SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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FABRICATION OF Ti-40Nb-10HA COMPOSITE AND Ti-40Nb ALLOY WITH SURFACE NANOTUBES FOR IMPLANT APPLICATION

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Fabrication of Ti-40Nb-10HA Composite and Ti-40Nb Alloy with Surface Nanotubes for Implant Application**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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Date: 25th May 2018

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LIST OF ABBREVATIONS

BCC	Body Center Cubic
CP-Ti	Commercially Pure Titanium
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-ray
E.G	Ehylene Glycol
FESEM	Field Emission Scanning Electron Microscopy
FDA	Food and Drug Administration
HA	Hydroxyapatite
HBSS	Hank’s Balanced Salt Solution
HCP	Hexagonal Closed-Packed structure
MMC	Metal Matrix Composite
PM	Powder Metallurgy
rpm	rotation per minute
SBF	Stimulate Body Fluid
SCE	Saturated calomel electrode
SEM	Scanning Electron Microscopy
TCP	Tricalcium Phosphate
TTCP	Tetracalcium Phosphate
XRD	X-Ray Diffraction

LIST OF SYMBOLS

GPa	Gigapascal
HV	Vickers Hardness
MPa	Megapascal
%	Percentage
pH	Potential of Hydrogen
wt %	Weight Percentage
vol %	Volume Percentage

FABRIKASI KOMPOSIT Ti-40Nb-10HA DAN ALOI Ti-40Nb BERPERMUKAAN NANOTIUB UNTUK APLIKASI IMPLAN

ABSTRAK

Kriteria bio-bahan pada hari ini dikehendaki memiliki sifat mekanikal yang baik dengan memiliki keupayaan untuk menumbuh sel-sel tisu dalam badan. Dua kaedah untuk menghasilkan bahan yang memiliki bioaktif adalah dengan menambah bahan bioaktif hidroksiapatit (HA) dan melakukan pengubahsuaian permukaan bahan. Sifat-sifat mekanikal dan kadar bioaktif komposit Ti-40Nb-10HA dan kebolehan penumbuhan nanotiub atas permukaan aloi Ti-40Nb telah dikaji. Komposit Ti-40Nb-10HA dan aloi Ti-Nb difabrikasi dengan menggunakan kaedah metalurgi serbuk dengan dipadatkan pada tekanan 500 MPa. Ti-40Nb-10HA adalah disinterkan ke suhu-suhu (900°C – 1300 °C). Keputusan menunjukkan nilai ketumpatan relatif komposit meningkat (91.54% - 97.09%) apabila suhu sinter meningkat. Selain itu, kadar kakisan komposit yang dikaji menggunakan kaedah elekrokimia adalah dalam julat 0.0348 – 0.1494 mm/tahun. Modulus keanjalan meningkat dari suhu 1000°C ke 1300 °C (17.6 GPa ke 20.03GPa). Ini bermaksud, modulus anjalan komposit tersebut serasi dengan modulus keanjalan tulang manusia (18GPa). Komposit menunjukkan peningkatan dalam kekerasan mikro (112.46 HV ke 183.85 HV) dan kekuatan mampatan (159 MPa ke 193.33 MPa) apabila suhu sinter menaik daripada 1000°C ke 1300 °C. Ujian in-vivo dijalankan dalam larutan HBSS selama 7 hari. Pertumbuhan apatite meningkat apabila suhu sinter meningkat dari 1000°C ke 1200°C manakala aloi Ti-40Nb (sinter pada suhu 1200°C) menerusi penganodan menunjukkan pembentukan nanotiub oksida dengan pengurangan diameter liang (dari 70nm ke 50 nm) apabila peratusan isipadu NH_4F dalam elektrolit meningkat 0.5 % isipadu ke 0.7 % isipadu.

FABRICATION OF Ti-40Nb-10HA COMPOSITE AND Ti-40Nb ALLOY WITH SURFACE NANOTUBES FOR IMPLANT APPLICATION

ABSTRACT

The criteria of today's biomaterials has included both physical properties and its ability to promote growth of body tissue. In today's technology, there are two methods to improve bioactivity of the biomaterials are by adding bioactive materials such as hydroxyapatite (HA) and surface modification of the materials. Hence, the mechanical properties and bioactivity of Ti-40Nb-10HA composite was studied and the investigation of the feasibility of forming nanotubes on Ti-40Nb alloy was also conducted. Ti-40Nb-10HA and Ti-40Nb was fabricated by powder metallurgy method with the compaction pressure of 500 MPa. Ti-40Nb-10HA was sintered at variation of temperature (900°C – 1300 °C). Mechanical testings' results show that the densification occurs when the sintering temperature increases. The relative density of the sintered composite increases as sintering temperature increases from 91.54% to 97.09%. The corrosion rates of the sintered Ti-40Nb-10HA composite is within the range of 0.0348 to 0.1494 mm/year. The modulus of the composite increase as the sintering temperature increase from 1000 °C to 1300 °C (17.6 GPa to 20.03 GPa) which is comparable with the modulus of human bone which is 18GPa. The Ti-40Nb-10HA composite sintered at 1100°C to 1300 °C show increasing micro hardness (112.46 HV to 183.85 HV) and compressive strength (159 MPa to 193.33 MPa). In-vivo evaluation in HBSS for 7 days, nucleation and growth of apatite increases as the sintering temperature increases from 1000°C to 1200°C while the surface modification of Ti-Nb (sintered at 1200°C) exhibited formation of oxide nanotube with reducing diameter from 70 nm to 50 nm when volume percentage of NH_4F in electrolyte increased from 0.5 vol% to 0.7 vol%.

