# MECHANICAL PROPERTIES AND BIOACTIVITY OF TI-NB-HA COMPOSITE FABRICATED BY MECHANICAL ALLOYING

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**UNIVERSITI SAINS MALAYSIA**

**2020**

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**by**

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**Thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy**

**July 2020**

# ACKNOWLEDGEMENT

All praise to the Almighty Allah for the blessings and allowing me to complete my dissertation and fulfil the requirements for PhD. I would like to express my humble gratefulness to my supervisor, Prof. Ir. Dr. Zuhailawati Hussain for her guidance, supervision, comments, encouragement and constant support rendered throughout the research and most importantly her willingness to spend her valuable time for discussion when needed especially during the preparation of the thesis.

I would like to thank the Higher Education Ministry of Malaysia and Universiti Teknologi MARA (UiTM) for financial support and the opportunity to pursue the degree of Doctor of Philosophy. My genuine gratitude is also deserved to all lecturers, administrative and technical staffs in the School of Materials and Mineral Resources Engineering (SMMRE), Universiti Sains Malaysia (USM) for their endless help in providing their co-operation and technical support. Not to forget, to my lab mates including Nazirah and Hazwani. It was pleasure working with them and I really appreciate for their friendship and knowledge sharing. I would like to extend my appreciation to all postgraduate students in SMMRE, USM and individual who indirectly involved in this research work.

Finally, my heartfelt gratitude goes to my beloved parents Ahmad bin Maidin and Noor'Aini binti Ahmad as well as my family members for their love, motivational support, continuous pray and encouragement along the process of completing this research work. I am also grateful to my sincere husband, Mohd Haizu bin Che Hassan for his moral support, patience and understanding, particularly in upbringing our beloved sons, Muhammad Adam Mikael and Muhammad Anas Mikael. May Allah bless all of you. Thank you.

## TABLE OF CONTENTS

**CHAPTER FOUR : RESULTS AND DISCUSSION**

## LIST OF TABLES

## LIST OF FIGURES

## LIST OF SYMBOLS

| | |
|---|---|
| α | Alpha phase |
| β | Beta phase |
| θ | Bragg angle |
| °C | Degree celcius |
| g | Gram |
| % | Percentage |
| wt.% | Weight percent |

## LIST OF ABBREVIATIONS

| | |
|---|---|
| BPR | Ball to weight ratio |
| BCC | Body center cubic |
| CaP | Calcium phosphate |
| CPP | Calcium pyrophosphate |
| cp-Ti | Commercially pure titanium |
| EDX | Energy dispersive x-ray |
| FESEM | Field emission scanning electron microscope |
| FTIR | Fourier Transform Infra-Red (FTIR) spectroscopy |
| GPa | Gigapascal |
| HBSS | Hank's balanced salt solution |
| HCP | Hexagonal close packed |
| HA | Hydroxyapatite |
| ICDD | International centre for diffraction data |
| MA | Mechanical alloying |
| MPa | Megapascal |
| MMC | Metal matrix composite |
| PM | Powder metallurgy |
| PCA | Process control agent |
| SEM | Scanning electron microscope |
| SBF | Simulated body fluid |
| TTCP | Tetracalcium phosphate |
| TCP | Tricalcium phosphate |
| XRD | X-ray diffraction |

