BIOCOMPATIBLE & BIOACTIVE COATING OF HYDROXY APATITE ON 316L STAIN LESS STEEL FOR ORTHOPAEDIC IMPLANTS

By

Ahsan Bashir

School of Chemical and Materials Engineering

National University of Sciences and Technology

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Name: Ahsan Bashir

Reg no. 00000171686

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Supervisor Name: Dr. Aftab Akram

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

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DEDICATION

I would like to dedicate this research work to my loving parents, beloved siblings, friends, teachers, and my supervisor on this work

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All praise and gratitude be to **ALLAH ALMIGHTY**, the most beneficent, gracious and merciful, who capacitated and enabled me to complete this research work.

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Abstract

Surface treatment of the metallic implants by depositing coatings of biomaterials is an important method for imparting new properties and applications into these implants. The coatings of hydroxyapatite (HA) were deposited over 316-L stainless steel (SS) substrate samples by using two different coating techniques. First, electrophoretic deposition (EPD) technique was used for depositing HA on 316-L SS substrate plates. The sintering process after the EPD to enhance the attachment between the substrate material and coating was avoided. Instead a polymer binder poly vinyl alcohol (PVA) was incorporated in HA before the deposition for this purpose. Deposition rate was controlled by varying 3 process variables including: voltage, time and pH of the suspension. Second coating technique used was spray pyrolysis. Sintering was used during this technique after deposition (to give strength to the coating) at 900 °C for 2 hours and temperature above that was avoided, so that both substrate sample and coatings can be saved from any high temperature damage. The deposition rate here was also controlled by varying 3 process variables including: substrate surface temperature, duration of the spray and nozzle-to-substrate distance. Structural properties of these coatings were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Surface roughness and dimensional analysis of coatings was studied by atomic force microscopy (AFM). Purity of the obtained coatings was confirmed by using Raman spectroscopy. Such HA coatings in combination with metallic biomaterials can be used for biomedical applications where properties like biocompatibility and bioactivity are required, such as orthopaedic implants and dental implants.

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List of Abbreviations

HA _____ Hydroxy Apatite

EPD _____ Electrophoretic Deposition

SBF _____Stimulated Body Fluid

SS _____Stainless Steel

CaP _____Calcium Phosphate

AISI _____American Iron and Steel Institute

CaPs _____Calcium Phosphates

PS _____Plasma spraying

PVA _____Poly Vinyl Alcohol

Chapter 1

INTRODUCTION

1.1 Background of the Research

A medical implant is a synthetic device produced for supplanting a missing natural body part, to provide strength to some injured part, or to improve a present structure of the body [1]. An orthopaedic implant device should necessarily be made of a biocompatible material so that it is non-damaging and non-toxic for human body. Such materials are basically called biomaterials including, orthopaedic implants, artificial blood vessels, heart valves, dental and surgical implants [2].

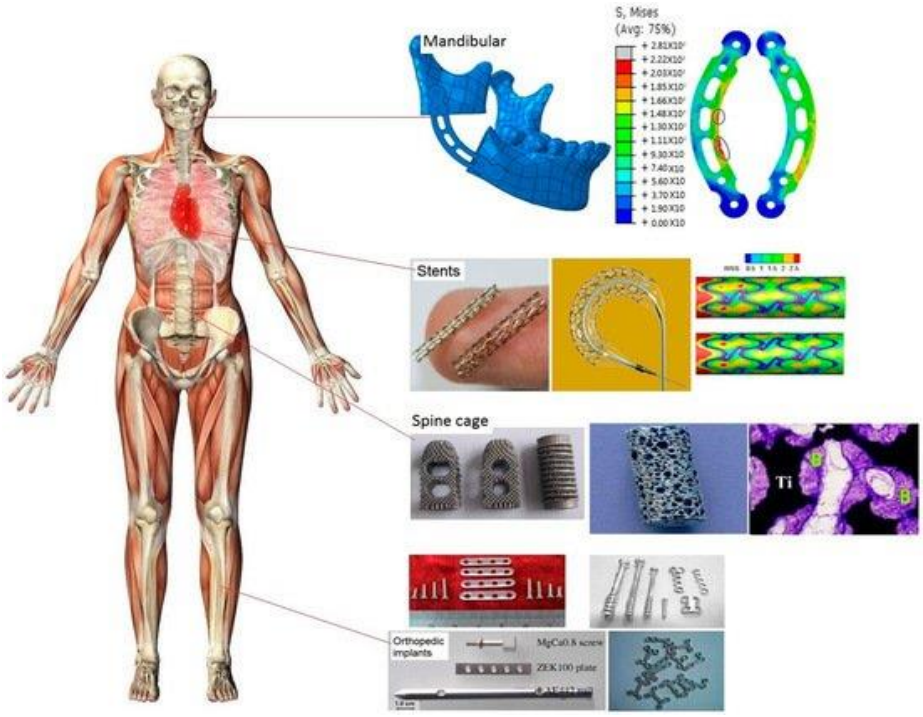

Figure 1-1: Different applications of medical implants in human body [3]

Presently the materials which have wide acceptance to be used for medical implants are mainly metals like titanium (Ti), cobalt (Co) and their alloys and stainless steels. These materials offer high biocompatibility along with great mechanical properties [4]. Some other biomaterials of metallic class like iron (Fe) and magnesium (Mg) based alloys are biodegradable which makes them useful as temporary medical

implants. Such applications include orthopaedic, cardiovascular and dental implants. They provide support to the damaged or affected parts of body through their good mechanical properties for a small time period and gradually start diminishing by either adsorption or resorption reactions caused by the physiological conditions [5].

A medical implant also required to have the capability of stimulating tissue growth. The metallic biomaterials individually could not accomplish this requirement of medical implants. The research work done in the past few decades have proved that by using hydroxyapatite (HA) as a coating material on the surface of medical implants (made from metallic biomaterials) could stimulate process of natural bone formation (osseo-integration) and also improve their overall mechanical stability and fixation with the surrounding tissue [6].

Plasma spraying technique has been most extensively used for coating HA onto the metallic implants in recent times [7-9]. It is a very simple technique with advantages like higher deposition rate, variable phase and structure, lower substrate temperature and coatings of variable porosity. The main disadvantage is the use of high temperature during this process which can go around 10,000 ºC and result in the phase changes of both metal substrate as well as HA. Other changes like dehydroxylation, alterations in the properties of surface and decrease in the crystallinity also occur. Also, the high cost of plasma spraying technique coupled with the wastage of coating material in extensive quantity makes this process impractical at commercial level [10].

There are other alternative coating methods available too, but so is the need to further explore these processes as well.

1.2 Problem Statement

Substantial number of studies had been done for HA coatings using electrophoretic depositions technique [11-13], but in this research work, it is tried to obtain coatings particularly at low value of voltages. Also the sintering of the coated sample was avoided to protect from any phase changes that might occur at high temperatures of sintering by incorporating a polymer binder into the colloidal solution obtained for coating purposes. The second coating procedure used was spray pyrolysis. Research works of using this approach of spray pyrolysis as a coating procedure for HA were not found. Spray pyrolysis was mainly used as a synthesis technique of HA before

[14-15]. In this research work it was tried to make this process a more time efficient for industrial applications.

Both these coating processes were performed to deposit HA onto 316L-stainless steel (SS) samples for orthopaedic applications.

1.3 Research Objectives

The main objective of this research work was to develop HA coatings onto 316L stainless steel using both electrophoretic deposition and spray pyrolysis techniques. The other related objectives in this study are given below:

1. To obtain HA coatings by using electrophoretic deposition (EPD) technique by using 3 different process variables and analyze to determine the best result and process conditions.
2. To obtain HA coatings by using spray pyrolysis technique by using 3 different process variables and analyze to determine best result and process conditions.
3. To understand after comparing results of both techniques, that which coating technique will produce overall better quality coatings within the process parameters that are used in this research work.
4. To study about the bioactive response of the coatings by immersing the coated samples in stimulated body fluid (SBF).

1.4 Research Significance

This research work offers an alternative methodology of coating hydroxyapatite onto 316L-SS metallic implant using electrophoretic deposition, a technique that has been increasingly used in researches as well as commercially in the past two decades [11-13]. Other method used for developing HA coatings onto metallic implant was spray pyrolysis and applied in a different approach compare to the conventional approaches that have been done in the past. Present approaches of spray pyrolysis are used for synthesizing HA onto metallic implants by using reactants of HA in spray guns, making this process more of a synthesis process for HA [14-15]. However, in this research work spray pyrolysis has been used as a coating method for depositing already synthesized HA onto metallic implant, making it a more time saving approach for HA coatings at commercial level.

Chapter 2

Literature Review

2.1 Biomaterials

> "A biomaterial is a nonviable material used in a medical device, intended to interact with biological systems." Williams D.F. [16]

Bio materials are materials which can be natural or man-made, alive or lifeless and typically prepared from a combination of multiple constituents, which interact with biological systems. Bio materials find frequent uses in medical applications to enhance or substitute a natural function [17].

Out of all known materials, only a small number fulfill the needs of grafting within the body. Such biomaterials are part of any five main materials classes: polymers, metals, ceramics, composites and natural materials. Various kinds of these materials employed in the field of medicine are actually the outcome of several researches performed in the past few decades by monitoring certain material properties like physical properties, purity and composition and manufacturing novel materials with novel and unique properties. Manufacturing of such biomaterials have been done per the requirements of pharmaceutical devices. For instance, vascular grafts need the use of woven fibers of polymer, hip replacements need implants of Ti alloys and hemodialysis require bundled together fibers of polymer [18].

The biomaterials classification on the basis of their applications for bone regeneration is shown schematically in the figure below.

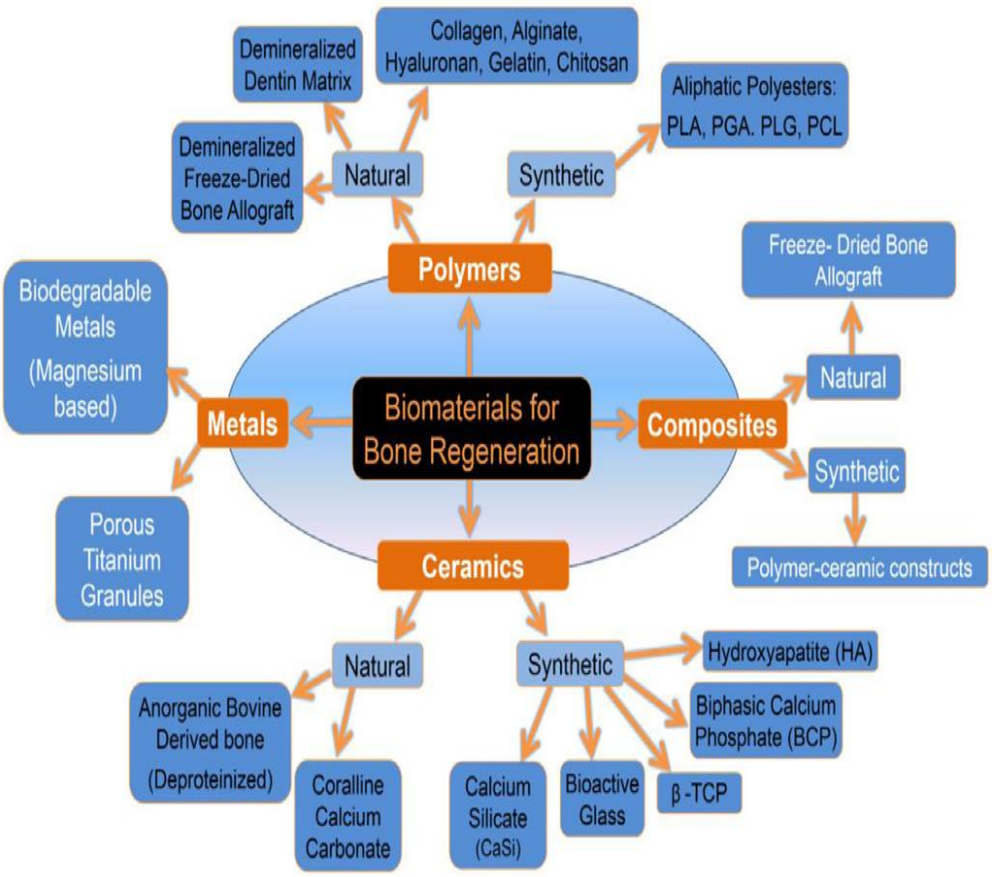

Figure 2-1: Biomaterials classification for bone regeneration applications [19]

The basic characteristic that all biomaterials have is their biocompatible nature that makes them easily acceptable to the body without suspecting them as any toxic alien material. Because body straightaway react to any alien substance with help of cells present in bodily fluid which begin process of inflammation and after that a process of healing wounds starts. When a medical device is implanted within the body, the response of tissues starts off against the injury which causes inflammation. Injury around implanted device results in instant growth of the temporary matrix that contains a combination of fibrous protein and inflammatory substance which are ejected from endothelial cells, inflammatory cells and activated platelets. Biomaterials are biocompatible but all are not unreactive within the body, only those of which have high bioactivity does integrate towards the responses of body, such as by producing a host matrix that helps in a controlled growth of the tissue or eventually converted into a fully grown tissue. Biomaterials which are good enough of avoiding attack from the immune system of body, and also stimulate tissue growth, are actually very effective and costs less too [18].

Another significant property to have in the biomaterial is mechanical similarity comparable to that of host or replaced tissue. Particularly replacements of hard tissue require biomaterial to provide sustenance or help in sharing the load to some extent. In these cases, biomaterials needed to have better hardness, fracture toughness and compressive strength [18].

2.2 Goals of Biomaterial field

The biomaterials as a field is going through a ground-breaking change where life sciences are getting equal significance as given to materials science and engineering. At the same time, developments in the field of engineering (such as nanotechnology) have significantly enhanced the way biomaterials are being designed today, that also made possible to manufacture materials having capability to perform otherwise difficult functions. For example, such biomaterials are specifically fabricated to provide practically similar physicochemical properties that are crucial in natural materials. Just like biomaterials, their methods of production are also inspired from nature. While synthetic man-made materials are mainly designed on millimeters scale or even larger and then further scaled down to micrometer or nanometer scale, the natural materials are fabricated by using self-assembly at smaller scales. It is a bottom-up type of material fabrication which helps in producing information-rich materials having complex structures with vastly reproducible method and that too by spending nominal input of energy [20].

2.3 Biomaterial Classifications Based on Tissue Response

Biomaterials are often divided mainly into 3 classes on the basis of the response of tissue. In more comprehensive terms, these classes are: inert, active and resorbable or degradable materials. Inert materials have minimum response of tissue. Active materials provide great help in bonding with the surrounding tissue, for instance, stimulating the growth of new bone. Resorbable or degradable materials are incorporated within the tissue which is adjacent to the affected tissue, or can be completely dissolved after some time. Metals normally are inert, polymers are either inert or degradable and ceramics can be active, inert or degradable [21].

Examples of some of the accepted biomaterials are given in the table below.

Table 1: Examples of some accepted biomaterials [18]

Metals	Ceramics	Polymers
316L stainless steel	Hydroxyapatite	Polyvinyl alcohol
Titanium	Alumina	Polyethylene
Ti_6Al_4V	Zirconia	Polyurethane
Co-Cr Alloys	Carbon	Polyamide

2.4 Bioceramics

Ceramics are one of the most versatile and commonly found materials. Out of all ceramics, the oxides are used most frequently and also available abundantly in nature. Also compared to other materials oxides have some of the simplest processes for synthesis, shaping and heat-treatment. All ceramics have some common properties like high hardness, good compressive strength, low density, low tensile strength and chemical stability. Because of these properties, ceramics offer load-bearing applications for mobile service parts in hostile surroundings, for example in refractories, engine blocks, and replacements for hard tissues [22].

