# Characterization of β-TCP coated on stainless steel 316

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**2022**

**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING**

**UNIVERSITI SAINS MALAYSIA**

# Characterization of β-TCP coated on stainless steel 316

By

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Dissertation submitted in partial fulfillment of the requirements for the degree of

Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

**AUGUST 2022**

## DECLARATION

I hereby declare that I have conducted completed the research work and written the dissertation entitled "**Characterization of β-TCP coated on stainless steel 316**". I also declared that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

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Date: 18/08/2022

## ACKNOWLEDGEMENT

Alhamdulillah. I have completed writing this report but with the help and encouragement of great people around me, of course. Foremost, I am profoundly grateful to my supervisor Dr. Nurazreena Binti Ahmad from the School of Materials and Mineral Resources Engineering at Universiti Sains Malaysia for her patience and enthusiasm. Her guidance and useful comments helped me throughout my research and writing this report.

Sincere thanks to all my friends during my study for their help and moral support. I also want to thank all the technicians in the School of Materials and Mineral Resources Engineering for their co- operations. My special thanks to my parents, family, special mate and others for their support, motivation and constructive suggestion for the completion of the report, from start until this project is finished.

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## LIST OF SYMBOLS

| | |
|---|---|
| amps | Ampere |
| BHN | Brinell hardness number |
| cm | Centimetre |
| ° | Degree |
| °C | Degree Celcius |
| °C/ min | Degree Celcius per minute |
| g | gram |
| g/cm³ | Gram per cubic centimetre |
| kV | Kilovolt |
| MPa | Megapascal |
| µm | Micrometre |
| ml | Mililitre |
| mm | Milimetre |
| nm | nanometre |
| % | Percentage |
| Hv | Vickers pyramid number |
| wt.% | Weight percentage |

## LIST OF ABBREVIATIONS

| | |
|---|---|
| β-TCP | beta tri-calcium phosphate |
| AFM | Atomic Force Microscopy |
| FTIR | Fourier Transform Infrared Spectroscopy |
| HA | Hydroxyapatite |
| HBSS | Hank's Balance Salt Solution |
| HCA | Hydroxycarbonated apatite |
| ICDD | International Centre of Diffraction Data |
| PVA | Polyvinyl Alcohol |
| PVC | Polyvinyl Chloride |
| SEM | Scanning electron microscope |
| SPS | suspension plasma spray |
| SS | Stainless steel |
| WL | Weight loss |
| XRD | X-Ray Diffraction |

## LIST OF CHEMICAL FORMULA

| | |
|---|---|
| As | Arsenic |
| Be | Berylium |
| C | Carbon |
| Cr | Chromium |
| Co | Cobalt |
| CoCrMo | Cobalt chromium alloys |
| Fe | Iron |
| Hg | Mercury |
| Mo | Molybdenum |
| Ni-Cr | Nickel-Chromium |
| Pb | Lead |
| SiC | Silicon carbide |
| V | Vanadium |
| W | Tungsten |

**Pencirian β-TCP bersalut pada keluli tahan karat 316**

## ABSTRAK

Bahan bio ialah bahan yang direka bentuk untuk berinteraksi dengan tubuh manusia. Keluli tahan karat, terutamanya jenis 316, adalah bahan bio logam yang sering digunakan untuk aplikasi bioperubatan kerana biokompatibiliti unggul, kos rendah, ketersediaan, dan kekuatan tinggi. Walau bagaimanapun, larut lesap ion logam ke dalam tisu sekeliling adalah satu kelemahan yang menyebabkan masalah buah pinggang dan jantung. Dengan menyalut ß-TCP pada permukaan 316 SS ialah cara menghalang ion besi daripada merebak dan memusnahkan tisu manusia. Dalam projek ini, objektif utama adalah untuk menyalut beta trikalsium fosfat pada 316 SS melalui teknik salutan semburan dan untuk menilai kesan bilangan salutan ke atas sifat salutan 316 SS. Parameter yang digunakan adalah bilangan salutan yang berbeza iaitu 1 hingga 5 lapisan. Cecair disediakan dengan mencampurkan PVA ke dalam air suling. Seterusnya, biarkan ia sejuk pada suhu bilik dan tambah serbuk β-TCP. Kemudian, cecair disembur pada subsrat 316 SS dengan bilangan lapisan yang berbeza dan disinter pada 700°C. Pencirian yang terlibat ialah Mikroskop Elektron Pengimbasan (SEM), Mikroskop Daya Atomik (AFM), kekerasan Vickers dan ujian bioaktiviti dalam HBSS. Daripada hasil yang diperolehi, salutan dengan lima lapisan mempunyai ketebalan dan kekerasan yang paling besar manakala bagi salutan kekasaran permukaan dengan tiga lapisan mempunyai nilai tertinggi iaitu 6.131 nm. Akhir sekali, untuk sampel ujian bioaktiviti dengan salutan tiga lapisan mempunyai berat yang kurang meningkat, manakala sampel dengan salutan lima lapisan mempunyai penurunan berat yang besar. Jumlah penurunan berat dipengaruhi dengan ketara oleh lapisan tambahan salutan, terutamanya pada lapisan ke lima. Meningkatkan bilangan salutan, meningkatkan penurunan berat.

