SYNTHESIS AND CHARACTERIZATION OF ULTRAFINE HYDROXYAPATITE (HAp) POWDER COATING ON STAINLESS STEEL SUBSTRATE BY ELECTROPHORETIC DEPOSITION

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

Bachelor of Technology

In

Metallurgical and Materials Engineering

By

DEEP K. BHAISARE (10604012)

&

PRIYADARSHI BEHERA (10604004)

Department of Metallurgical and Materials Engineering

National Institute of Technology

Rourkela

2010

SYNTHESIS AND CHARACTERIZATION OF ULTRAFINE HYDROXYAPATITE (HAp) POWDER COATING ON STAINLESS STEEL SUBSTRATE BY ELECTROPHORETIC DEPOSITION

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

Bachelor of Technology

In

Metallurgical and Materials Engineering

By

DEEP K. BHAISARE (10604012)

&

PRIYADARSHI BEHERA (10604004)

Under the Guidance of

Prof. D. CHAIRA

Department of Metallurgical and Materials Engineering

National Institute of Technology

Rourkela

2010

National Institute of Technology Rourkela

Certificate

This is to certify that the thesis entitled "**Synthesis and characterization of ultrafine hydroxyapatite (HAp) powder coating on stainless steel substrate by electrophoretic deposition**" submitted by **Deep K. Bhaisare and Priyadarshi Behera** in partial fulfilment of the requirements for the award of Bachelor of Technology in Metallurgical and Materials Engineering with specialization in "Metallurgical and Materials Engineering" at National Institute of Technology, Rourkela (Deemed University) 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 the award of any degree or diploma.

Place:

Date:

Supervisor
Prof. Debasis Chaira
Department of Metallurgical & Material Engineering
National Institute of Technology,Rourkela- 769008

ACKNOWLEDGEMENT

With deep regards and profound respect, I avail this opportunity to express my deep sense of gratitude and indebtedness to Prof. D. Chaira, Metallurgical and Materials Engineering Department, NIT Rourkela, for introducing the present research topic and for his inspiring guidance, constructive criticism and valuable suggestion throughout in this research work. It would have not been possible for me to bring out this thesis without his help and constant encouragement.

I am sincerely thankful to Dr B.B. Verma, Professor and Head Metallurgical and Materials Engineering Department for his talented advice and providing necessary facility for my work.

Special thanks to my friends and other members of the department for being so supportive and helpful in every possible way.

Last but not the least; I am highly grateful to laboratory members of the Department of Metallurgical and Materials Engineering, N.I.T., Rourkela, especially, R. Pattanaik, Mr. Shyamu Hembram , U.K. Sahu for their help during the execution of experiments.

Date:
Place: Deep K. Bhaisare

ABSTRACT

In recent years, synthesis and characterization of ultrafine hydroxyapatite (HAp) powder coating on stainless steel substrate by electrophoretic deposition gives an active area of research due to their enhanced applicability in the medical field. This makes them very attractive as prosthetic replacements.

Ultrafine HAp powder was obtained by milling elemental calcium phosphate mineral. The HAp powder was dispersed into isopropyl alcohol by ultrasonication and magnetic stirring. The HAp powder was deposited by electrophoretic deposition (EPD) using lead as anode and stainless steel substrate as cathode. Powder was coated on stainless steel substrate at a voltage of 60 volt and time was varying from 15 minutes to 1.5 hours. It was observed that HAp powder deposited at 60 volt for 45 minute gives the best coating. In another set of experiment, coating time was 45 minutes having periodic time of 10 minutes with gap of 2 minutes. It was also observed that there is lack of adherence of powder particles with the substrate. To improve adherence of particles with substrate a surfactant sodium dodecyl sulfate (SDS or NaDS) ($C_{12}H_{25}SO_4Na$) was added during EPD process and subsequently sintering was performed at 800^0C for 2 hours in open atmosphere. X-ray diffraction (XRD) shows the peaks of HAp after deposition.

It was observed from XRD spectra that XRD patterns of HAp powder that was prepared by planetary milling and HAp powder was deposited on stainless steel substrate by EPD at 60 volts for 15 minutes. Here the some peaks of HAp are visible in the coated substrate along with peaks of stainless steel. The intensity of HAp peaks in the coated substrate is lesser than pure HAp powder. This is due to the presence of large peak of stainless steel along with HAp.

It was observed from SEM analysis that HAp deposited on stainless steel substrate at 1 hour shows smooth and good adherence where as for deposition of 1.5 hours shows discontinuous and non-adherence deposition. As the time of deposition is increased there may be formation of thick layer which may generate cracks.

Contents

List of Figures

List of Tables

CHAPTER 1

1. INTRODUCTION

Coating is a worldwide scientific technique to enhance the mechanical properties of surface. It has also found its use in biomedical purpose where prosthetic implants like bones and teeth are to be replaced. The substrates used in these implants are usually metallic devices having superior metallurgical properties like high strength, corrosion resistance and biocompatibility with internal human environment. Even though these metallic device satisfy these conditions they are still corrode because of inconsistent environment. Hence they are coated with an inorganic, stable and biocompatible material called Hydroxy Apatite.

These coated metallic device mostly stainless steel of higher grades found tremendous application in biomedical purpose mainly in implants of teeth and prosthetic bones. The HAp is stable and neutral without having any positive or negative charge but they have special property to carry charge when set in electric field. Hence coating techniques like Electrophoretic Deposition, Electro Coating, elctrophoretic coating etc. are being used. The coating thickness varies with applied condition like time, voltage, time-intervals, organic medium used, surfactants, area of coating and sintering In this project these parameters have been varied to study the coating thickness and adherence on 316 grade stainless steel.

1.1Objectives and Scope of Thesis

This project studies the electro-phoretic deposition of HAp coating on 316 grade stainless steel. The substrate was negatively biased and the lead plate was positively charged with applied potential of 60 volts (DC). The coating thickness and adherence varies on the parameters like time of coating, voltage applied, time intervals, organic medium and area of coating. Deposition times were varied from 15 minutes to 1.5 hours. In another set of experiment, total deposition time was 45 minutes with interval of 2 minutes. To improve adherence of HAp particles with the substrate, wetting agent sodium dodecyl sulphate was added and also sintering was done at 800°C for 2 hours in open atmosphere.

Chapter 1 describes the brief introduction of the project. Chapter 2 discusses about the theory of HAp coating, grade of stainless steel used and the deposition technique. It also presents a brief literature review of HAp coating on stainless steel substrate by EPD technique. Chapter 3 describes experimental procedure that is carried out for electrophoretic deposition in this project work. Chapter 4 includes the results of x-ray diffraction (XRD) and scanning electron microscopy (SEM) of coated samples. Chapter 5 describes conclusion of the project and scope for future work.

1.2 THEORY

1.2.1 HYDROXYAPATITE (HAp)

Liping He et al. (1) discusses that the worldwide biomaterials industry has an annual turnover of $2.3 billion in the field of hard tissue repair and replacement with increasing tendency. The factors affecting the success of an implant is highly dependent on the simultaneous achievements of good biocompatibility and mechanical properties of it because normally its failure is attributed to the factors of infection, loosening, fracture and wear. So far, only the hydroxyapatite coated metal implants, which result in a combination of biochemical stability of hydroxyapatite [HAp, $Ca_{10}(PO_4)_6(OH)_2$] and good mechanical strength of metals, have been widely used and growing.