CHAPTER 1

INTRODUCTION

1.1 Background

The development of metallic implants was initially intended to be applied in bone repair, typically internal fracture fixation of long bones in the 19^{th} century. Since then, metallic materials is applied in orthopaedic surgery to invent temporary orthopaedic devices such as bone plates, pins and screws and permanent implants such as total joint replacement, dental and orthodontic practice including tooth fillings and roots.

There are increasing research in metallic biomaterials but only a few are biocompatible and durable. These materials is categorized into 4 groups based on major alloying elements: stainless steels, cobalt-based alloys, titanium-based alloys and miscellaneous. Most of the metallic implants in the first three group have been approved by United States Food and Drug Administration (FDA) (Chen and Thouas, 2015).

Titanium and titanium alloys are commonly used as implant materials in orthopaedics, cardiology and dentistry due to high strength and high biocompatibility. The most well-known titanium alloys which is widely used in implant application is Ti-6Al-4V. The addition of alloying element, Al and V greatly improved the mechanical properties of titanium. However, corrosion or wear processes released metal ions that may induce aseptic loosening of the implantation in long term. Hence, niobium is suggested to be used as alloying element in titanium alloy added with HA as niobium is not harmful to human body and it stabilizes the β-phases in titanium.

In 2017, Gonzalez *et al.* (2017) research on surface coating of Ti-Nb alloy on stainless steel. The finding shows that the surface coating on stainless steel has lower elastic modulus and equal or higher hardness value as compared to commercially used alloys such as stainless steel. It has high value of joint plastic deformation between coating and substrate. Balbinoti *et al.* (2011) use powder metallurgy method to produce Ti/HA biocomposite. Result shows that micro α-Ti, $CaTiO_3$, $Ca_3(PO_4)_2$ and Ti_xP_y phase(s) found in composite which HA decompose into $CaTiO_3$ and β-$Ca_3(PO_4)_2$. Then β-$Ca_3(PO_4)_2$ decompose into $CaTiO_3$ layer and nucleation and growth of Ti_xP_y .The compression strength of nanometric HA composite is 40 % higher than micrometric HA, because nanometric HA is better dispersed in composites.

Titanium and titanium based alloys have relatively poor tribological properties because of their low hardness. One of the methods that allows the change of biological properties of Ti alloys is to produce a composite, which will exhibit the favourable mechanical properties of titanium and excellent biocompatibility and bioactivity of ceramics. The main ceramics, used in medicine are hydroxyapatite, silica or bioglass. Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) shows good biocompatibility because of its chemical and crystallographic structure being similar to that of living bone. HA has porous nature and is bioactive which means that after some time it is partially resorbed and replaced by natural bone. Besides, HA has the ability to form strong chemical bonds with natural bone (Niespodziana *et al.*, 2010).

Various types of surface modification methods has also been explored to further improve the bioactivity and biocompatibility of Ti. The surface treatment included surface coating with HA or chemical treatment that enhance HA formation. Chemical modification of Ti surface such as anodization has also been proven that it enhance biocompatibility which typically leads by formation of rough porous TiO_2 layers (Tsuchiya *et al.*, 2006). In addition, Young's modulus of TiO_2 nanotubes is lower than Ti substrate and the HA coating has poor adhesion strength at the HA/Ti interface (Chernozem, Surmeneva and Surmenev, 2016).

It was found that fluorite concentration, anodization temperatures and applied potential differences has effects on the formation and dimensions of the titania nanotubes in ethylene glycol/water mixture electrolyte (Xie and Blackwood, 2010).

1.2 Statement of Problem

In the early period of medical implant development, the only criteria for implant material suitability were appropriate physical properties and non-toxicity. There are a lot of studies of Ti-alloy with β-stabilize that fulfil the as mentioned criteria in biomedical application such as Ti–13Nb–13Zr, Ti–12Mo–6Zr–2Fe (TMZF), Ti–35Nb–7Zr–5Ta (TNZT) Ti–29Nb–13Ta–4.6Zr, Ti–35Nb–5Ta–7Zr–0.40 (TNZTO), Ti–15Mo–5Zr–3Al and Ti–Mo (Geetha *et al.*, 2009). Today, the criteria of the biomaterials has included the physical properties of the bone implant material and its ability to promote the growth of body tissue (Arifin *et al.*, 2014). In the early period of implant material development, a material was considered suitable to replace natural tissue when it had minimal or zero toxicity. Later on, the ability to promote natural tissue growth was considered. Biomaterials for implants should not be cytotoxic which is caused by increased metallic ion content in the blood (Arifin *et al.*, 2014). Hydroxyapatite (HA) is a bio ceramic material with poor mechanical properties, especially for load-bearing applications.

However, HA has a similar structure to bones and can promote the growth of natural tissues. Combining a titanium alloy with HA creates a new bio-composite with excellent mechanical and biological properties. Somehow, there are very little studies and research for metal matrix composite (MMC) with ceramic reinforcement such as Ti-Nb-HA alloys since bio ceramic materials can enhance corrosion resistance of the Ti-alloy by increasing its service period. In addition, HA has high intergradation with surrounding bone which helps to form bony tissues around the implant materials and Nb element is one of the β-stabilizers that give high strength and low modulus to the biomaterials. In this study, further investigation on Ti-Nb-HA will be carried out to determine the effect of sintering temperature to the mechanical properties and microstructure of the Ti-Nb-HA. Bioactivity performance of Ti-Nb-HA will also be determined by using SBF solutions.