Body is a naturally dynamic system repeatedly sustaining itself by the help of its defensive mechanism in order to provide best possible working circumstances. An endless process of continuous growth and decomposition of bio structures offers a challenging hostile environment for body components. The body's immune system responds with the actions of living cells of size in nano scale and these essentially are chemical suspension and surface assimilation processes. After a biomaterial comes into contact with body tissue, the proteins from surrounding body fluid quickly start covering its bare surface and adsorption begins. The nature of adsorbed protein layer is controlled by the chemical nature of underlying substrate material, because the surface charge and wettability are affected by the substrate. Surface chemistry governs the processes of platelet adhesion and macrophage fusion. Even though in vitro studies suggest that cells can adhere, spread and grow while comes in contact with bare surfaces of biomaterial, but the adsorbed proteins from adherent cells and surrounding adjacent tissues further increase growth, migration and cell attachment. The cytoskeletally linked receptors in the cell membranes will facilitate cell adhesion by interacting with the material surface because of the protein layer adsorption over

it. Therefore, the chemistry of the biomaterial implant that is placed inside the body is very vital for the optimal body functions. While testing ceramics in vivo conditions, there are certain ceramics which on dissolving inside bodily fluid does not create an increase in the activity of body's immunity system or when make a direct interaction with the tissues, these ceramics are called bio-ceramics. Mostly bio-ceramics are oxides in nature, and have the benefit to be naturally compatible inside body conditions. These biocompatible properties comes from the presence of certain ions in their chemical composition which are also normally present in the biological environment, for example Na+, K+, Ca^{2+}, Mg^{2+}, and some other ion like $Al^{3+}$and Ti^{2+} which show toxicity of some degree towards body tissue [22].

Structural ceramics like polycrystalline alumina and toughened zirconia have exceptional tri-bological properties, better fracture toughness and reliability. These properties make them perfect materials for hard tissue replacement. The bio-ceramics are being used as implant materials over the past two decades and this leads to a rise in the clinical usage of bioactive ceramics, because these ceramics provide a particular biological response at material interface which results in very strong bonding between the tissue and the material. Bioactive ceramics are mostly calcium phosphates and hydroxyapatite is one of the main family members. Other family members include bio-active glasses and glass-ceramics. But because of some limitations like high brittleness of ceramics, e.g. alumina and low strength of bio-active ceramics, e.g. hydroxyapatite lower their scope for medical applications [22].

Bio ceramics are normally used for repairing or replacing hard skeletal tissues but the stable bonding that they form with connective tissues vary considerably. Therefore on the basis of their type of bonding to the surrounding connective tissues, bio-ceramics can be categorized into four different groups:

1. Dense and almost inert
2. Inert and porous
3. Surface reactive and dense
4. Resorbable

Dense and almost inert bio ceramics through morphological fixation make bonding with the bone, and the growth of the bone takes place within surface irregularities, e.g. Al_2O_3. Inert and porous bio-ceramics make bone bonding beyond tissue growth,

i.e. by biological fixation, e.g. HA coated porous implants. Surface reactive and dense bio-ceramics make a direct attachment with the bone by chemical bonding or through bioactive fixation, e.g. hydroxyapatite. Resorbable bio-ceramics forms bonding with the bone by means of one of the before mentioned processes and then gradually superseded by the bone, e.g. tricalcium phosphate [22].

2.4.1 Bone

Bone is a composite material of organic-ceramic nature and structurally a very complex substance. The core components of bone include calcium phosphate ($Ca_3(PO_4)_2$), collagen ($C_{65}H_{102}N_{18}O_{21}$) and water. The weight percentage of these constituents is 69%, 20% and 9% respectively. Moreover, very small amounts of other organic materials are also present, including proteins, polysaccharides, and lipids. Collagen serves as a matrix and comprises of small microfibers of diameters ranging between 100-2000 nm, and these provide a net-like look of collagen which makes it difficult to distinct between individual microfibers. While the reinforcement phase contains nanoparticles of calcium phosphate, which make the bone stiffer and present as crystallized carbonated hydroxyapatite and/or amorphous calcium phosphate [23].

Collagen molecules offer small empty interstitial compartments, which are regularly spaced and here the deposition of apatite nano crystals take place via a controlled bio-mineralization method which involve over 200 acid proteins of different nature. These proteins serve as inhibitors or nucleators, so that anchored nano crystals in collagen undergo epitaxial growth. The process of crystallization for low solubility apatite and complex structures favourably advances via the creation of intermediate metastable products by kinetically controlled process [23].

Bones are regarded as the living bio-minerals because of the fact that inside them, permanently active cells are present. The bone formation process is initiated by unique cells called ‘osteoblasts’, which produce collagen matrix and release in the shape of a jelly like substance called ‘osteoid’, then mineralization occurs by the controlled deposition of nano crystals of calcium phosphate. The osteoblasts stayed trap within mineral phase as they evolved into ‘osteocytes’ that constantly preserve the bone formation process. Simultaneously, bone cells of another kind catabolize the bone by destructive metabolism, which known as ‘osteoclasts’ [24].

The method of bone growth and decay is very dynamic, because of the evolution which takes place when the body is under development, and helps in maintaining the shape and consistency of bone as well as facilitating its regeneration process if fracture occurs. It also comprises mechanisms for storage and transport of two vital elements present in bones, calcium and phosphorus. In bones there are varying sorts of incorporation of inorganic and organic materials, resulting in noteworthy differences in their mechanical properties. For example, high inorganic content will result in low toughness, and low inorganic content can result in low resiliency or fracture strength of the bone [24].

2.4.1.1 Required Properties in Bone Implants

A bone implant should definitely have certain properties like biocompatibility, bioactivity, osteo-conductivity, osteo-inductivity, structure similarity with bone, and bio-resorbable in nature. For instance, a hip implant must exhibits similar response as of a real bone when under loading conditions and should also have ability to undergo remodeling. Bio-ceramics provides lower density and higher porosity and that offers greater surface area for the process of vascularization and bony ingrowth. The ideal circumstances for osteo-conductivity are a fine distribution of inter-connective pores of the size of 150-300μm range. The pores arrangement and the inter-connectivity pore sizes greatly affect the osteo-conductivity of the bone and its mechanical properties. The osteo-conductive bone scaffold offers a suitable environment for both cells and proteins of the bone. Osteo-conductive ceramic when placed newly in the body lacks mechanical properties of the bone, but slowly attains required mechanical strength equivalent of a bone because of the growth that takes place after initial placement in the body [25].

Currently the bio-ceramic bone grafts design is not very optimal because of them being naturally rigid and breakable, which makes them not suitable for load bearing applications. Still they are used in non-loadbearing applications, for example as bone filling materials for both orthopaedic and oral surgery, in parts used for surgery of middle ear, and as coatings for metallic and dental implants. This shortcoming in bio-ceramics can be overcome by producing ceramics with enhanced mechanical strength and having complex hierarchical structural similarity with the hard tissues. An artificial bone should have its strength comparable with that of the cancellous bone that is being replaced and that is around or greater than 200MPa. Its elastic

modulus value should also be similar to that of bone and that is around 20GPa. This should maintain tolerable toughness of bone and avoid both fatigue fracture caused by cyclic loading and stress shielding [26].

2.4.2 Hydroxyapatite

Hydroxyapatite is a bio-material comes from a family of minerals named 'apatite'. It is a hydrated calcium phosphate compound. The name 'apatite' was originated from the Greek word 'apate' which means 'to deceive'. The reasoning behind this was that these minerals are available in various different colors and crystal habits, and that is why most of the times were wrongly identified as the precious minerals like amethyst or aquamarine. The calcium phosphates are naturally resorbable within the body [27].

In HA the molar ratio of Ca/P is 1.67. Based on these ratios of Ca/P, the calcium phosphate (CaP) ceramics exhibits some diverse phases. HA is one of such phases and also very commonly available CaP ceramic in the body. These variable phases of calcium phosphates are given in the table below [28].

Table 2: Different phases of CaP based on Ca/P ratio [28]

S. No.	Ca/P Ratio	Compound Name	Chemical Formula
1	0.5	Monocalcium phosphate	$Ca(H_2PO_4)_2$
2	1	Dicalcium phosphate	$CaHPO_4$
3	1.33	Tricalcium phosphate	$Ca_3(PO_4)_2$
4	1.5	Octacalcium phosphate	$Ca_8(HPO_4)_2(PO_4)_4$
5	1.67	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$

2.4.2.1 Crystal Structure of HA

$Ca_{10}(PO_4)_6(OH)_2$ is the chemical formula of HA and that indicates the nature of unit cell in its crystal structure which include molecules of two types. The crystal structure of HA comes under hexagonal system, while few monoclinic system exceptions are there. The hexagonal system has the reflection plane and rotational symmetry of hexagonal nature. The HA unit cell have values of lattice parameters as 0.942 nm and 0.688 nm for 'a' and 'c' axes respectively. The unit cell skeleton is mainly made up of phosphate (PO_4^{3-}) groups in the form of tetrahedral arrangement.

An entire unit cell is composed of 44 atoms which are present as mutually arranged ionic groups of OH^-, PO_4^{3-}, Ca^{2+} in a hexagonal system [29].

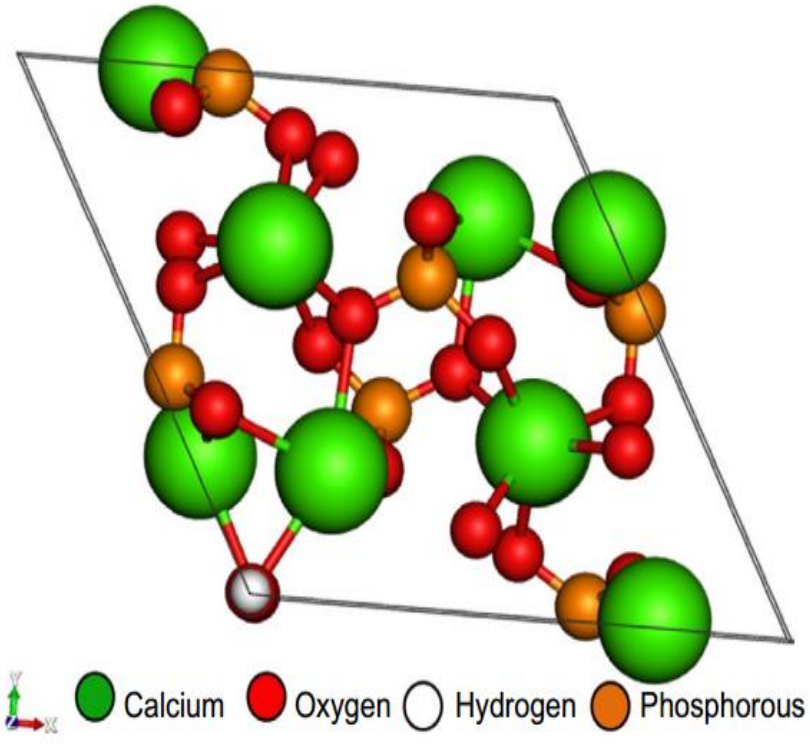

Figure 2-2: A unit cell in the crystal structure of HA [29]

2.4.2.2 Applications of HA

HA offers applications in prosthetics because of its chemical composition and crystallographic resemblance with the bone. Because of that, HA can be synthesized in various different forms on the basis of required application, for instance, different forms of HA include: porous material, coating material, powdered material and dense material. Other than its similarity with the bone, the other properties of HA that are essential for it to be used in prosthetic applications are: biocompatibility, osteoconductivity, biodegradability, bioactivity and chemical affinity at physiological conditions [28]. Other applications of HA include: bone scaffolds, drug delivery, vascular grafts, skin tissue repairing, antimicrobial membranes and water treatment [30].

Applications of HA in biomedical and some other fields are shown in the figure below.

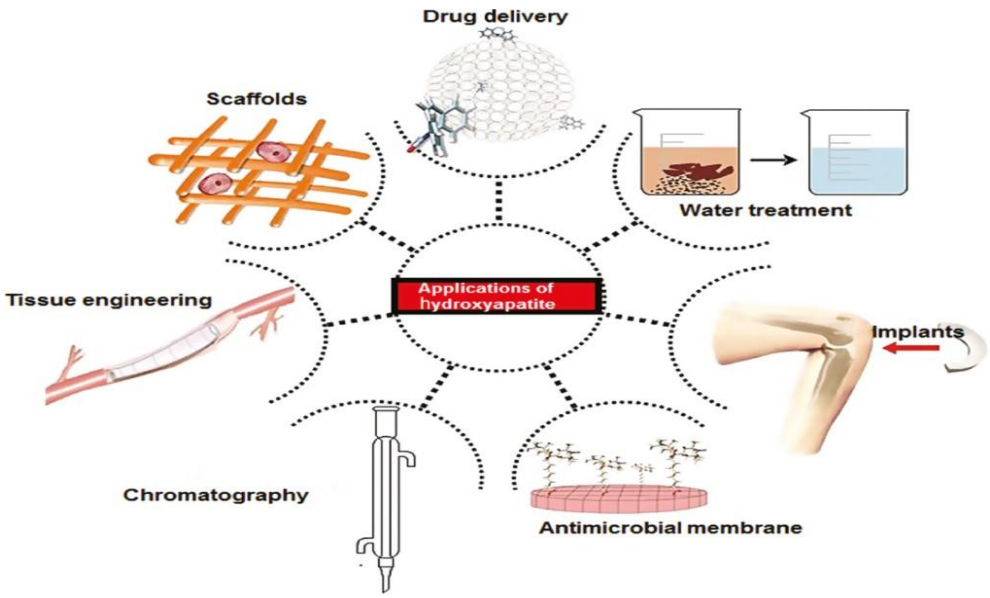

Figure 2-3: Different applications of HA [30]

In this research work, HA as a coating material on 316L stainless steel has been used. Usually, the mechanical strength of HA alone as a dense material is not enough to be used in load bearing applications for longer durations, therefore, HA as a coating material on metallic biomaterial has been used. Several techniques of depositing HA onto metallic biomaterial are available; some of those will be discussed later on in this chapter.

2.5 Metallic Biomaterials

Metallic biomaterials found applications for medical implant devices since the very beginning of this field. These mainly include iron (Fe), cobalt (Co) ant titanium (Ti) based systems. The mechanical properties (including strength, ductility, and modulus) of these alloy systems have been used for making devices required for replacing skeletal structures and also needed to have in vivo stability for longer periods of time. In these systems, the presence of a passive surface covering of oxides has provided chemical inertness inside body conditions [31].

2.5.1 Stainless Steel

The first ever metallic biomaterials used for orthopedic implants were the alloys of stainless steel. Initially, the results were not that great because some incidents reported that failure took place due to severe corrosion and fatigue failures. But as the development in research continues, the usage of stainless steel as an implant material increases tremendously with the inception of a medical grade stainless steel

designated by American Iron and Steel Institute (AISI) as AISI 316L [32]. This type of steel is a low carbon austenitic stainless steel which has a percentage composition of chromium (Cr) 17%, nickel (Ni) 12%, molybdenum (Mo) 2.5%, manganese (Mn) 2%, silicon (Si) 1% and carbon (C) maximum of 0.03%. Mo addition provides increased resistance against normal corrosion, enhances pitting resistance against the ionic solutions containing chloride ions and also at higher temperatures ensure an increase in strength. The extremely low amount of C reduces the chances of dangerous carbide formation during welding process. 316L stainless steel offer applications in orthopaedic, dental and cardiovascular implants [33].