T. M. Sridhar et al. (2) studied that metals and alloys are used in restoration of anatomical structures for centuries owing to their superior mechanical properties. However, the degradation of most metals implanted in the human body has narrowed the choice of clinically usable metals and alloys to mainly—stainless steels, cobalt–chromium and titanium and its alloys. These metallic devices are unique that they are exposed to living cells, tissues and biological fluids which are not only dynamic but are also a hostile environment for the survival of the implant. Type 316L stainless steels (SS) are widely used for implantation purposes in orthopaedic surgery owing to their corrosion resistance, mechanical properties and low cost. However, clinical experience has shown that they are susceptible to localised corrosion in the human body causing the release of metal ions into the tissues surrounding the implants. Several incidences of failures of such devices have demanded the application of biocompatible and corrosion resistant coatings and surface modification of the alloys.

Ryan K. Roeder et al. (3) studied that pure HAp has very poor mechanical strength and thus cannot be used directly as a replacement materials, hence it is to be used as a composite. Titanium is generally used as the substrate but due to high cost of titanium stainless steel is to be used as a cheap replacement of titanium. Various other microstructurally controlled HAp ceramics such as whiskers reinforced HAp and others may give a good platform for future replacements.

Pure HAp ceramics has low mechanical reliability; hence not used as artificial teeth or bones. Hence various HAp-based composites are fabricated, but only the HAp-coated titanium alloys have found wide application. Among the others, the microstructurally controlled HAp ceramics such as fibers/whiskers-reinforced HAp, fibrous HAp-reinforced polymers, or bio-mimetically fabricated HAp/collagen composites seem to be the most suitable ceramic materials for the future hard tissue replacement implants (3).

Cook, Gerhard A. et al.(4) mentioned that calcium is an important element as the constituent of bone but it is not the only element in the bone as it includes several of the other mineral like magnesium, phosphorus and other trace elements. Hydroxyapatite is generally the crystalline structure of calcium and phosphorus in 2:1 ratio.

The importance of calcium on preventing osteoporosis is undeniable. Yet, calcium does not work alone in creating strong, healthy bones. Although calcium is a major constituent of bone, the whole bone matrix is composed of a variety of other minerals including phosphorus and magnesium, trace elements, proteins, collagen, and glycosaminoglycans. Calcium and phosphorus occur in bone in a 2 to 1 ratio predominantly as crystalline structures called hydroxyapatite (5).

Hydroxyapatite is a naturally occuring mineral of calcium apatite with the formula $Ca_5(PO_4)_3(OH)$, but is usually written $Ca_{10}(PO_4)_6(OH)_2$ to denote that the crystal unit cell comprises two entities. It crystallizes in the hexagonal crystal system. It has a specific gravity of 3.08 and is 5 on the Mohs hardness scale. Pure hydroxylapatite powder is white. Naturally occurring apatites can however also have brown, yellow or green colorations, comparable to the discolorations of dental fluorosis (5).

Junqueira, Luiz Carlos et al. (6) Up to fifty percent of bone is made up of a modified form of the inorganic mineral hydroxylapatite. Carbonated-calcium deficient hydroxylapatite is the main mineral of which dental enamel and dentin are comprised. Hydroxyapatite crystals are also found in the small calcifications (within the pineal gland and other structures) known as corpora arenacea or ‘brain sand’.

1.2.2 Medical uses

HAp can be used to replace amputated bones, coating to promote bone growth inside prosthetic implants. The coral skeletons through heat treatment process can be converted to HAp. The porous structure allows rapid growth but decreases the mechanical strength and burns the proteins and other organic molecules which increase the immunity i.e. preventing GHVD and rejection. They have found use as hip replacement and dental implants as coating on metals. They also promote osseo-integration.

1.2.3 HAp Coating on Metal Substrate

Sridhar T. M. Et al. (7) As Metals and alloys have superior mechanical properties they found use in restoration of anatomical structures. However, due to degradation of most metals implanted in the human body very limited clinically usable metals and alloys mainly to — stainless steels, cobalt–chromium and titanium and its alloys are being used. These metals are not dynamic and have higher degree of inertness in human body. Type 316 L stainless steel (SS) is widely used for implantation purposes in orthopaedic surgery because of their exceptional corrosion resistance, mechanical properties and low cost. However, clinical experience has shown that they are susceptible to localised corrosion in the human body causing the release of metal ions into the tissues surrounding the implants. Several incidences of failures of such devices have demanded the application of biocompatible and corrosion resistant coatings and surface modification of the alloys.

HAp is biocompatible and bioactive and is capable of interacting with the surrounding bone and teeths. It has a simulating effect on bone formation, which is known as osseo-induction. It enhances the osseo-ìntergration, and also some chemical bonding may occur between HAp and bone. Due to poor mechanical properties it is proposed in this work to develop thin layers of HAp on the surface of type 316L SS by electrophoretic deposition. The excellent biocompatibility and biostability of HAp coatings have become well established and the use of this material for prosthetic applications are being rapidly popularised in the past few years (7).

The dominant requirements connected with the development of HAp coatings on metallic implants are—preparation of stoichiometric powder material with required chemical and phase composition. This is established by their chemical identity (Ca/P ratio 1.66) and by close crystallographical affinity with bone tissue. Another essential criterion is their deposition as coatings without the presence of non-stoichiometric phases of the powder. A number of novel methods offering the potential for better control of film structure for coating HAp include hot isostatic pressing, flame spraying, ion beam deposition, laser ablation and electrochemical deposition along with plasma spraying which has been widely studied over the decade. The major problems associated with plasma spraying process are that it is a line of sight process that produces a non-uniform coating with heterogeneous structure. The high temperature involved alters the HAp and metal substrate phases. Hence, electrophoretic deposition of HAp on metal substrates was used to overcome the above drawbacks and to achieve the uniform distribution of fine HAp deposits. The advantages of this technique include high purity of layers formed, ease of obtaining the desired thickness and stronger adhesion to the substrate. The present work was undertaken to optimise the applied coating potential required to produce adherent HAp coatings on SS and electrochemically evaluate their corrosion resistance and impedance behaviour in simulated body conditions (7).

Many technologies of coating HAp onto metallic substrates like physical vapour deposition, electrochemical deposition, plasma-spraying pulse laser melting and electrophoretic deposition. Due to their high stiffness, degradation of the HAp coatings caused by poor quality control, de-lamination of the coating due to cyclic fatigue and/or thermal expansion mismatch between the HAp coating and metal substrate. Hence an improved coating technique is required to over these drawbacks (7).

Chen Z. et al. (8) suggested one such technique is electro-codeposition for fabricating composite coatings, in which solid particles are incorporated in a metallic matrix. Its been widely studied and used for erosion resistant and wear resistant applications. The electro-codeposition technique is for the first time applied to fabricate biomedical coatings on metal substrates at low ambient temperature. This is expected to avoid the high temperature post-treatment in some other fabrication processes, which sometimes can result in decomposition or phase transition of HAp. The objective of this work is to investigate the applicability of the electro-codeposition technique in fabricating HAp/metal biomedical coatings. In particular, this paper investigates the composition and microstructure of HAp/Ni composite coatings, discusses the growth process of composite coating, and studies the influence of process conditions on the fraction of HAp in the fabricated composite coatings.

1.2.4 Electrophoretic Deposition (EPD)

Ilaria Corni et al. (9) electrophoretic deposition (EPD) is attracting increasing interest as a materials processing technique for a wide range of technical applications.This technique enables the production of unique microstructures and nanostructures as well as novel and complex material combinations in a variety of macroscopic sHApes, dimensions and arrangements starting from micron-sized or nanosized particles

The electrophoretic deposition (EPD) is an electrochemical method attracting increasing interest as a material processing technique. EPD is usually carried out in a two electrode cell. The mechanism of electrophoretic deposition involves two steps. In the first step an electric field is applied between two electrodes and charged particles suspended in a suitable liquid move toward the oppositely charged electrode (electrophoresis). In the second step the particles accumulate at the deposition electrode and create a relatively compact and homogeneous film (deposition). In order to effectively apply this technique to process materials, it is essential to produce a stable suspension containing charged particles free to move when an electric field is applied. Therefore EPD can be applied to any solid that is available as a fine powder (e.g. <30micrometer particle size) or as a colloidal suspension, including metals, polymers, ceramics and glasses. After the deposition, a heat-treatment step is normally needed to further densify the deposit and to eliminate porosity (9).

