UNIVERSITI TEKNIKAL MALAYSIA MELAKA

PREPARATION AND CHARACTERIZATION OF SOL-GEL DERIVED HYDROXYAPATITE COATING ON STAINLESS STEEL SUBSTRATE

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

ZURIANEE BT LOKMAN LOGANATHAN

B050910174

890203075596

FACULTY OF MANUFACTURING ENGINEERING

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ABSTRAK

Tujuan kajian ini adalah untuk menyediakan dan mencirikan salutan *hydroxyapatite* yang disalut pada substrat *stainless steel*. *Stainless steel* digunakan sebagai biobahan kerana sifat mekanikal yang baik. Dalam usaha untuk meningkatkan daya tahan kakisan *stainless steel*, salutan *hydroxyapatite* dengan dan tanpa kehadiran HCl pemangkin disediakan oleh teknik sol-gel digunakan kerana ia mempunyai ciri-ciri yang menyerupai tisu badan. Asid *phytic* juga digunakan sebagai pra-salutan kerana ia memiliki besar kakisan rintangan. Sampel yang dianalisis oleh XRD menunjukkan puncak fasa hydroxyapatite yang lemah. Sampel diperhatikan di bawah Mikroskop Optik (OM) menunjukkan bahawa substrat *stainless steel* yang telah di pra-salut dengan asid *phytic* mempunyai permukaan kurang berkarat berbanding dengan sampel lain. Kemudian, pemerhatian di bawah Mikroskop Elektron Imbasan (SEM) menunjukkan salutan tidak seragam hadir pada substrat. Data dari EDX menunjukkan bahawa semua elemen yang membentuk *hydroxyapatite* pada substrat wujud dan dengan itu membuktikan bahawa lapisan salutan *hydroxyapatite* berjaya terbentuk pada substrat *stainless steel*.

ABSTRACT

The purpose of this research is to prepare and characterize the sol-gel derived hydroxyapatite coating on stainless steel subtrate. Stainless steel is being use as biomaterial due to its high mechanical strength and toughness. In order to enhance corrosion resistance of stainless steel, hydroxyapatite coating with and without presence of HCl catalyst prepared by sol-gel technique is being used as it has characteristic close to body tissue. The use of phytic acid conversion coating is also being implemented as it posses great corrosion resistivity. The coated samples analyzed by XRD shows that a weak peak of hydroxyapatite phase present in the coating. Samples observed under Optical Microscope shows that stainless steel substrate that being pre-coated with phytic acid has less corroded surface compared to other samples. Then, observation under Scanning Electron Microscope shows non-uniform coating present on the substrate. Data from EDX show that all element from hydroxyapatite present on the substrate and thus prove that hydroxyapatite coating layer manage to be form on stainless steel substrate.

DEDICATION

Dedicated to my beloved family and friends.

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest gratitude to my supervisor Dr. Zulkifli Bin Mohd Rosli of Faculty of Manufacturing Engineering, University Technical Malaysia Malacca. He had provide me not only his valuable knowledge, but also his time to help me overcome the difficulties encountered during this study.

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LIST ABBREVIATIONS, SYMBOLS, NOMENCLATURE

Al	=	Aluminium
ASTM	=	American Society for Testing Materials
Ca	=	Calcium
Cu	=	Copper
Fe	=	Iron
HA	=	Hydroxyapatite
HCl	=	Hydrochloric Acid
JCPDS	=	Joint Committee on Powder Diffraction Standard
L	=	Length
ml	=	Milliliter
Mn	=	Manganese
Ni	=	Nickel
P	=	Phosphate
T	=	Thick
W	=	Width
Zn	=	Zinc
µ	=	Micro

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Biomaterials have been use for quite a long time ago by humans. The Romans, Chinese, and Aztec used gold in dentistry more than 2000 years ago. Besides, glass eyes and wooden teeth have been used trough much of the recorded history. During that period of time, there were no medical device manufacturers, no formalized regulatory approval processes, no understanding of biocompatibility and certainly no academic courses on biomaterials (Ratner, 2004). Yet, crude biomaterials have been used, generally with poor to mixed results, throughout history. Earlier of the 21st century, biomaterials are widely used throughout medicine, dentistry and biotechnology.