In this research work, 316L stainless steel samples were used as substrate material for the production of HA coatings, mainly because they cost lesser than other metallic biomaterials.

2.6 Key Properties of Biomaterials

The most important property that a biomaterial should offer is that, it should not cause any adverse effect when place within the body. Also the biomaterials should offer a wide range of applications. Another important thing is to have different number of biomaterials having different properties. However, in general:

- ✓ Metallic biomaterials find uses mostly in load bearing application and because of their appropriate fatigue strength can withstand the severities of everyday life activities such as, walking, chewing etc.
- ✓ Ceramic biomaterials offer good wear resistance and high hardness, which are required in applications involving articular surfaces, as in case of teeth and joints, and also used for bone bonding implants.
- ✓ Polymer biomaterials have uses where properties like high flexibility and stability are required, and also have applications in low friction articulating surfaces [34].

2.7 Mechanical properties of bio materials

To classify a bio-material for biomedical applications, certain requirements needs to be met, one of such requirements is that the mechanical properties of material must be equivalent to that of the bone to guarantee high performance, reliability and medical success [35].

2.7.1 Elastic modulus

Elastic modulus of a material is defined as the stress over strain ratio that is inside the proportional limit. It signifies a material's stiffness inside elastic region under the application of tensile or compressive stress. It has medical importance as it shows that selected biomaterial offer equivalent deformable properties to that of the material they going to be replaced with. Load bearing biomaterials need high modulus of elasticity along with low deflection. High elastic modulus of material results in its low fracture resistance. Elastic modulus of biomaterial is required to be equivalent to that of the bone, because if higher than that, then applied load only be borne by the biomaterial and if lower, then all load be borne by bone only. Normally, for measuring elastic modulus bend test is utilized as it is easier to measure deflection in it compared to tensile or compressive loading. But for bone replacement, the biomaterials are typically porous with samples of small sizes. Hence, for these materials nano-indentation testing is used. This test offer high precision and appropriate for samples of micro-scale sizes. Non-destructive method for the measurement of elastic modulus can also be used [36].

2.7.2 Hardness

Hardness is basically the resistance of a material to mechanical indentation, and a measure of the plastic deformation caused by it. It has importance in selecting a biomaterial for medical applications. Hardness of the biomaterial should be equivalent to that of the bone, because if it is higher that will result in the penetration of biomaterial into the bone. As mentioned above, sizes of biomaterials used are very small, hence hardness test on micro- and nano-scale levels are used including Vickers and Knoop indenters [36].

2.7.3 Fatigue

Fatigue is defined as the material failure caused by the cyclic or repeated loading and unloading. This loading can be either tensile or compressive. Fatigue is also very important for biomaterials as they are constantly under such mode of loading during their life time in service. Under cyclic loading, flaws or micro cracks generation takes place. These micro cracks then propagate into large cracks and results in the failure of the material. Other than cyclic loading various other factors also help in cracks propagation like frictional sliding of surfaces, grain boundary residual stress, progressive wear and shear stress [36].

2.7.4 Fracture Strength

The highest amount of stress that a material can bear before its fracture is known as the fracture strength of that material. Fracture strength of biomaterials especially bio-ceramics is of real importance because of their brittle nature. In bio-ceramics, cracks propagation is easier under tensile loading rather than under compressive loading. Various tests are at disposal for measuring tensile strength of these materials, biaxial flexural strength test, bending flexural strength test and the Weibull strength analysis. Flaws have an impact on the strength and reliability of bio-ceramics during the course of manufacturing and implantation. In bio-ceramics, flaws creation can be done by many different processes like heating and thermal sintering. Having high reliability than high strength is more important in bio-ceramics [37].

2.7.5 Fracture Toughness

A material which have the capability of resisting fracture when there are complications of cracks or flaws can be called a tough material and this property is known as fracture toughness. This property helps to assess the performance, reliability and medical success of biomaterials. Biomaterials with higher fracture toughness provide better medical performance and serviceability. Several methods used for its measurement, for example, indentation fracture, single-edge notched beam, indentation strength, double cantilever beam, and single-edge pre cracked beam [37].

Mechanical properties of the bone and a few biomaterials are given in the table below.

Table 3: Mechanical properties of bone and some biomaterials [35]

Material Name	Tensile strength (MPa)	Compressive strength (MPa)	Elastic modulus (GPa)	Fracture toughness (MPa. $m^{-1/2}$)
Cortical bone	50-151	100-230	7-30	2-12
Stainless steel	465-950	1000	200	55-95
Ti-alloys	596-1100	450-1850	55-114	40-92
Hydroxyapatite	40-300	500-1000	80-120	0.6-1

2.8 Applications of Biomaterials

Biomaterials conventionally are being used in medical devices for a very long time, but of late the scope of their application has increased considerably. Today the biomaterials are made with the use of loads of information at our disposal, and with the incorporation of various biologically active components obtained from nature. The future holds even greater things with biomaterials finding application beyond medical, by using biologically stimulated design with the combination of dynamic behaviour [38].

In early 20th century, naturally obtained materials were starting to be replaced with synthetically produced materials (ceramics, polymer, metals alloys) because they offer better performance, more functionality and increased reproducibility compared to their naturally obtained equivalents. These developments lead to an evident rise in the range of applications of biomaterials. Also biomaterials become more proficient and help saved millions of lives, because of their incorporation in devices like vascular stents, artificial hips, contact lenses, and dental restoratives. The kind of applications they offer, biomaterials were considered as the type of materials that used for medical devices, and the foundation laid for the field of materials science. Materials were thought to perform mainly mechanical functions: to avoid biological rejection, that results in hindered device performance and health of the patient. It was desirable that, bio-materials should be inert and do not interact with host organism's biology. These early researches in material science deliver the basis for the evolution of inert biological substrates and given a foundation to biomaterials as a scientifically discrete discipline [38].

2.8.1 Orthopaedic Applications

All biomaterials (metallic, polymeric and ceramic) have been used for orthopaedic devices. Metallic biomaterials typically find applications in load bearing devices, for instance, in plates, pins, and femoral stems etc. Polymeric materials have applications for joint replacements of bony articular surfaces, which are normally used against ceramic components. Ceramic materials (like zirconia and ammonia) offer wear applications in joint replacements, whereas hydroxyapatite have uses in bone bonding applications for assisting implant integration. Porous alumina provide great uses being a bone spacer material for replacing affected parts of the bone, which require removal because of injury or disease [38].

Figure 2-4: Orthopaedic Applications including: Stents and orthopaedic implants [3]

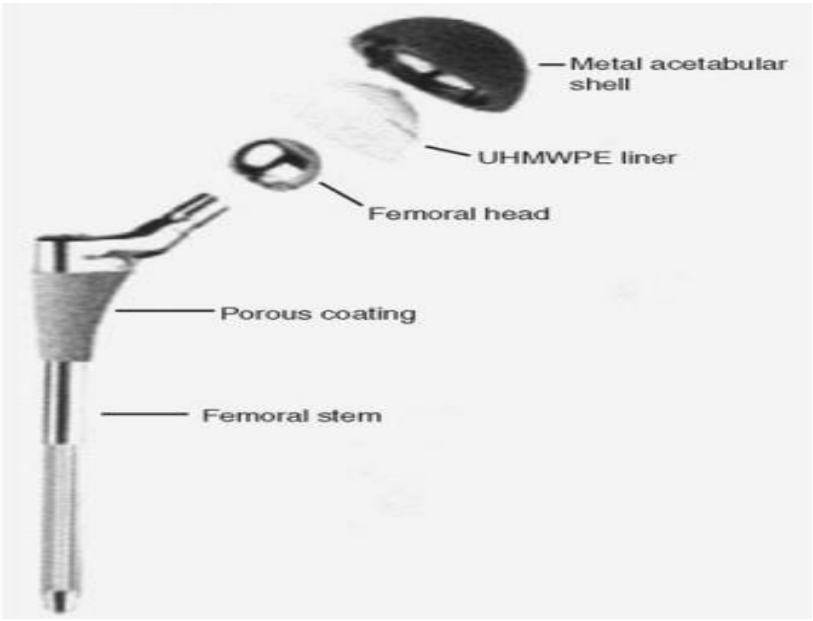

Figure 2-5: Components of a total-hip replacement implant used in orthopaedic surgery [2]

2.8.2 Dental Applications

Metallic bio-materials find uses in dental orthopedics, also used as pins in tooth implants for anchoring purposes. Polymeric materials as dentures and plates are used in orthodontic devices. Ceramic materials like alumina, offer applications in tooth implants and in dental porcelains. Hydroxyapatite has uses in tooth implants, metallic pin coatings, and as a bone filling material for bone voids caused by disease or injury [38].

Figure 2-6: Examples of different dental implants [39]

2.8.3 Cardiovascular Applications

Numerous biomaterials find uses for cardiovascular devices according to the particular needs and requirements. Such as, carbon has been in use for making heart valves, while polymer like polyurethanes have uses in making cardiac pacemaker leads [38].

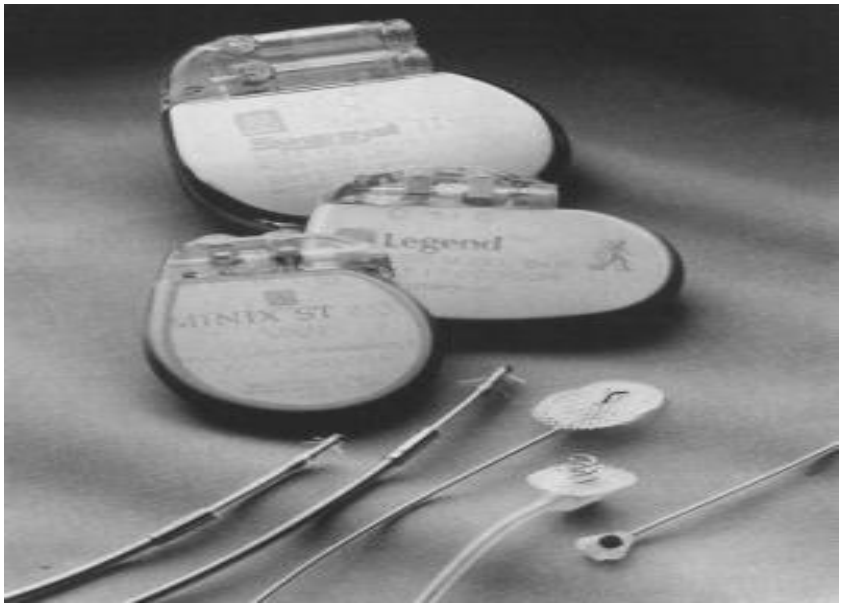

Figure 2-7: Different component designs of pacemaker including: pulse generators, connector blocks and pacemaker leads [2]

2.8.4 Cosmetic Surgery

Biomaterials also offer applications in cosmetic surgery, for instance, silicone implants has been used for breast augmentation [38].

2.9 Coating Processes

For improving properties of the substrate material surfaces, selection of suitable coating materials is not enough. Selecting the proper technique and procedure for depositing coating material onto the substrate surfaces of the implant material is also of great importance. Continuous researches have been performed in past few decades by utilizing several coating techniques and procedures. The most commonly used biomaterials group for coating purposes is of calcium phosphates (CaPs). Various coating processes that have been explored are plasma spraying, spray pyrolysis, sol-gel deposition, laser deposition, electrophoretic deposition, biomimetic deposition and dip coating [40].

Table 4: Characteristics of different coating techniques [40]

Coating Technique	Coating thickness	Advantage	Disadvantage
Plasma spraying	50-250 μm	High deposition rates	Non-uniform coating crystalinity; line of sight technique
Pulsed laser deposition	0.05–5μm	Controlled coating chemistry and morphology	Line of sight technique
Biomimetic deposition	<30μm	Coating of complex geometries; co-deposition of biomolecules	Time consuming; requires controlled pH
Sol-gel deposition	<1μm	Coating of complex geometries; low processing temperature	Requires controlled atmosphere processing; expensive raw materials
Electrophoretic deposition	0.1–5μm	Co-deposition of biomolecules; Controlled composition and morphology	Low mechanical strength; Line of sight technique

In this research work, the electrophoretic deposition and spray pyrolysis are used for the deposition of HA onto 316L stainless steel.

2.9.1 Plasma spraying

Plasma spraying (PS) is the most commonly adopted dry deposition technique for industrial purposes. That is because this technique offers higher deposition rates and large covering areas for coatings. The processing involved in the plasma spraying include the generation of a hot plasma flame or jet by introducing the feedstock or precursor materials into the plasma producing torch at certain pressure conditions. Through this plasma jet the feedstock particles bombarded onto the surface of the implant causing either complete or partial melting of these powder particles which results in the formation of an adherent coating [40].

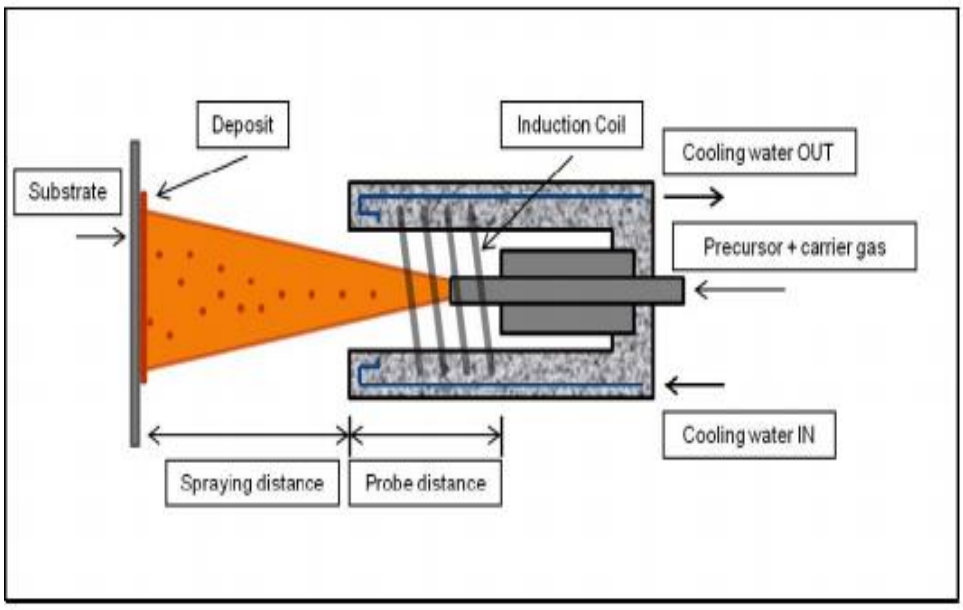

Figure 2-8: Schematic representation of plasma spraying technique [40]

On the basis of the variable pressure conditions the plasma spraying can be classified into 3 different processes:

1. Low Pressure Plasma-Spraying (LPS) is performed at low or reduced pressure conditions.
2. Vacuum Plasma-Spraying (VPS) is performed in a vacuum chamber.
3. Atmospheric Plasma-Spraying (APS) is performed at air pressure conditions [40].

2.9.2 Pulsed laser deposition

Pulsed laser deposition (PLD) is another dry deposition technique in which a thin film is deposited by using the mechanism of physical vapor deposition (PVD). The setup of this technique consists of: laser source of krypton fluoride (KrF), substrate holder fixed to its position, deposition chamber of ultrahigh vacuum, pumping systems and rotating target. The solid target is irradiated when the pulsed laser beams are focused onto it, producing certain compounds. This creates a plasma cloud of high energy which contains electrons, atoms, ions, molecules, clusters of molecules and might also include fragments of target material and droplets. The expansion of this plasma cloud occurs whether in gaseous or vacuum environment and deposition of adherent thin film over the substrate is achieved at a temperature between 350–600 °C [40].

