD process, suspended charge particle are migrated to-ward the opposite charged electrode under the dc electric charged field [6, 7, 13].

In the experimental work first the sample of Ti 6Al 4V process through different processing technique. Hydroxyapatite is prepared from calcium nitrate tetra-hydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and di-ammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ). Suspension solution concentration 20gm per liter of ethanol was taken. Samples were prepared by varying the pH value and deposition time. Before deposition, solution of HAp and ethanol are mixed at magnetic stirrer for 30 minutes for better mixing. The electrophoretic deposition is done at constant voltage of 30 Volt (V). Deposition was done by varying the time and pH value of solution for preparation of the sample. The characterization was done from SEM for surface morphology and XRD done for the phase identification and EDS for the element identification.

# *CHAPTER 2*

**LITERATURE**

**REVIEW**

## **2.1 Bio-materials:-**

Any natural or synthetic materials, which have interaction with the living tissue and biological fluid and used to repair damage parts of the body or to replace the damage parts of the body are called bio-material. Bio-compatibility is the basic requirement of the biomaterial due to which material producing effectively producing the host response for the desired application. The research field of biomaterials is considered challenging and attractive because of its potential applications to enhance the quality of life. The research field of bio-material faces various complexities when it is implant in the biological environment for restoring or maintaining the organ functions. Many numbers of medical devices are made from the bio-materials for orthosis or prosthesis applications. Various medical devices have made from the biomaterials including elbow implant, hip implant, teeth implant, eye implant, artificial heart valve, eye lenses, artificial pancreas, artificial heart, and many other types of bone implants. Initially, in the past only few type of material were used for implantation but now various types of biomaterials were used for the bio-medical application. Many type of bio-materials, that are used for the bio-medical application are metallic, polymeric, ceramic and composite biomaterial. According to the requirement of the implants, composites of the same material or the composites of the different materials were used for the implant formation.

Many bio-materials are used for the biomedical application like stainless steel is used for the joint replacement, bone fixation, heart valve and titanium and its alloys are used for joint replacement, dental bridge and dental implant formation. Gold are used for dental filling and silver is used for pacemaker wire, dental amalgams.

Ceramic biomaterial that are used for the bio-medical application are aluminum oxides ie used for hip implant and dental implant, zirconia ie. Used for the hip implant, calcium phosphate i.e used for bone graft substitutes and surface coating on the total joint replacements, calcium sulfate, carbon e.i used for heart valve coating and orthopedic implant.

Polymer biomaterials that are used for the biomedical applications are nylon e.i used for making surgical suture and tracheal tube, silicon rubber i.e used for the formation of cell scaffold and fracture fixation, polyethylene i.e used for formation of hip and knee joint and artificial tendons and ligaments.

### **2.1.1. Ti alloy (Ti 6Al 4V)**

Metallic materials are sensitive to corrosion attack by the body fluids, with subsequent release of metallic ions which might cause adverse affects to the surrounding tissues [8]. Thus, the properties of the surface oxide layer, such as roughness, topography and composition, takes place an important role in the biocompatibility of a Ti alloy (Ti 6Al 4V) implant [6]. Many numbers of techniques have been developed to improve the surface properties of Ti implants. These include electrophoretic deposition, ion implantation, chemical vapor deposition, electrolytic deposition, plasma spray deposition etc [4-6, 8, 10].

## **2.2. Surface modification**

Surfaces of commercially purchased biomaterials implants are not found so good both with respect to their surface morphology and their surface chemistry. Surface modification is not just modify the surface, it improves adhesion properties, micro-cleaning, functionalization of amine, hydroxyl, carboxyl etc, also produces bio-compatibility, create permanent wet ability and also produces hydrophobic characteristics. Through the surface modification technique, many types of surfaces can be designed which direct proper biological response in a particular cell/tissue situation, with the purpose of shortening healing time and minimizing toxic reaction. Surface modification is used to improving the mechanical properties, reliability, stability and long-term performance of the medical device. Surface modification of materials provides ideal bulk properties to the surface of implant material (e.g. Tensile strength or stiffness) with the desired surface properties (e.g. Bio-compatibility or bio-activity).

### **2.2.1. Hydroxyapatite**

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , HAp) a bio-ceramic which has similar mineral constituents of the human bones and teeth [1-8, 13, 14]. In hydroxyapatite Ca and P ratio is 1.67 [1, 3]. The hap coating would decrease the release of the metallic ions by acting like a barrier, and at the same time it enhanced the bioactivity of the implants [10, 12, 16]. HAp is the most important calcium compounds found in natural hard tissues as mineral phase. HAp acts as a support in hard tissues and is responsible for stiffness of bone, dentin and enamel. HAp is being widely used in medical and dental applications due to its close matching in chemical composition and high biocompatibility with natural bone tissue [5]. However, its application in the human body has been limited due to its poor mechanical properties. Unluckily, the poor mechanical properties of hap devices severely inhibit its clinical applications for high load bearing conditions [5, 6, 10]. As a result, the significant research activity has been associated with the development of hap coatings on metals or hap composites. Due to osteo-integration properties of the hydroxyapatite, the coating of hap is done on to the other implants like titanium alloys and stainless steel 316L [4]. Titanium is suitable metal substrate for hap coating, due to its similar mechanical properties to bone and also high corrosion resistance. Many types coating techniques have been used for the preparation of hap coatings, such as plasma spraying, sol-gel deposition, dip coating, chemical solution deposition, sputter coating, bio-mimetic coating and electrophoresis [10-16]. HAp can prepare from synthetic chemicals or obtained from natural constituents of hydroxyapatite. HAp can prepare from precipitation method, emulsion or micro-emulsion technique, sol-gel method, solid state reaction [10].

### **2.2.2 Surface modification technique for Ti6Al4V**

Titanium and its alloys are generally use in aeronautical, marine and chemical industries owing to their specific properties such as excellent corrosion, oxidation and high temperature resistance and high strength. Nevertheless the application of application of titanium alloys under severe were and friction conditions is highly restricted due to their poor tri-biological properties such as high friction coefficient and high hardness. Main properties of biomaterials that are seen during the selection of the biomaterial are biocompatibility, resistance to corrosion or controlled

degradability, elastic modulus, fracture toughness and fatigue strength for the specific biomedical application. Titanium and its alloys have many biomedical applications, especially as hard tissue replacements because of their relatively low modulus, excellent fatigue strength, excellent formability, as well as superior biocompatibility and corrosion resistance [18]. Titanium and its alloys are generally considered to be bio-inert materials because they cannot bond directly to bone tissues in the human body. Surface modification is the fundamental of physiochemical interaction between the biomaterial and the physiological environment at the molecular, cellular and tissue level. The function of surface modification is to change the physical and chemical properties of the surface to improve the functionality of the original material. There are many ways through which combat wear, corrosion and galling can be divided into three categories.

First by changing the surface metallurgy in which titanium and its alloys are heat treated to achieve different properties such as ductility, machinability, structural stability. Laser melting is one of the methods of changing surface metallurgy in which high power laser beam is used to melt the surface.