**Characterization of β-TCP coated on stainless steel 316**

## ABSTRACT

Biomaterials are materials designed to interact with the human body. Stainless steels, particularly 316 types, are the most often used metallic biomaterials for biomedical applications due to their superior biocompatibility, low cost, availability and high strength. However, leaching of metallic ions into surrounding tissues is a huge disadvantage which can cause renal and cardiac problems. By coating ß-TCP onto the surface of 316 SS is an alternate way for preventing iron ions from spreading and destroying human tissues. In this project, the main objective are to coat beta tricalcium phosphate on 316 SS via spray coating technique and to evaluate the effect of number of coatings on the properties of the coated 316 SS. The parameter used is different number of coatings which is 1 to 5 layers. The slurry was prepared by mixing PVA into distilled water. After that, let it cool to room temperature and the add β-TCP powder with the right composition. Then, the slurry is sprayed on the 316 SS substrate with different number of layers and sintered at 700°C. Characterization involved are Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM), Vickers Microhardness Test and Bioactivity test in HBSS. From the result obtained, the coating with five layers had the greatest thickness and hardness while for the surface roughness coating with three layers had the highest value of 6.131 nm. Lastly, for bioactivity test sample with coating of three layer has less gained in weight, while sample with coating of five layer has great weight loss. The amount of weight loss was influenced significantly by the addition layer of coating, particularly at layer five. Increasing number of coatings, increased weight loss.

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Human organs and tissues are quite resistant to the wear and use of daily life, yet they can nevertheless fail for a variety of reasons. Regenerative medicine is the study of innovative methods for repairing and replacing damaged organs and tissues. Stem cell therapy and biomaterials are two examples of regenerative medicine therapies. Biomaterials are materials designed to interact with the human body. They can be built from a variety of materials and physically comparable to the organ or tissue that has to be restored. Biomaterials have developed from improvised medical adjuncts based on commercially accessible materials to an organised, multidisciplinary discipline with thousands of researchers and scientific societies, a plethora of journals, a vibrant industry, and a wide range of applications (Buddy Ratner, 2019). Biomaterials can be made from a number of materials depending on their intended function. They can be formed of natural components like as collagen, synthetic materials such as metal, or a mix of the two (Caitlin et al, 2019).

When synthetic materials were first used in biomedical applications, the requirements were effective physical properties to match those of the replaced tissue with a minimal toxic response of the host, so biologically inert or nearly inert materials were used to reduce corrosion and the release of ions and particles after implantation to minimize the immune response and foreign body reaction. Mechanical characteristics and toxicity are also important considerations in the choosing of materials for implant manufacturing. When inert biomaterials are introduced into the body, a foreign fibrous capsule forms around the substance, protecting it from the surrounding tissue. These

materials were usually made from a variety of metals, ceramics, or substances such as rubber (University of Babyloon, 2020).

These early materials were unable to interact with the body on a cellular level, as today's biomaterials do. Advances in the creation of innovative biomaterials have resulted in materials that can interact with the body to aid healing and regeneration. These newer biomaterials were termed bioactive, which meant they could interact with the body and create chemical interactions with tissues. This is found in hip implants that stimulate bone formation, allowing a calcium coating known as hydroxyapatite to form atop the implant. The most recent biomaterials, known as third generation biomaterials, are designed to interact with the body and stimulate a specific reaction from cells. Third-generation biomaterials can also resemble the body's natural three-dimensional structure and promote tissue regeneration (Caitlin et al, 2019).

Outstanding biocompatibility and mechanical features, controlled corrosion profile (high chemical inertness and corrosion resistance for permanent implants, and a controlled degradation profile for resorbable platforms), adequately high wear resistance (particularly for articulating components), and osteointegration are the important benchmarks for metallic biomaterials (for implants interfacing with bone tissues). These benchmarks' meanings are always changing. For example, biocompatibility descriptors have developed to include non-sensitizing, non-allergenic, and non-tumorigenic characteristics, among many others. However, with the discovery of multiple feedback loops within materials–host systems, a more accurate definition of biocompatibility may be the capacity of a material to execute its function in a given application while generating an acceptable host response (Prasad et al, 2017).

Stainless steels, particularly 316L type, are the most often used metallic biomaterials for biomedical applications due to their superior biocompatibility, low cost, great corrosion resistance, availability, ease of processing, and high strength. With these excellent features, 316L stainless steel has become the most appealing biomaterial for dental implants, stents, and orthopaedic implants. It is utilised in a range of dental applications, including temporary crowns, sterilised equipment, arch wires, orthodontic brackets, and so on. The first step in determining biocompatibility is to evaluate an implant material's corrosion in biological solution in vitro (Nicoleta et al, 2017).

According to ASTM A240, type 316 and 316L are chromium nickel austenitic steels. Element molybdenum addition can improve stainless steel corrosion resistance, which is why 316/316l is more corrosion resistant than 304/304l. When the strength level of 316L steel with reduced carbon content is just slightly greater than that of 316 steels. As a result, grade 316l is sometimes extremely similar to grade 316. Another distinction is that 316l can be utilised for weld treatment due to its reduced carbon content. 316/316L steel offers excellent corrosion resistance properties in both ambient and oxidising environments (Agico Group, 2022).

The issue of iron ion breakdowns and producing harmful effect within the human body is a problem in medical implantation, thus the 316 SS must be modified before being used as an implant. As a result, the substrate will be modified to improve the substrate's bonding with the bone and to resist corrosion and ions discharged from the substrate (Dahotre et al, 2009). Implant dysfunctionality due to corrosion, mechanical failure, and poor biocompatibility, on the other hand, has been described. Zierold reported on the effect of different metals on the surrounding tissues in 1924. When introduced into bone, copper and nickel discoloured the surrounding tissue

significantly, but iron and steel disintegrated quickly and worsened tissue erosion. Although pure metals such as gold, silver, and aluminium did not stain tissue, they were too soft for most medical equipment. The 18Cr-8Ni (wt.%) stainless steel was initially used in implants in 1926. In vivo, this steel was both more corrosion resistant and stronger than vanadium steel. Molybdenum was added to the steel later that year to enhance its corrosion resistance in chloride-containing water. This alloy is referred to as 316 stainless steels. Titanium and its alloys were initially considered for orthopaedic use in 1940. These materials have previously been employed in aircraft applications and demonstrated exceptional corrosion resistance in seawater. As a result, good corrosion resistance in vivo could be expected. This was noticed upon implant removal. Maurice Down introduced a variety of orthopaedic devices, including titanium plates and screws, in 1947 (Noam Eliaz, 2019).