The process is useful for applying materials to any electrically conductive surface. The materials which are being deposited are the major determining factor in the actual processing conditions and equipment which may be used (9).

1.2.4.1 Non-aqueous electrophoretic deposition

In some coating requirement, maximum voltage applied is 3-4V in liquid medium water to avoid electrolysis of water. To achieve higher coating thickness and higher rate of deposition higher voltage has to be applied and hence some organic solvents are used as liquid medium. These solvents are alcohols ketones of which ethanol, acetone and methyl ethyl ketone are used widely.

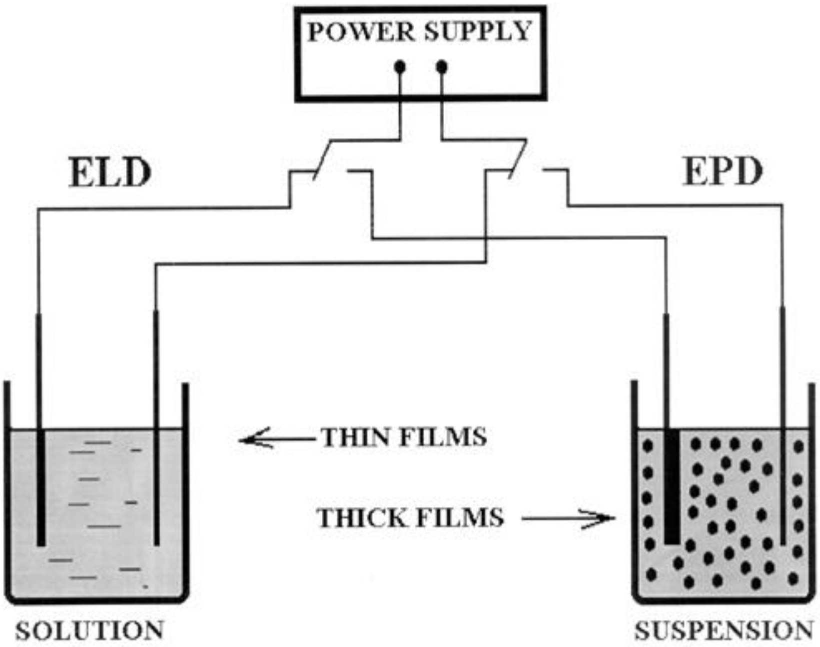

Figure 1: Typical electrophoretic deposition set-up.

1.2.5 Selection of 316L Stainless Steel

Chemical Formula(316 SS)
Fe, C<0.03%, Mn<2.0%, Si<0.75%, P<0.045%, S<0.03%, Cr=16-18%, Mo=2-3%, Ni=10-14%, N<0.1%

Grade 316 is the standard molybdenum-bearing grade, second in importance to 304 amongst the austenitic stainless steels. The molybdenum gives 316 better overall corrosion resistant properties than Grade 304, particularly higher resistance to pitting and crevice corrosion in chloride environments (10).

Grade 316L, the low carbon version of 316 and is immune from sensitization (grain boundary carbide precipitation). It is extensively used in heavy gauge welded components (over about 6mm). The austenitic structure also gives these grades excellent toughness, even down to cryogenic temperatures. Compared to chromium-nickel austenitic stainless steels, 316L stainless steel offers higher creep, stress to rupture and tensile strength at elevated temperatures (10).

Composition

Table 1: Composition ranges for 316L stainless steels.

Grade		C	Mn	Si	P	S	Cr	Mo	Ni	N
316L	Min	-	-	-	-	-	16.0	2.00	10.0	-
	Max	0.03	2.0	0.75	0.045	0.03	18.0	3.00	14.0	0.10

Mechanical Properties

Table 2: Mechanical properties of 316L stainless steels.

Grade	Tensile Str (MPa) min	Yield Str 0.2% Proof (MPa) min	Elong (% in 50mm) min	Hardness Rockwell B (HR B) max	Brinell (HB) max
316L	485	170	40	95	217

Corrosion Resistance

Excellent in a range of atmospheric environments and many corrosive media - generally more resistant than 304. Subject to pitting and crevice corrosion in warm chloride environments, and to stress corrosion cracking above about 60°C (10).

316 is usually regarded as the standard “marine grade stainless steel”, but it is not resistant to warm sea water. In many marine environments 316 does exhibit surface corrosion, usually visible as brown staining. This is associated with crevices and rough surface finish (10).

Applications

Typical applications include:

- Food preparation equipment particularly in chloride environments.
- Pharmaceuticals
- Architectural applications
- Medical implants, including pins, screws and orthopedic implants like total hip and knee replacements (10).

Kannan S. et al. (11) suggested that type 316L SS plays a key role in the bone replacement surgery due to its excellent mechanical features, availability at low cost and ease of fabrication. However it fails miserably in vivo conditions due to corrosion-related problems. Hence are alternative method on the development of hydroxyapatite (HAp) coatings has been elucidated to impart corrosion resistance of the base metal and ensure biocompatibility of the ceramic on the metal surface. This also could not match the implant at the host site due to the continuous interaction of hostile environment with the implant and results in the dissolution of both ceramic and metal. An artificially induced passive layer on the metal surface prior to coating may improve the nature of implant on the resistance to corrosion. In the present study, the effect of HNO_3 treatments on 316L SS and the coatings on passivated 316L SS is being explored. Electrochemical studies involving cyclic anodic polarization experiments and impedance analysis in Ringer's solution were done to determine the corrosion resistance of the coatings.

CHAPTER 2

2. LITERATURE REVIEW

Liping He et al. (8) studied fabrication of HAp/Ni biomedical coatings using an electro-codeposition technique and concluded that nickel is the matrix in the fabricated composite coatings and HAp particles are incorporated in the nickel matrix. The growth process of composite coating is similar to the electro-codeposition model proposed by Xiang et al. The results also show that the operation conditions, such as the temperature (T), pH, current density (D), have remarkable effect on the composition of the fabricated HAp/Ni composite coatings. It is worth to mention the somewhat toxic effect of nickel in the human body. Further work is to prepare HAp/Ti or HAp/Ti alloy composite coatings for investigating the reliability of the electro-codeposition technique on fabricating biomaterials for hard tissue replacement (8).

T. M. Sridhar et al. (7) studied Preparation and characterisation of electrophoretically deposited hydroxyapatite coatings on type 316L stainless steel and concluded that the optimum coating parameters for electrophoretic deposition of HAp on type 316L SS was established at 60 V and 3 min. XRD and SIMS studies confirm the presence of stoichiomertic structure and presence of Ca and P on depth profiling of the HAp coatings. The OCP and breakdown potentials of HAp coated samples shifted towards the nobler direction when compared with the uncoated 316L SS. Marginal changes observed in the impedance parameters (|Z|, R_p and C) for the coated samples before and after polarisation indicating the stable nature of the coatings. The increase in polarisation resistance and a decrease in capacitance on immersion for 200 h indicate that HAp coatings are electrochemically stable and evince improved corrosion resistance in simulated body fluids.