Second by changing surface chemistry of the titanium and its alloys to increase the wear and corrosion resistance, decrease the coefficient of friction. Methods used for changing surface chemistry are oxidation through chemical methods, oxidation through electrochemical methods, oxidation through thermo-chemical methods, nitriding through gas nitriding, nitriding through plasma nitriding, carburization, diffusion process, ion implantation, laser surface alloying by laser gas alloying, laser surface alloying by laser surface alloying.

Third, By adding a surface layer or coating on titanium and its alloys to improve its surface properties. Following methods are used for improving the surface properties are thermal spray coating by plasma spraying, electro-chemical deposition, thermal spraying, laser cladding, chemical vapor deposition, physical vapor deposition, electrophoretic deposition.

#### ***2.2.2.1 Electrophoretic deposition (EPD):***

In late 1950s, electrophoretic coating began to take its present shape. In 1965, the first electrophoretic product was patent. It has been found that application in the past 40 years mainly in the ceramic technology [6]. Electrophoretic deposition is actually a two step process in which in the first step suspended charge particle in the liquid is migrated toward the oppositely charged

electrode and in the second step the deposited particles on the electrode forming a relatively dense and homogeneous film [6, 5, 11]. Another EPD processing is required for the further densify the deposits and to eliminate porosity that's also include suitable heat treatment. Generally EPD can be used to any solid that can be present in the form of powder or a colloidal suspension. Electrophoretic deposition of any material can be found that can be polymer, metal carbides, oxides, nitrides and glasses. EPD has been widely used due to following advantages:- requirement of simple apparatus, low process cost, uniformity of the deposited layer , the possibilities to control the film thickness and uniformity by the simple control over the process parameters, complex fabricated objects can easily be coated, both inside of the cavities as well as on the outside cavity surfaces. The process has relatively high purity. Applicability of wide range of bio-materials(ceramics, metals, polymers etc.) [17]. This process has also some following disadvantages : - the low flexibility and reproducibility along with the hidden parameters involve within the EPD process have put the restriction on its industrial applications [5,8], the reliability of the electronics devices fabricated through EPD process is highly affected by the microstructure of the deposited layer [8]. After electrophoretic deposition, deposit remains in loosely held coating particles which is densified by sintering at elevated temperature, this heating may create problem in term of degradation of hydroxyapatite coating and character of metal implants [15]. Many researchers have investigated that the microstructure of the deposited layer is the function of the deposited parameter such as voltage, suspension composition and surface modifying additives [8]. Suspending media is another important parameter that controlling the deposition pattern in the electrophoretic deposition [4]. Organics liquids eliminates the electrodes reaction and gas evaluation so it is preferred over the water these reactions are occur due to electrolysis of water on application of the electric field. Another advantages are concerned with the organic solvent is that it is chemically stable and low conductivity due to low dielectric constant [4].

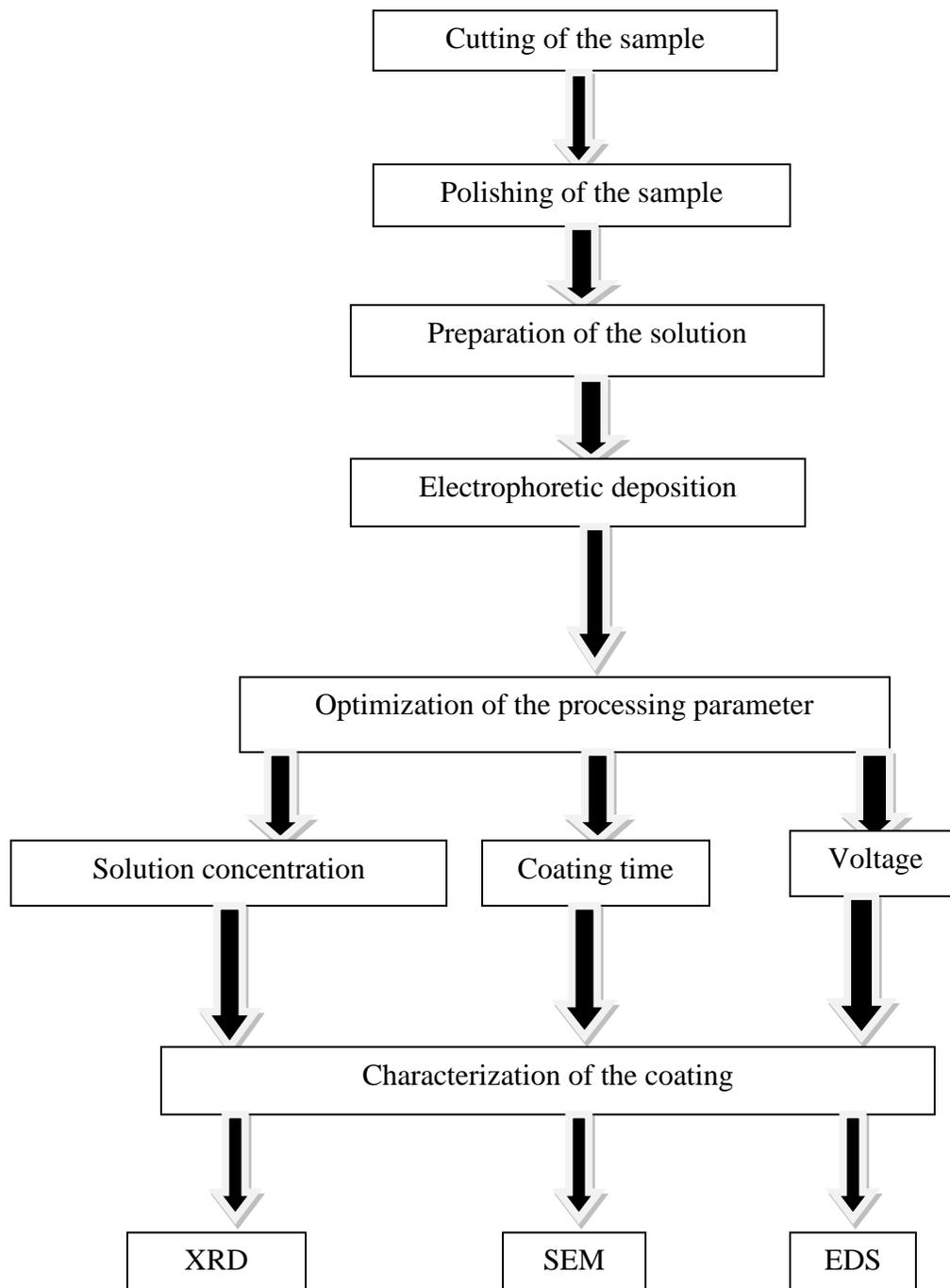
### **2.3 Objective:**

- a. Development of uniformly coated HAp on titanium alloys for biomedical application.
- b. The optimization of processing parameter (voltage, coating time, solution concentration).
- c. Characterization of the coated layer.
- d. To see difference between sintered and non-sintered hydroxyapatite deposition.
- e. To see the deposition at different pH.
- f. To see the difference in deposition at same pH in varying coating time.