In general, the biomaterials used have a higher affinity for a wide range of proteins and hence become encapsulated with a plasma protein, primarily albumin, fibrinogen, IgG, fibronectin, and von Willebrand factor, following injection. Protein interactions and adsorption change the structure of the produced biomaterial. When biological tissue interacts with biomaterial or implant surfaces, fibrinogen becomes increasingly adherent and causes biomaterial denaturation. As a result, there is an urgent need to change the biomaterial surface to reduce the degree of neoepitopes exposure following cell and tissue interactions in order to safeguard the biomaterial over its expected shelf life. The surface chemistry and structure of a biomaterial are critical factors that influence protein adsorption, cell interference, and host reactivity. For example, in vitro cell adsorption can be accomplished by modifying the surface chemistry of a biomaterial. Nonetheless, the in vivo process of an externally applied biomaterial is unaffected by ordinary chemistry. Biomaterials, for example, are often

polymer, ceramic, or metal-based, with surface qualities ranging from hydrophilic to hydrophobic, tough to soft, and all evoke the same reaction in vivo. It could result in nonspecific protein adsorption. These biomaterials' surface modification aids in modulating their protein interaction behaviour. Precisely, a large number of results have been discovered, and surfaces that are unaffected by protein adsorption are referred to as nonfouling surfaces. As a result, the literature demonstrates a surface modification of biomaterial employing a wide range of approaches, including physical changes, chemical modifications, and radiation, to achieve a highly biocompatible biomaterial architect. In general, biomaterial surface modification, such as changing polymer chemistry, wetting ability, domain structure, and shape, has significantly influenced protein adsorption and cellular reactions in vitro (Nidhi et al, 2019).

## 1.2 Problem Statement

Stainless steel 316 is a biocompatible material. Iron ion, on the other hand, may be dissolved from the substrate in human body conditions. A high iron content can be harmful to live tissue (Bociaga et al, 2008). Metallic materials are highly preferred for implants due to their great strength, ductility, and toughness; however, implant corrosion caused by leaching of metallic ions into surrounding tissues is a huge disadvantage. Every stage of the implantation operation, from design to finished product manufacture, requires a greater understanding of basic electrochemical reactions. The presence of a passive coating on the surface of metallic implants during implantation should limit the corrosion process by releasing low-level corrosion products, allowing for effective implantation. However, due to the complicated physiology of human fluids, particularly dissolved gases, proteins, and different ions, as well as temperature effects, an oxygenated saline solution creates an aggressive environment that might lead

to implant corrosion. Metal ion leaching has been discovered to be extremely hazardous to cells. Pb (lead), Hg (mercury), As (arsenic), and Be (beryllium) are known to be poisonous and are avoided in clinical applications. Other metals, such as Fe (iron), Al (aluminium), Cr (chromium), V (vanadium), and Co (cobalt), have been reported to stimulate tissue regeneration. These metal ions may cause protein denaturation and even an immune reaction, followed by organ damage due to deposition. Ion accumulation in an organ can disrupt normal metabolism and cause renal and cardiac problems. Furthermore, mechanical load under normal living conditions has the potential to increase the rate of corrosion due to mechanical impacts in action (Priyadarshini et al, 2019).

So, the surface modification by using ceramic coating is needed. Attaching ß-TCP to the surface of 316 SS is an alternate way for preventing iron ions from spreading and destroying human tissues. As a result, the spraying method was used to solve this problem. The number of coatings on the substrate was the manipulated variable in this experiment.

## 1.3 Research Objectives

The objectives of this project are as follows:

1. To coat beta-tricalcium phosphate on 316 SS via spray coating technique.

2. To evaluate the effect of number of coatings on the properties of the coated 316 SS.

## 1.4 Scope of Research

This thesis is divided into five chapters. Chapter 1 describes a brief overview of the study, including a problem statement and objectives for this project. In Chapter 2, a comprehensive review on the biomaterial, metallic elements used in biomedical, ceramic coating and also technique used during coating. Chapter 3 describes the methodologies used in this project, including sample and slurry preparation, coating procedure, and coating characterization techniques. Chapter 4 presents the experimental results of the ceramic coating as well as a discussion of the ceramic coating immersed in hbss. Finally, Chapter 5 summarizes the findings of the research and makes recommendations for future work. Figure 1.1 shows the flowchart for this project.