A biomaterial can be any substance or combination of substances having natural or synthetic origin, which can be used on a clearly defined period as a whole or a part of a system that treats, heals or replaces a tissue or organ function of living body (Choubey, 2005). In other words, biomaterial is a materials designed to work under biological compulsion. Biomaterial is being used and adapted for a medical application. It is a nonviable material used in a medical device intended to interact with biological systems which performs or replaces a natural function. Biomaterials should be biocompatible with human body which means the material should be biologically compatible by not producing a toxic and injuries in living tissue. The human body has an extraordinary ability to be able to tell whether an object is foreign or not. This is part of the body protection against invasion from an outside organism. If a substance is placed in the body and the body can tell it is foreign, then

an immune system response will be generated. When an object is incorporated into the body without any immune responses it is said to be biocompatible. In order for a device to be biocompatible, it must follow a very strict requirement from the body.

Stainless steel has enjoyed clinical success because of their superior strength, biocompatibility, durability, and resistance to corrosion in physiological environment. The high mechanical strength and toughness of these bio-metals are the most important advantages over bioactive ceramics, which are inherently weak and brittle. Upon implantation, a close contact of the metal prostheses with surrounding host tissue is required for a subsequent ingrowths of bone tissue into the pre-design cavities on the implant surface. The change of relative position between implant and the surrounding tissue is highly undesirable and therefore immobilization of a patient may be needed before the implant fixation is strong enough to bear load.

However, there are concerns about their corrosion resistance upon the body physiologic fluids and also their bioactivity, since the probability of pitting corrosion is high in stainless steel. Corrosion is constituted of the material loss that causes an implant to become weak. The more significant matter is the release of the corrosion products in the body tissues which causes some adverse effects, which increases the rate of formation of fibrous tissue around the implant. On the other hand, stainless steel are not capable of forming a suitable bond between the implant and tissues. For this reason, developing the techniques for increasing their corrosion resistance and bioactivity become significant.

In response, hydroxyapatite sol-gel coatings have been suggested as a key factor in controlling these corrosion rates. Hydroxyapatite, HA ceramics belong to a class of calcium phosphate-based materials, which have been widely used as bone substitutes. Due to the chemical similarity between hydroxyapatite and mineralized bone of human tissue, synthetic hydroxyapatite exhibits strong ability to host body tissues. Formation of chemical bond with the host tissue offers hydroxyapatite a greater advantage in clinical applications than most other bone substitutes. Hydroxyapatite coatings on metallic offer great improvement in orthopedic and dental applications and are used in successful clinic practices (Liu et al, 2001).

1.2 Problem Statement

Due to high mechanical strength and toughness, stainless steel is being use as biomaterial. Besides, other factors that makes stainless steel as a success biomaterial are its durability, biocompatibility and resistance to corrosion. However, the corrosion resistance of stainless steel towards body fluid and their bioactivity become a concern. Thus, hydroxyapatite coating is being used over stainless steel substrate as hydroxyapatite is a material that has characteristic close to body tissue. Furthermore, phytic acid will be used as a conversion coating on stainless steel substrate to enhance its corrosion resistivity. In this research, stainless steel will be coated with sol-gel derived hydroxyapatite by using dip coating technique. The use of catalyst and conversion coating will be studied in order to prepare sample that can restrain corrosion and degradation.

1.3 Objectives

The objectives that need to be achieved during this study include:

a. To prepare hydroxyapatite coating solution via sol-gel technique.
b. To implement the use of catalyst and conversion coating in the coating preparation.
c. To develop a coating layer on substrate by using dip coating technique.