# *CHAPTER 3*

**MATERIALS**  
**AND**  
**METHODOLOGY**

### 3.1. Work methodology:



## **3.2. Preparation of titanium sample:**

### **3.2.1 Cutting**

Samples of Ti 6Al 4V were cut from a titanium sheet in the dimension of 12mm×10mm×5mm. Hexa-blade were used as a cutting tool for cut the sample.

### **3.2.2 Grinding**

Grinding was done on a belt grinder. Grinding was done for making smooth edges.

### **3.2.3 Paper polishing**

Paper polish was done through four types of emery paper namely 1/0, 2/0, 3/0 and 4/0. These papers have abrasive particles on their surface. 1/0 has more roughness than the other three papers. The roughness of the paper decreases from 1/0 to 4/0. Effective polishing was achieved by using two consecutive emery papers in the perpendicular fashion on the Ti samples. Paper polishing was mainly done to remove the particle roughness of the cut titanium samples.

### **3.2.4 Cloth polishing**

Cloth polishing was done after paper polishing. Cloth polishing was done on a nylon pad on a cloth polishing wheel. This cloth polishing is also called buffing; this is used for only finishing the polishing process. Alumina paste was used as a polishing material in the diamond polishing. This cloth polishing was done for removing the lines that remained after paper polishing.

### **3.2.5 Diamond polishing**

Diamond polishing was done after cloth polishing. Diamond polishing was done only for removing very light scratches that remained after cloth polishing. In, this procedure, diamond paste was used along with Hi-Fin spray. This was the finishing step of polishing of the sample. Finally, a mirror-like surface was produced after diamond polishing was done.

### 3.3. Preparation of hydroxyapatite:

Hydroxyapatite required in the study was prepared using wet chemical method. The raw material used were calcium nitrate tetra hydrate and di-ammonium hydrogen phosphate and ammonium water.

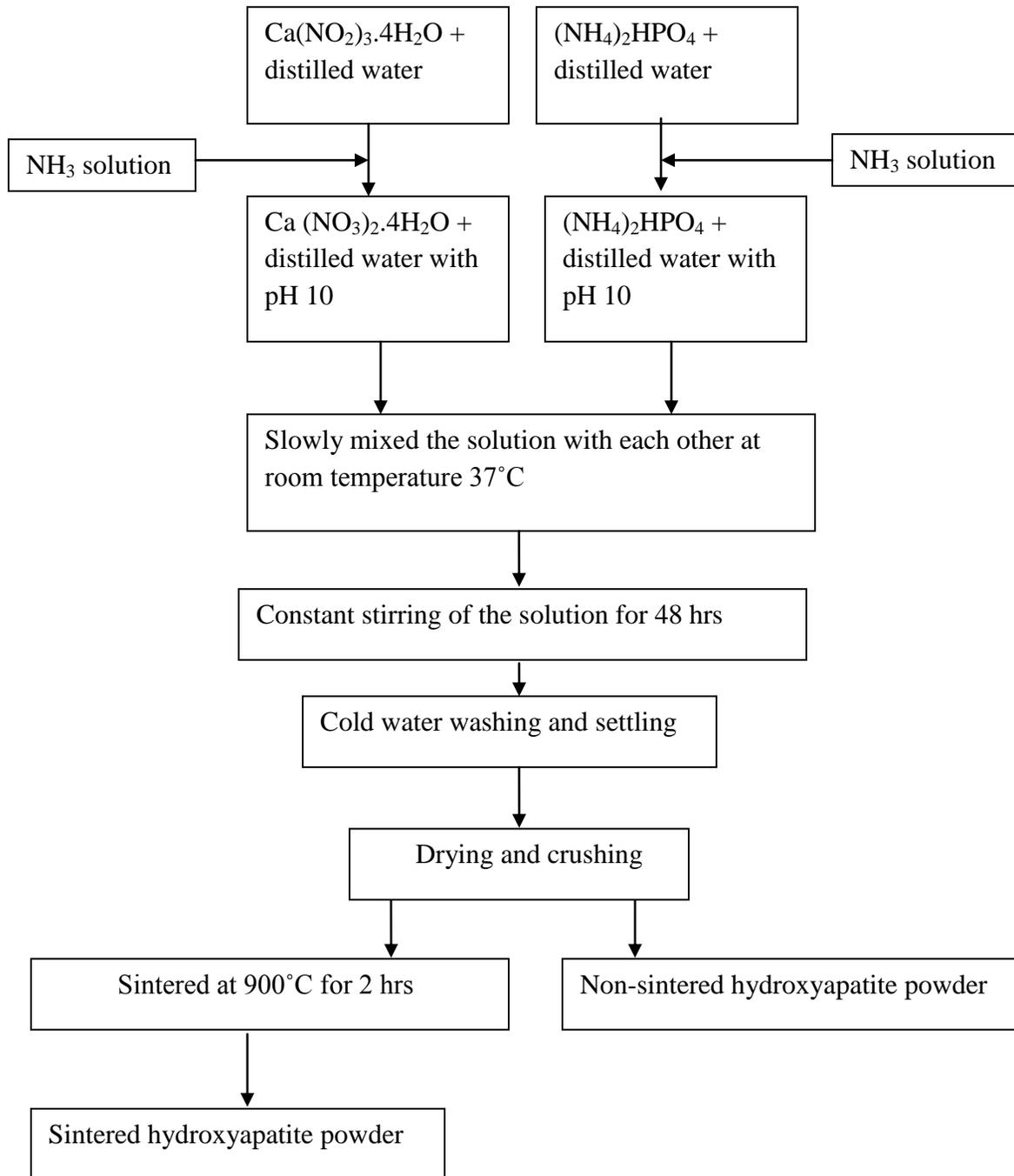
The following reaction will take place in the synthesis can be given by:



0.5 mole solution of calcium nitrate tetra-hydrate and 0.3 mole solution of di-ammonium hydrogen were taken for the synthesis of hydroxyapatite. The solutions were prepared in the de-ionized water. pH of the solution was maintained to 11 with the help of ammonium water on to a magnetic steering. After balancing the pH of the solutions, solution of calcium nitrate tetra-hydrate was slowly mixed with the solution of di-ammonium hydrogen phosphate on to a magnetic steering. Then mixture of the calcium nitrate tetra hydrate and di-ammonium hydrogen phosphate was left of 48 hrs on to a magnetic steering. Because particles size of the formed hydroxyapatite were depend on to the stirring time, if steering time is more, the particle size get more smaller. Then after two days of magnetic stirring, the prepared hydroxyapatite was filtered out with the help of filter paper. Then after filtering the solution, a cake like precipitate was formed. Then precipitate was dried for 3-4 days at 65°C. Then after drying the precipitate of HAp were crushed in to powder. Then power of the HAp was sintered at 900°C for 2 hrs. HAp preparation steps are explained in the *Figure.3.1*.