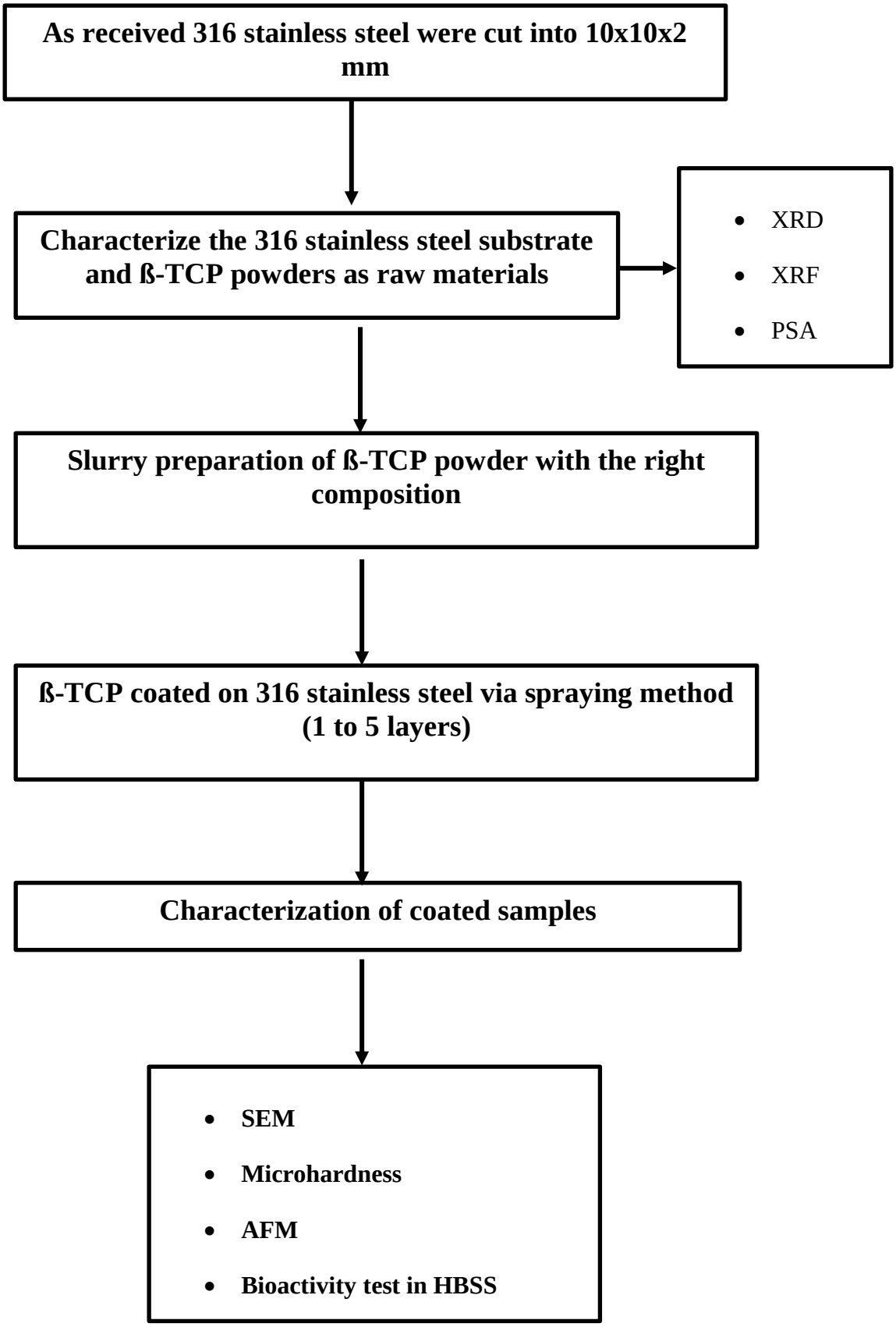


Figure 1. 1: Experimental Flow Chart

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Biomaterial

Any materials, surface, or structure that interacts with biological processes is referred to as a biomaterial. Biomaterials can be created or obtained from nature, and they can also be produced for use in bioengineering to help, improve, or replace damaged tissue or a biological function. The scope of applicability is really broad (Pavlovic et al, 2015). Metals, ceramics, plastic, glass, and even living cells and tissue can all be utilised to create a biomaterial. They can be reengineered into moulded or machined parts, coatings, fibres, films, foams, and textiles for application in biomedical goods and devices. These may include heart valves, hip joint replacements, dental implants, or contact lenses. They are frequently biodegradable, and some are bio-absorbable, which means they are gradually expelled from the body after performing a role (NIH, 2022). The first and most significant condition for a biomaterial for implantation or medical usage is that they be non-toxic, non-immunogenic, chemically inert, and acceptable to the human body (Silvio et al, 2020). The biomaterial must have sufficient physical and mechanical characteristics to enhance or replace biological tissues (Thouas et al, 2014).

Corrosion resistance is required for biomaterials. This is especially difficult with metal implants. Metal implants can produce metallic ions due to the presence of human fluids, which can collect in body tissue or be transported to other places of the body. Corrosion is one of the most significant processes affecting the life and performance of orthopaedic equipment composed of metals and alloys that are used as implants in the body. Biomaterials are often exposed to crucial humidity levels and an environment with a high proportion of localised corrosion. The low corrosion resistance of implants

in bodily fluid leads in the release of metal ions that are incompatible with implants in the body. It has been discovered that the discharged ions produce allergic and harmful responses. Corroded implants in the human body release an accumulation of toxic and dangerous metal ions such as Fe, Cr, Ni, Co, and Ti into the bodily fluid (Silvio et al, 2020).

Biocompatibility is one of the required conditions for the clinical usage of biomaterials in orthopaedics. It refers to a biomaterial's capacity to fulfil its job without causing hazardous or harmful effects on biological systems but yet triggering an adequate host reaction in a given circumstance. The materials used in implants are supposed to be non-toxic and to produce no inflammatory or allergic responses in the human body (Silvio et al, 2020). Biocompatibility now encompasses not just bio-inertia, but also bio functionality and biostability. High biocompatibility and functional qualities are greatly desired in new biomaterials. Biocompatibility can be influenced by the chemical, mechanical, and structural features of biomaterials, their interaction with biological environments, and even the assessment technique. The biological assessment of biomaterials covers a wide range of in vitro and in vivo studies for cytocompatibility, genotoxicity, sensitization, irritation, acute and chronic toxicity, hemocompatibility, reproductive and developmental toxicity, carcinogenicity, and other factors (Bogdan et al, 2020).

## 2.2 Metals and metal alloys

Metallic materials are the most significant engineering materials; they are employed as biomaterials owing to their outstanding heat conductivity and mechanical qualities. The information and knowledge required of a metal as a biomaterial is that it does not cause an adverse reaction when used in services, i.e., it is biocompatible.