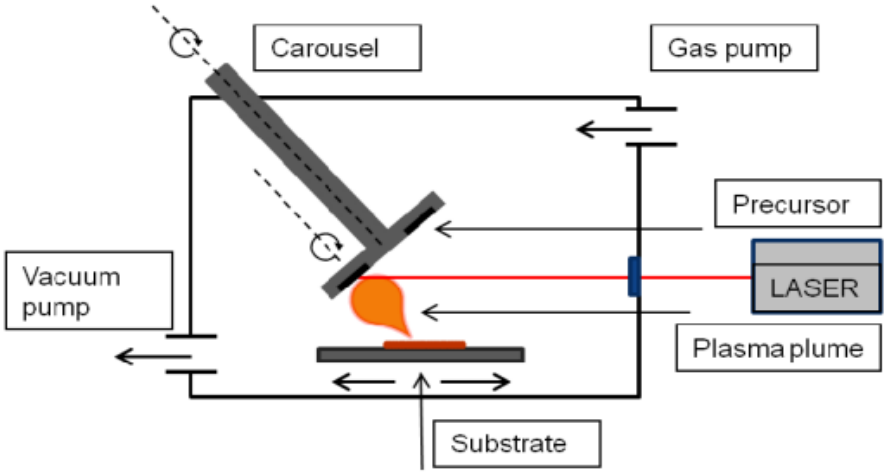

Figure 2-9: Schematic representation of the pulsed laser deposition (PLD) coating system [40]

2.9.3 Sol-Gel deposition

The sol-gel deposition is a wet chemical deposition technique in which a liquid solution is formed (which is called ‘sol’) having solid particles of the sizes ranging 1-500 nm in the form of colloidal suspensions. Different coating methods can then be used (such as, dip-coating, spraying or spin-coating) for applying the sol over the substrate material. This sol coating while still present in the form of a ‘gel’ is placed on the surface of target material and then subjected to drying. During drying, the transition from sol to gel phase completed resulting in the formation of a thin coating of precursor materials only [40].

2.9.4 Biomimetic deposition

Biomimetic deposition is another wet deposition technique firstly introduced in 1990 [41] by Kokubo *et al.* in which the coating is made in similar biological conditions which are as follows:

- ✓ pH value 7.4
- ✓ Temperature 37 °C
- ✓ Pressure of CO_2 0.05 atmospheric
- ✓ suitable concentration of electrolytes

The process includes formation of a stimulated body fluid (SBF) which mimics the in vivo conditions. Then pretreated substrate samples of Ti are placed within SBF to achieve the bone-like surface deposition of CaP coating over the samples [42].

2.9.5 Electrophoretic deposition

Electrophoretic deposition (EPD) process is different from both dry and wet deposition techniques and lies under the category of electrochemical deposition. This type of deposition processes usually performed at room pressure and temperature conditions and the precursor materials that need to be coated are present in the form of distributed particles within electrolytic solutions and have the ability to transport electrical charge. The substrate material used in these processes is also electrically conductive in nature [40].

EPD uses the mechanism of electrophoresis for the coating purposes which involves the movement of charged precursor particles suspended in the liquid solution under the effect of an electric field and gets deposited on the substrate surfaces which serve as electrode. The organic solvents are mainly used as a liquid medium in EPD like methanol, ethanol or isopropanol [40].

The EPD processes can be of two types: cathodic and anodic processes. The main electrochemical reactions that take place during EPD are related to the process of water electrolysis and are given below:

Anodic reaction: $H_2O \rightarrow 1/2(O_2)\ (g) + 2H^+ + 2e^-$

Cathodic reaction: $2H_2O + 4e^- \rightarrow 2OH^- + H_2\ (g)$

Anodic EPD involves the anodic reaction where the colloidal suspended particles carry negative charge and react with the H^+ ions that are generated at anode. This results in the neutralization of colloidal particles resulting in their deposition at the substrate material which serve as an anode in anodic EPD. Cathodic EPD involves the cathodic reaction where the colloidal suspended particles carry positive charge and are neutralized by reacting with the OH^- ions that are generated at cathode. In this process, the substrate material is acting as a cathode [43].

There are certain factors that can control the deposition rate when their values are varied. These factors are given below:

- ✓ time
- ✓ electrode voltage
- ✓ electrode materials
- ✓ size of particles needs to be deposited
- ✓ conductivity
- ✓ pH of the suspensions/solutions [43]

Both thin and thick coatings can be obtained, also because it is a submersion coating process it can facilitate the deposition on porous implants as well. Coatings of composite materials and both inorganic and organic materials can be achieved for biomedical implants [40]. The overall low cost of the materials and equipment used, makes this process a good choice to be used in this research work.

2.9.6 Spray Pyrolysis

The process of spray pyrolysis involves the spraying of a solution (which contains the coating material) onto the substrate material (that is heated to a desired temperature) to obtain a nanostructure onto the substrate material surface. Apart from the coating material, the other constituents in the spraying solution are volatile at the deposition temperature so that the coating of only desired material can be obtained. Spray pyrolysis has various process variables that determine the properties of the deposited nanostructure such as its thickness, shape and particle size. These process variables are:

- ✓ substrate surface temperature
- ✓ solution flow rate

- ✓ solution concentration
- ✓ nozzle-to-substrate distance
- ✓ carrier gas flow rate
- ✓ ambient temperature
- ✓ duration of the spray

Spray pyrolysis can be used for developing thin nano-scale coatings and clusters at the commercial level provided that certain process parameters have been kept constant. For instance, coatings of CdSe, CdS, TiO_2 and Cu can be produced by this process [44].

In this research work, the deposition of HA on 316L stainless steel have been done.

Chapter 3

Experimental Procedures

In this chapter, the two coating techniques that were used to produce coatings of HA onto 316L stainless steel are discussed in detail.

3.1 HA coatings by EPD method

3.1.1 Materials and Equipment Used

The main materials and equipment that were used during this process are as follows:

- ✓ Synthesized hydroxyapatite (HA) powder
- ✓ Methanol (CH_3OH)
- ✓ Poly vinyl alcohol (PVA)
- ✓ De-Ionized water
- ✓ Nitric acid (HNO_3)
- ✓ Acetone (C_3H_6O)
- ✓ Drying Oven
- ✓ Hotplate Magnetic Stirrer
- ✓ Ultrasonic Bath Sonicator
- ✓ Vacuum Filtration apparatus
- ✓ Electrochemical Workstation
- ✓ 316L stainless steel samples
- ✓ Silicon carbide (SiC) papers of different grit sizes

3.1.2 Purpose of using PVA

PVA is a synthetic polymeric binder material. PVA is highly soluble in water and does not have any effect on the bioactivity of HA coatings. The purpose of using PVA is to improve the HA coating adhesion with the substrate material. This is because the attachment between the metallic substrate and HA coating is poor. Sintering process to enhance the bonding strength of coating can also be used. But high temperatures used in sintering causes deterioration of the substrate material as well as phase changes in HA coatings can also take place producing coatings which have higher dissolution rates in the body.

3.1.3 PVA coated HA Preparation

First of all, the HA powder was coated with the PVA powder (5 wt%). For this procedure, a suspension was obtained by suspending 4 grams of HA powder in de-ionized water and 0.2 grams of PVA powder (which corresponds to 5 weight %) was added to this suspension to make a mixture. This mixture was stirred and heated at 50°C for half an hour on a hot-plate magnetic stirrer. The filtration of the mixture was done by using the vacuum filtration apparatus to remove the water. The resulting product was dried in a drying oven at 80°C for 24 hours to eliminate any remaining water content. The dried product was then grounded into a fine powder by using mortar pestle.

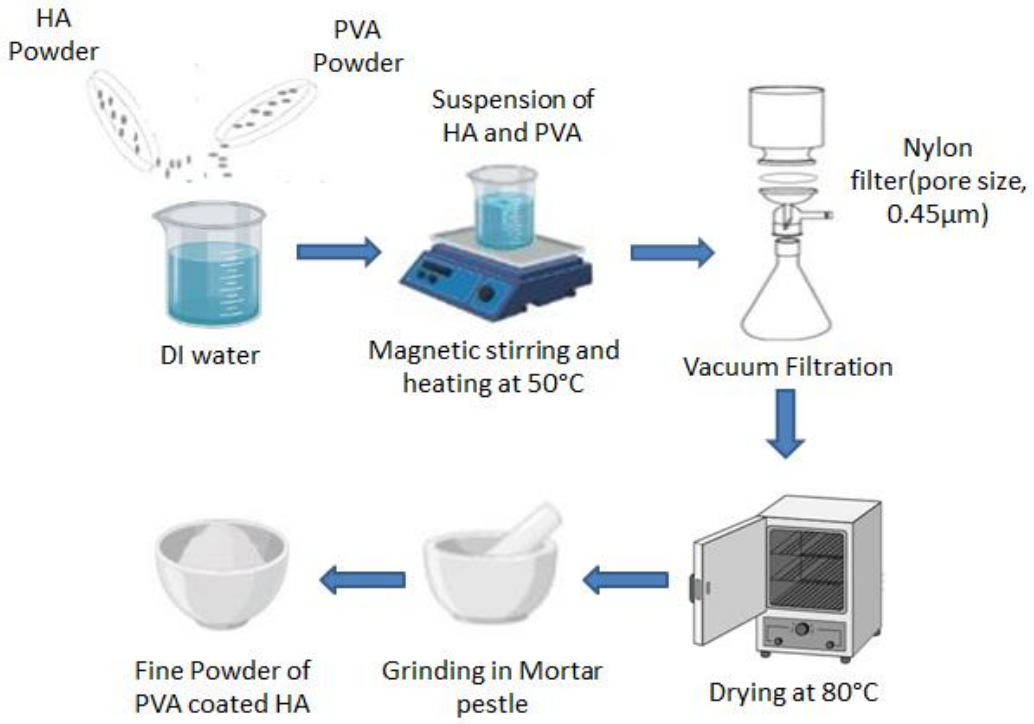

Figure 3-1: Schematic of the Preparation of PVA coated HA

3.1.4 EPD Procedure

The EPD procedure starts with the formation of a 2% suspension of that finely grounded powder of HA which is coated with PVA, in methanol. In this process, 2 grams powder of PVA coated HA was suspended by using ultrasonic bath sonicator in 100 ml of methanol for half an hour. The pH of this suspension was 10. Coating of one sample was done by using this suspension. For another sample, the pH was adjusted to 8 by using 1ml of nitric acid in the suspension. And for the remaining

samples, the pH of the sample was adjusted to 6 by adding 2 ml of nitric acid in the suspension.

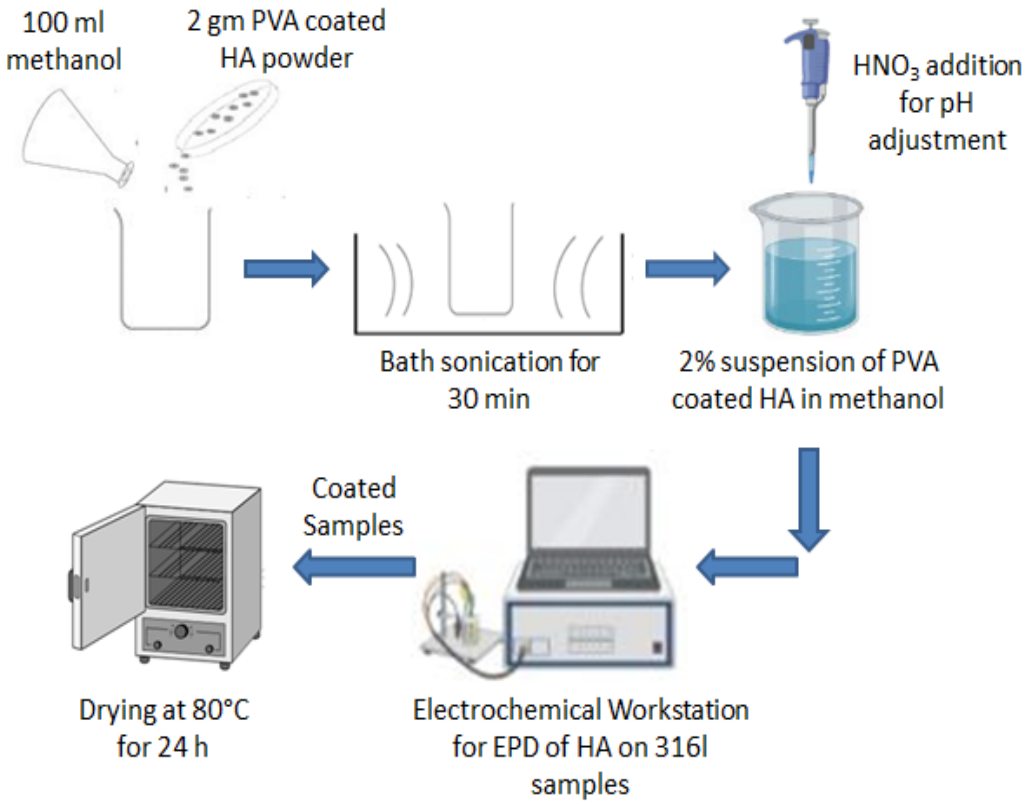

Figure 3-2: Schematic of producing HA coatings by EPD

Substrate samples used were of 316L stainless steel plates. In order to remove any scratching marks their polishing was done by using upto 1000 grit sized papers of SiC. The samples were thoroughly washed and rinsed by using de-ionized water. The degreasing of the samples with acetone was done in ultrasonic bath sonicator followed by drying in the oven.

The substrate samples were used as cathode in the EPD setup. A Platinum (Pt) electrode was used as an anode. In the suspension, both of these electrodes were dipped by keeping a distance of 1cm between them. Direct current was passed through the suspension to achieve the deposition of the suspended particles onto the substrate electrode. The coated substrate was then taken out and kept in the heating oven for drying at 80°C for 24 h.

A diagram of showing the EPD process for coating HA on 316l-SS is shown in the figure below.

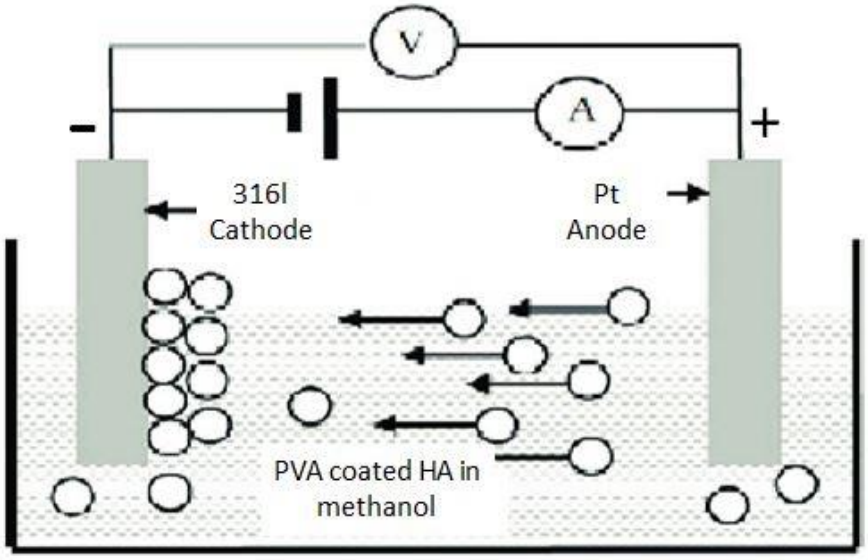

Figure 3-3: Diagram of the EPD process for coating HA on 316l stainless steel

The seven different samples were coated with EPD procedure by changing 3 parameters that control the deposition rate, including: voltage, time and pH of the suspension. Details of these prepared samples, given in the table below.