### 3.4. Preparation of hydroxyapatite solution for electrophoretic deposition:

Hydroxyapatite solutions were prepared for the electrophoretic deposition of hydroxyapatite on to the titanium plate. Suspension solution was made from ethanol. The concentration of the hydroxyapatite was 20gram per liter of ethanol [7]. Before deposition the solution was mixed for 30 min so that concentration of the hydroxyapatite in the ethanol solution remained same.



**Figure 3.1** Flowchart of preparation of sintered and non-sintered hydroxyapatite

### 3.5 Parameters used for sample preparation:

Samples were prepared at constant voltage of 30 volts with varying pH value and deposition time from non-sintered hydroxyapatite and sintered hydroxyapatite.

**Table 3.1** *Samples prepared from non-sintered HAp at different time and temperature.*

Sample number	pH	Time (minute)	Voltage(V)
1	3.5	5	30
2	3.5	10	30
3	3.5	15	30
4	2.5	5	30
5	2.5	10	30
6	2.5	15	30
7	1.5	5	30
8	1.5	10	30
9	1.5	15	30

**Table 3.2** *Samples prepared from sintered HAp at different time and temperature.*

Sample number	pH	Time(minute)	Voltage(V)
1	1.5	5	30
2	1.5	10	30
3	2.5	5	30
4	3.5	5	30

### 3.6 Characterization of the hydroxyapatite and the coated surface of the titanium sample:

#### 3.6.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive technique that extracts detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. The powder diffraction method is generally done for characterization and identification of polycrystalline phases. XRD analysis is usually based on the principle of constructive interference, i.e. when a monochromatic X-ray beam with wavelength  $\lambda$  is projected onto a crystalline material at an angle  $\theta$ , diffraction occurs only when the distance travelled by the rays reflected from consecutive planes differs by a number  $n$  of wavelengths. When x-rays are scattered from a crystal lattice, peaks of scattered intensity are observed and which correspond to the following two conditions:

1. The angle of incidence = angle of scattering.
2. The path-length difference is equal to an integer number of wavelengths.

In this XRD analysis graph is plotted between  $2\theta$  and counts [1-7]. In XRD analysis the Bragg's equation is considered.

$$n\lambda = 2d\sin\theta$$

where,

$n$  is the number of wavelength,

$\lambda$  is the wavelength,

$d$  is spacing between the planes in the atomic lattice,

$\theta$  is the angle between the incident ray and the scattering planes

The XRD analysis of the sintered and non-sintered hydroxyapatite powder as well as that of the deposited surface was done by using Philips X-Ray diffractometer which has nickel filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV voltage and 30mA current having a scanning range( $2\theta$ ) of 10-80° at a scan speed ( $2\theta/\text{sec}$ ) of 0.15.

### **3.6.2 Scanning Electron Microscopy (SEM)**

A scanning electron microscopy (SEM) is used for the check the surface morphology of the sample. It is a type of electron microscope that takes images of the sample by scanning it with the help electrons. The electrons interact with the atoms that generate the sample producing signals that contain information about the sample's surface composition, topography, and other properties such as electrical conductivity. Through this scanning electron microscope the surface topography of metal surface and deposited layer has analyzed by magnifying image. Whether crack is formed or not and the bond formed between the coating and the surface of the sample was analyzed through this scanning electron microscope.

### **3.6.3 Energy Dispersive Spectroscopy (EDS)**

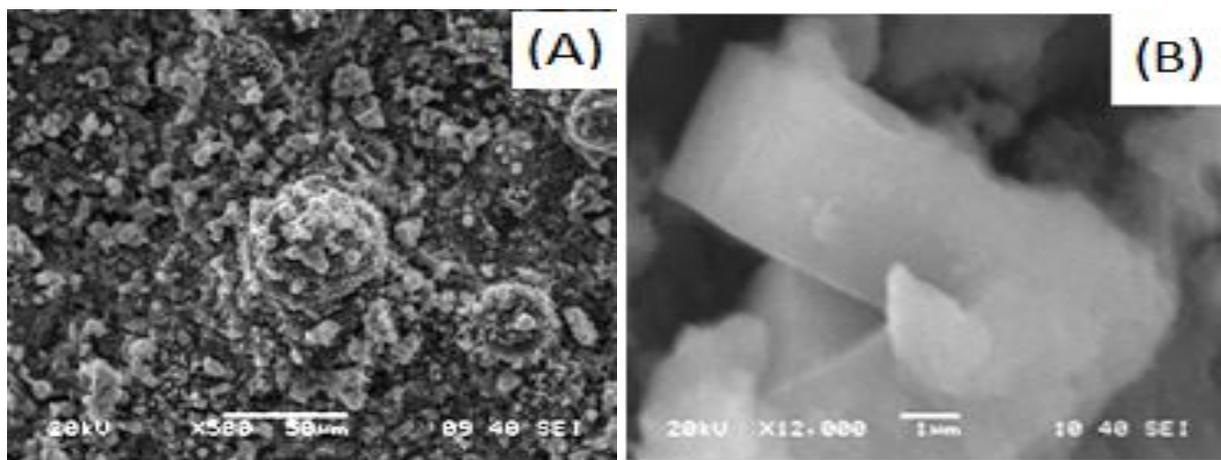
This is energy dispersive spectroscopy in which X-ray is used for the analysis of the sample. EDS has characterization capabilities because each element has a unique atomic structure allowing only unique set of peaks on its X-ray spectrum. In this EDS, high energy particles are incident on to the surface of the sample. EDS tells about the chemical composition of the coating layer of the coated surface. EDS shows peaks associated with Ca and P and also peak for Ti and O [8]. EDS is used to reveal the elements present in the coating or samples.

# *CHAPTER 4*

**RESULTS  
AND  
DISCUSSIONS**

#### 4.1. Morphological characterization

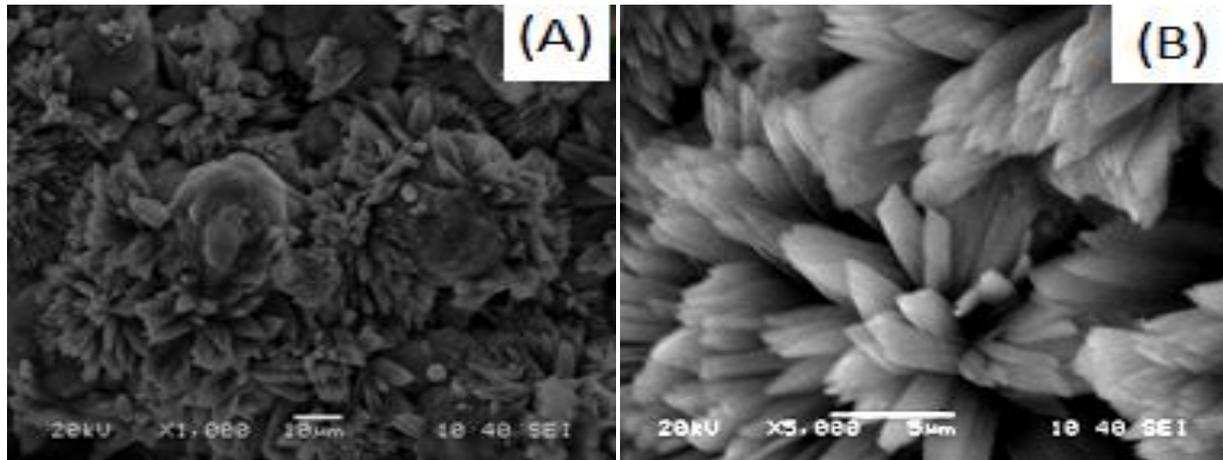
**Figure 4.1** shows continuous, uniform and crack free coating. This image shows some globular hydroxyapatite is deposited on the surface. And it is found that flake shaped HAp is deposited on to the sample in irregular manner. After magnification from 500X to 12000X then flake shaped structure of the hydroxyapatite is found but not any rod or needle shaped hydroxyapatite deposition is found in the coating. *Wang et al.* [19] found a fluffy region composed of a fine acicular structure less than 100 nm in diameter after electrochemical deposition of hydroxyapatite on Mg alloy for 30 minute at 85°C.