Metallic biomaterials are typically utilised for load bearing applications and must have adequate fatigue strength to withstand the rigours of daily life. 316L stainless steel, cobalt chromium alloys (CoCrMo), titanium-based alloys (Ti-6Al-4V), and several others (including tantalum, gold, dental amalgams, and other "specialty" metals) are now used in biomedical applications. Metals are technologically interesting because their characteristics may be changed based on the production procedures utilised, making them more abundant and varied than polymeric materials and ceramics (Santos, 2017).

Surface modification, such as surface structuring or coating with bioactive ceramic and polymer thin films, is commonly used to impart multifunctionality on bio-inert metals such as Ti- and Co-based alloys. Bio-inert materials, most frequently based on Ti, Co, and steel, are crucial for many load-bearing applications, where their corrosion resistance gives great long-term stability and dependable mechanical strength, with low long-term toxicity to the host locally or on a systemic basis. These materials have good tensile strength, fracture toughness, and fatigue stress, and they have found uses in orthopaedics as artificial joints, plates, and screws, orthodontics as braces and dental implants, cardiovascular and neurosurgical devices such as components of artificial hearts, staples, stents, and wires. Titanium is a popular bio-inert material because of its favourable combination of biocompatibility, corrosion resistance, strength and elastic modulus, and low weight and density when compared to ordinary steel and Co-Cr alloys (Karthika, 2017).

Because of their good mechanical qualities, strong corrosion resistance, and high wear resistance, Co-Cr alloys have been established as metallic biomaterials vital for orthopaedic, cardiovascular, and dental fields. When compared to other metallic

biomaterials such as stainless steels and Ti alloys, their wear resistance qualities are quite good (Takayuki, 2015). Cobalt-Chromium (Co-Cr) alloys are primarily base-metal alloys that are frequently used in orthopaedic and dental applications. Co-Cr alloys are extensively used in dentistry for the fabrication of metallic frameworks for removable partial dentures and have lately been employed as metallic substructures for the fabrication of porcelain-fused-to-metal restorations and implant frameworks. The growing global interest in using Co-Cr alloys for dental applications is due to their inexpensive cost and acceptable physicomechanical characteristics. Furthermore, among base-metal alloys, Co-Cr alloys are increasingly being utilised to replace Nickel-Chromium (Ni-Cr) alloys in several nations. This is mostly due to growing worry about the harmful effects of nickel on the human body when nickel-containing alloys are exposed to the oral cavity (Youssef, 2014).

Stainless steel, CoCr alloys, and Ti alloys have been the three most often utilised metals for implants up to this point. The first stainless steel used for implants includes 18wt.% Cr and 8wt.% Ni, making it stronger and more corrosion resistant than steel. Molybdenum (Mo) addition has increased corrosion resistance, resulting in type 316 stainless steel. Following that, the carbon (C) content was lowered from 0.08 to 0.03 wt.%, improving its corrosion resistance to chloride solution and naming it 316L. Titanium is distinguished by its low weight. It has a density of 4.5g/c$m^3$ vs 7.9g/ c$m^3$ for 316 stainless steel and 8.3g/ $cm^3$ for cast CoCrMo alloys. Ti and its alloys, such as Ti6Al4V, are noted for their high tensile strength and resistance to pitting corrosion. Titanium alloyed with Ni, i.e. Nitinol, produces alloys with shape memory, making them useful for a variety of applications such as dental restorative wiring. CoCr alloys have been used in the fabrication of artificial joints for many decades. They're well-known for their high wear resistance. The wrought CoNiCrMo alloy, in particular, has

been utilised to manufacture severely loaded joints such as ankle implants (Hendra et al, 2010). Table 2.1 shows the metallic materials and alloys used for biomedical application.

Table 2. 1: Metallic materials and alloys used for biomedical application (Baibourine et al, 2008)

| **Metallic biomaterial** | **Applications** |
|---|---|
| 316L stainless steel | Fracture fixation, stents, surgical instruments |
| CP-Ti, Ti-Al-V, Ti-Al-Nb, Ti-13Nb-13Zr, Ti-Mo-Zr-Fe | Bone and joint replacement, fracture fixation, dental implants, pacemaker encapsulation |
| Co-Cr-Mo, Cr-Ni-Cr-Mo | Bone and joint replacement, dental implants, dental restorations, heart valves |
| Ni-Ti | Bone plates, stents, orthodontic |
| Gold alloys<br>Hg-Ag-Sn Amalgam | Dental restoration |
| Platinum and Pt-Ir | Electrodes |
| Silver alloys | Antibacterial agents |

## 2.3 History of 316 stainless steel

The first stainless steel used for implants had an 18 wt.% Cr and an 8 wt.% Ni content. Ni makes it tougher and more corrosion resistant than steel. The presence of molybdenum (Mo) has increased its corrosion resistance, resulting in type 316 stainless steel. Following that, the carbon (C) concentration was lowered from 0.08 to 0.03 wt.%, improving its corrosion resistance to chloride solution and naming it 316L. One of the most significant factors to consider for many applications is corrosion. Metal corrosion is caused by the composition of the metal as well as the presence of corrosive agents in

the surrounding environment. Once the corrosive environment has been established, the most frequent and easiest method of avoiding corrosion is careful metal selection. Nonferrous metals, stainless steel, and nonmetallic materials have strong corrosion resistance due to the existence of a protective passive layer (Hermawan et al, 2011).

304 SS, with its high chromium-nickel composition and low carbon content, is the most versatile and commonly used austenitic stainless steel. Its alloys are all variations on an 18% chromium, 8% nickel austenitic alloy. 304 SS shows resistance to oxidation, corrosion, and durability. 316 SS is an austenitic chromium-nickel stainless and heat-resistant steel with exceptional corrosion resistance when subjected to several types of chemical corrodents such as sea water, brine solutions, and the like. Because it contains molybdenum, 316 SS alloy is more resistant to chemical attack than 304 SS. 316 SS is long-lasting and simple to construct, clean, weld, and polish. It is significantly more resistant to high-temperature solutions of sulfuric acid, chlorides, bromides, iodides, and fatty acids. Certain medications require stainless steels containing molybdenum to avoid excessive metallic contamination (Nema, 2017).