**SIFAT MEKANIKAL DAN BIO-AKTIVITI KOMPOSIT TI-NB-HA DIFABRIKASI SECARA PENGALOIAN MEKANIKAL**

## ABSTRAK

Titanium adalah logam biobahan yang paling popular untuk implan ortopedik kerana sifat mekanik dan ketahanan kakisan yang baik. Walaubagaimanapun, ketidaksepadan elastik modulus dan ikatan yang lemah dengan tulang disebabkan oleh sifat biolengai telah dikenalpasti sebagai punca utama yang menyebabkan implan longgar dan akhirnya mengalami kegagalan implantasi. Kajian ini bertujuan untuk mengkaji sifat mekanikal dan bioaktiviti komposit titanium-niobium-hidroksiapatit (Ti-Nb-HA) yang dihasilkan melalui pengaloian mekanikal dan metalurgi serbuk. Bagi mengkaji kesan HA dan Nb, komposisi HA dan Nb diubah dalam julat 0 hingga 15% berat dan 0 hingga 40% berat. Serbuk Ti, Nb and HA dicampur menggunakan pengisar bola tenaga tinggi selama 2 jam pada kelajuan 200 rpm dan diikuti dengan pemadatan di bawah 500 MPa dan pensinteran pada 1200°C. Kesan daripada kerapuhan HA, penambahan HA mengurangkan kekuatan mampatan (1001.24 MPa hingga 160.94 MPa) dan mikrokekerasan (300.53 HV hingga 85.47 HV). Penambahan HA menyumbang kepada ikatan yang lemah dengan matrik menyebabkan ianya amat mempengaruhi pengurangan elastik modulus dari 65.10 GPa hingga 29.91 GPa. Peningkatan kandungan HA didapati memberikan penilaian ciri bioaktiviti yang baik kepada komposit apabila direndamkan di dalam HBSS selama 30 hari. Sifat bioaktiviti tertinggi dicatatkan oleh 15% berat HA disebabkan oleh apatit paling banyak (3.40%). Faktor yang mempengaruhi sifat bioaktiviti dipercayai disebabkan oleh dekomposisi HA semasa proses pensinteran yang menghasilkan CaO dan $CaTiO_3$. Akibatnya,

kehadiran ion $Ca^{2+}$ ini meningkatkan keamatan kalsium lalu mempercepatkan pertumbuhan apatit. Penambahan Nb meningkatkan kekuatan mampatan (199.95 MPa hingga 300.11 MPa) dan mikrokekerasan (120.97 HV hingga 269.90 HV) disebabkan oleh penguatan larutan pepejal. Bagaimanapun, kehadiran $TiO_2$ dan $Ti_2P$ merendahkan kekuatan mampatan pada 40% berat Nb. Selain itu, elastik modulus mengalami penurunan dengan penambahan Nb. Amaun fasa β yang tertinggi dicatatkan oleh 30% berat Nb (76%). Pada 40% berat Nb, penurunan elastik modulus disebabkan oleh pengurangan fasa β akibat dari kesan HA terurai yang menghasilkan $TiO_2$ dan $Ti_2P$. Kehadiran fasa β, kelarutan tinggi $Ti_2P$ dan kumpulan fungsi $OH^-$ membantu meningkatkan pertumbuhan apatit di komposit yang mempunyai amaun Nb berbeza. Pada ujian rendaman dalam HBSS selama 30 hari, bioaktiviti tertinggi dicapai oleh 30% berat Nb dan diikuti 40% berat Nb, 20% berat Nb, 10% berat Nb dan 0% berat Nb. Peningkatan pertumbuhan apatit pada 40% berat Nb disebabkan oleh kehadiran fasa bioserasi seperti $TiO_2$ dan $Ti_2P$. Komposit dengan penambahan 10% berat HA dan 30% berat Nb mempamerkan keputusan terbaik dan berpotensi besar bagi menyediakan sokongan mekanikal dan peningkatan bioaktiviti bagi mencapai keserasian sifat bagi tulang kortikal.