In addition, Tsuchiya *et al.* (2006) has done research that presence of the nanotubes on a titanium surface enhances the apatite formation. Hence, the feasibility of anodization on Ti-40Nb alloys pellets in ethylene glycol electrolyte with ammonium fluoride which start from raw materials was also another issues that most researchers are trying hard to figure out. Research works are focus on anodization on Ti foil (Xie and Blackwood, 2010) and anodization on Ti-Nb alloy been investigated in phosphoric acid added with ammonium fluoride as electrolyte (Jang *et al.*, 2009). However, there are very few research or investigation of the feasibility of anodization of Ti-Nb alloy which is sample preparation involves powder metallurgy and sintering to produce bulk alloy.

1.3 Objectives

The primary aim for this study is to examine the influence of β-stabilizing element, Niobium to microstructure and mechanical properties of Ti-alloy. In addition, bioactivity of HA in Ti-alloy is determined. The specific objectives of the research work are:

i. To investigate the effect of sintering temperature (900 °C - 1300°C) on the microstructure, mechanical properties and corrosion behaviour of Ti-Nb-HA composite

ii. To determine the bioactivity of HA in Ti-Nb-HA composite

iii. To determine the feasibility of forming nanotubes by anodization on Ti-40Nb pellets

1.4 Research of Work

The project aimed to investigate mechanical properties of Ti-40Nb-10HA at various sintered temperature and the bioactivity performance of Ti-40Nb-10HA. Ti-40Nb-10HA composite (50 wt % Ti, 40 wt% Nb, 10 wt% HA) which sintered at different temperature were synthesized by powder metallurgy method. The microstructure and mechanical properties of the specimens were investigated by carried out compressive test and hardness test to determine the maximum compressive strength and modulus of elasticity of the composites. Corrosion testing of Ti-40Nb-10HA was also carried out to determine corrosion behaviour of the specimens. The surface bioactivity of composites was evaluated by characterizing the apatite layer of specimens that soaked in HBSS. Bioactivity of the Ti-alloy can be enhanced by surface treatment and adding bioactive element. Anodization of Ti-40Nb alloy was conducted to determine the feasibility of growing nanotubes of the alloy. Anodization of bulk alloy, Ti-40Nb (60 wt% Ti, 40 wt% Nb) prepared by powder metallurgy method, and sintered at optimum temperature of

1200 °C in this project. SEM observation was carried out to determine the morphology of the TiO_2 nanotubes and determine the length and pore size of the nanotubes.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents a review on existing research and information of the topics relates to biomaterials, titanium and modification and improvement of titanium alloy in biomedical field, important fabrication parameter of titanium alloy.

2.2 Biomaterials

Biomaterials are the non-living materials that are manufactured to survive and function as foreign bodies within biological environment such as in living human system. The common feature of biomaterials is that it is used in intimate contact with human living body. In other word, biomaterials are used biocompatible materials which can be either natural or man-made which function to replace or assist organ or tissue part in intimate contact (Chen and Thouas, 2015).

In 1976, the first Consensus Conference of the European Society for Biomaterials (ESB) define biomaterial as ‘a nonviable material used in medical device, intended to interact with biological systems’. In recent, field of biomaterials has evolved. The current definition of biomaterial is a material intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body’. Biomaterials have been evolved from a material that interacting with the body by influencing biological processes towards tissue regeneration (O’Brien, 2011).

Implant materials can be categorized as in Table 2.1 based on the type of material used and the biological response when implanted (Saini *et al.*, 2015).

Table 2.1 Classification of Implant Materials based on its Biodynamic Activity (Saini *et al.*, 2015).

Biodynamic Activity	**Chemical Composition**		
	Metals	**Ceramics**	**Polymers**
Biotolerant	Gold Co-Cr alloys Stainless steel Niobium Tantalum		Polyethylene Polyamide Polymethylmethacrylate Polytetrafluroethylene Polyurethane
Bioinert	Commercially pure titanium Titanium alloy (Ti-6Al-4V)	Al oxide Zirconium oxide	
Bioactive		Hydroxyapatite Tricalcium phosphate Bio glass Carbon-silicon	

Titanium is an ideal metal in intra-osseous dental implants. It triggers a spontaneous formation of oxide layer on its surface which protect the metal from chemical attack including aggressive body fluids. The titanium oxide layer is insoluble and it prevents the release of ions which could react with organic molecules. Thickness of oxidized titanium surface layer increase after implantation (Allegrini *et al.*, 2006). Chemical surface treatment of titanium implants help to accelerate the osseous connection and increase strength of bone-implant adherence. Chemical surface treatment such as coating implant with hydroxyapatite can help to accelerate the osseointegration on bone-implant contact.

2.3 Metallic Biomaterials

The most commonly used metallic biomaterials are stainless steel, cobalt-based alloy and titanium alloys. These materials are bio-inert materials, which are used widely in load-bearing functions, where it has high corrosion resistance which provides excellent long-term stability and reliable mechanical strength with minimal toxicity to the host. Over the year, these materials were used in applications 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. Implant materials are generally made of stainless steel, cobalt-based alloy and titanium alloys. A metallic implant should possess the following important characteristic; excellent biocompatibility (non-toxic), high corrosion resistance, suitable mechanical properties, high wear resistance and osseo-integration (Chen and Thouas, 2015).