Table 5: Processing conditions for different samples coated by EPD

Sample #	Voltage (volts)	Time (hours)	pH
1	9	1	6
2	9	2	6
3	9	4	6
4	9	4	8
5	9	4	10
6	8	4	6
7	9.9	4	6

3.2 HA Coatings by Spray Pyrolysis

The main materials and equipment that were used during this process are as follows:

- ✓ Synthesized HA powder

- ✓ Methanol (CH_3OH)
- ✓ Magnetic Stirrer
- ✓ Ultrasonic Bath Sonicator
- ✓ Spray Gun
- ✓ Air compressor Pump
- ✓ Hot Plate
- ✓ Infrared Thermometer
- ✓ Muffle Furnace

3.2.1 Preparation of Spraying Solution

The spraying solution was obtained by adding 1 gm of powdered HA into 100 ml of methanol. This suspension was stirred by using a magnetic stirrer for 4 hours and this was followed by sonication in the ultrasonic bath sonicator for half an hour to achieve a uniform distribution of HA particles into methanol. The methanol as a solvent was used because of its low boiling point of 64.7°C, which is lower than all of the different substrate surface temperatures that were used during this coating process. So that, methanol gets evaporated when coating solution sprayed onto substrate surface and the coatings of pure HA can be obtained.

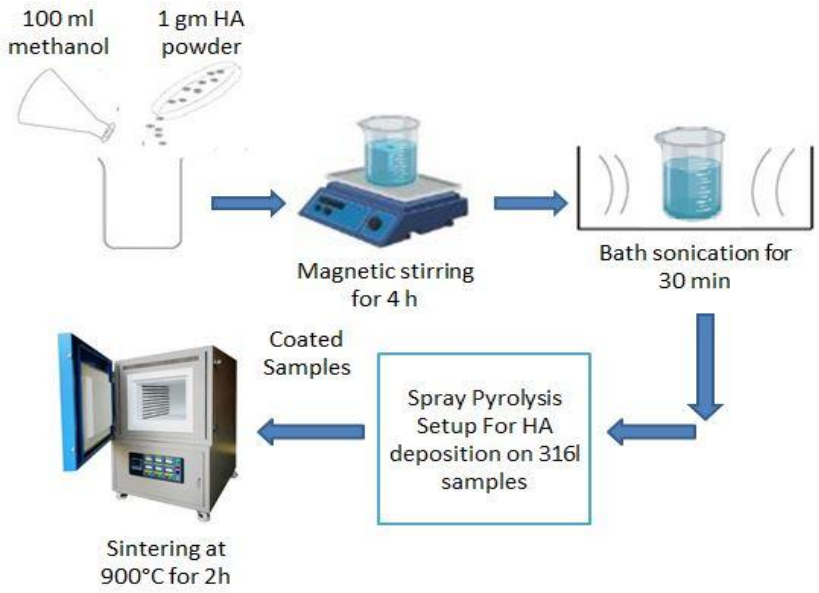

Figure 3-4: Schematic of producing HA coatings by spray pyrolysis

3.2.2 Spray Pyrolysis Procedure

After bath sonication, the HA coating solution was transferred into the container of spraying gun. The spraying gun was connected to an electric air compressor pump.

The pressure was kept constant for all the samples at around 80 psi. The substrate sample was placed onto the hot plate for heating the substrate surface upto the desired temperature. To hold the substrate in place for sustaining the air pressure during spraying kapton tape was used. The temperature of the substrate surface was monitored closely by using the infrared thermometer. Right after the desired surface temperature was reached, the spraying was started. The coated sample was then sintered at 900°C for 2 hours in a muffle furnace. The following figure shows the diagram of spray pyrolysis setup used for coating HA on 316l-SS.

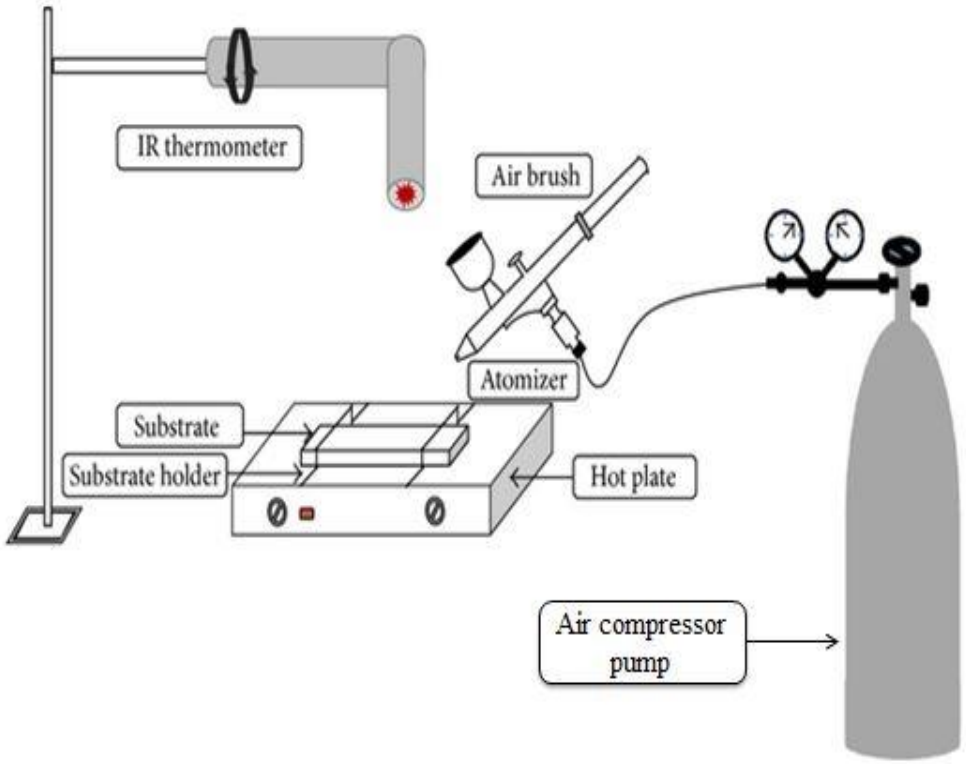

Figure 3-5: Diagram of spray pyrolysis process for coating HA on 316l stainless steel [45]

The duration of the spraying for most samples was 1 minute and was changed for some samples. The substrate surface temperature used for most samples was 250°C. Also the distance between the surface of the substrate and nozzle of the spraying gun was 25 cm for most samples.

The seven different samples were coated with this procedure by changing 3 process variables including: substrate surface temperature, duration of the spray and nozzle-to-substrate distance. Details of these prepared samples, given in the table below.

Table 6: Processing conditions for different samples coated by spray pyrolysis

Sample #	Surface temperature T (°C)	Nozzle-to-substrate distance d (cm)	Duration of spray t (seconds)
1	250	25	30
2	250	25	60
3	250	25	90
4	200	25	60
5	150	25	60
6	250	20	60
7	250	15	60

Chapter 4

Characterization Results and Discussion

4.1 Scanning Electron Microscope (SEM)

To analyze the structural morphology of the obtained HA coatings, Scanning Electron Microscope (SEM) was used. The equipment used for SEM was JEOL-instrument JSM-6490A. SEM is a non-damaging characterization technique and causes no harm to the sample after the electrons interact with the coated surface.

The first step in SEM is to make the testing surface conductive which in this case was HA coating (non-conductive), and for this purpose gold sputtering on HA coatings was done before the actual SEM process was started. The operating conditions while the SEM analysis was performed include:

- ✓ Operating voltage of 10-20 kV
- ✓ Applied current 90 mA
- ✓ 10mm of working distance

4.1.1 Spray Pyrolysis Samples

The SEM images at two different magnifications (2,000 or 2,500 and 10,000) and known distances (1μm and 10μm) are given below. The figure 4-1 to 4-6 are of the HA coated samples by spray pyrolysis technique.

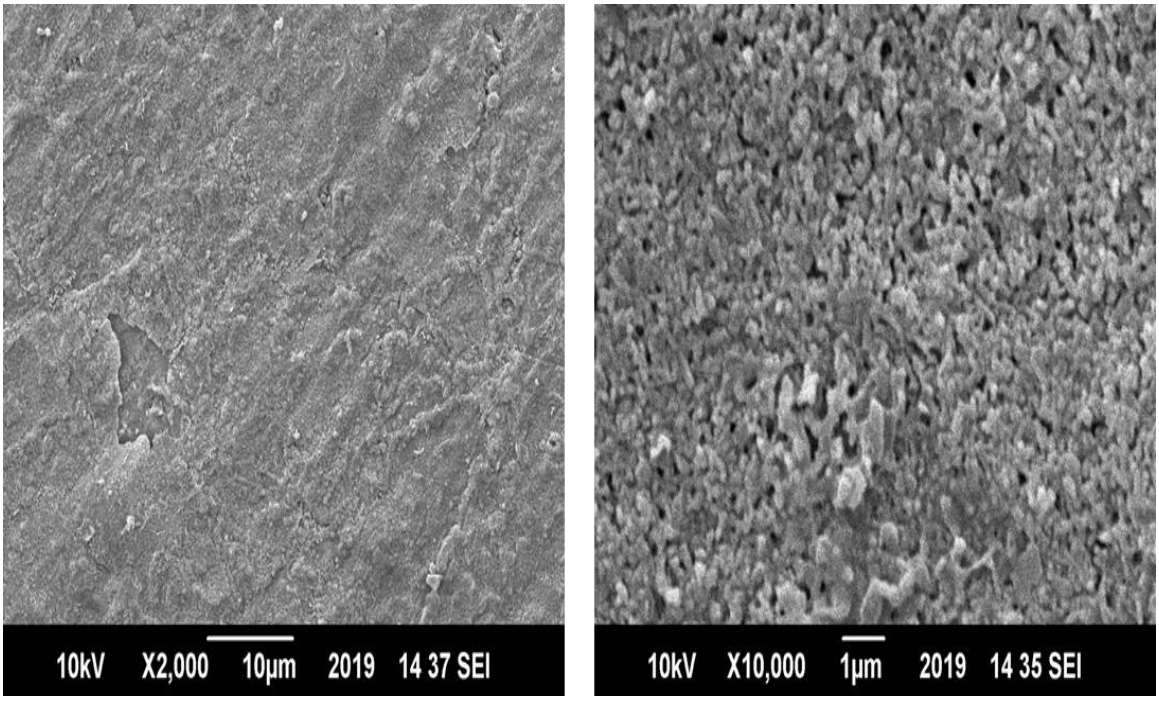

Figure 4-1: SEM image of the sample with processing conditions of (1 min, 150 °C, and 25 cm) at 2,000 and 10,000 magnifications

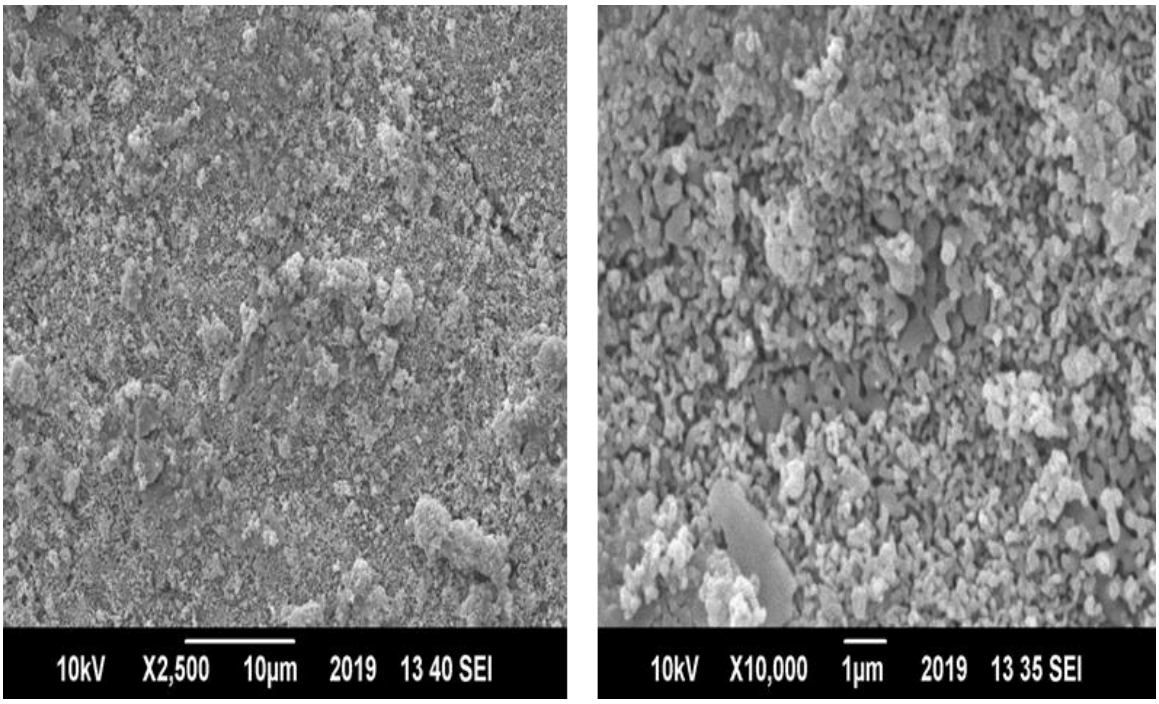

Figure 4-2: SEM image of the sample with processing conditions of (1 min, 200 °C, and 25 cm) at 2,500 and 10,000 magnifications

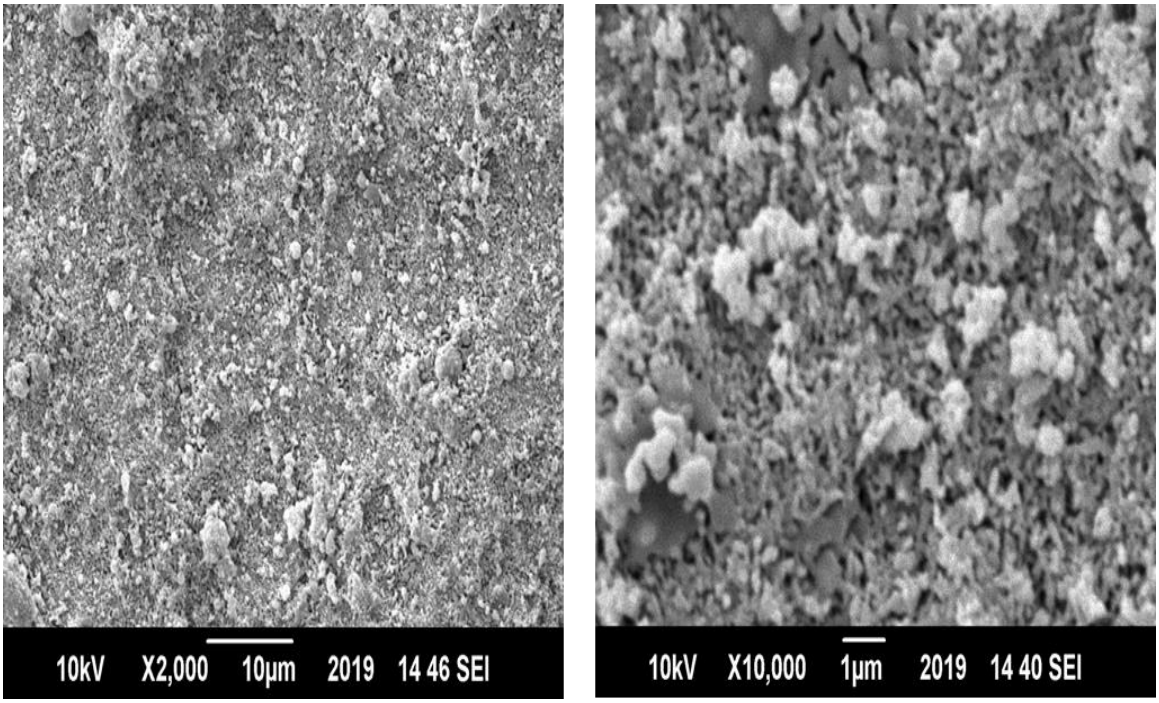

Figure 4-3: SEM image of the sample with processing conditions of (1 min, 250 °C, and 25 cm) at 2,000 and 10,000 magnifications