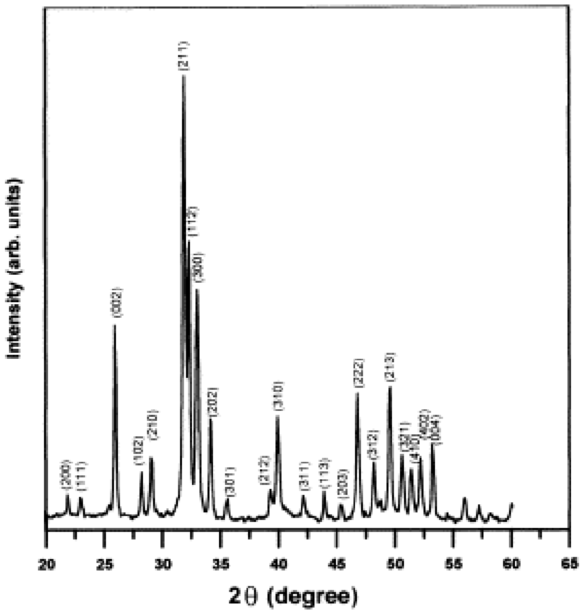

Figure 2: XRD graph of HAp coated on 316L SS obtained at optimum coating parameters of 60 V & 3 min.

Josefina Ballarre et al. (12) studied Improving the osteointegration and bone–implant interface by incorporation of bioactive particles in sol–gel coatings of stainless steel implants and concluded that The protection of surgical grade stainless steel implants against corrosion can be achieved by applying hybrid organic–inorganic sol–gel silica-based coatings. The addition of silica nanoparticles and glass–ceramic particles to the sol–gel coating enables the isolation of potentially toxic ions coming from the alloy to the surrounding environment. The in vitro bioactivity and implant–tissue integration is promoted by the addition of such silica nanoparticles. The TEOS–MTES–$SiO_2$with GC system coatings on stainless steel, promotes the formation and growth of non-stoichiometric hydroxyapatite during in vitro tests when the amount of silica particles is less. The different amount of colloidal silica slightly affects the quality of the mineral crystals formed in the new bone in vivo conditions. The stiffness of the newly formed bone in the implant with a lower amount of silica nanoparticles seems to be similar to the values for old cortex bone, showing short periods of maturation and mineralization of newly formed bone tissue around the implant.

Kazuaki Kanamoto et al. (13) studied Formation characteristics of calcium phosphate deposits on a metal surface by H_2O_2-electrolysis reaction under various conditions and concluded that the deposit of calcium phosphate was formed by the H_2O_2-electrolysis under a wide range of conditions. However, the formation of a smooth and uniform layer comprised solely of HAp was found to form under restricted conditions, pH 3–4.5; $[Ca^{2+}] \geq 25$ mM and < 42 mM; $[PO_4^{3-}] \geq 15$ mM and <25 mM; the ratios of $[Ca^{2+}]/[PO_4^{3-}]$, around 1.67; the applied potential ≤ -0.6 V vs Ag/AgCl and > -1.0 V vs Ag/AgCl. The pH range for HAp formation on a stainless steel surface was lower than that on a titanium surface. SEM images revealed that the HAp deposit was made up of a net-like matrix and domes, comprised of morphologically amorphous HAp flakes. In both cases of the formation of HAp and brushite, 20–30 nm sized calcium phosphate aggregates in an amorphous state were formed at the early stage of the H_2O_2-electrolysis treatment and then rearranged. The assemblies were converted to ribbon-like flakes of HAp or to brushite plate, depending on the pH used. Judging from the unique thin and ribbon-like morphology, the HAp flakes may be possibly used as a novel type of HAp adsorbent as well as an HAp coating for the artificial implants.

Ning Ma et al. (14) studied Ag–TiO_2/HAp/Al_2O_3 bioceramic composite membrane: Fabrication, characterization and bactericidal activity and concluded that g–TiO_2/HAp/Al_2O_3 bioceramic composite membrane was prepared by two-step approach. Membrane morphology characterization showed a microporous structure which was comprised of Ag–TiO_2/HAp composite layer overlaid on α-Al_2O_3 disk support. A superior ability of promoting interfacial charge-transfer reactions leads to the reduction of electron–hole recombination in Ag–TiO_2 photocatalytic processes. The proposed two-step approach offers a convenient method for fabricating and immobilizing Ag–TiO_2/HAp nanocomposite system on the ceramic support with a certain control over mass area ratio of Ag–TiO_2 and HAp. The inherited microporous membrane structure resulted in low loss of water permeability during the procedure of membrane fabrication, compared with α-Al2O3 support. E. coli removal results demonstrated the excellent bactericidal activity of as-prepared membranes, which was ascribed to the integrated performance of membrane filtration, high bacterial adsorption of HAp, enhanced photobiocide activity of Ag–TiO_2 nanocomposite as well as chemical activity and bacterial adherence of metallic Ag, with the aid of weak UV illumination. In addition, membrane fouling was alleviated due to the photocatalytic processes at membrane surface under UV illumination, compared with that under dark condition. It is believed that this novel membrane system may show extensive and efficient bactericidal ability for various pathogenic agents with weak UV light and even sunlight illumination for antibacterial treatment of groundwater and drinking water (13).

Suprabha Nayar et al. (15) studied hydroxyapatite coating on stainless steel pre-coated with bovine serum albumin at ambient conditions and concluded biomimetic process of in situ coating of HAp on a functionalized metallic surface has been demonstrated. Unlike, the SBF route where one makes use only of the inorganic constituents of body fluids, the present process mimics the philosophy of biomineralization, responsible for the highly sophisticated morphological features of bio-inorganic particles. Biomimetic coating produced at ambient conditions presents compositional/structural features and optimum crystallinity akin to bone.

A. Balamurugan et al. (16) studied Elaboration of sol–gel derived apatite films on surgical grade stainless steel for biomedical applications and concluded Sol–gel dip coating of substrates using viscous precursor solutions and subsequent drying and sintering enables the formation of thin and fully dense HAp coatings. FT-IR, EDXA and SEM analysis revealed the stoichiometric and micro porous nature of the hydroxyapatite coatings. Shear bond strength analysis showed that the 15 μm HAp coating adheres very well to 316L SS substrate when compared to other coating thicknesses. The potentiodynamic polarization measurement and ICP-AES analysis shows the protective nature of the HAp coatings on low carbon 316L SS and also it acts as a barrier for corrosion attack in simulated body fluid environment. It is thus concluded that sol–gel is a potential and practical method applied to prepare HAp bioceramic films on 316L SS surface to improve both the corrosion resistance and biocompatibility.

S. Kannan et al. (17) studied Hydroxyapatite coatings on sulfuric acid treated type 316L SS and its electrochemical behaviour in Ringer's solution and concluded that this treatment helps like resistance to pit initiation, less susceptibility to localized attack, and no change of HAp phase during sintering, will be a welcome feature for possible applications in the areas of total joint replacement, endoprosthesis and long-term survival in the human body. The presence of HAp coatings over the passive layer plays a dual role in preventing the release of metal ions (rendering it more corrosion resistant) and in making the metal surface more bioactive. Future work will be focused on the characterisation of the treated metal surface to find out surface changes that occurred and to analyse the leach out of metal ions during polarization studies.

Nasser A.M. Barakat et al. (18) studied physiochemical characterizations of hydroxyapatite extracted from bovine bones by three different methods: Extraction of biologically desirable HAp and concluded that the proposed and the traditional processes can be exploited to extract natural biological apatite bioceramic from the bovine bone bio-waste. Subcritical water extraction has the advantage of producing carbonated hydroxyapatite which is preferred in the biomedical applications. The alkaline hydrothermal process also relatively maintains the carbonate ion present in the biological apatite but less than the subcritical water method. The thermal process almost produces hydroxyapatite carbonate-free. The apatite obtained by the thermal process has higher particle size and better crystallinity than the proposed processes. The alkaline hydrothermal process produces relatively better nanoparticle shape (nanorods) than the other two processes.

CHAPTER 3

3. EXPERIMENTAL PROCEDURE

Figure 3 shows the photograph of electrophoretic deposition set up that was used for the deposition of HAp powder on stainless steel substrate.