The basic reason for the creation of superaustenitic stainless steels was that these very corrosive conditions led steel manufacturers to design steels with higher chromium, molybdenum, and nitrogen concentrations for greater resistance to pitting and crevice corrosion. Superaustenites provide a price advantage over nickel-base alloys, which can also be employed for certain purposes. Different amounts of chromium, as well as other materials, can be utilized to fabricate variable degrees of corrosion resistance. The most popular stainless-steel grades are 304 and 316. To retain an austenitic composition at lower temperatures, both 304 and 316 stainless steel (as well as other 300-series grades) require nickel. Austenitic steels provide an ideal

mixture of strength, workability, and corrosion resistance. The addition of molybdenum in 304 and 316 stainless steel gives a considerably better degree of corrosion resistance. The "moly" is added to increase corrosion resistance to chloride, such as that found in sea water (Mori et al, 2004). Table 2.2 shows the chemical compositions of 304 and 316 stainless steel**,** Table 2.3 shows typical chemical composition of 316 SS and Table 2.4 shows typical mechanical properties of 316 SS.

Table 2. 2**:** Chemical compositions of 304 and 316 stainless steel (Rodriguez et al, 2011)

| **Chemical composition** | **Type** | |
|---|---|---|
| | **304 SS** | **316 SS** |
| Carbon | 0.08% max. | 0.08% max. |
| Manganese | 2.00% max. | 2.00% max. |
| Phosphorus | 0.045% max. | 0.045% max. |
| Sulphur | 0.030% max. | 0.030% max. |
| Silicon | 1.00% max. | 1.00% max. |
| Chromium | 18.00-20.00% max. | 16.00-18.00% max. |
| Nickel | 8.00-10.50% max. | 10.00-14.00% max. |
| Molybdenum | - | 2.00-3.00% max. |

Table 2. 3: Typical Chemical Composition of 316 SS (United Performance Metal, 2021)

| **wt.%** | **316 SS** | **316L SS** |
|---|---|---|
| Carbon | 0.08 max | 0.03 max |
| Manganese | 2.00 | 2.00 |
| Silicon | 0.75 | 0.75 |
| Chromium | 16-18 | 16-18 |
| Nickel | 10-14 | 10-14 |
| Molybdenum | 2-3 | 2-3 |
| Phosphorus | 0.045 | 0.045 |
| Sulphur | 0.03 | 0.03 |
| Nitrogen | 0.10 | 0.10 |
| Iron | Bal. | Bal. |

Table 2. 4: Typical mechanical properties of 316 SS (United Performance Metal, 2021)

| | |
|---|---|
| Density | 8.03 g/cm$^3$ |
| Yield Strength | 205 MPa |
| Ultimate Tensile Strength | 515 MPa |
| Elongation Percent | 40% |
| Hardness | 95 BHN |

## 2.4 Metallic elements used in medical implant

The first metal produced especially for human use was "Sherman Vanadium Steel," which was used to make bone fracture plates and screws. Most metals used in implant fabrication (for example, Fe, Cr, Co, Ni, Ti, Ta, Mo, and W) may be tolerated by the body in low contents. Those metallic elements are sometimes needed in cell functioning (Fe), vitamin B12 production (Co), and aortic crosslinking (Cu) but cannot be tolerated in excess amounts in the body. The biocompatibility of implant metals is a major problem because they can deteriorate in the hostile bodily environment. Corrosion causes material loss, which weakens the implant, and, perhaps more importantly, corrosion chemicals leak into tissue, causing undesired effects (Park and Lakes, 2007).

Metals have a number of unique features. One is malleability, which allows metal to be shaped into implants; another is ductility, which refers to the ability to pull out metal in the shape of wire and is a crucial feature in permitting the fabrication of intramedullary rods, screws, and long stems. Improved characteristics can be obtained by mixing multiple metallic components in alloys. Alloys used in orthopaedic surgery must have certain characteristics. Because the implant's alloy is immersed in bodily fluid, low corrosion rates and relative inertness are required. As a result, significant research has focussed on modifying the physical surfaces of allow implants (Arturo et al, 2022).

As a result, biocompatibility is generally a factor in the selection of materials for medical purposes. When it comes to metals and alloys, the susceptibility of the material to corrosion and the effect of corrosion on the tissue are the most important components of biocompatibility. Corrosion resistance of currently utilised 316L

stainless steel, cobalt-chromium, and titanium-based implant alloys is dependent on a thin surface layer of oxide passivation. Stainless steel is the least corrosion resistant of the metals and is only used for temporary implantation. Although titanium and Co-Cr alloys do not corrode in the body, metal ions progressively penetrate through the oxide layer and accumulate in tissue. When a metal implant is implanted in the human body, it is surrounded by a layer of fibrous tissue which thickness is proportional to the amount and toxicity of the dissolution products, as well as the degree of movement between the implant and the nearby tissues. Under some situations, pure titanium may cause little fibrous encapsulation, but stainless-steel implants can cause the development of a fibrous layer up to 2 mm thick. Metals are the materials of choice for typical load-bearing applications due to their superior fracture and fatigue resistance (Irena, 1997).