The most widely used stainless steel and cobalt-based alloy are SUS316L and Co-Cr alloy which have Young's Modulus around 180 GPa and 210 GPa respectively. For titanium alloy, the widely used implant device such as Ti-6Al-4V ELI has lower Young's Modulus of 110 GPa (Niinomi and Nakai, 2011). The first generation biomaterials, Ti-6Al-4V have excellent reputation for corrosion resistance and biocompatibility. However, long term performance of these alloys raised some concerns due to release of Al and V ions from the alloy. Both Al and V ions released form the alloy found to be causing long term health problems such as Alzheimer disease, neuropathy and ostemomalacia (Geetha *et al.*, 2009). Ti-6Al-4V have high coefficient of friction, leading to formation of wear debris that causes inflammatory reaction at the surrounding bone tissue, these causes the service period of implants are restricted to 10-15 years (Geetha et al., 2009). The Ti-6Al-4V alloy is $\alpha + \beta$ biomedical alloy. The $\alpha + \beta$ titanium treated structures have high strength, higher ductility, and higher low cycle fatigue. However, α + β biomedical alloy is also high stiffness and high modulus which prevent stress needed to transferred to adjacent bone. This results in bone resorption around the implant and causes implant loosening. This bio incompatible situation leads to death of bone cells which is known as "stress shielding effect" (Geetha *et al.*, 2009). Hence, the materials replaces for bone is expected to have modulus equivalent to bone with modulus varied in the magnitude from 4 to 30 GPa depending on the type of bone and direction of measurement to prevent "stress shielding effect". β treated structure has higher fracture toughness and low modulus. The strength of an alloy increases with increasing β stabilizer content. In addition, low modulus beta titanium consist compatible alloying elements and have modulus close to bone (Geetha *et al.*, 2009). Theoretical studies have shown that β-isomorphous elements (Mo, V, Nb, Ta) are the most suitable alloying elements to be added in Ti alloy because it decreases the modulus of elasticity of Ti which is in body centered cubic structure (BCC) without compromising the strength and these elements are non-toxic element due to it high solubility in titanium and less preferably form intermetallic compounds which will affect the mechanical properties and microstructure of the alloy (Campbell, 2006).

Materials design of novel Ti-alloys for such as implants application is limited to 2 conditions. First condition is all alloyed chemical elements should be biocompatible and the second condition is implant materials should elastically match human bones as closely as possible. In order to fulfill the first condition, elements from the Periodic table are limited to metal such as Au, Ag, Ti, Zr, Nb, or Mo to ensuring biocompatibility can be used. The second criterion can be conveniently quantified in terms of the polycrystalline Young's modulus.

2.4 Metal Matrix Composite (MMC)

Titanium is a bio-inert material, it forms an interlocking bonding with bone, but it might cause loosening of implant and failure of the implant. Bioactive material such as hydroxyapatite can help titanium alloys forming long term stable bonding with bone. Hence, some hydroxyapatite is often added inside titanium or titanium alloy to form metal matrix composite.

Hydroxyapatite has similar chemical and crystallographic structure with bone. However, it cannot be used alone as implant's materials due to its poor mechanical properties. Hence, hydroxyapatite are often mixed with other high mechanical properties materials such as titanium alloys to make composite that is more suitable to be used for load-bearing implant (Balbinotti *et al.*, 2011).

The bio-active and biodegradable properties of hydroxyapatite (HA) make it a preferred candidate for implants such as bone replacement in replacing natural tissues damaged by diseases and accidents. However, the low mechanical strength of HA hinders its application. Combining HA with a biocompatible material with a higher mechanical strength, such as a titanium (Ti) alloy, to form a composite has been of interest to researchers. A HA/Ti composite would possess characteristics essential to modern implant materials, such as bio-inertness, a low Young's modulus, and high biocompatibility.

The interaction between titanium alloys and hydroxyapatite has been studied by several researchers. Thermal stability has been observed to affect the synthesis of HA, such that in the thermal processing of a HA/Ti system, tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP) are commonly produced after dehydroxylation and decomposition (Arifin *et al.*, 2014)

The surface charge of the substrate in immersion of Hank's Balance Salt Solution (HBSS) also play essential role in reaction of apatite formation. Yoshida and Hayakawa (2017) research show that negatively charged surface with PO_4H_2 or COOH groups have more apatite formation than positively charged surfaces with NH_2 groups. The apatite formation is initiated by adsorption of calcium ions on negatively charged surface and the phosphate ions bound to the adsorbed calcium ions. The amount of calcium ions and phosphate ions attracted to substrate to form apatite crystals will increase as immersion time increase (Figure 2.1).