Figure 3: Electrophoretic deposition setup

3.1 Procedure for sample preparation

a. A sheet of stainless steel was taken and cut into 10mmx10mm dimension.
b. The sample was then polished by belt grinder followed by emery paper of 3/0 and 4/0.
c. Then sample was then polished by diamond spray polish in cloth emery.
d. After obtaining mirror finish the sample was kept in dil. H_2SO_4.
e. 1% HAp solution (volume) was prepared in isopropanol solution with the help of magnetic stirrer.
f. 2% by weight of sodium dodecyl sulphate was added as wetting agent during EPD.

3.2 Experimental preparation

3.2.1 Materials

a) Ultrafine HAp powder was obtained by high energy planetary milling.
b) Type 316L SS electrodes of 10×10×2 mm size samples were mechanically polished from 3/0 and 4/0 emery papers followed by using a 1 μm diamond paste to get a mirror finish.

3.2.2 Electrophoretic deposition

a) The electrodes were washed thoroughly in running distilled water, rinsed and ultrasonically degreased with acetone and dried.
b) The electrophoretic deposition process was carried out at room temperature from a 1% suspension of HAp in isopropyl alcohol in a 100 ml glass beaker. The suspension was stirred with a magnetic stirrer.
c) A lead sheet was used as the anode and the working electrode was used as the cathode.
d) The distance between the two electrodes is nearly 2 cm.
e) Deposition was carried out on a 1 cm^2 surface area on one side of the specimen.
f) HAp powder was electrophoretically deposited on type 316L SS samples of 1 cm^2 area from a 1% suspension in isopropanol.
g) The electrophoretic deposit on 316L SS metal substrate was determined at 60V at a constant time of 1 hr, 15 mins, 30 mins, 45 mins(2 mins interval after each 10 minutes).
h) The voltage was set to 60 volts and the experiment was commenced. Although voltage, 60V was set but no deposition takes place.
i) For better adherence of HAp powders to the substrate sintering of coated samples were carried out at 800^0C for 2 hours in open atmosphere.

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1 X-ray diffraction (XRD) study

Figure 4 shows the XRD patterns of HAp powder that was prepared by planetary milling. The pattern shows the different peaks of HAp.

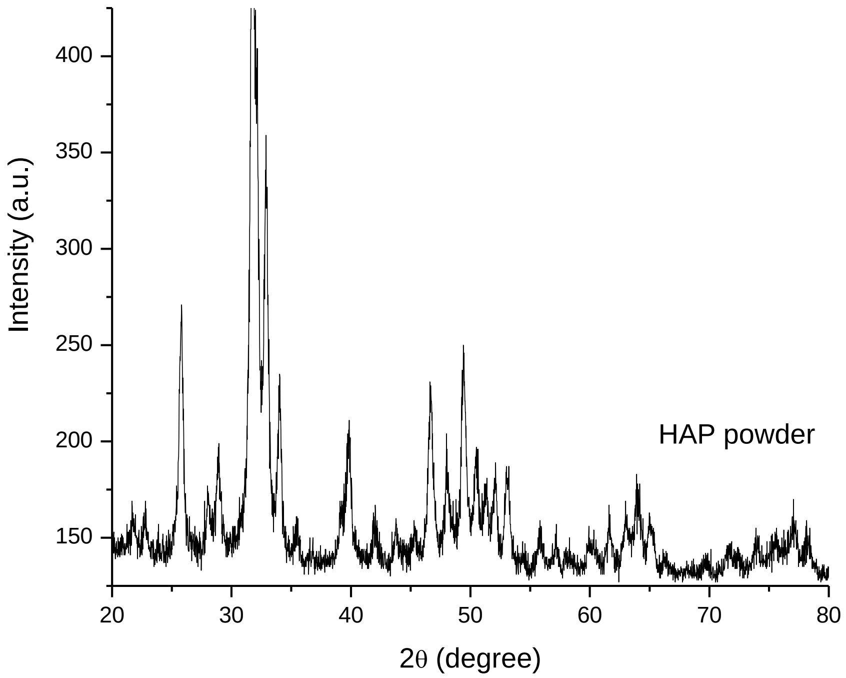

Figure 4: XRD patterns of pure HAp powder prepared by planetary milling.

Figure 5 shows the XRD patterns of HAp powder that was coated on SS samples for 15 minutes continuously and 45 minutes periodically having periodic time of 10 minutes with gap of 2 minutes. To improve the adherence properties of the HAp particle with the substrate, wetting agent sodium dodecyl sulphate was added during EPD process. XRD patterns show the strong HAp peaks along with Fe peaks. In the XRD patterns, only the peaks of Fe are shown, rest are the peaks of HAp.

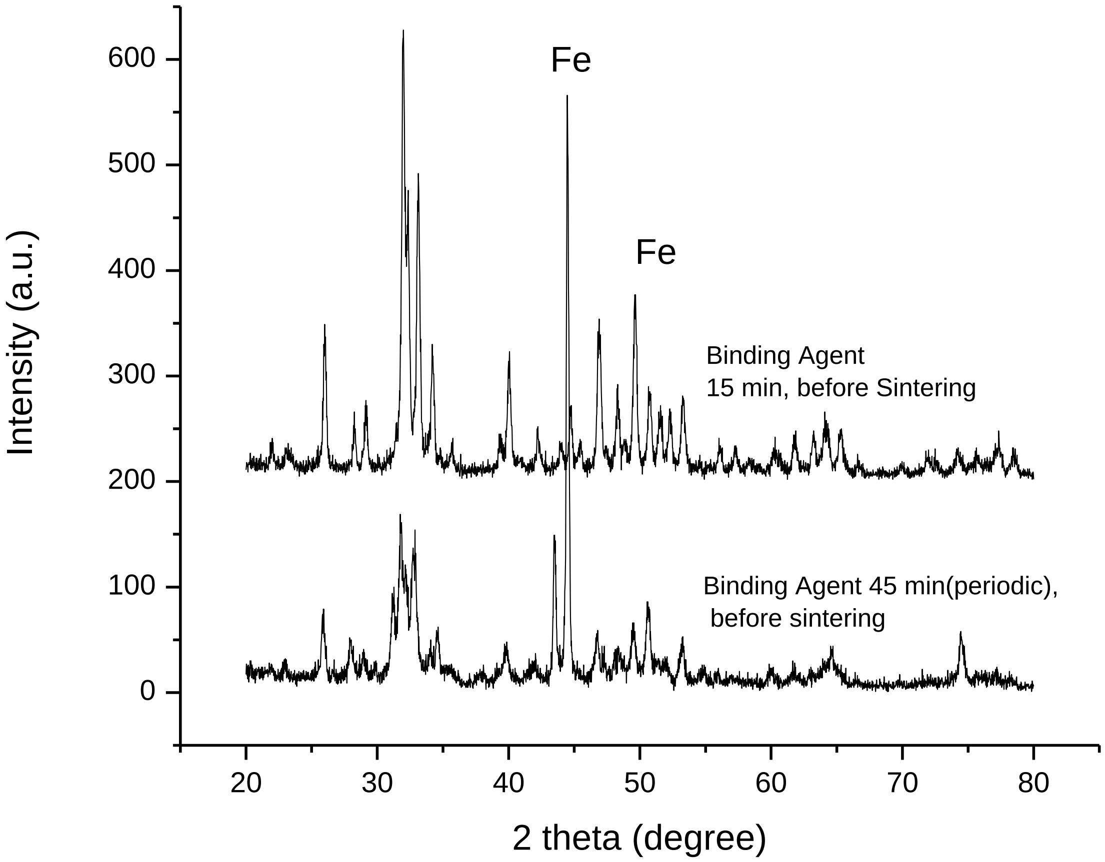

Figure 5: XRD graph for HAp coated substrate on SS for deposition time of 15 continuously and 45 minutes (periodic).