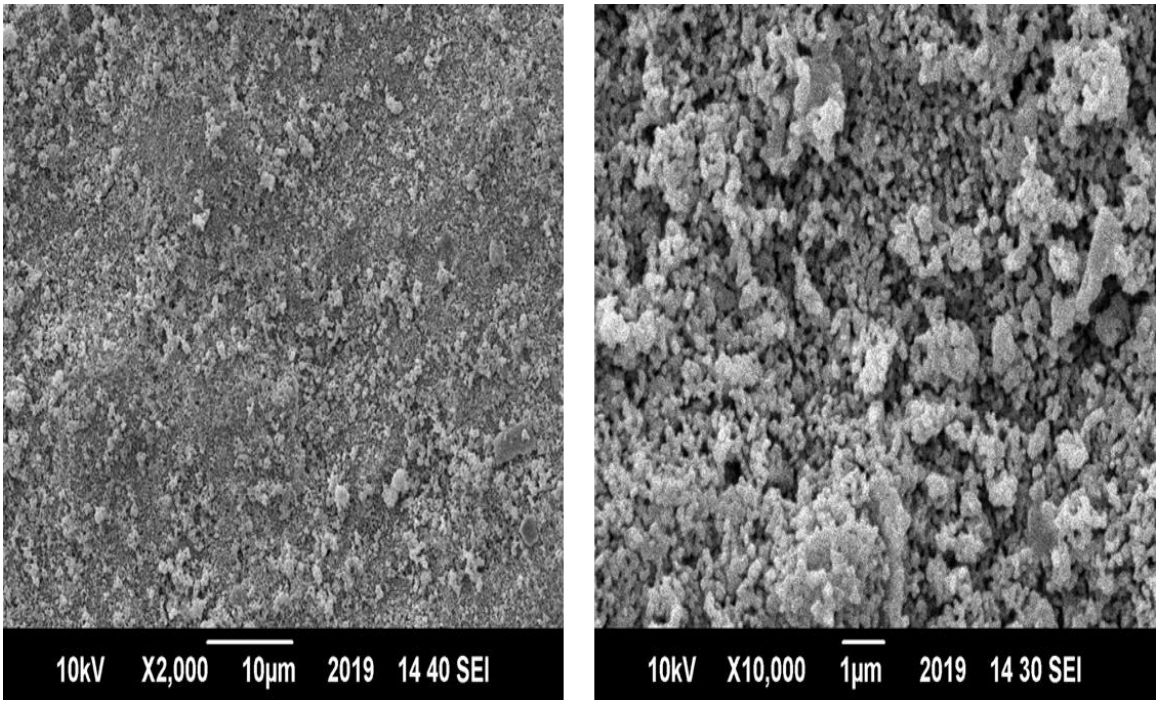

Figure 4-4: SEM image of the sample with processing conditions of (1 min, 250 °C, and 20 cm) at 2,000 and 10,000 magnifications

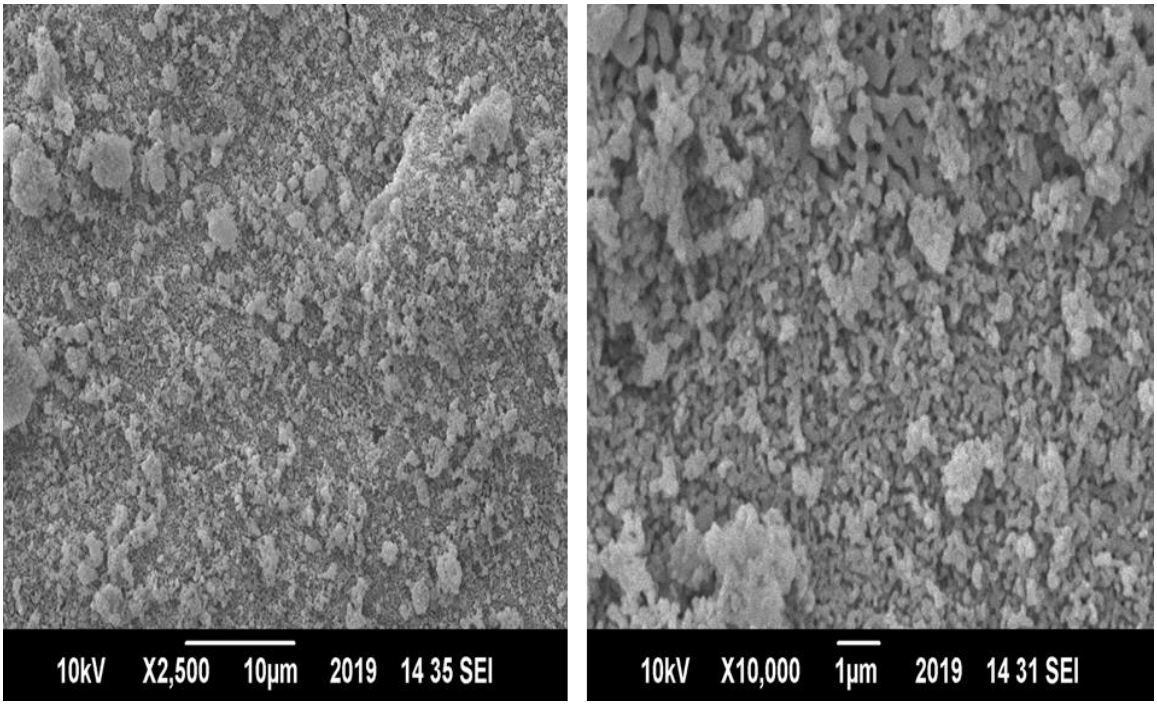

Figure 4-5: SEM image of the sample with processing conditions of (1 min, 250 °C, and 15 cm) at 2,500 and 10,000 magnifications

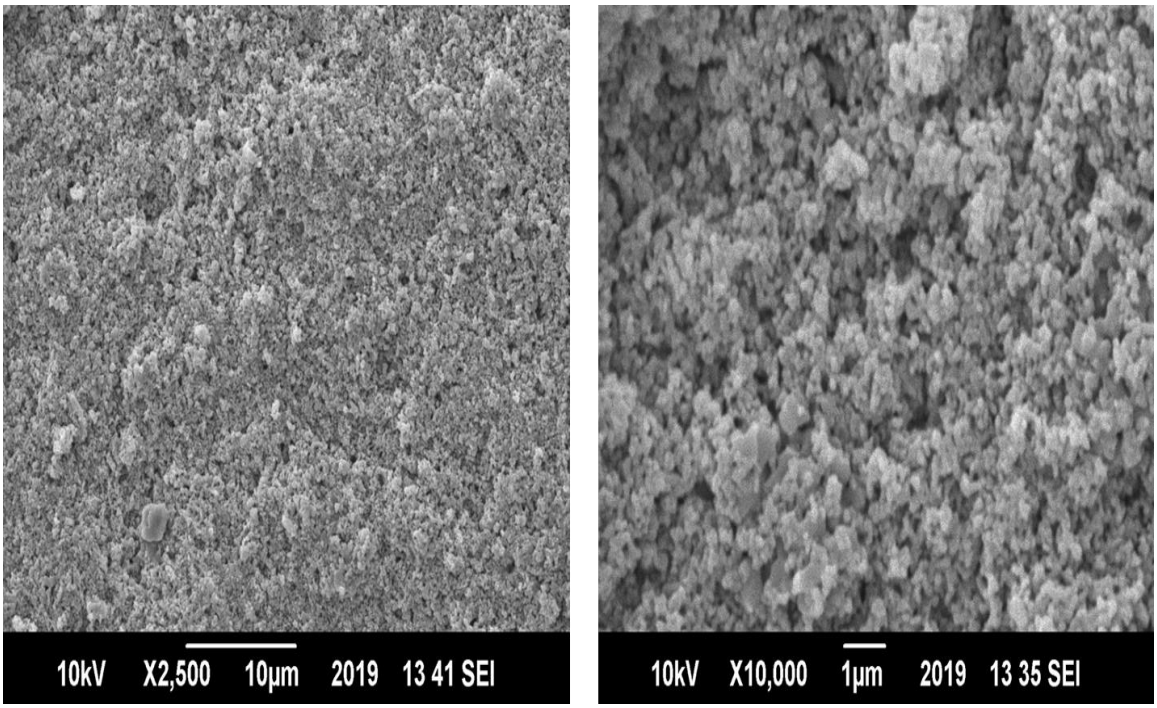

Figure 4-6: SEM image of the sample with processing conditions of (1 min 30 sec, 250 °C, and 25 cm) at 2,500 and 10,000 magnifications

4.1.1.1 Variable Substrate Surface Temperature

The figure 4-1 to 4-3 belongs to the samples in which the two constant process variables used were duration of the spray (1 minute) and nozzle-to-substrate distance (25 cm). The only variable was the substrate surface temperature which was 150 °C, 200 °C, and 250 °C respectively.

The coating in fig. 4-1 was found to be the deposited homogenously but does have some minor cracks visible in there. The coating in fig.4-2 was also homogenously deposited and does have a few minor visible cracks in it as well. The coating in fig. 4-3 had homogenous deposition but no visible cracks were found in there. All three coatings had surface level porosity in them. Overall, the coating thickness or the visible deposited mass on the surface of the substrate was found to be the highest on the sample where deposition took place at 250 °C of substrate surface temperature. In other words the deposited mass was increased with increasing substrate surface temperature from 150 °C to 250 °C.

4.1.1.2 Variable Nozzle-to-Substrate Distance

The figure 4-3 to 4-5 belongs to the samples in which the two constant process variables used were duration of the spray (1 minute) and substrate surface temperature (250 °C). Nozzle-to-substrate distance was the variable in these samples and its values used were 25 cm, 20 cm, and 15 cm respectively.

The surface morphology of coating in fig. 4-3 is discussed above. The coating in fig. 4-4 was found to have similar homogeneous deposition having no visible cracks as in case of third sample (fig. 4-3). The only visual difference in both these samples was of coating thickness (deposited materials mass), which was found to be thicker in third sample. The coating in figure 4-5 was relatively less homogenously deposited with more irregularly placed agglomerates having few minor visible cracks as well. Surface level porosity was also present in all these samples. Overall, the thickness and homogeneity of the coating was found to be the highest on the sample where deposition took place at 25 cm of nozzle-to-substrate distance. In other words, homogeneity and thickness of the coating was improved when nozzle-to-substrate distance was increased from 15 cm to 25 cm.

4.1.1.3 Variable Duration of the Spray

In figure 4-5 and 4-6 the constant process effecting factors were substrate surface temperature (250 °C) and nozzle-to-substrate distance (25 cm). The variable factor

was duration of spray with values used were (1 min) and (1 minute 30 sec) respectively.

The surface morphology of coating in figure 4-5 is discussed above. The coating in fig. 4-6 has shown the best results overall in terms of homogeneity and thickness of the coating if compared with all other samples that were coated by spray pyrolysis technique. Overall, the trend here was found to be that while increasing the duration of spraying from 30 seconds to 1 min and then from 1 min to 1 min and 30 sec, the overall coating results were came better.

4.1.2 EPD Samples

The figure 4-7 and 4-8 belongs to the HA coated samples that were obtained by using EPD.

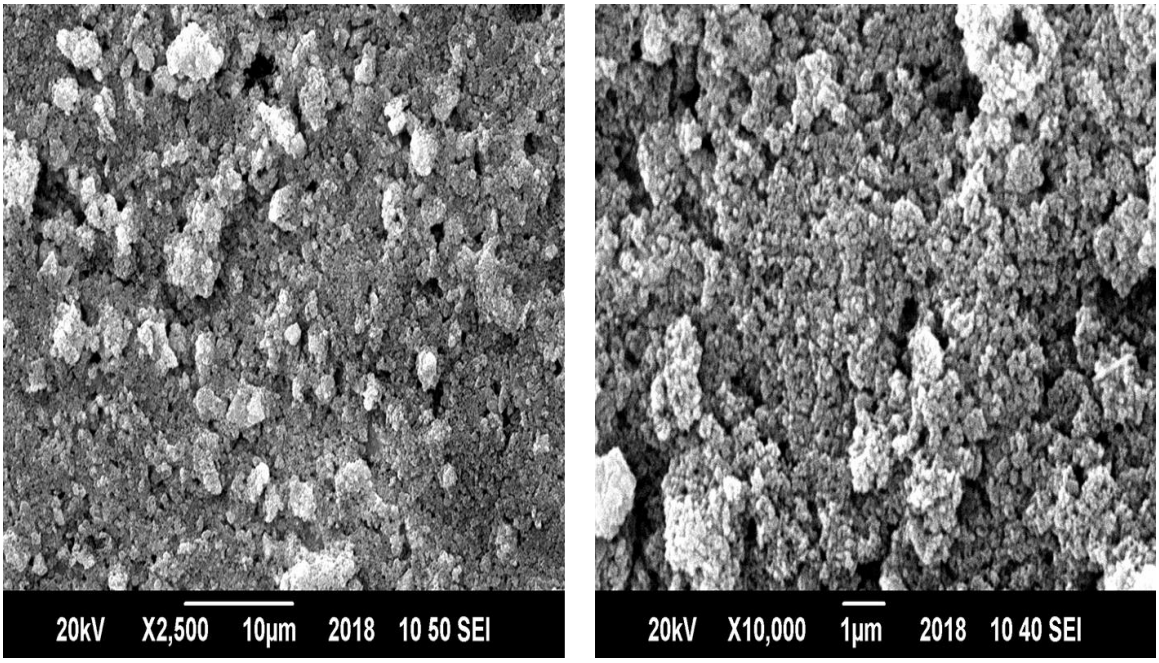

Figure 4-7: SEM image of the sample with processing conditions of (9 volts, 4 hours, and 8 pH) at 2,500 and 10,000 magnifications

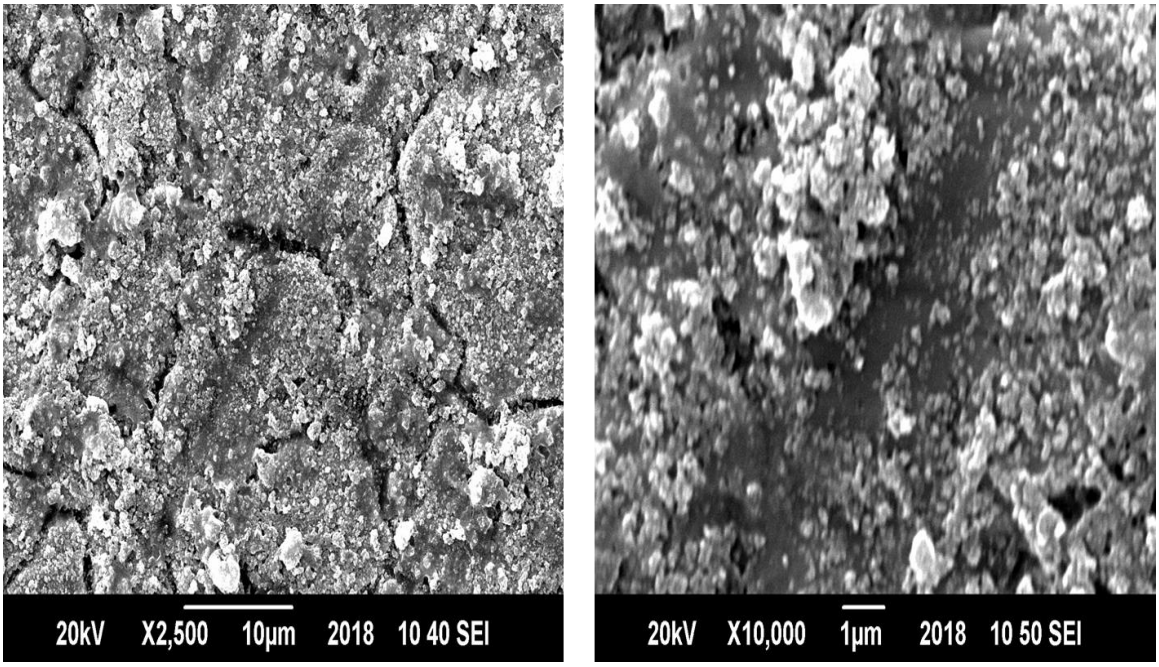

Figure 4-8: SEM image of the sample with processing conditions of (9 volts, 4 hours, and 10 pH) at 2,500 and 10,000 magnifications

4.1.2.1 Variable pH of the Suspension

The two process effecting factors that were kept constant for the samples represented in figure 4-7 and 4-8 were applied voltage (9 volts) and time of the coating process (4 hours). The variable process factor was the pH of the suspension and its values used were 8 and 10 respectively.