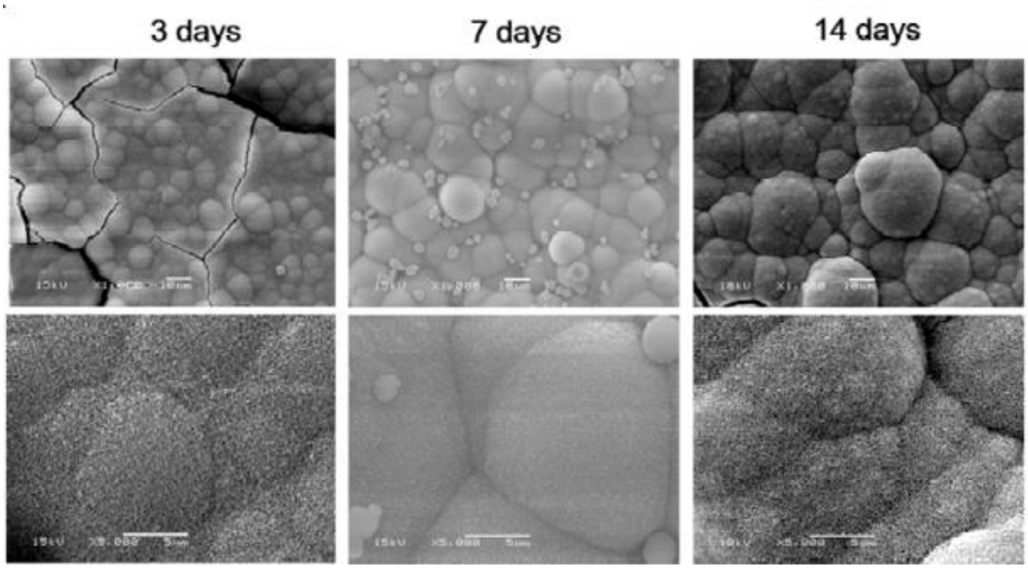

Figure 2.1 SEM pictures of the surface appearance of Ti disks after horizontal immersion in Hank's balanced salt solution (HBSS) for 3, 7, and 14 days (Suzuki *et al.*, 2016)

2.5 Effect of Niobium to Titanium Alloy

Titanium undergoes allotropic transformation at 883 °C which above this temperature, titanium has the BCC crystal structure which also know as β-phase. This transformation temperature can be changed by changing the level of the interstitial content as well as using different alloying element. The addition of different amount of alloying element change the α/β structure transformation temperature such as the oxygen and aluminum stabilize the α-phase and elements like vanadium and niobium stabilize the β-phase.

There are a lot of researches investigate on the replacing the vanadium in Ti-6Al-4V to niobium due to vanadium was found toxic to the human body (Gonzalez, Afonso and Nascente, 2017; Hon, Wang and Pan, 2003). Niobium acts as strong β-phase stabilizer. Adding niobium inside Ti alloy will result in lowering the α to β phase transformation temperature. Ti-Nb binary alloys with more than 40mass % Nb can retain β-phase at lower temperatures (Sharma *et. al.*, 2015).

In addition, main drawback of the Ti-Al alloys is that, in high temperature application, it will experience a severe oxidation at temperature about 750°C to 850°C. High Nb content Ti alloy are widely used in high heat-resistance application with because they can applied at high operating temperature, and Niobium possess a good oxidation resistance compared to traditional Ti-Al alloys (Peter *et. al.*, 2015).

Niobium is a refractory metal that has the BCC structure and it has good biocompatibility and passivity characteristic, which this characteristic is actually similar to Ti. Niobium has high passivity in terms that it is highly reactive with atmospheric oxygen, at even short time exposed to oxygen, a thin layer niobium oxide is formed on the surface. This layer of niobium oxide helps in prevent the ion release in a human body-like environment. In short, niobium is non-toxic, non-allergenic. In mechanical characteristic standpoint, it promotes the reduction of elactic modulus when is acts as alloying element in titanium (Kuromoto *et al.*, 2015).

2.6 Effect of Calcium Phosphate to Titanium Alloy

Biocompatibility of titanium alloy can be enhanced by adding calcium phosphate such as hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), calcium pyrophosphate (DCP, $Ca_2P_2O_7$), tricalcium phosphate (TCP, $Ca_3(PO_4)_2$), and tetracalcium phosphate (TTCP, $Ca_4P_2O_9$) which are used extensively in implant application. Among the calcium phosphate group, hydroapoxyapatite (HA) is the most biological stable phase. The stoichiometry of HA has very stable crystal structure up to 1350 °C. HA contains for nearly 2/3 of the weight of bone. HA components provide compression strength to bone. The rest of the 1/3 of weight of bone is from collagen fiber. Hydroxyapatite is not only biocompatible, it is also highly bioactive to produce strong bonding with the bone tissue. Its surface transformed into biological apatite when implanted, through some reactions such as dissolution, precipitation and ion exchange (Lee *et. al.*, 2002).

2.7 Titanium Alloys in Medical Application

The very beginning of commercial development of titanium as surgical implant material was by the late 1940s. This is due to commercially pure (C.P) titanium has better corrosion resistance and tissue tolerance than stainless steel and comparatively lower strength. However, C.P titanium has restricted wear resistance which restricted the usage of applications such as pacemaker cases, heart valve cages and reconstruction devices (Wang, 1996).

In 1970s, titanium and its alloy grades started gaining attention and used widely as implant materials. The cold worked C.P titanium alloy was applied for dental implant and maxillofacial applications. This is because C.P titanium alloys can be further increase its strength through cold pressing (Wang, 1996). Application of Ti-6Al-4V ELI alloy in total joint prostheses increase significantly in United States in the late 1970 due to its attractive mechanical properties; high strength, low elastic modulus, excellent corrosion resistance and good tissue tolerance. Currently, its applications include hip and knee prostheses, trauma/fixation devices (nails, plates, screws, and wires), instruments and dental implants (Wang, 1996).

In early 1980s, high levels of black debris from titanium, vanadium and aluminium were found in surrounding tissues under high wear conditions (Wang, 1996). This condition is especially found in application such as knee and modular hear components. This leads to the inflammation of surrounding tissues and loosening of implants (Mantripragada *et al.*, 2013). Soon to be realized that Ti-6Al-4V has relatively poor wear resistance which makes Ti-6Al-4V wasn't suitable for bearing surface applications such as hip heads and femoral knees without surface treatment or coating (Wang, 1996). In order to increase wear resistance, thermomechanical processing of titanium microstructure is being studied as temperature plays an important role in the evolution of microstructures. Besides, Al and V from Ti-6Al-4V alloys have shown to be associated with diseases such as like Alzheimer's disease, neuropathy, and osteomalacia because V is toxic in elemental state and oxide state at the implant's surface. Therefore, V-free Ti alloys such as Ti-6Al-7Nb and Ti-5Al-2.5Fe were created. Then, V-and Al-free Ti alloys such as Ti-Zr and Ti-Sn alloys were also developed (Mantripragada *et al.*, 2013).