After EPD process was over, the samples were sintered at 800°C for 2 hours in open atmosphere to impart better adherence of the particles with the substrate. Figure 6 shows the XRD patterns of the samples deposited for 15 minutes (without wetting agent) of two samples after and before sintering. It is clear from the graph that peaks of HAp are present after sintering which shows that there is no decomposition HAp during sintering.

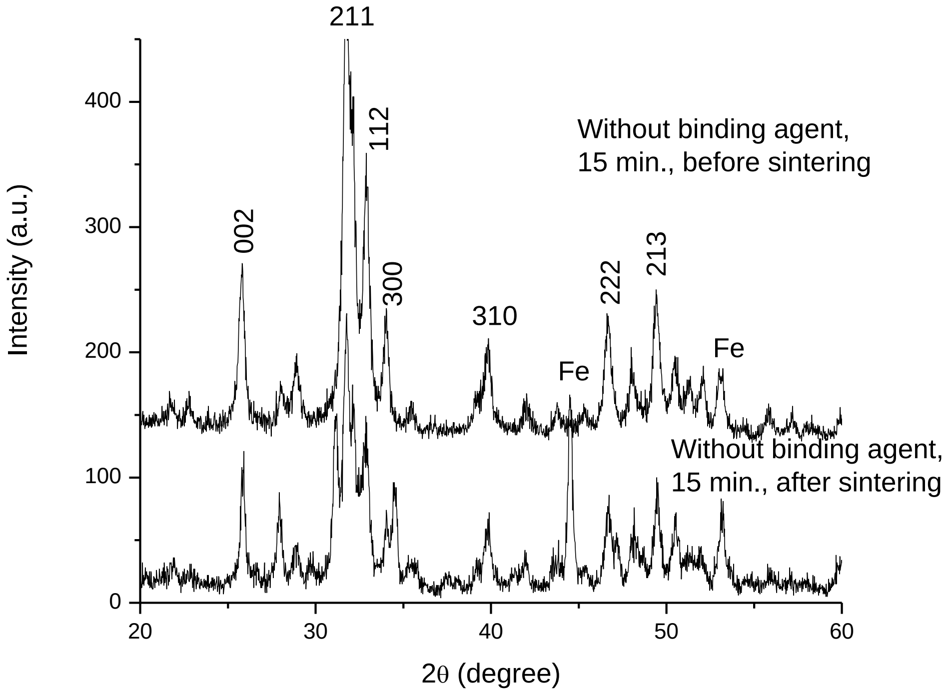

Fig. 6: XRD graph for HAP coated substrate on SS for deposition time of 15 minutes of two samples before and after sintering.

4.2 Scanning electron microscopy (SEM) study

To study the morphology and size of coated Hap powder on stainless steel substrate SEM was carried out. Figure 7 and 8 show the SEM micrographs of Hap coated stainless steel samples.

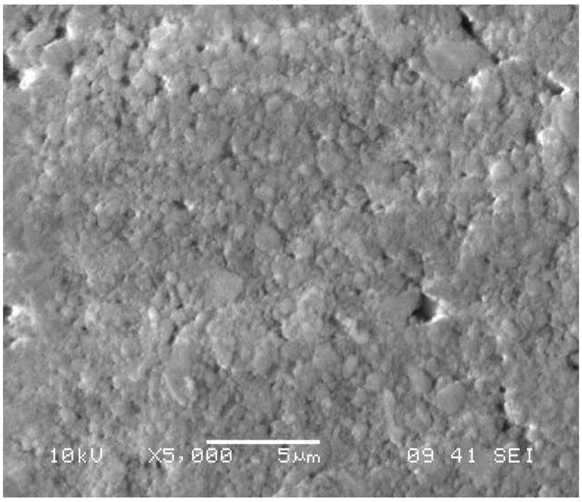

Figure 7: HAp coated SS for deposition time 1 hour without sintering.

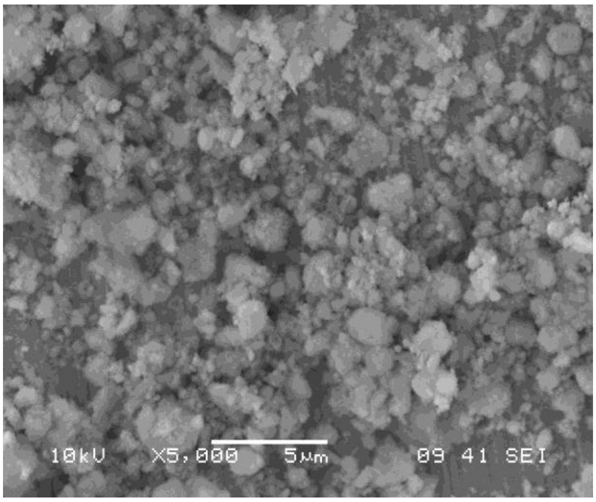

Figure 8: HAp coated SS for deposition time 1.5 hour without sintering.

Here the deposition time was 1 hour and 1.5 hours respectively at 60 volt. It is observed that deposited layer is smooth and good particle contact for 1 hour deposited sample. But in case of 1.5 hour sample, deposition layer is not smooth and also particles are not adhered to each other. As the time of deposition is increased there may be formation of thick layer which may generate cracks.

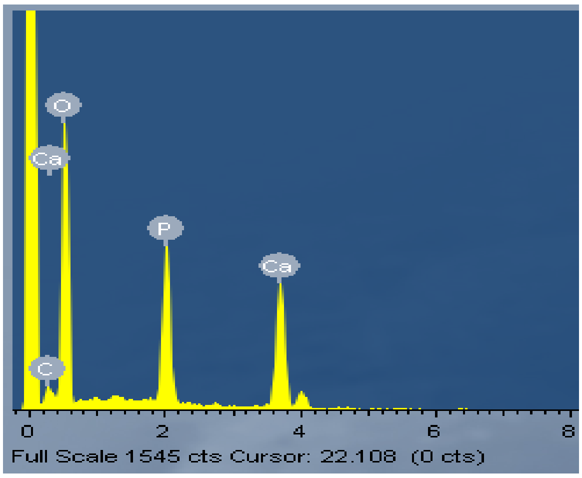

Figure 9: EDS spectra of HAp coated SS for deposition time 1.5 hours without sintering.

Element	**Weight%**
C K	2.87
O K	49.97
P K	16.30
Ca K	30.85
Totals	100.00

Table 3: Weight percentage of different elements present in HAp powder.

Figure 9 shows the EDS spectra of HAp coated SS for deposition time 1.5 hours without sintering. The EDS spectrum shows the peaks of Ca, P, and O along with a weak peak of C. Table 3 shows the weight % of different elements that are present in coating. The calculated Ca/P ratio is 1.89 which is close to the stoichiometric ratio of HAp (1.66).

To improve the bonding properties to the SS substrate, wetting agent was added followed by sintering at 800°C for 2 hours. Figure 10 and 11 show the SEM micrographs of HAp coated SS using binding agent and deposition time 15 minutes before and after sintering respectively. From the figure it was found out that there is particle coarsening after sintering. This may be due to agglomeration of the particles at high temperature. Before sintering particles are more or less same in size and are uniformly distributed. But after sintering due to coarsening, particles are seem to be randomly arranged.