1.4 Scope

This project will focus primarily on the experimental work on synthesizing sol-gel derived hydroxyapatite coating on stainless steel substrate. Besides, there are also several variables to be evaluated when preparing the sample and the coating solution which are conversion coating solution and catalyst. After finishing the coating process, characterization towards the hydroxyapatite coating on stainless steel substrate will be done in order to obtain the coating characteristics.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

This chapter reviews on the related study based on the previous research conducted by other researchers on the hydroxyapatite derided by sol-gel method as a coating process on stainless steel substrate. Through this chapter, the study on hydroxyapatire sol-gel is being studied and discussed. Besides, the literature review will also focus on the principle of stainless steel as biomaterials and coating technique used which is dip coating.

2.2 Biomaterial

Biomaterials improve the quality of life for an ever increasing number of people each year. The range of applications is vast and includes such things as joint and limb replacements, artificial arteries and skin, contact lenses, and dentures. The biomaterials community is producing new and improved implant materials and techniques to meet this demand, but also to aid the treatment of younger patients where the necessary properties are even more demanding. To meet these urge needs it is necessary to have reliable methods of characterisation of the material and material-host tissue interactions.

As stated by Rodriguez et al (2004), biomedical materials can be divided roughly into three main types governed by the tissue response. Inert (more strictly, nearly inert) materials allow no or minimal tissue response. Active materials encourage

bonding to surrounding tissue. For example, new bone growth being stimulates. Degradable or resorbable materials are incorporated into the surrounding tissue, or may even dissolve completely over a period of time. Metals are typically inert, ceramics may be inert, active or resorbable and polymers may be inert or resorbable. Some examples of biomaterials are provided in **Table 2.1**.

Table 2.1 : Example of Biomaterials (Rodriguez et al, 2004)

Metals	Ceramics	Polymers
316L stainless steel Co-Cr Alloys Titanium Ti6Al4V	Alumina Zirconia Carbon Hydroxyapatite	Ultra high molecular weight polyethylene Polyurethane

The main property required of a biomaterial is that it does not prohibit an adverse reaction when placed into service. The range of applications for biomaterials is large. The number of different biomaterials is also significant. However, in general, metallic biomaterials are used for load bearing applications and must have sufficient fatigue strength to endure the needs of daily activity such as walking. Ceramic biomaterials are generally used for their hardness and wear resistance for applications such as articulating surfaces in joints and in teeth as well as bone bonding surfaces in implants. Polymeric biomaterials are usually used for their flexibility and stability, but have also been used for low friction articulating surfaces (Navarro, 2008). **Table 2.2** explain the advantages and disadvantages of ceramic, polymeric and metallic biomaterial (Ratner, 2004).

Table 2.2 : Advantages And Disadvantages Of Each Class Of Biomaterial.

Class of material	Advantage	Disadvantage	Example
Ceramics	• High compression strength • Can be highly polished • Wear & corrosion resistance • Inert	• Low strength in tension • Low fracture toughness • Mismatched with bone • Difficult to fabricate	Alumina, Zirconia, Silicate glass, Calcium phosphate, Calcium carbonate
Polymeric	• Easy to make • Tailorable properties • Surface modification • Immobilize • Biodegradable	• Leachable • Absorb water & proteins • Surface contamination • Cells Wear & breakdown • Biodegradation • Difficult to sterilize	PMMA, PVC, PLA/PGA, PE, PTFE, PET, Silicones
Metallic	• High strength • Fatigue resistance • Wear resistance • Simple to fabricate • Easy to sterilize • Shape memory	• High modulus • Corrosion • Metal ion toxicity • Metallic looks	Stainless Steel (316L), Co-Cr alloys, Au-Ag-Cu-Pd alloys, Amalgam (AgSnCuZnHg) Ni-Ti, Titanium

2.2.1 Biocompatibility

According to Mihov et al (2010), biocompatibility is the ability of a material to perform with an appropriate host response in a specific application. The material should posses the quality of not having toxic or injurious effects on biological systems. There are many factors which influence implant biocompatibility such as implant size, shape, material composition, and surface wettability, roughness and charge. For a material to be considered biocompatible, any adverse reactions which may ensue at the blood/material or tissue/material interface must be minimal. This requires a biomaterial to interact as a natural material would in the presence of blood and tissue. Biomaterials should not alter plasma proteins (including enzymes) so as to trigger undesirable reactions, cause adverse immune responses, cause thrombus formations, cause cancer, produce toxic and allergic responses and destroy or sensitize the cellular elements of blood.