Stress shielding is another major problem occurs in metallic implant. Stress shielding is define as stress transfer between implant device and bone is not homogenous when Young's Moduli of implant and bone is different (Niinomi and Nakai, 2011). This causes bone resorption and loosening of the implant. It fractures after removal of the implant. Therefore, it is important to lower the modulus of metallic implant in order to match with the modulus of the bone. The addition of non-toxic elements such as Nb, Zr, Mo, and Ta to the titanium alloy decrease the modulus of elasticity (Mantripragada *et al.*, 2013).

2.8 Physical Metallurgy of Titanium Alloys

Titanium has high melting point (1678°C) in elemental form. It exhibits two crystalline forms of titanium, alpha (α) and beta (β) at different temperature. Alpha (α) is stable at room temperature and exists in HCP structure, beta (β) is stable at elevated temperature and it is in BCC form. Alpha phase is stable up to 1620°F (882°C), the transition temperature which is know as beta transus. At beta transus, alpha phase transforms to beta phase. Beta phase is stable from the beta transus up to its melting point 3130°F (1827°C) (Long and Rack, 1998).

Alpha phase is the primary phase in commercial pure titanium at room temperature. However, when some alloying elements is added to pure titanium, the amount of each phase will change as well as the beta transus temperature. The alloying element that increase beta transus temperature is called alpha stabilizer. Alloying element such as aluminium (Al), oxygen (O), nitrogen (N), and carbon (C) stabilize the alpha phase in titanium alloy. On the other hand, those alloying elements that decrease beta transus temperature is called beta stabilizer, and it can be further categorized into beta isomorphous elements and beta eutectoid elements. Niobium, vanadium, molybdenum and tantalum are examples of beta eutectoid elements. Those elements have high solubility in titanium. Beta eutectoid has very limited solubility in titanium and prone to form intermetallic compound. Examples of beta eutectoid are manganese, chromium, silicon, iron, cobalt, nickel, and copper (Campbell, 2006).

HCP structure has very limited slip system. Hence, alpha phase is less ductile and more difficult to undergo deformation compared to BCC structure beta phase. In addition, alloys containing only alpha phase cannot be strengthened by heat treatment due to limited slip system. Figure show the 2 mains crystal structure exist in titanium and titanium alloy.

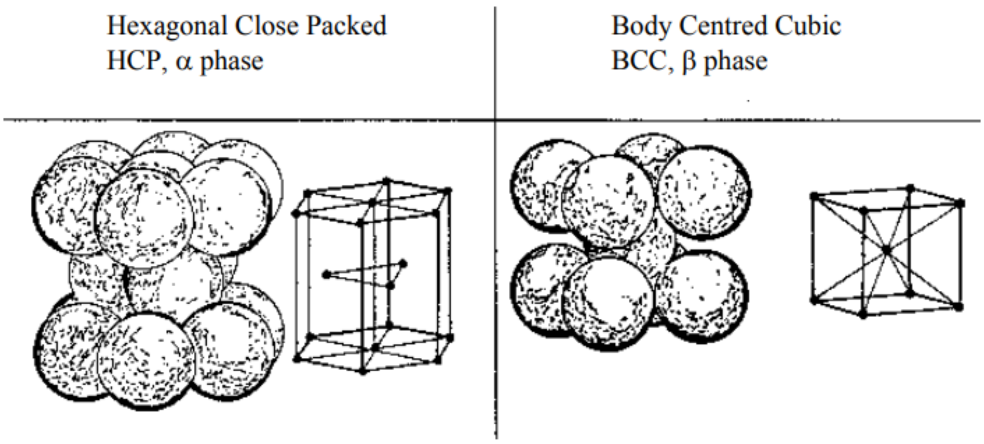

Figure 2.2 The 2 mains crystal structure in titanium (Campbell, 2006)

Ti-6Al-4V is the more commonly utilized titanium alloy. It is an alpha-beta alloy, which the aluminium stabilizes the alpha phase and vanadium stabilize the beta phase. One big advantage of alpha-beta alloy is it exhibit best balance of mechanical properties of both phases, and it have high strength at room temperature and not significant for their creep resistance. Due to it consists of two-phase structure, it has poor weldability compared to beta alloys.

With sufficient amount of beta stabilizing elements, beta phase can be retained to room temperature in beta alloys. BCC beta phase exhibit better deformation capabilities than HCP alpha phase. Beta alloy also exhibit better formability than alpha and alpha-beta alloys. It can be formed at room temperature. The beta alloys can be solution treated and aged (STA) to higher strength levels than the alpha–beta alloys while still retaining sufficient toughness. The disadvantage of beta alloy is alloying elements increase densities and it might reduce ductility when heat treated to peak strength, and it has low weldability (Campbell, 2006).

Titanium alloy is classified to α, near-α, α+β, metastable β or stable β which depends on their room temperature microstructure. (Wanhill and Barter, 2012).

(1) α alloys;

Examples: commercially pure grades of Ti, containing well- defined amounts of oxygen, and Ti-2.5Cu and Ti-5Al-2.5Sn.