The coating in figure 4-7 was found to have homogeneous deposition of particles having no visible cracks but does have surface level porosity. Visible Deposited mass was found to be relatively higher as compared to the sample shown in fig. 4-8. The coating in figure 4-8 was lower in uniformity of the deposited particles, had some visible cracks and porosity. Overall, it was found out that by lowering pH of the suspension from 10 to 8 and then 6, the better homogeneity and thickness of the coating was achieved.

4.2 Atomic Force Microscope (AFM)

Surface roughness analysis of the HA coatings was done by using atomic force microscope (AFM). This characterization technique can also provide information regarding thickness of the obtained coatings. The equipment used for AFM was JOEL JSPM-5200. AFM data analysis of three EPD coated samples (with variable applied voltage but constant coating time and pH of the suspension) is discussed

below. AFM images of these samples in 2d and 3d and their histogram analyses are also given below.

4.2.1 AFM Analysis of EPD coated samples

The topographical image space of these samples was (2µm × 2µm × maximum particle height) as shown in the 3D AFM images below. The white spots in these images represents the deposited HA particles.

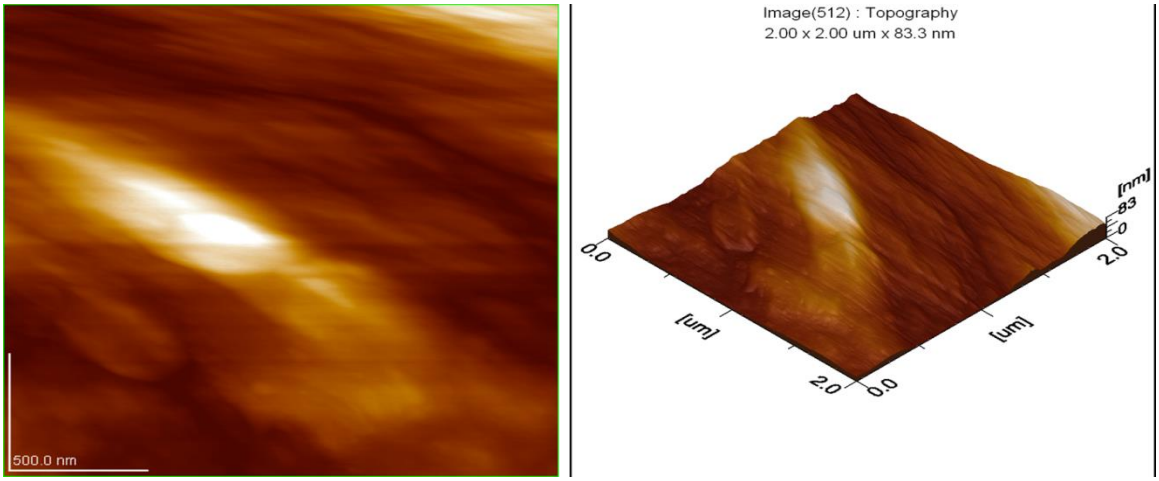

Figure 4-9: AFM images in 2D and 3D of the sample coated at (8v, 4h, and 6pH)

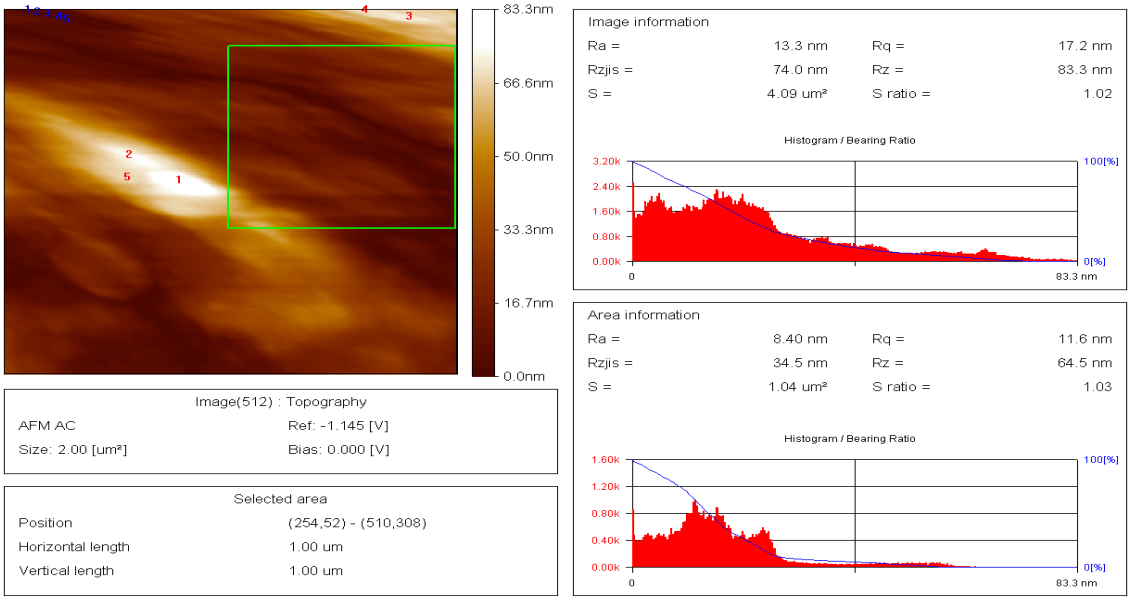

Figure 4-10: Histogram analysis of sample coated at (8v, 4h, and 6pH)

The fig. 4-10 shows the histogram analysis of the EPD coated sample with processing conditions of (8v, 4h, and 6pH). In this sample, the maximum particle

height which also corresponds to the thickness of the coating was 83.3 nm. The average roughness (Ra) of the deposited particles was 13.3 nm.

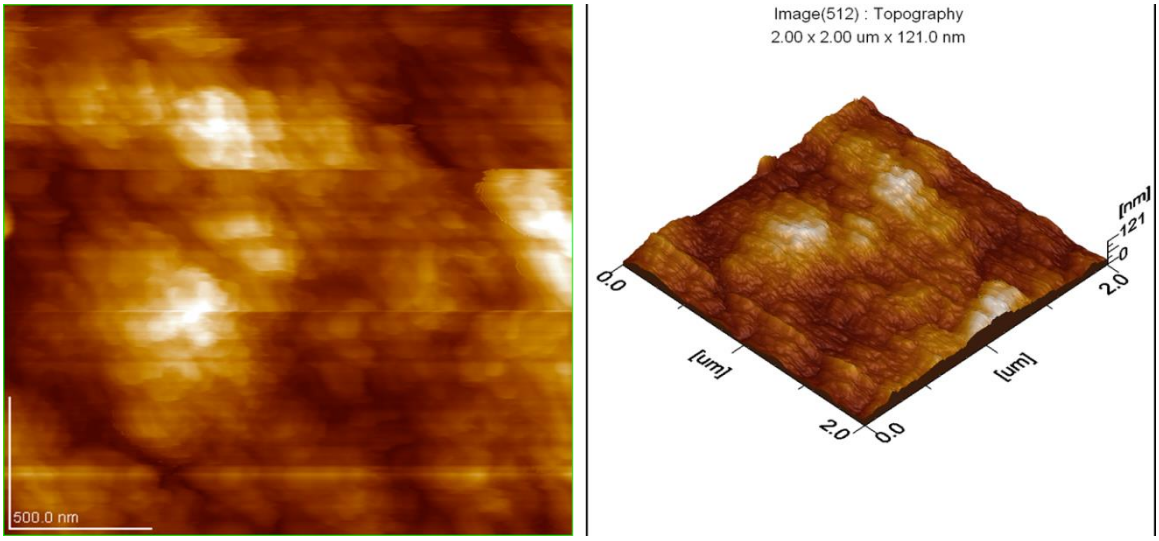

Figure 4-11: AFM images in 2D and 3D of the sample coated at (9v, 4h, and 6pH)

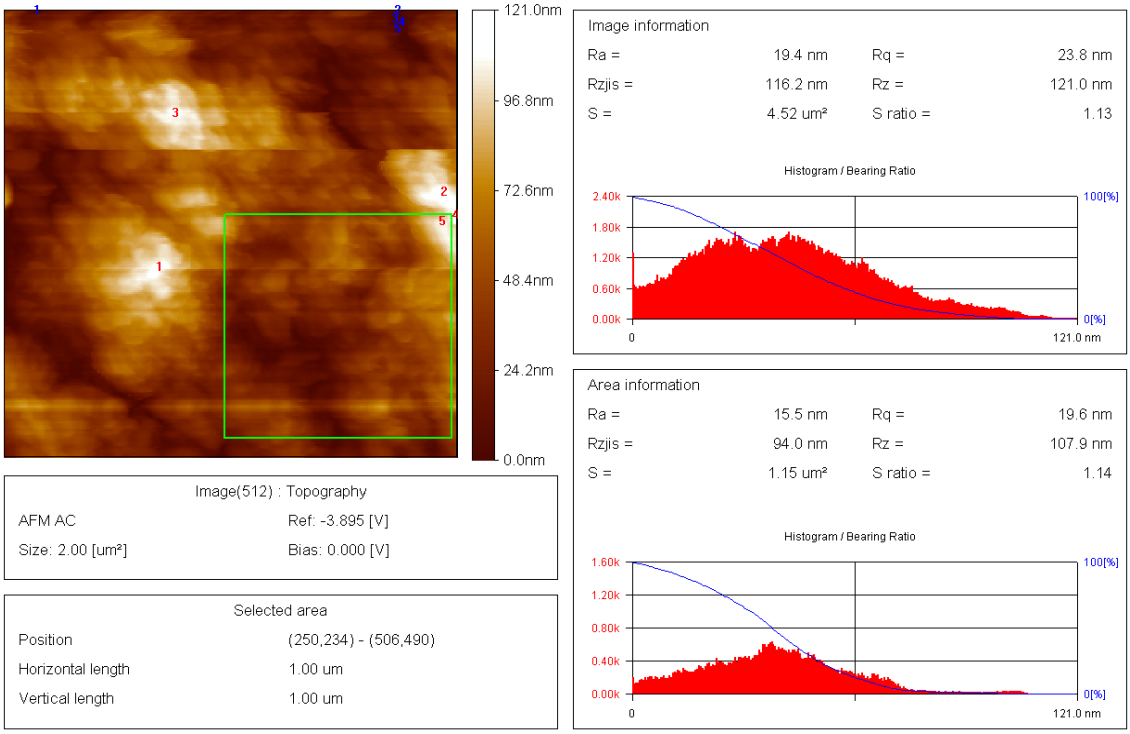

Figure 4-12: Histogram analysis of sample coated at (9v, 4h, and 6pH)

The fig. 4-12 shows the histogram analysis of the EPD coated sample with processing conditions of (9v, 4h, and 6pH). In this sample, the maximum particle

height or coating thickness was 121 nm. The average roughness (Ra) of the deposited particles was 19.4 nm.

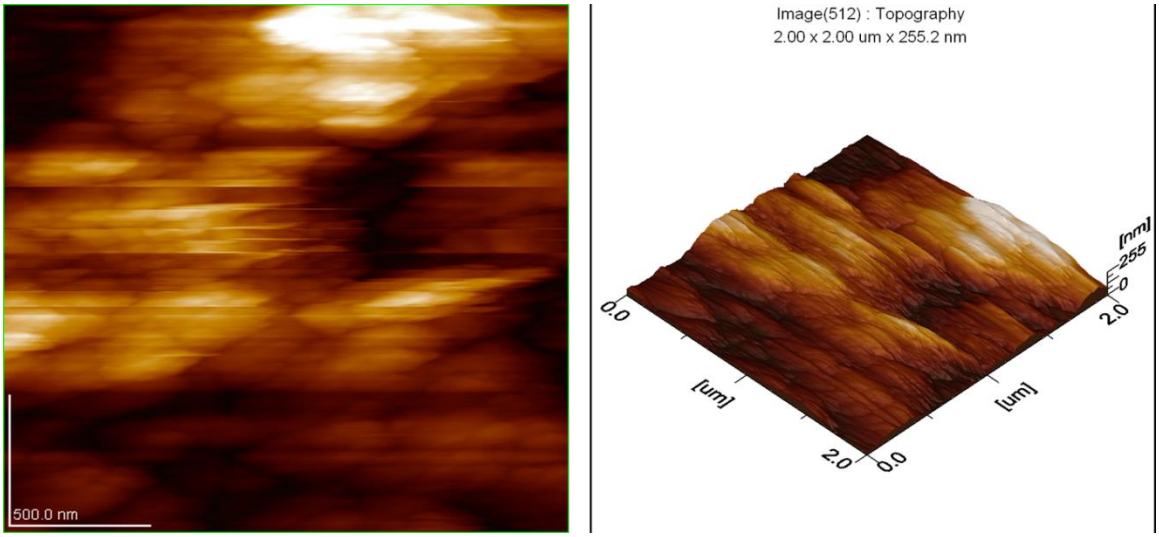

Figure 4-13: AFM images in 2D and 3D of the sample coated at (9.9v, 4h, and 6pH)

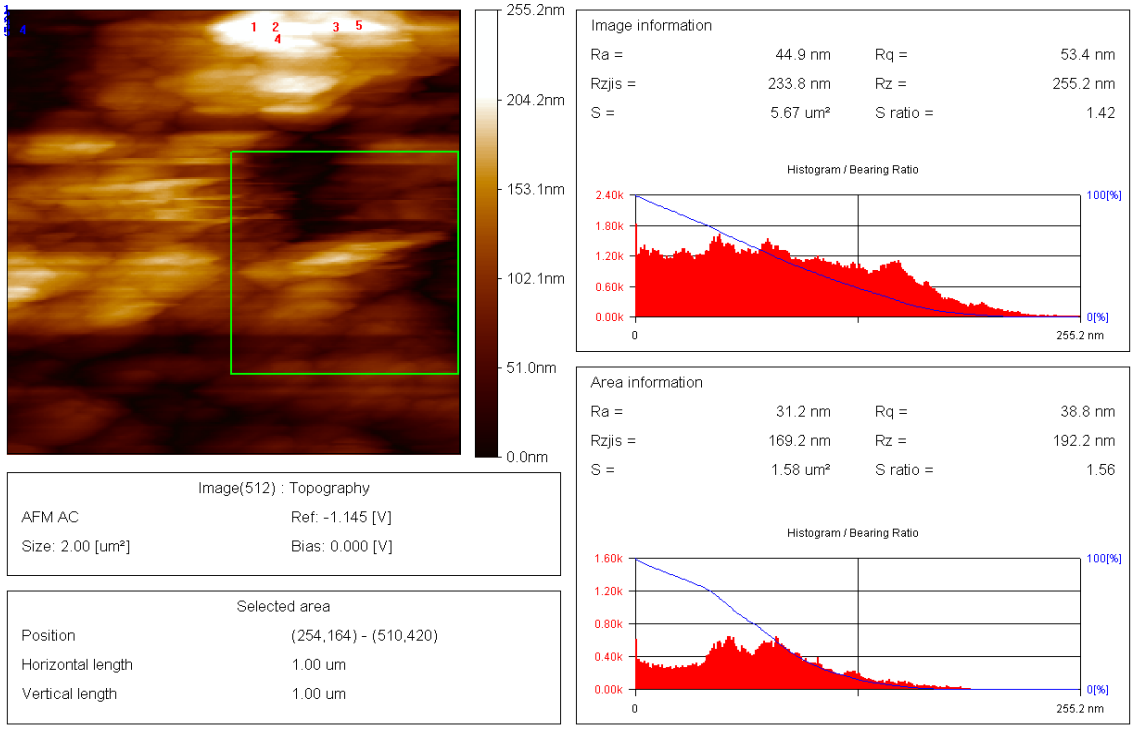

Figure 4-14: Histogram analysis of sample coated at (9.9v, 4h, and 6pH)

The fig. 4-14 shows the histogram analysis of the EPD coated sample with processing conditions of (9.9v, 4h, and 6pH). In this sample, the maximum particle or coating thickness was 255.2 nm. The average roughness (Ra) of the deposited particles was 44.9 nm.