**Figure 4.1:** Scanning electron micrograph of non-sintered HAp coating for 5 minutes at different magnification (A)500X (B) 12000X.

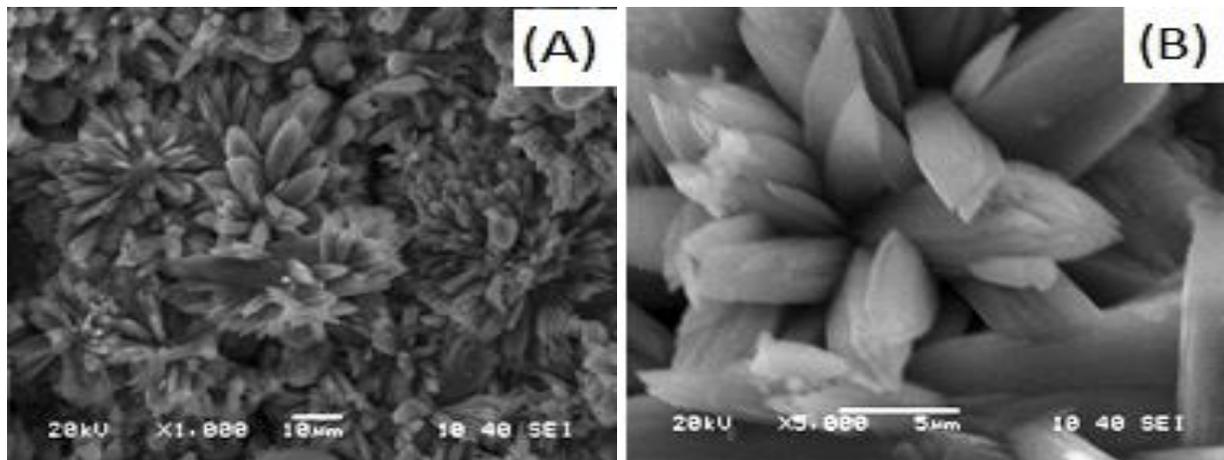
**Figure 4.2** shows continuous, uniform and crack free deposition and also some globular structures are formed on the surface. This figure showed that after increasing the deposition time from 5 minutes to 10 minute then flaked shaped hydroxyapatite is clearly visual and also some rod or needle shaped hydroxyapatite is deposited where flake shaped hydroxyapatite is not deposited. This image showed that flake like structured HAp is deposited in irregular manner and also needle shaped HAp deposited in the fluffy region. After magnification from 1000X to (B)

5000X in the tabular region of **Figure 4.2 (A)** then it shows that many numbers of flake shaped structure hydroxyapatite is deposited on to the sample.



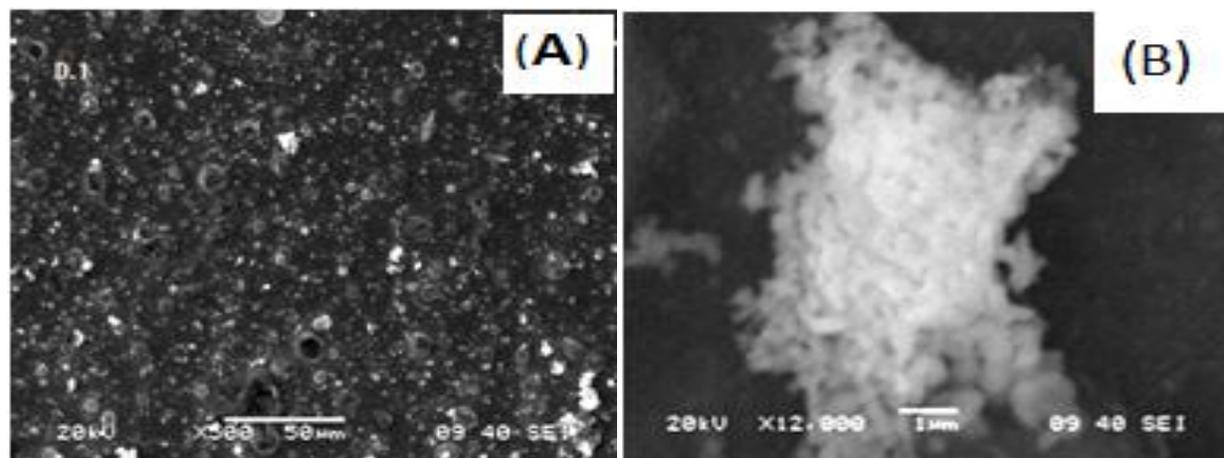
**Figure 4.2:** Scanning electron micrograph of non-sintered HAp coating for 10 minutes.

**Figure 4.3** shows continuous, uniform and crack free deposition. It shows after 15 minutes of deposition, size of deposited flake shaped hydroxyapatite increases. Additionally, some of the flakes shaped deposited HAp may develop almost perpendicularly to the substrate, through which adjacent curled flakes fusing together at one joint and construct the macro-porous structure, as presented in **Figure 4.3 (B)**. *N. Ravishankar et al.*[20] found that it is beneficial to have a flake-like structure for bone growth [20]. **Figure 4.3 (B)** shows adjacent curled flakes are fused together with one flake which is deposited almost perpendicular to the deposition surface.



**Figure 4.3:** Scanning electron micrograph deposited non-sintered HAp coating for 15 minutes

**Figure 4.4** shows that deposition of sintered hydroxyapatite at 30V and 1.5 pH for 5 minutes. The deposition is uniform, continuous and crack free coating. And it has found that spherical shaped hydroxyapatite deposited on to the surface through EPD. After magnification of the image 500X to 12000X then it is seen that white color hydroxyapatite is deposited on the surface.