(2) Near-α alloys;

Near-α Ti alloy contains only a small amount of β phase. They are heat- treatable and stronger than α alloys. Early examples are Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V. More complex alloys have been developed for improved creep resistance. These include Ti-Al-Zr-Mo-Si-Fe and Ti-Al-Zr-Sn-Nb(Mo,Si) alloys.

(3) α–β alloys;

α–β Ti alloys contain limited amounts of β-stabilizers, the majority of which cannot strengthen the α phase. Hence α-stabilizers are also added. The mechanical properties depend on the relative amounts and distribution of the α and β phases. These variables are controlled by processing and heat treatment. Examples are Ti-6Al-4V and Ti-6Al-2Sn-4Zr-6Mo.

(4) β alloys;

It has sufficiently high β-stabilizer contents that commercially useful microstructures are predominantly β phase. They have been developed mainly because of excellent formability (e.g. cold-rolling) and very good response to heat treatment. Examples are Ti-15Mo-3Nb-3Al-0.2Si and Ti- 10V-2Fe-3Al.

The effect of alloying elements for titanium on β-transus fall into three categories; α-stabilizer (Al, O, N, C), β- isomorphous stabilizer (Mo, V, Nb, Ta), β eutectoid stabilizer (Fe, W, Cr, Si, Ni, Co, Mn, H) and neutral (Zr, Sn) (Long and Rack, 1998).

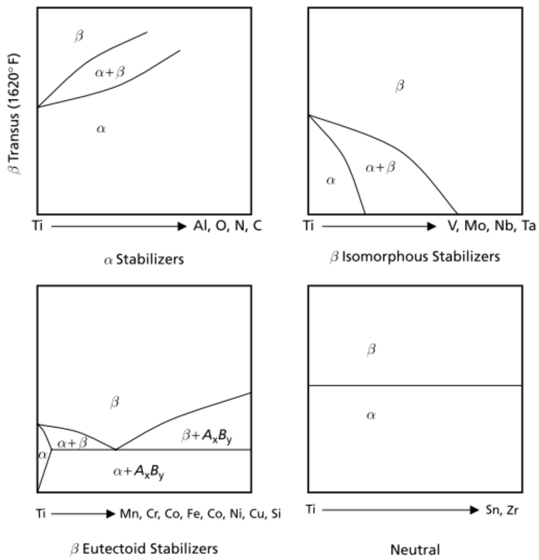

Figure 2.3 Phase Diagrams for Binary Titanium Alloys (Campbell, 2006)

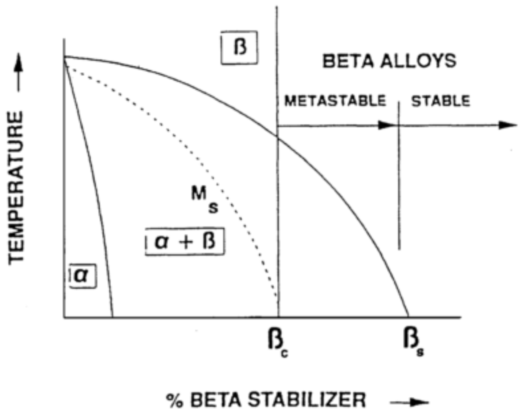

Figure 2.4 Pseudo-binary Phase Diagram of Ti-β stabilizer (Long and Rack, 1998)

β-alloy is defined as alloy with chemical composition lies above $β_{c.}$ It contains sufficient total β stabilizer content to retain 100% β upon quenching from above the β-transus. Alloys lying above the critical minimum level of β -stabilizer content may still lie within a two-phase region, with the resulting as-quenched β -phase being metastable with the potential of precipitating a second phase upon aging. Alloys with increasing alloying content ultimately exceeding a critical $β_s$ value are considered stable β alloys, in which no precipitation takes place during practical long-time thermal exposure (Long and Rack, 1998).

The equilibrium phase diagram of Ti-Nb binary alloy system is shown in Figure 2.5. The phase diagram shows that the α to β allotropic phase transformation, for pure titanium, occurs at 1155 K (882 °C).

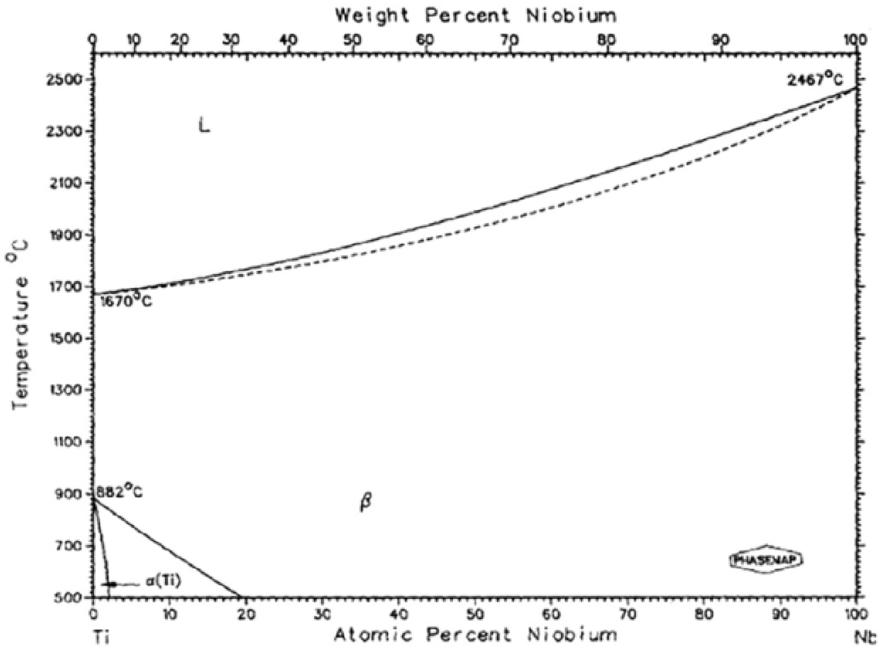

Figure 2.5 Phase diagram of titanium and niobium (Sharma *et. al.*, 2015)

Since niobium acts as a strong β phase stabilizer, niobium additions result in a significant lowering of α to β phase transformation temperature. It can be seen that Ti-Nb binary alloys with more than 40 wt% Nb can retain the beta phase at very low temperatures (Sharma *et. al.*, 2015).