2.3 Corrosion

According to Hansen et al (2008), corrosion is degradation of materials due to interactions with their environments, and corrosion of most metals and other materials is inevitable. Corrosion is one of the major degradation processes that might occur in vivo, and should thus be considered when evaluating new biomaterials and new designs of medical devices. Metals and alloys, which are extensively used in medical devices, might corrode severely in this bioenvironmental in accordance with both thermodynamic and kinetic considerations. This degradation process is undesirable because it limits the functionality and lifetime of medical devices. Besides, it releases corrosion products that may cause an adverse biological reaction in the host. Ceramics may also undergo selective leaching, although they more often fail in situ due to mechanical processes such as wear.

Corrosion is a complex phenomenon that depends on geometric, metallurgical, mechanical and chemical parameters. Thus, a firm understanding of these parameters and their synergistic effects is required in order to control biomaterials corrosion.

Corrosion is something that has to be avoided. Approaches available for controlling corrosion include the application of protective coatings to metal surfaces to act as a barrier or perhaps provide sacrificial protection. The coating functions to inhibit corrosion by altering the alloy chemistry to make it more resistant to corrosion (Shaw, 2006).

2.4 Stainless Steel

Stainless steel materials are resistant to a wide range of corrosive agents due to their high Cr content (more than 12 wt%), which allows the formation of a strongly adherent, self-healing and corrosion resistant coating oxide of Cr_2O_3. Several types of stainless steel are available and the most widely used for implant manufacture is austenitic stainless steel. In order to be austenitic at room temperature, stainless steel needs to contain a certain amount of austenite stabilizing elements such as Ni or Mn. The stainless steel most widely used in clinical applications is AISI 316L that contains 0.03 wt% C, 16–18 wt% Cr, 10–14 wt% Ni, 2–3 wt% Mo and minor amounts of nitrogen, manganese, phosphorus, silicon and sulphur as can be seen in **Table 2.3** below.

Table 2.3 : 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

Stainless steel is widely used in traumatological temporary devices such as fracture plates, screws and hip nails among others, owing to their relatively low cost, availability and easy processing. Their use in orthopaedic joint prosthesis is restricted because other metallic alloys such as Ti-based and Co–Cr-based alloys exhibit superior mechanical and corrosion properties. At present, new austenitic stainless steel with high Cr content (over 20%), where Ni has been partially substituted by Mn and with a high N content (between 0.3 and 0.4%), is being used in joint prosthesis.

N stabilizes the austenitic phase and induces an increase in both the corrosion resistance and the mechanical properties (yield stress). This is a clear example of new materials with an improved performance that have been developed chronologically during the second generation, but that from a conceptual point of view belong to the first generation.

Stainless steels are characterized by corrosion resistance higher than other steels due to the formation of a passive oxide film. That film reduces the corrosion rate by blocking the transport of metallic ions and electrons. The stainless steels are classified into three categories according to their microstructures: ferritic, martensitic and austenitic. Among them, the austenitic stainless steels (face centered cubic structure, nonmagnetic) which contains Cr (16-18 wt. (%)) and Ni (12-15 wt. (%)) in its composition are responsible for increasing corrosion strength and ensure the stability of the austenitic phase, respectively (Karimi et al, 2012).

According to the interfacial response caused by biological interactions between the implant material and adjacent tissue, stainless steels are classified as biotolerable material being not able to form chemical bond with the bone. When the materials is implanted, occurs the formation of a fibrous tissue capsule around the implant with variable thickness, which depending on the amount of relative movement can lead to deterioration of the implant functions or damage in the tissue at interface. An alternative to improve the response at the tissue-implant interface is the development of stainless steel 316L biocomposites with a bioactive material, such as hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$).