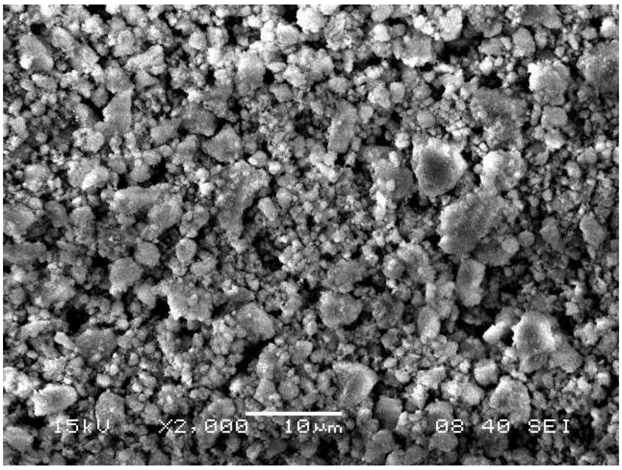

Figure 10: HAp coated SS using binding agent and deposition time 15 minute (before sintering).

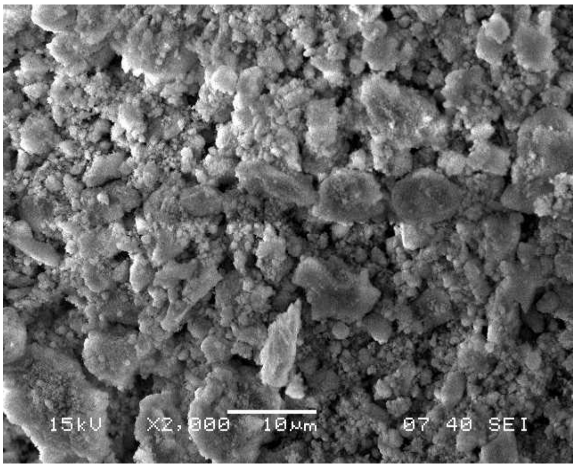

Figure 11: HAp coated SS using binding agent and deposition time 15 minute (after sintering).

Figure 12 and 13 shows the HAp coated SS with binding agent and deposition time of 45 minutes (periodic) before and after sintering. After sintering the there is particle coarsening but the adherence of the coated layer is better. Due to addition of binding agent there is also some increase in adherence than without binding agent. In Figure 12 we can see small sized HAp particles and smooth layer of the coat, whereas in Figure 13 particle coarsening occurs after sintering and the smoothness vanishes.

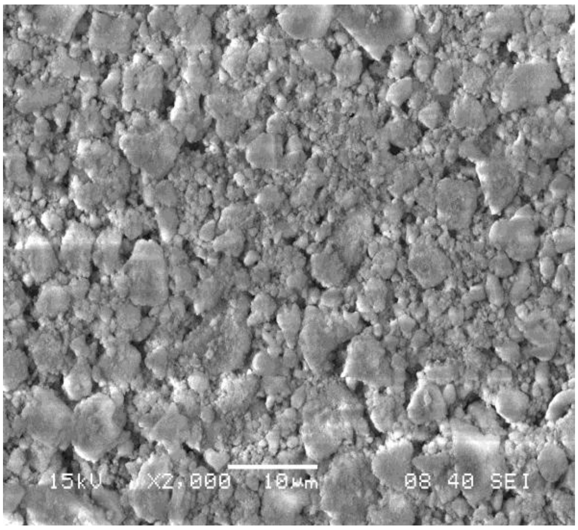

Figure 12: HAp coated SS with binding agent and deposition time of 45 minutes (periodic) before sintering.

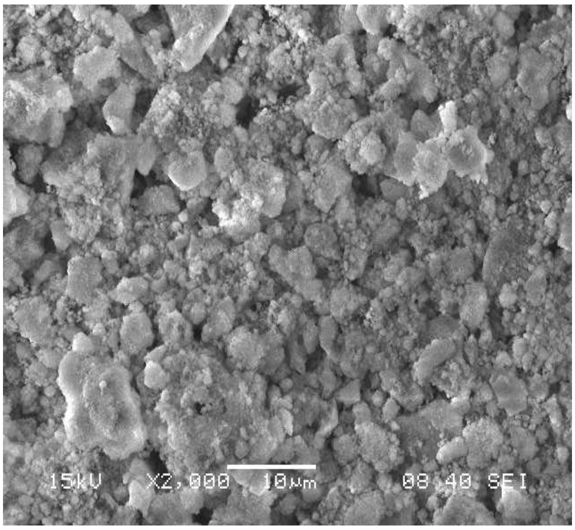

Figure 13: HAp coated SS with binding agent and deposition time of 45 minutes (periodic) after sintering.

Figure 14 and 15 shows HAp coated SS deposition without using binding agent for time of 15 minutes before and sintering. The fine particles deposited on SS agglomerates to coarse particles after sintering. By addition of binding agent also the deposit formed has not attained adequate sticking properties with the substrate here. Thus sintering is done to increase the sticking properties.

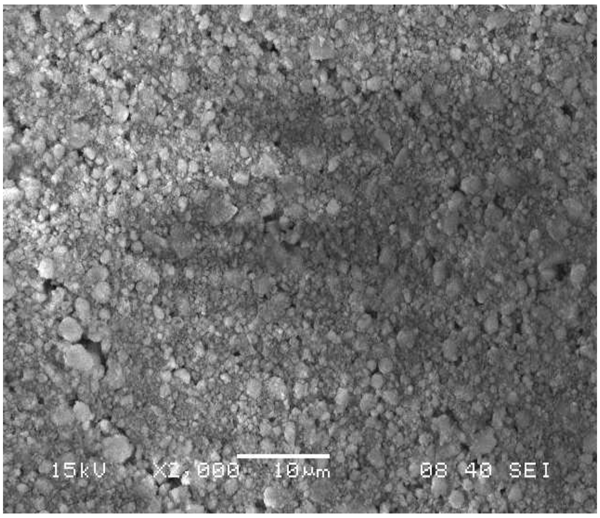

Figure 14: HAp coated SS deposition without using binding agent for time of 15 minutes and before sintering.

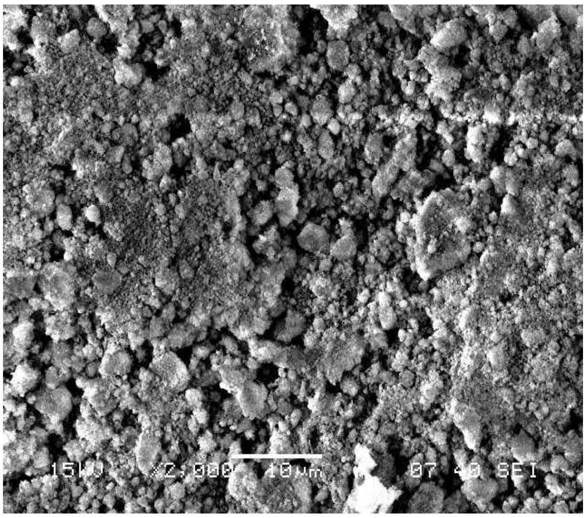

Figure 15: HAp coated SS deposition without using binding agent for time of 15 minutes and after sintering.

To measure the thickness of HAp coating, cross-section of samples were studied under SEM. Figure 16 shows the SEM micrograph of the cross-section of coated HAp on SS without using binding agent for 15 minutes after sintering. It is seen from the micrograph that thickness is around 2 to 3 micrometer.