Sherman is regarded as the pioneer of steel plates for fracture therapy. Surgical stainless-steel alloys (316L) with different quantities of iron, chromium, and nickel are being employed in the fabrication of prostheses. The low carbon (L) content of surgical stainless steel reduces corrosion as well as undesirable tissue reactions and metal allergies. Although many implants are still made from this great material, their usage is presently limited to plates, screws, and intramedullary devices that are not designed to sustain weight for a lengthy period of time. Fatigue failure and relatively high corrosion rates make it an unsuitable choice for the production of current joint replacement implants (Arturo et al, 2022). Figure 2.1 shows the stainless steel Charnley stem (left) and a cobalt-chromium Mueller (right)

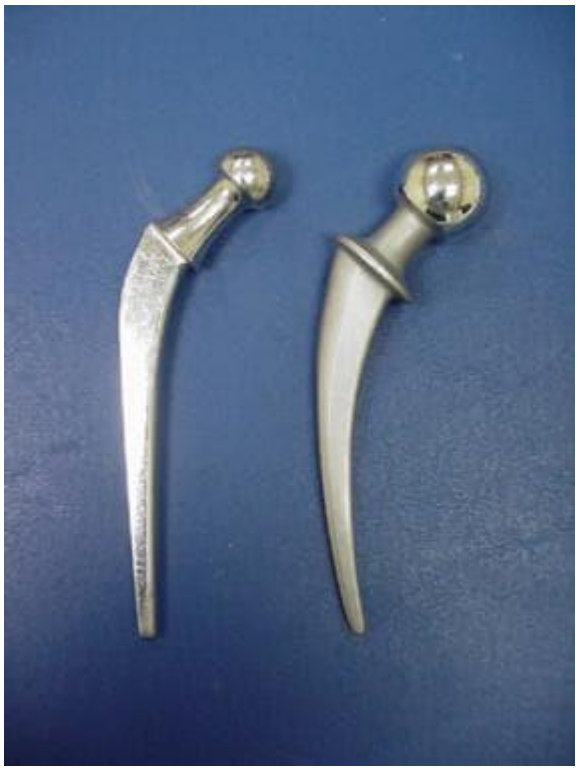

Figure 2. 1: Stainless steel Charnley stem (left) and a cobalt-chromium Mueller (right) (Arturo et al, 2022).

The surface of chromium-containing iron (and cobalt base) alloys is chromium oxide–based as a result of passivation or oxidation. The chromium oxide generates a very thin invisible layer that is resistant to biodegradation. These alloys have a relatively high corrosion rate because the oxide layer dissolves slowly in vivo. This is seen as a susceptibility for fretting and crevice corrosion, which restricts the potential of biologic fixation or the fabrication of modular implants. Heise et al, discovered that macrophages may influence the oxide surfaces of both stainless steel and titanium oxide discs in an in-vitro investigation. The macrophage activity formed corrosive pits and emitted statistically significant amounts of nitric oxide from the stainless-steel discs (Arturo et al, 2022).

Titanium and titanium alloys have a strong corrosion resistance due to their stable passive layer. As a result, titanium surfaces are frequently referenced in the context of electrochemical corrosion processes when they react as a cathode in contact with other metallic materials. Some surface treatments, such as sandblasting, resulting in rough and dirty surfaces, which may raise the risk of corrosion susceptibility. Electrochemical studies of the corrosion behaviour of Ti and Ti alloys have usually revealed excellent surface passivation. It may be demonstrated in physiological conditions that some alteration of the surface oxide composition occurs or that deposition of Ca and P, in the case of exposure to Ringer's solution, slows the stability of $TiO_2$ surface oxide. Ti alloys dissolve in acidic environments (0.5M $H_2SO_4$) and are less stable than pure Ti. These circumstances, however, are very strong in comparison to what is expected in the human body and can only be imagined in the crevice situation (Patrick et al, 2008).

For many decades, CoCr alloys have been used to make prosthetic joints. They are well-known for their high wear resistance. The wrought CoNiCrMo alloy, in particular, has been utilised to make severely loaded joints such as ankle implants. Figure 2.2 shows a set of ankle implants made from wrought CoNiCrMo alloy (Hermawan et al, 2010).

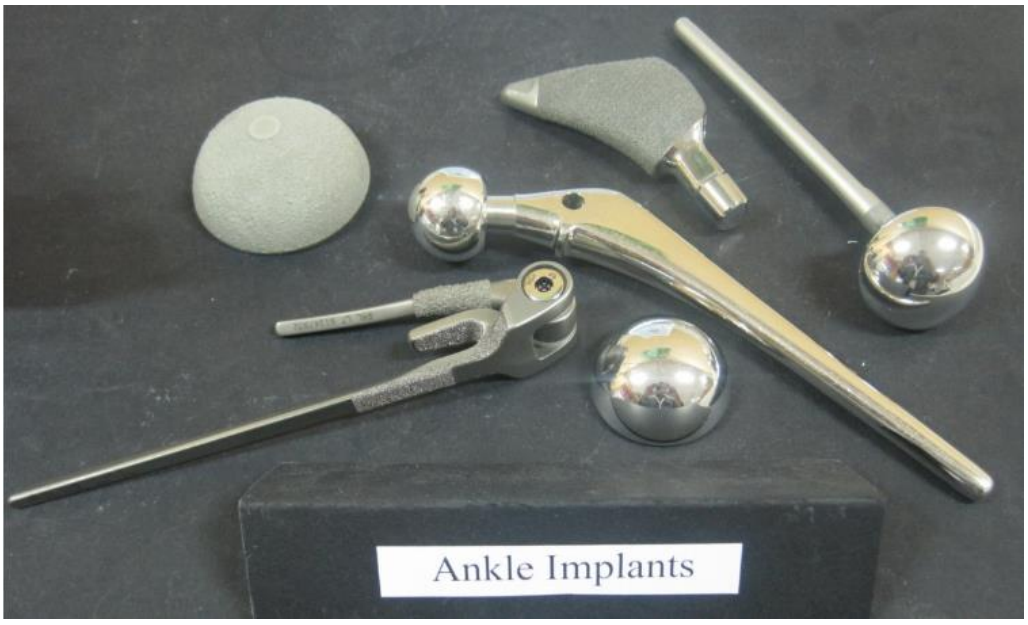


Figure 2. 2: A set of ankle implants made from wrought CoNiCrMo alloy (Hermawan et al, 2010).