Process variations are traditionally used to control the alloy microstructure and therefore to optimize titanium alloys properties, i.e. ductility, strength, fatigue resistance or fracture toughness. The effects of various microstructures are then correlated with engineering properties, with the most common microstructural features studied in metastable β alloys being β grain size and the size and distribution of aged α. Apart from α phase, precipitation of transient β' or α' phases and/or intermetallic compounds may be observed in metastable β alloys depending upon alloy composition, heat treatment, processing (Long and Rack, 1998).

2.9 Important Parameters in Fabrication of Titanium Alloy

Various parameters need to be considered in fabrication of composite. Densification and microstructure of biomaterials are depends on parameters such as raw materials, processing method, particle size and their chemical and morphologic characteristic.

Sintering temperature is one of the parameter that control the microstructure and mechanical properties of the Ti alloy. Different phase present at different sintering temperature and there's also change of the dissolution of alloying element in the titanium as the sintering temperature is increased.

Martins *et. al.*(2010) states that by increasing the sintering temperature, microstructural analysis showed an acicular two-phase ($\alpha + \beta$) microstructure growing with the dissolution of the niobium particles that act as β-phase nucleation agent.

2.10 Powder Metallurgy of Titanium Alloy

Powder metallurgy (PM) is a cost-effective metal forming technology that provides various benefits for industrial metal production compared to melting and casting. The products manufactured by PM techniques exhibit a near net shape that requires few or no further machining steps. In addition, PM provide the ability to produce products with controlled porosity and microstructure. Mechanical milling (MM) is an efficient technique to refine powder particles, which is beneficial for improving the densification and mechanical properties of the PM alloys in the subsequent sintering process.

Density is a very crucial factor of the performance of powder metallurgy components. The control of final properties of sintered materials often requires control of final density. As density increases, almost all properties such as hardness, strength, fatigue life, toughness, ductility, electrical conductivity, magnetic saturation , and corrosion resistance are improved (Xiaolin Chen, 1998).

PM process usually involves pressing the powder within dies then followed by heating or sintering of the powder compact under controlled environment which is below melting temperature of the metal. Sometimes, various proportions of non-metals, metallic compounds or chemical additions are added to the metallic powders to get desired properties.

Powder metallurgy process is a method that can prepare wide range of metals and lloys with fine-grained microstructure and high mechanical properties. This method is effective in prepare the complex alloy system where the alloying elements have high difference in melting temperature. Thus, powder metallurgy is a more conventional method for preparation for complex alloy system compared to liquid metallurgy (Sharma, Vajpai and Ameyama, 2015).

2.11 Corrosion Behaviour of Ti Alloy

Corrosion resistance is important property for an implant materials. Internal partial pressure of oxygen in human body is about one quarter of atmospheric oxygen pressure, the oxidation is less reactive compared to outside of body. Which the formation of protective passive oxide film on the metal surface would slow down when implant is broken or removed.

Biomaterials such as stainless steel, cobalt-based alloys and titanium-based alloys are favorable in terms of mechanical property because they are able to bear loads and undergo plastic deformation prior failure. They have high modulus of plasticity. Corrosion resistance and biological effects of release metal ion determines the biocompatibility of metallic implant biomaterials. Metallic implant is expect to be made up of non-toxic elements and cause no significant inflammatory or allergic reaction to human body. The implant is stress-shielded and it will deteriorates, this weaken the bone's interface or the implant (Chen and Thouas, 2015). The release of metal ions from metallic implants should be at lowest level in harsh condition in the body. And even at satisfactory low level after long service period (after 30 years) under normal physiological conditions (Chen and Thouas, 2015).

The combination of stress shielding, wear debris, and motion at an interface is especially damaging and often accelerates implant failure. There also are concerns about the elements released from cobalt-based alloys, as Ni, Cr and Co, are all found to be toxic. They may cause systemic allergic reactions in the host body, which can increase inflammation (Chen and Thouas, 2015).

The elastic modulus for pure titanium is 105 GPa, Ti-6Al-4V (α+β phase) has the elastic modulus in range of 101 to 110 GPa and for the β- Ti alloy (bcc) alloys has even lower elastic modulus of 55GPa. Thus, the β-Ti alloy has elastic behavios compatible with the human bones (10-40GPa) (Gonzalez *et.al.*, 2017).

Differences in elastic moduli of the implant material and bone are very important. For example, Ti-6Al-4V alloy and cortical bone (18 GPa), can lead to a possible failure of the implant procedure due to stress shielding effect. In addition, Ti-6Al-V release toxic Al and V species that can be really harmful to the human body. Hence, Zr, Nb, Mo, Sn and Ta have been investigated as non-toxic β-stabilizing alloying elements in Ti alloys in last 20 years. Out of all, Nb is shown to be a suitable substitude of V in implant