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2.5 Hydroxyapatite

Hydroxyapatite Ca_{10} $(PO_4)_6(OH)_2$, abbreviated as HA is an inorganic compound whose chemical composition is similar to the composition of the bone. It is a very attractive material for biomedical applications such as a bone substitute material in orthopedics and dentistry due to its excellent biocompatibility, bioactivity and osteoconduction properties (Navarro, 2008). Hydroxyapatite has been used

extensively in medicine and dentistry for implant fabrication owing to its biocompatibility with human bone and teeth. However due to its poor mechanical properties, hydroxyapatite ceramics cannot be used for heavy load bearing applications, but common uses include bone graft substitution and coatings on metallic implants. **Table 2.4** shows the mechanical properties of hydroxyapatite.

Table 2.4 : Typical Mechanical Properties of Dense Hydroxyapatite Ceramics

Source : Sina, 2010

Theoretical density	3.156 g/cm3
Hardness	500-800 Vickers
Tensile strength	40-100 MPa
Bending strength	20-80 MPa
Compressive strength	100-900 MPa
Fracture toughness	1 MPa/m1/2
Young's modulus	70-120 GPa

Among the different classes of biomaterials, bioceramic is one of the promising classes of available biomaterials used as human body-implants. Few of the bioceramics have similarity with the mineral part of our bone but do not match with the intricate structure of the bone. There are several calcium phosphate ceramics that are considered biocompatible. Of these, most are resorbable and will dissolve when exposed to physiological environments. Hydroxyapatite is the most important bioceramic materials for its unique bioactivity and stability. According to Nath et al (2006), unlike the other calcium phosphates, hydroxyapatite does not break down under physiological conditions. In fact, it is thermodynamically stable at physiological pH and actively takes part in bone bonding and forming strong chemical bonds with surrounding bone. This property has been exploited for rapid bone repair after major trauma or surgery. While its mechanical properties have been found to be unsuitable for load-bearing applications such as orthopedics, it is used as a coating on load bearing implant materials such as titanium and titanium alloys or composites with other materials.

There are several methods to produce hydroxyapatite powder. The most popular and widely researched route is solution precipitation. Hydroxyapatite nanoparticles can be prepared using microwave irradiation. Sol-gel and hydrothermal routes are the two other important routes for hydroxyapatite synthesis. Even hydroxyapatite can be produced by mechanosynthesis route, in which case no heat treatment is required to produce crystalline nano hydroxyapatite. Some other routes for synthesis of hydroxyapatite are solid state reaction, plasma technique, hydrothermal hot pressing, ultrasonic spray pyrolysis, and emulsion system (Nath et al, 2006).

Porous hydroxyapatite has better biocompatibility as tissues can grow much faster into the available pores. The pore size can be controlled and also complex shaped materials can be fabricated. Several efforts have been made to improve the mechanical properties of hydroxyapatite (Nawawi et al, 2011). Thermal treatment is necessary to improve the mechanical properties. Even sometimes some amount of additives can be added to improve the sinterability and mechanical properties without affecting the bioactivity. Using $C(OH)_2$ additives the sintering temperature can be increased without any dissociation (Sina, 2010).

Hydroxyapatite is an important inorganic biomaterial which has attracted the attention of researchers related to biomaterials field in recent years. Hydroxyapatite is chemically similar to the mineral component of bones and hard tissues in mammals. It is one of few materials that are classed as bioactive, meaning that it will support bone ingrowth and osseointegration when used in orthopaedic, dental and maxillofacial applications (Rodriguez,2004). As a result, this inorganic phosphate has been studied extensively for medical applications in the form of powders, composites or even coatings. According to Agrawal et al (2011), it is also observed that dense sintered HA has many bone replacement applications and is used for repairing bone defects in dental and orthopedic sites and immediate tooth replacement. For substituting or repairing the bone, the designed material must has the ability to create a bond with the host living bone.

Hydroxyapatite has the abilty to integrate in bone structures and support bone ingrowth without breaking down or dissolving. Hydroxyapatite may be employed in

forms such as powders, porous blocks or beads to fill bone defects or voids. These may arise when large sections of bone have had to be removed for example in the case for bone cancer or when bone augmentations are required. The bone filler will provide a scaffold and encourage the rapid filling of the void by naturally forming bone and provides an alternative to bone grafts. It will also become part of the bone structure and will reduce healing times compared to the situation where no bone filler was used.