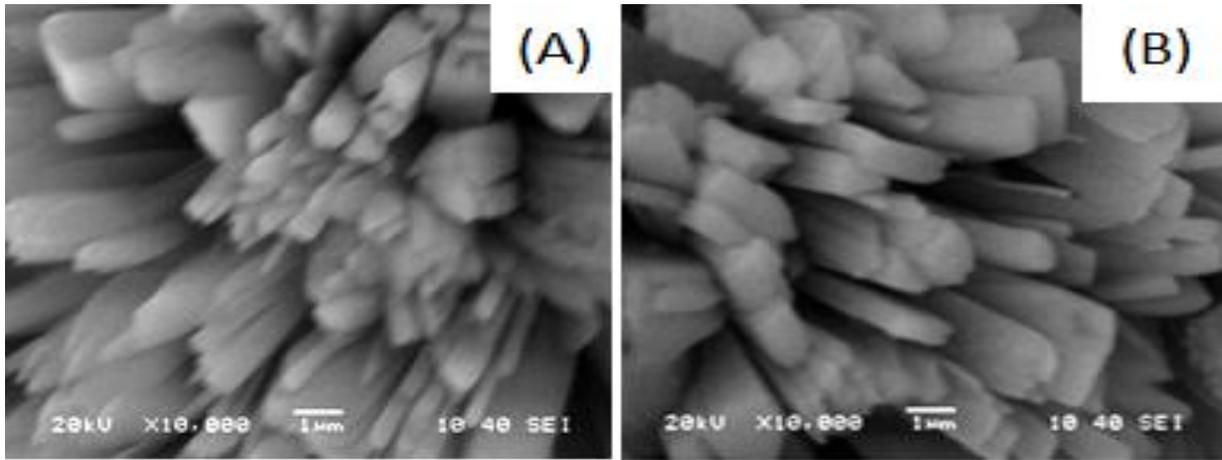
**Figure 4.4:** Scanning electron micrograph deposited non-sintered HAp coating for 5 minutes.

#### 4.1.1 Difference between sintered and non-sintered hydroxyapatite coating:-

##### 4.1.1.1 At same pH for different coating time for non-sintered hydroxyapatite coating:-

**Figure 4.5** (A) and (B) are the images of the deposition at pH 1.5 for 10 minutes and 15 minutes at 10000X magnification. These two figures show that after increasing the deposition time from

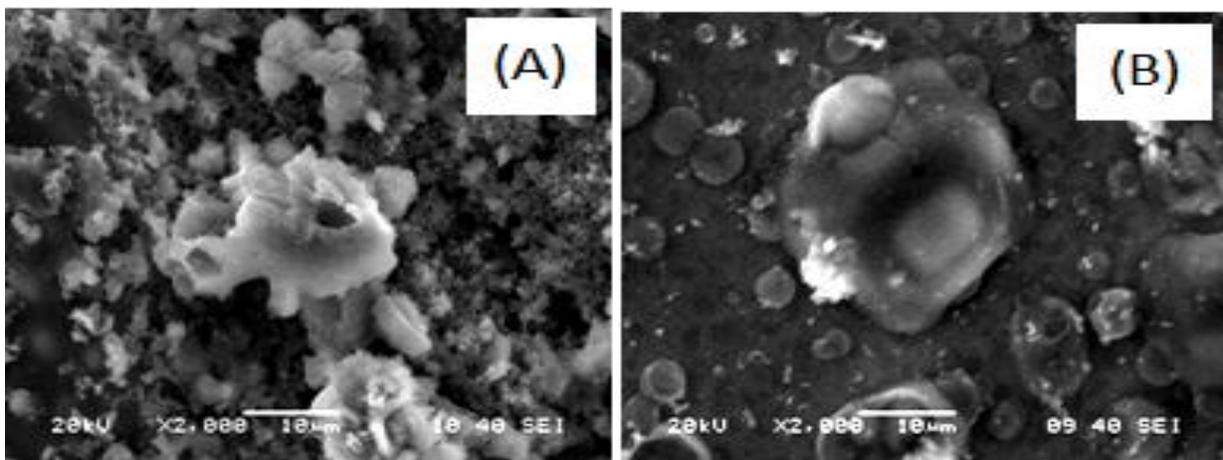
10 minutes to 15 minutes at constant pH then diameter of the deposited flake shaped hydroxyapatite increases.



**Figure 4.5:** Scanning electron micrograph of non-sintered HAp coating at 10000X magnification for varying deposition time (A) 10 minutes, (B) 15 minutes.

#### **4.1.1.2 Difference between deposition of sintered and non-sintered HAp at pH 1.5 and 5 minutes time:-**

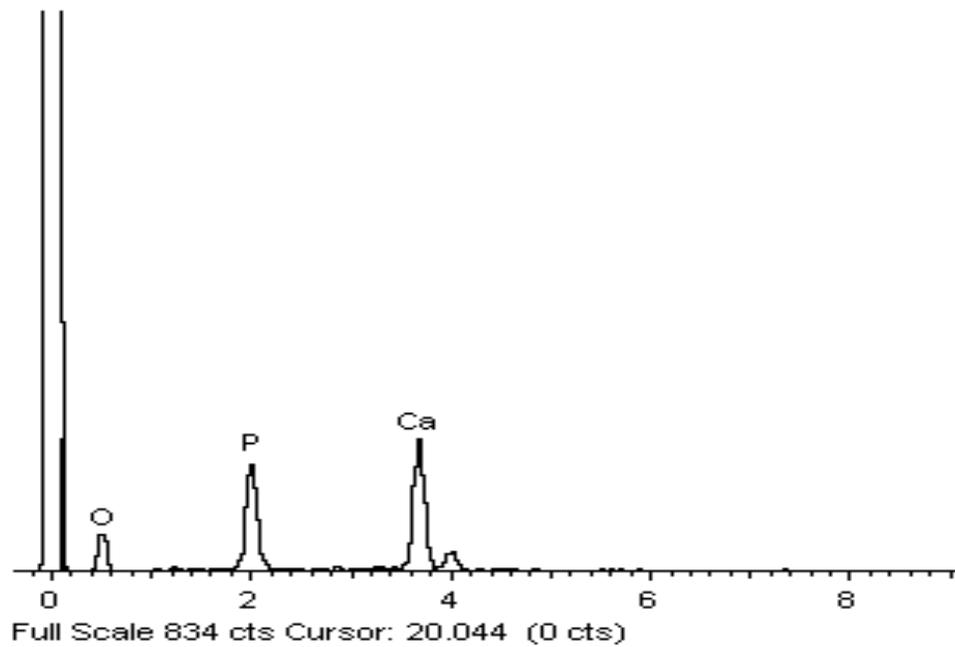
The **Figure 4.6 (A)** shows that in case of non-sintered hydroxyapatite deposition globular deposition is happened and in case **(B)** sintered hydroxyapatite deposition spherical shaped hydroxyapatite deposited on the surface. In case of non-sintered hydroxyapatite deposition is uniform but in case of sintered HAp deposition is continuous but not uniformly distributed deposition is happen,