Overall, the coating thickness was increased with increasing the voltage used (from 8v to 9.9v) during EPD process. The average coating particle roughness was also increased in the same fashion.

4.3 X-Ray Diffraction (XRD)

To find out the crystal structure and the overall crystallinity of the HA coatings, X-ray diffraction (XRD) analysis was done. XRD is another non-damaging characterization technique and does no harm to the sample after the interaction of X-rays takes place with the coated surface.

XRD of the samples was done within the scanning angle (2Θ) of 20º to 70º. The XRD patterns for HA exhibit prominent peaks at 2Θ= 25.91°, 28.94°, 31.78°, 32.93°, 34.1°, 39.8°, 46.7°, 49.5° which corresponds to the preferred diffraction planes of (002), (210), (211), (300), (202), (310), (222), (213) respectively (JCPDS card no. 00-009-0432). The presence of high intensity peak at diffraction plane of (211) confirms the pure crystalline nature of the HA coatings. The overall peaks intensity was found to be higher in case of spray coated samples showing higher degree of crystallinity as it should be for pure crystalline HA coatings. Whereas, in case of EPD samples the overall peaks intensity was found to be lower, this is because of the incorporation of PVA into HA before the EPD coatings. PVA generally exhibits semi-crystalline structure, which lead to the overall reduction in the degree of crystallinity of obtained HA coatings and hence the presence of lower intensity peaks for EPD samples.

The XRD analyses for both spray pyrolysis and EPD coated HA samples are given in the figures below.

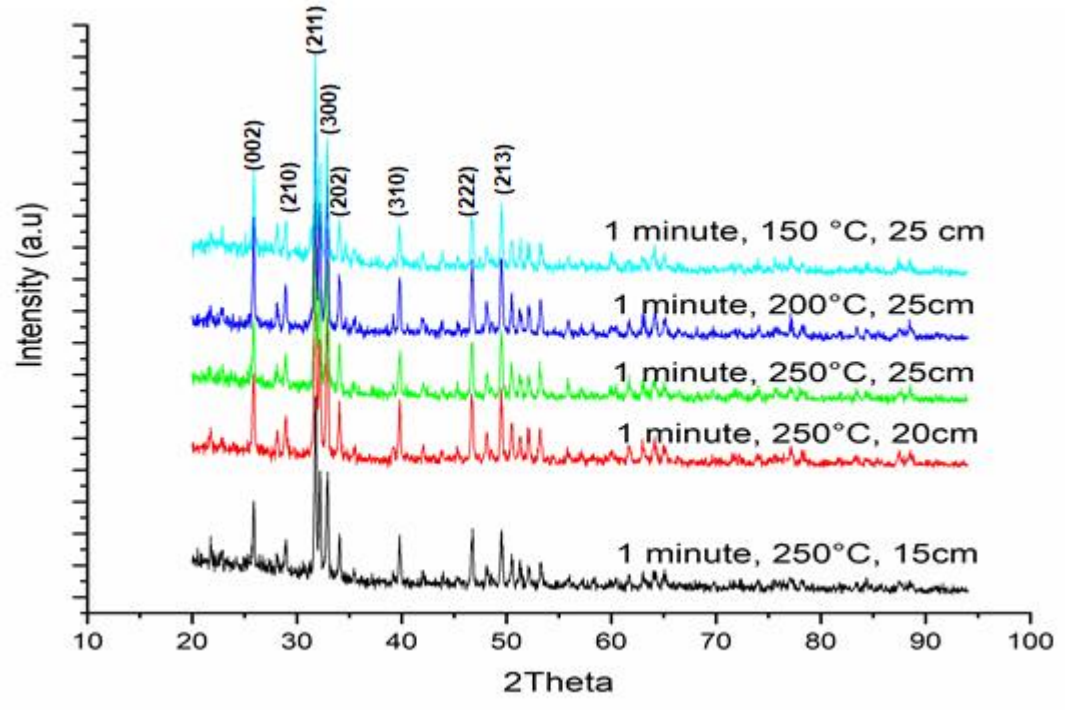

Figure 4-15: XRD analysis of different spray pyrolysis Samples

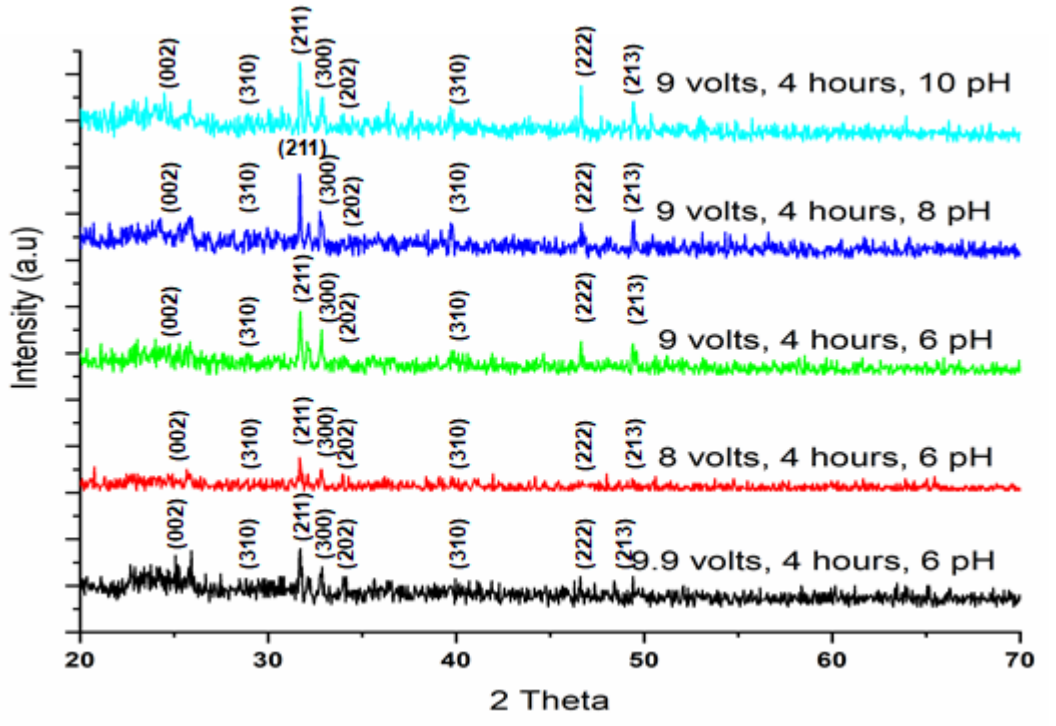

Figure 4-16: XRD analysis of different EPD Samples

4.4 Raman Spectroscopy

Purity of the HA coatings was further confirmed by performing the Raman spectroscopy for one sample of both the coating techniques used. Raman Spectrum showed all the characteristic peaks for HA which are attributed to the four different vibrational stretching modes of P-O bonds in phosphate (PO_4^{-3}) group. Raman spectroscopy of spray pyrolysis coated sample with processing conditions of 250 °C, 25 cm and 1 min 30 sec was done. For EPD coatings, the Raman spectrum of the sample with processing conditions of 9.9 volts, 4 hrs and 6 pH was obtained.

The most prominent peak which is characteristic to HA found at 958 cm^{-1} for both the samples.

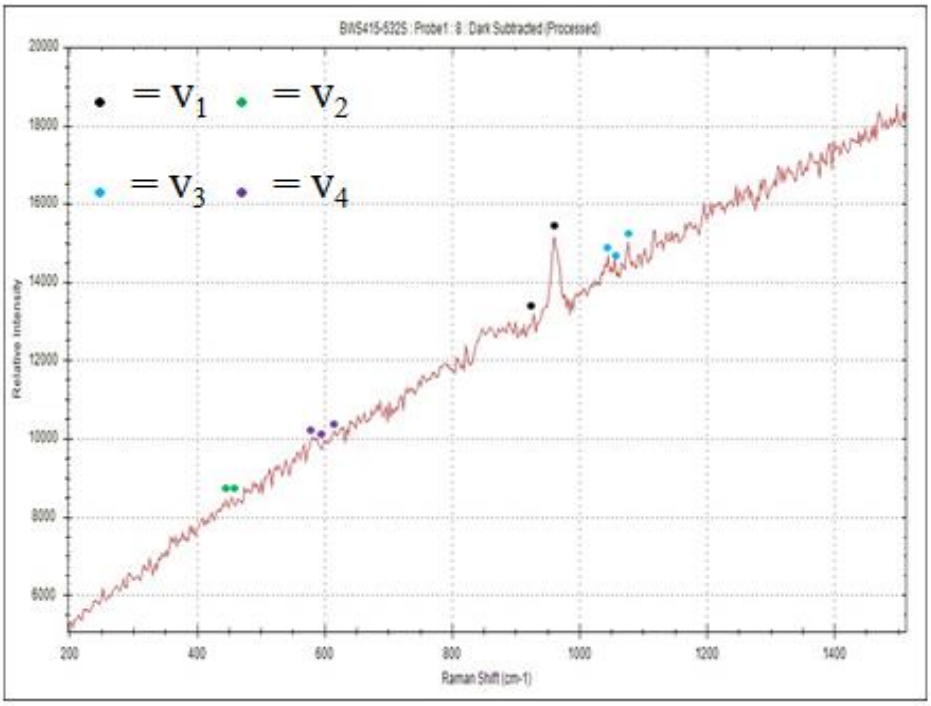

Figure 4-17: Raman spectrum of spray pyrolysis coated sample

4.4.1 Peaks attribution of Spray coated Samples

Peaks attributed to four different vibrational stretching modes of P-O bonds include:

1. V_1: 926, 958 cm^{-1}
2. V_2: 446, 452 cm^{-1}
3. V_3: 1046, 1054, 1076 cm^{-1}
4. V_4: 580, 599, 612 cm^{-1}

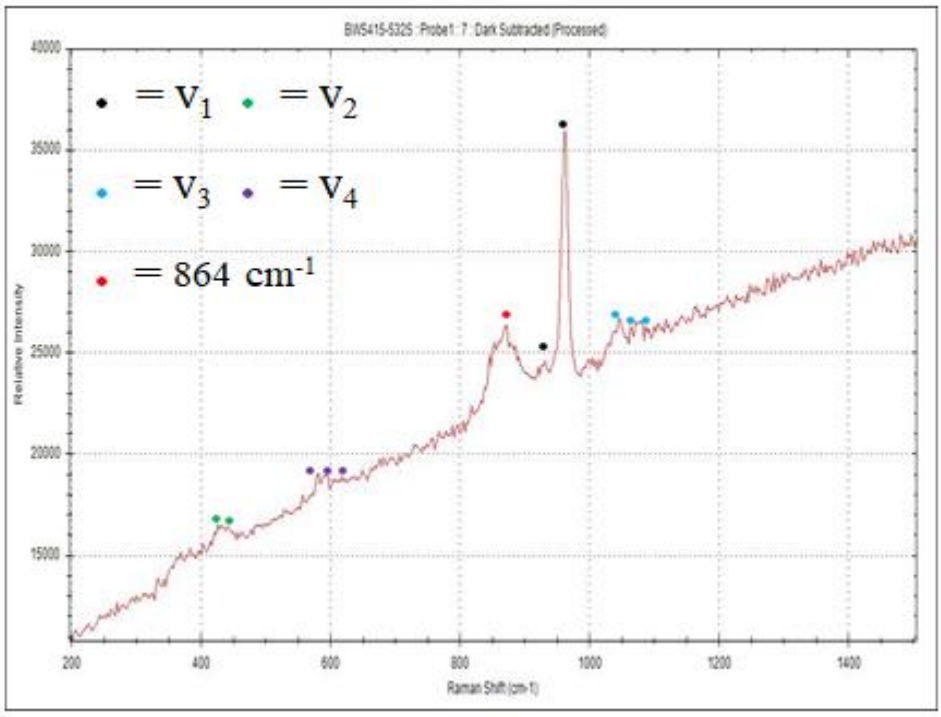

Figure 4-18: Raman spectrum of EPD coated sample

4.4.1 Peaks attribution of Spray coated Samples

Peaks attributed to four different vibrational stretching modes of P-O bonds include:

1. V_1: 932, 958 cm^{-1}
2. V_2: 428, 442 cm^{-1}
3. V_3: 1046, 1058, 1082 cm^{-1}
4. V_4: 584, 597, 622 cm^{-1}

One extra prominent peak was observed in EPD coated sample at 864 cm^{-1} which was attributed to the vibrational stretching of C-C bond present in the PVA which was incorporated into HA during EPD coatings.

Conclusions

In this study, the HA coatings were successfully deposited over the 316-L SS samples by using EPD and spray pyrolysis techniques. Structural morphology of the obtained coatings was studied by using SEM. The coating roughness and thickness was analyzed by using AFM. A total of 14 samples were coated (seven for each technique) by changing a combination of three different process variables in both these techniques. The overall best results of HA coatings in case of EPD technique were obtained with processing conditions of 10 v of applied voltage, 4 hrs of coating time, and 6 pH value of the suspension. The best results by spray pyrolysis technique were achieved with processing conditions of 250 °C of substrate surface temperature, 25 cm of nozzle-to-substrate-distance, and spraying time of 1 min 30 sec. By comparing the results of both coating techniques, overall the spray pyrolysis coatings were thicker and more crystalline in nature than the EPD coating. Such HA coatings in combination with metallic biomaterials can be used for biomedical applications where properties like biocompatibility and bioactivity are required, such as orthopaedic implants and dental implants.

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