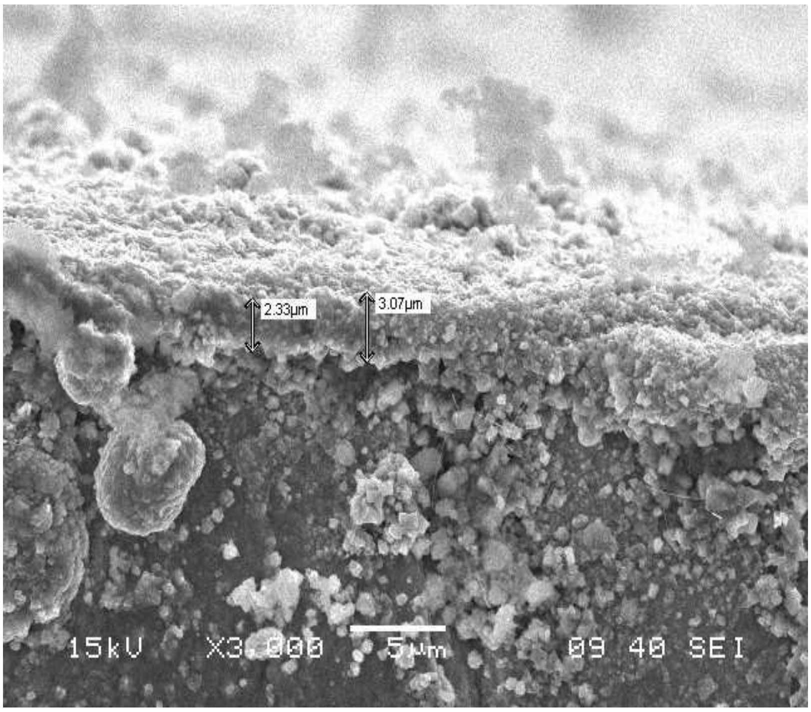

Figure 16: SEM micrograph of the cross-section of coated HAp on SS without using binding agent for 15 minutes after sintering.

CHAPTER 5

5. Conclusions

Ultrafine HAp powder obtained by planetary milling was deposited on stainless steel substrate by electrophoretic deposition. In EPD process, lead was used as anode and stainless steel was used as cathode. The operating voltage was 60 V and time was varying from 15 minutes to 90 minutes. Although when lower voltage was applied, no deposition took place. XRD shows the different peaks of HAp after deposition.

To improve the adherence of HAp particles on stainless steel substrate, wetting agent (sodium dodecyl sulfate) was added and also sintering was carried out at 800^0C for 2 hours in open atmosphere. After sintering no decomposition of HAp takes place. SEM also shows the morphology and size of HAp particles on stainless steel substrate. It is observed that after sintering, particle coarsening takes place. EDAX shows the peaks of calcium, phosphorus and oxygen of the HAp particles. The calculated Ca/P ratio is 1.89 which is close to stochiometric ratio (1.66). It is concluded from SEM micrograph that the deposition is best when 60 V is applied for 1 hour which is indicated by the presence of continuous HAp particles and also smooth surface. But small cracks have been found. To measure the coating thickness, cross section of the samples was also observed under SEM. The coating thickness is around 2-3 microns.

CHAPTER 6

6. Future work

1. Although we have varied deposition time and voltage, the effect of several other deposition parameters like particle size, cathode to anode distance, medium, substrate, anode material, and temperature can be studied.

2. The biocompatibility as test of the HAp deposited on stainless steel samples can be investigated.

7. Reference

1. Liping He, Hairong Liu, Dachuan Chen, Zongzhang Chen and Xiaojun Bai, Fabrication of HAp/Ni biomedical coatings using an electro-codeposition technique, Surface and Coatings Technology, Volume 160, Issues 2-3 (2002), pages 109-113.
2. T. M. Sridhar, U. Kamachi Mudali and M. Subbaiyan, Preparation and characterisation of electrophoretically deposited hydroxyapatite coatings on type 316L stainless steel, Corrosion Science, volume 45, Issue 2 (2003), pages 237-252.
3. Ryan K. Roeder, Gabriel L. Converse, Robert J. Kane and Weimin Yue, Hydroxyapatite-reinforced polymer biocomposites for synthetic bone substitutes, Journal of the Minerals, Metals and Materials Society, volume 60, Number 3 (2008), pages 38-45.
4. Cook, Gerhard A.; Lauer, Carol M. "Oxygen" in Clifford A. Hampel. The Encyclopedia of the Chemical Elements, New York: Reinhold Book Corporation. (1968), pages 499–512. LCCN 68-29938.
5. As mentioned on site http://www.microalgaeoil.net/hydroxyapatite.html, dated 05/05/2010.
6. Junqueira, Luiz Carlos; José Carneiro, Basic Histology, Text & Atlas (10th ed.), McGraw-Hill Companies (2003), pages 144. 2003 ISBN 0071378294.
7. Sridhar T. M., Mudali U. K. and Subbaiyan M., Preparation and characterisation of electrophoretically deposited hydroxyapatite coatings on type 316L stainless steel, Corrosion Science, Volume 45, Issue 2 (2003), pages 237-252.
8. He L., Liu H., Chen D., Chen Z. and Bai X, Fabrication of HAp/Ni biomedical coatings using an electro-codeposition technique, Surface and Coatings Technology, Volume 160, Issues 2-3 (2002), pages 109-113.
9. Ilaria Corni, Mary P. Ryan, Aldo R. Boccaccini; Electrophoretic deposition: From traditional ceramics to nanotechnology Journal of the European Ceramic Society, Volume 28, Issue 7 (2008), pages 1353-1367
10. As per site http://www.azom.com/details.asp?articleid=2382 with date added of Feb 18, 2004
11. Kannan S., Balamurugan A. and Rajeswari S., Electrochemical characterization of hydroxyapatite coatings on HNO_3 passivated 316L SS for implant applications; ElectrochimicaActa Volume 50, Issue 10 (2005), Pages 2065-2072.
12. Josefina Ballarre, Damián A. López, Wido H. Schreiner, Alicia Durán and Silvia M. Ceré ; Protective hybrid sol–gel coatings containing bioactive particles on surgical grade stainless steel: Surface characterization, Applied SurfaceScience Volume 253, Issue 17 (2007), pages 7260-7264.
13. Kazuaki Kanamoto, Koreyoshi Imamura, Nobuhide Kataoka, Jun Oshitani, Hiroyuki Imanaka and Kazuhiro Nakanishi; Formation characteristics of calcium phosphate deposits on a metal surface by H_2O_2-electrolysis reaction under various conditions, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 350, Issues 1-3 (2009), pages 79-86.

14. Ning Ma, Xinfei Fan, Xie Quan and Yaobin Zhang; Ag–TiO_2/HAp/Al_2O_3 bioceramic composite membrane: Fabrication, characterization and bactericidal activity, Journal of Membrane Science , Volume 336, Issues 1-2 (2009), pages 109-117.
15. Nayar S., Pramanick A. K., Sharma B. K., Mishra R. K., Bansal S. K., Prajapati A., Sahu K. K., Das S. K., Pathak L. and Sinha A.; Hydroxyapatite coating on stainless steel pre-coated with bovine serum albumin at ambient conditions; Colloids and Surfaces B: Biointerfaces, Volume 48, Issue 2 (2006), pages 183-187.
16. Balamurugan A., Balossier G., Kannan S., Michel J., Faur J. and Rajeswari S.; Electrochemical and structural characterisation of zirconia reinforced hydroxyapatite bioceramic sol–gel coatings on surgical grade 316L SS for biomedical applications; Ceramics International, Volume 33, Issue 4, (2007), pages 605-614.
17. S. Kannan, A. Balamurugan and S. Rajeswari; Hydroxyapatite coatings on sulfuric acid treated type 316L SS and its electrochemical behaviour in Ringer's solution , Materials Letters, Volume 57, Issues 16-17 (2003), pages 2382-2389.
18. Barakat N. A.M., Khalil K.A., Sheikh F. A., Omran A.M., Gaihre B., Khil S. M and Kim H.Y., Physiochemical characterizations of hydroxyapatite extracted from bovine bones by three different methods: Extraction of biologically desirable HAp , Materials Science and Engineering: C, Volume 28, Issue 8 (2008), pages 1381-1387