**Figure 4.6** Scanning electron micrograph of surface Coated from (A) non-sintered HAp, (B) sintered HAp for 5 minutes

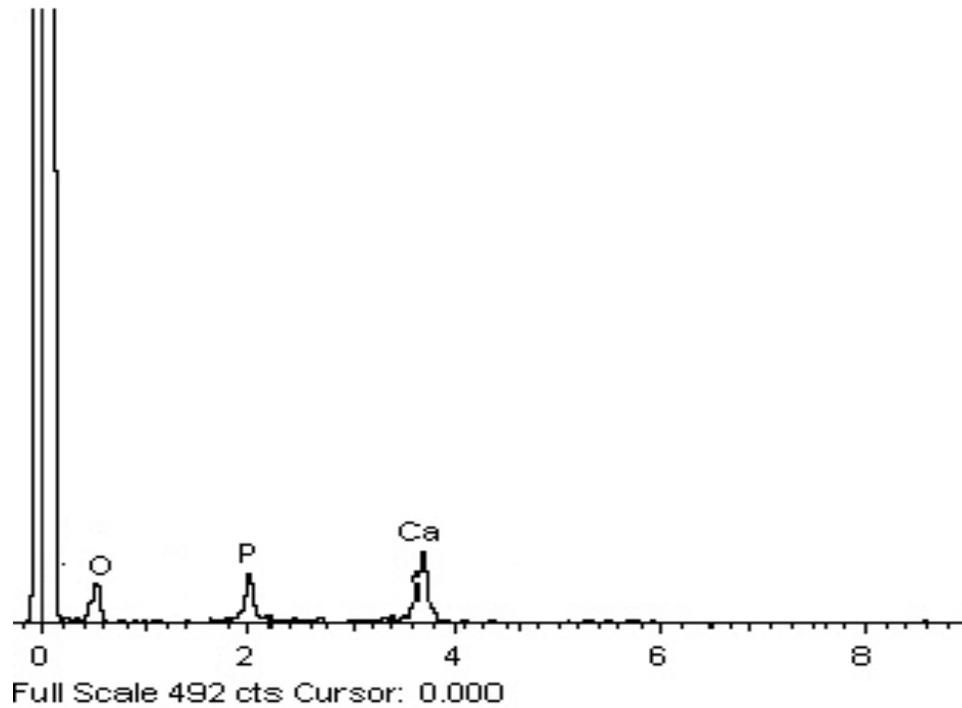
## 4.2 Energy dispersive Spectroscopy:

It has been observe that there are no cracks in the deposited layer after drying. Energy dispersive spectra clearly show the presence of Ca and P compound, and also some amounts of other elements were detected. The  $Mg^{2+}$  and  $Na^{+}$  ions may substitute the  $Ca^{2+}$  positions.



**Figure 4.7:** Energy dispersive spectra of deposited non-sintered HAp coated surface.

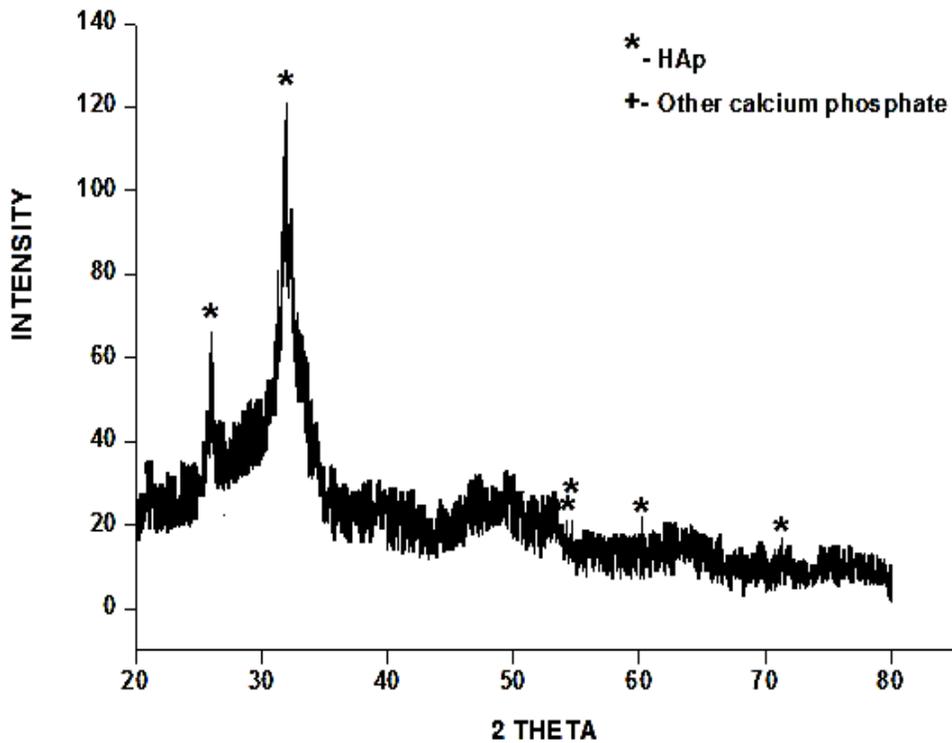
Energy dispersive spectroscopy EDS of sintered hydroxyapatite (*Figure 4.8*) shows main elements Ca and P are presents in the deposition surface and also some amount of oxygen are present.



*Figure 4.8: Energy dispersive spectra of sintered HAp coated surface.*

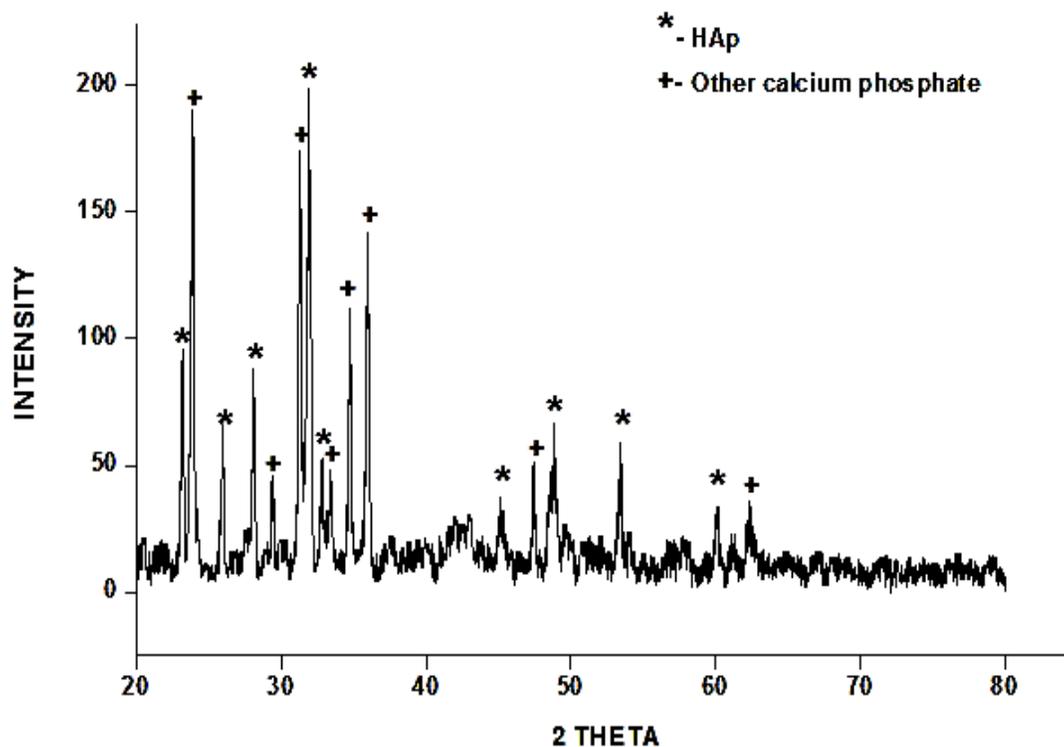
### 4.3. Phase identification:

From X-ray diffraction plot of *Figure 4.9* and *Figure 4.10* it can be seen that the amount of crystalline hydroxyapatite increases after sintering the prepared hydroxyapatite. It is revealed from diffraction pattern of hydroxyapatite that first peak found at  $25.88^\circ$  and after that second peak found at  $31.96^\circ$  in the sintered hydroxyapatite. In the non-sintered hydroxyapatite the first peak of HAp was also found at  $23.18^\circ$ . the crystalline peaks of syn HAp is found at  $25.88^\circ$ ,  $31.96^\circ$ ,  $54.01^\circ$ ,  $54.24^\circ$ ,  $60.43^\circ$ ,  $71.41^\circ$  in the non-sintered hydroxyapatite.

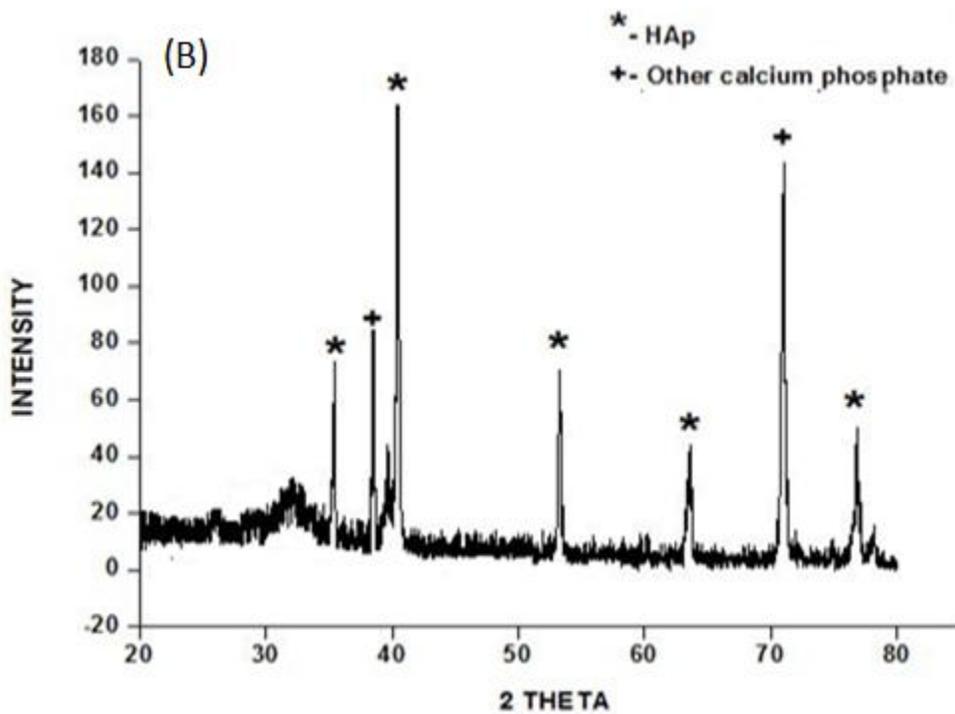
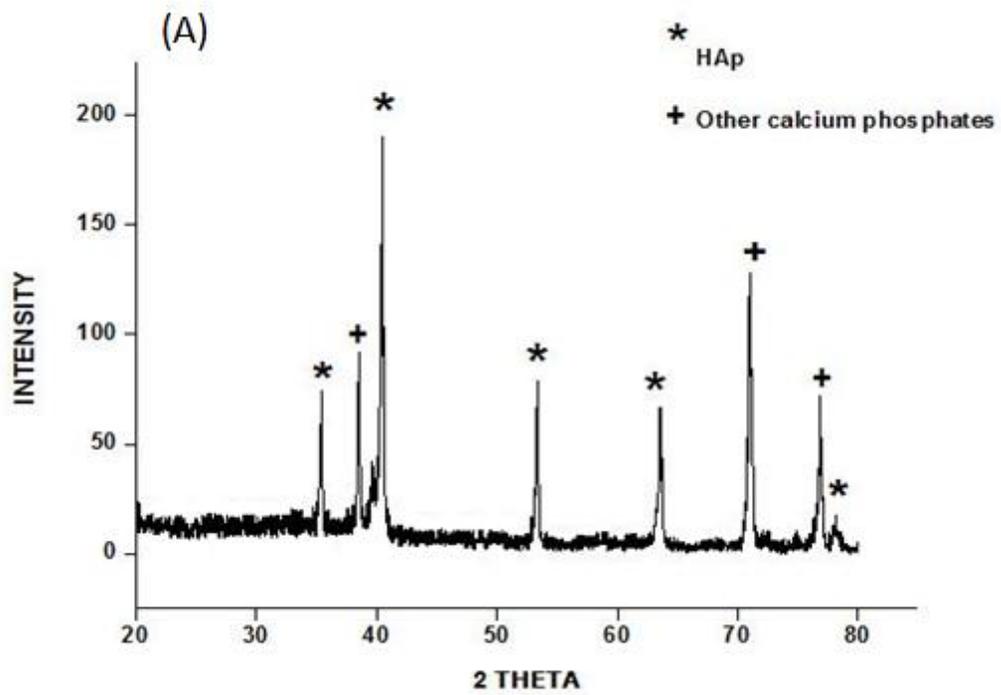


*Figure 4.9* X-ray diffraction plot of sintered HAp.

Now, **Figure 4.10** shows that some other calcium phosphates are present in the powder with the hydroxyapatite powder before the sintering. First of crystalline synthetic hydroxyapatite peak is detected at  $23.18^\circ$ .



**Figure 4.10** : X-ray diffraction plot of Nonsintered HAp.



**Figure 4.11** X-ray diffraction plot of Non-sintered HAp for (A) 10 minutes, (B) 15 minutes at 3.5 pH,

# *CHAPTER 5*

## **CONCLUSIONS**

## Conclusions:

- The electrophoretic deposition of hydroxyapatite on the Ti 6Al 4V at pH 1.5 and at constant voltage of 30V showed an enhanced deposition.
- SEM images also revealed the morphological properties of HAp.
- It was found that coating obtained with non-sintered HAp was better than that obtained in sintered HAp.
- XRD analysis showed distinct peaks of HAp and also some peaks of TiO<sub>2</sub> are present of due to formation of oxide on the surface of the sample.
- SEM analysis revealed the fabrication of a uniform deposit thickness at a constant pH of 1.5 with varying reaction time. The thickness of the coating also increased with time.
- EDS analysis shows the presence of different elements like Ca, O, P on the deposit surface.

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