**MECHANICAL PROPERTIES AND BIOACTIVITY OF TI-NB-HA COMPOSITE FABRICATED BY MECHANICAL ALLOYING**

## ABSTRACT

Titanium is the most popular metallic biomaterial for orthopaedic implant owing to their excellent mechanical properties and good corrosion resistance. However, the mismatch of elastic modulus and poor bonding with bones due to its bioinert behaviour has been identified as the major reason that lead to the implant loosening and eventual failure of the implantation. The present work investigates the mechanical performances and bioactivity of titanium-niobium-hydroxyapatite (Ti-Nb-HA) composite prepared by mechanical alloying and powder metallurgy. To study effect of HA and Nb , HA and Nb were varied from 0 to 15 wt.% and 0 to 40 wt.%, respectively. The powders of Ti, Nb and HA were mixed in a high energy ball mill for 2 hours at 200 rpm and followed by compaction under 500 MPa and sintering at 1200°C. Due to the brittleness of HA, the incorporation of HA decreased the compressive strength (1001.24 MPa to 160.94 MPa) and microhardness (300.53 HV to 85.47 HV). Adding HA contribute to the poor bonding with matrix which is more pronounced to reduce the elastic modulus from 65.10 GPa to 29.91 GPa. With the increasing in HA content, the composite displayed good bioactivity characteristics evaluation in HBSS for 30 days. The highest bioactivity was exhibited by composite with 15 wt.% HA due to the highest apatite (3.40%). Factor affecting the bioactivity are believed to be caused by HA decomposition during sintering process that produces CaO and $CaTiO_3$. As a result, the presence of these $Ca^{2+}$ ions increased the calcium concentration and accelerated the apatite growth. Higher Nb content improved the compressive strength (199.95 MPa to 300.11 MPa) and

microhardness (120.97 HV to 269.90 HV) due to solid solution strengthening. However, the presence of $TiO_2$ and $Ti_2P$ decrease compressive strength with 40 wt.% Nb. Apart from that, the elastic modulus was slightly decreased with the rise of Nb content. The highest amount of β phase is obtained by 30 wt.% Nb (76%). Increasing in Nb content to 40 wt.% decreases elastic modulus owing to decrement in β phase as a consequence of HA decomposition that lead to the formation of $TiO_2$ and $Ti_2P$. The presence of β phase, high solubility of $Ti_2P$ and functional groups of $OH^-$ act as favourable site for apatite growth in composite consisting different amount of Nb. Upon immersion test in HBSS for 30 days, the highest bioactivity was attained by 30 wt.% Nb and followed by 40 wt.% Nb, 20 wt.% Nb, 10 wt.%. The enhanced of apatite growth in 40 wt.% Nb was found to be caused by the presence of biocompatibility phases of $TiO_2$ and $Ti_2P$. Composite with addition of 10 wt.% HA and 30 wt.% Nb displayed the best properties and holds great potential in providing mechanical support and bioactivity enhancement in getting similar cortical bone characteristics.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Introduction

There are numerous biomaterials that can be placed in the human bodies such as metals (e.g. titanium alloys, stainless steel, cobalt alloys), ceramics (zirconia, calcium phosphates, aluminium oxide) and natural/synthetic polymers. Among these, titanium (Ti) and its alloys have been considered to be some of the most important significant biomaterials due to its remarkable behaviour. Excellent biocompatibility, high corrosion resistance, high strength-to-weight ratio and good mechanical properties make Ti as a perfect candidate for implantable metal-based biomaterials. Therefore, much attention has been diverted to the Ti and its alloys as compared to conventional metallic biomaterials such as cobalt-chromium alloys and stainless steel (Zhao et al., 2015; Zakaria et al., 2018).

Generally, commercially pure titanium cp-Ti (α-type) and Ti-6Al-4V (α+β type) are the most commonly used as permanent implant materials. However, the current Ti materials exhibit higher elastic modulus (100-120 GPa) than human cortical bone (10-40 GPa) (Nazari et al., 2015). This can result in stress shielding problem that been the most highlighted issues associated with the use of permanent implants. Stress shielding leads to critical clinical issues such as resorption to the bone, implant loosening, damage the healing process and adjacent anatomical structures, skeleton thickening, chronic inflammation and refracturing of the bone (Salahshoor & Guo, 2012; Yilmazer et al., 2013; Guo et al., 2015). Moreover, cytotoxic elements such as aluminum (Al) and vanadium (V) eventually released from Ti-6Al-4V, may cause severe problems once performed inside the human body. As mentioned by other authors, the release of ion Al and ion V from Ti-6Al-4V into the body might cause long-term health problems as