Hip joints are replaced with metal implants. Because prosthetic hip joints are being implanted in younger and more active patients, there was a need to extend their life expectancy. The hip resurfacing joint is a relatively new type of hip replacement that includes "metal-on-metal" articulation between a metal cover on the femoral head and a metal lined acetabular cup. These are manufactured of CoCrMo due of its corrosion and wear resistance. There are two types of CoCrMo alloys often utilised in biomedical applications, based on the amount of carbon supplied. However, both alloys have a cobalt balance that may be as low as 60% by weight. There contains around 28% chromium, which produces a chromium-rich passive oxide layer (Cr2O3) that develops spontaneously on the metal's surface. By isolating the metal from the air and water conditions, this provides superior corrosion resistance. Molybdenum is often added at 5-7 wt %to improve the mechanical characteristics of the alloy because it offers solid solution strengthening and strong localised corrosion resistance. On the surface of the

alloy is an oxide layer that creates a thin passive film enriched in chromium (George, 2010).

## 2.5 Beta Tri-Calcium Phosphate (ß-tcp)

Calcium phosphate ceramics (CPCs) have received a lot of interest as bone substitute materials for biomedical purposes because of their outstanding biocompatibility, bioactivity, and osteoconductivity, CPC coatings on metallic implants, in particular, benefit from both metals' high mechanical strength and ceramics' good biocompatibility and osteoconductivity, making them appropriate for load-bearing implants. They promote new bone formation along the implant from the interface in touch with natural bone tissue, resulting in a more fast and durable attachment of the implant to the surrounding bone tissue. Furthermore, CPC coatings can prevent metal ion discharge from metallic implants into the body. A bone-calcium phosphate-coated implant bonding method has been proposed, which begins with the partial breakdown of the coating and the subsequent creation of apatite on the coating surface. This apatite layer allows the coating to adhere to active the bone. If the coating dissolves too slowly in bodily fluid, intimate bone–implant bonding may take considerably longer, whereas quick breakdown of the coating might degrade the coating. As a result, obtaining coatings with an optimal dissolving rate is critical for sustained bone–implant bonding. Recently, there has been a growth in interest in producing biphasic calcium phosphate (BCP) ceramics, which are composed of a combination of the more stable hydroxyapatite (HA) and the more soluble tricalcium phosphate [$Ca_3(PO_4)_2$, TCP] (Byung et al, 2009).

It is a potential material for biomedical applications since it has great biocompatibility, strong biological affinity and activity, and reacts well to physical conditions. It is regarded as an appropriate bone replacement material since it resorbs well in vivo, with new bone development replacing the implanted tricalcium phosphate. It is one of the most appealing bioceramics due to its potential bioactivity and biocompatibility, and it is widely employed in medicine and dentistry. It is a high temperature phase of calcium phosphates that can only be created by thermal degradation, for example, of CDHA (calcium deficient hydroxyapatite), at temperatures above 800 C. Aside from chemical methods, ion-substituted ß-TCP may be produced by calcining bones. This form of ß–TCP is also known as "bone ash." At room temperature, the ß–TCP phase is more stable and less soluble in water than the α–TCP phase. It converts into the high-temperature phase α–TCP at temperatures above 1125 C (Rosli, 2009).

## 2.6 Coating Technique

Surface coating can allow the bulk materials to remain unchanged, while the surface functionality is engineered to afford a more wanted characteristic. Ceramic coatings are considered as ideal coatings on metal which can significantly improve the surface properties of metal materials including anti-fouling, self-cleaning, corrosion resistance, wear resistance, oil/water separation and biocompatibility. Furthermore, various techniques have been utilized to fabricate a range of different ceramic coatings with more desirable properties on metal materials, which make the materials widely used in service environment (Zang et al, 2020).

Hydroxyapatite (HA) is the predominant inorganic component of human and animal bones in terms of non-oxide ceramics. It is a bioactive ceramic substance that is

commonly utilised in bone tissue engineering. The HA ceramic coating has been widely employed to surface functionalize metallic biomaterials. Hiromoto et al. developed HA coatings on AZ31 magnesium alloy, and the findings shown that the HA coatings may significantly reduce Mg ion-release and corrosion current density. Furthermore, it was discovered that HA coating on 316 L stainless steel increased the corrosion behaviour and biocompatibility of metallic implants while also improving bone Osseointegration. Surmeneva et al. also created HA coatings with varying Ti concentrations on a Ti-6Al-4 V alloy, which was thought to be a potential biological material (Zang et al, 2020).

### 2.6.1 Method to coat 316 SS

#### 2.6.1(a) Magnetron sputtering technique

The main principles of the magnetron sputtering process are illustrated in Fig. 2, which depicts a magnetron from the side. The idea is to improve the ionization of the atoms before they hit the target, increasing the amount of sputtered material compared to conventional sputtering. This is accomplished by introducing magnetic fields close to the target surface using horseshoe magnets arranged on the magnetron's back side, as shown in Fig. 2. Since ions and electrons are separated here, the discharge created in front of the target is often referred to as magnetron "plasma." The most basic magnetrons have a circular geometry, but square magnetrons and other shapes are also quite common. On the market today, there are also cylindrical-shaped targets that rotate around an inner array of permanent magnets. Permanent magnets are typically used, but electromagnets can perform the same function and even be more flexible in attempting to arrange the desired magnetic field configuration, though the mechanical construction of the magnetron will be more complex. The magnetic field lines in Figure2.3 begin at the two outer north poles and end at the centrally arranged south pole. In addition to the magnetic field lines, a perpendicular to the target surface electric field E is created by