Coatings of hydroxyapatite are often applied to metallic implants (most commonly titanium or titanium alloys and stainless steels) to alter the surface properties. In this manner the body sees hydroxyapatiteas the type of material which is happy to accept. Without the coating the body would see a foreign body and work in such a way as to isolate it from surrounding tissues (Costan et al, 2011). Synthetic HA is classified as polycrystalline ceramics since its material structure is derived from individual crystals that have been fused together by a high temperature sintering. **Figure 2.1** shows the structure of hydroxyapatite.

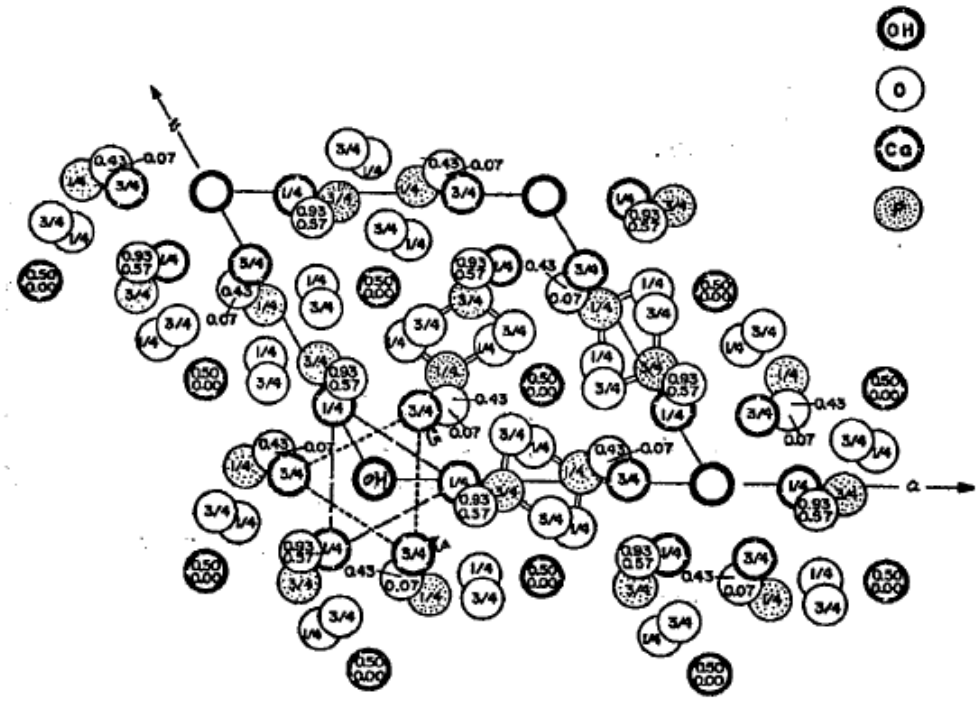

Figure 2.1 : Structure on Hydroxyapatite (Ratner, 2004)

2.5.1 Advantages Of Hydroxyapatite

Many biocompatibility studies prove that hydroxyapatite has a very similar chemical composition as the inorganic part of human hard tissue, such as bone and teeth. According to Liu et al (2011), the most important advantage of hydroxyapatite being a bioactive material is that bone will form a direct chemical bonding to hydroxyapatite implant without forming a collagen interface layer which is usually found in many other bioinert materials after implantation. Thereby the relative micro-movement between the implant and bone is dramatically reduced by this direct bonding, and no fibrous tissue capsule can be found between the implant and bone. This is important for the patient's recovery in the early period after implantation. Due to this chemical bonding interface, the bonding strength of hydroxyapatite and bone is much higher than other materials, such as Al_2O_3, ZrO_2 and Titanium alloy (Bosco et al, 2012).

2.5.2 Disadvantages Of Hydroxyapatite

The main disadvantage of hydroxyapatite is the poor mechanical property. Like most ceramics, the low toughness and impact resistance limit the clinical application of these materials (Rodriguez et. al, 2004). Hydroxyapatite cannott be used as a bulk material sustaining tension or impact. The tensile strength and compressive strength of the synthetic dense hydroxyapatite are $10\text{-}28x10^3$ psi and $30\text{-}130x10^3$ psi. The tensile strength and compressive strength of cortical bone are $10x10^3$psi and $20\ x10^3$ psi. There are two problems with hydroxyapatite mechanical properties which affect the clinical use of hydroxyapatite which are:

a. Hydroxyapatite is stiffer than bone. There is a modulus difference between cortical bone and dense hydroxyapatite. The Young's Modulus of cortical bone is $2x10^6$ psi, while $5\text{-}15x10^6$ psi for dense hydroxyapatite.
b. Bulk hydroxyapatite implants have low reliability under tensile loads. Cracks inside hydroxyapatite could cause catastrophic failure under use. Biologically, the hydroxyapatite in bone has very unique molecular structure, microstructure,

and macrostructure as can be seen in **Figure 2.2.** These structures give bone a unique ceramic/collagen fiber composite structure, which successfully prevent bone from breaking under mechanical load. Among them the microstructure plays an important role in this protection. The osteons are composed of concentric lamellae. Each lamella is composed of collagen fibers helixes. The apatite crystals can be found both inter-and intra-fibrillarly within the collagen layer. In this way, the bone elastic modulus drops but the elasticity increases. Certainly this microstructure is an ideal model for all hydroxyapatite composite, while the synthesis methods already developed are not capable of simulating this structure (Haibo, 2004).

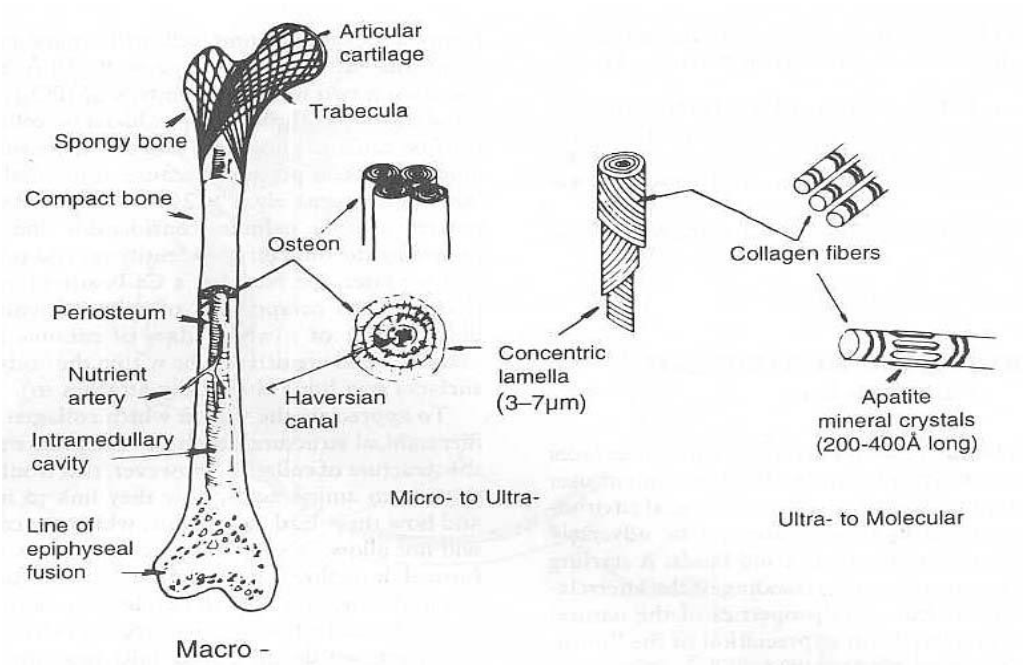

Figure 2.2 : The Molecular Structure, Macrostructure and Microstructure of Hydroxyapatie In Bone (Haibo, 2004)

Hence, the advantages and the disadvantages of hydroxyapatite has make it interested to be used as coating element on stainless steel substrate for the orthopaedic application.