

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

FARRAH NOOR BINTI AHMAD

UNIVERSITI SAINS MALAYSIA

2020

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

by

FARRAH NOOR BINTI AHMAD

**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

	Page
ACKNOWLEDGEMENT.....	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	ix
LIST OF SYMBOLS	xvii
LIST OF ABBREVIATIONS	xviii
ABSTRAK	xix
ABSTRACT.....	xxi

CHAPTER ONE : INTRODUCTION

1.1 Introduction	1
1.2 Problem statement	5
1.3 Research objective	7
1.4 Research outline	7

CHAPTER TWO : LITERATURE REVIEW

2.1 Introduction	9
2.2 Biomaterials	9
2.3 Types of bone	14
2.4 Metallic biomaterials	15
2.5 Titanium as metallic biomaterials	18
2.5.1 Introduction	18
2.5.2 Characteristics and properties of titanium	21
2.5.3 Phase transformation of titanium and its alloys	21
2.6 Introduction to solid solution	27
2.7 Metal matrix composite (MMC)	29
2.7.1 Effect of hydroxyapatite in titanium	30
2.7.2 Effect of niobium in titanium	32

2.8	Fabrication of titanium-based composite by mechanical alloying and powder metallurgy	39
2.8.1	Mechanical alloying	39
2.8.2	Powder metallurgy	41
2.8.3	Powder compaction	42
2.8.4	Sintering	44
2.9	Considerations for titanium alloy to be used in implant applications	47
2.9.1	Mechanical properties	47
2.9.2	Weight gain	49
2.10	Summary of review	50

CHAPTER THREE : RESEARCH METHODOLOGY

3.1	Introduction	53
3.2	Raw materials	55
3.3	Experimental procedures	56
3.3.1	Mechanical alloying and powder metallurgy	56
3.3.2	Compaction	59
3.3.3	Sintering	59
3.4	Characterization techniques	61
3.4.1	Phase and microstructural evaluation	61
3.4.1(a)	X-ray diffraction (XRD).....	61
3.4.1(b)	Microstructure analysis under field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX).....	62
3.4.1(c)	Microstructure analysis under optical microscopy (OM)	63
3.4.1(d)	Compression test	64
3.4.1(e)	Microhardness measurement.....	64
3.4.2	Physical evaluation	65
3.4.2(a)	Particle size analysis.....	65
3.4.2(b)	Density measurement	66
3.4.2(c)	Water contact angle measurement.....	67
3.4.3	<i>In vitro</i> bioactivity evaluation of Ti-Nb-HA composite	67
3.4.3(a)	Immersion test in Hank's balanced salt solution (HBSS)....	67
3.4.3(b)	Fourier transform infra-red (FTIR) spectroscopy	71

CHAPTER FOUR : RESULTS AND DISCUSSION

4.1	Introduction	72
4.2	Characterization of raw materials	73
4.2.1	Particle size analysis	73
4.2.2	X-ray diffraction (XRD)	74
4.2.3	Microstructure under field emission scanning electron microscope (FESEM)	75
4.3	Effect of varying the content of HA	77
4.3.1	Phase, chemical composition and morphological characterization	77
4.3.1(a)	X-ray diffraction (XRD).....	77
4.3.1(b)	Microstructure evaluation	84
4.3.2	Physical and mechanical properties	93
4.3.2(a)	Density and porosity measurement	93
4.3.2(b)	Microhardness measurement.....	96
4.3.2(c)	Compression test	97
4.3.2(d)	Fractographic analysis.....	100
4.3.3	Characterization and bioactivity assessment in Hank's balanced salt solution (HBSS)	103
4.3.3(a)	Microstructure evaluation	103
4.3.3(b)	Fourier transform infra-red (FTIR) spectroscopy	112
4.3.3(c)	Water contact angle.....	113
4.3.3(d)	pH analysis	116
4.3.3(e)	Weight gain	119
4.3.4	Result summary	121
4.4	Effect of varying the content of Nb	122
4.4.1	Phase, chemical composition and morphological characterization	122
4.4.1(a)	X-ray diffraction (XRD).....	122
4.4.1(b)	Microstructure evaluation	125
4.4.2	Physical and mechanical properties	135
4.4.2(a)	Density and porosity measurement	135
4.4.2(b)	Microhardness measurement.....	138
4.4.2(c)	Compression test	139
4.4.2(d)	Fractographic analysis.....	143

4.4.3	Characterization and bioactivity assessment in Hank's balanced salt solution (HBSS)	146
4.4.3(a)	Microstructure evaluation	146
4.4.3(b)	Fourier transform infra-red (FTIR) spectroscopy	155
4.4.3(c)	pH analysis	156
4.4.3(d)	Weight gain	158
4.4.4	Result summary	159

CHAPTER FIVE : CONCLUSION AND FUTURE RECOMMENDATIONS

5.1	Conclusion	162
5.2	Future recommendation	164

REFERENCES	165
-------------------	-----

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

	Page
Table 2.1 Biomaterials used in human body (Vallet-Regí, 2010; Chen & Thouas, 2015)	11
Table 2.2 Classification of implant-tissue responses (Wilson et al., 1993; Srivastav, 2011; Saini et al., 2015; Eliaz & Metoki, 2017)	12
Table 2.3 Composition of bone (wt.%) (Eliaz & Metoki, 2017)	14
Table 2.4 Metallic biomaterials in medical applications (Hosseini, 2012; Park et al., 2013)	17
Table 2.5 Comparison of physical and mechanical properties of metallic biomaterial with cortical bone (Ravaglioli et al., 1992; Gupta & Sharon, 2010; Nazari et al., 2015)	18
Table 2.6 Properties of titanium (Arifin et al., 2014)	21
Table 2.7 Types of stabilizer in titanium alloys (Chen & Thouas, 2015)	23
Table 2.8 Classification of titanium and titanium-based alloys (Polmear, 2006; Gu et al., 2018)	24
Table 2.9 Comparison between mechanical properties of Ti and Ti alloys developed in orthopaedic implants (Chen & Thouas, 2015)	25
Table 2.10 Comparative compositional and structural parameter of bone and HA (Al-Sanabani et al., 2013)	31
Table 2.11 Properties of niobium (Turchi, 2018)	38
Table 3.1 List of raw material used in experimental method	55
Table 3.2 Details of n-heptane	55
Table 3.3 Summary of investigated variable parameters	56
Table 3.4 Composition of composite	57
Table 3.5 Ionic compositions and concentration of HBSS solution and human blood plasma (Rabadjieva et al., 2011)	68
Table 4.1 Distribution of average particle size of Ti, Nb and HA powders	73
Table 4.2 Phase percentages of α and β in Ti-Nb-HA composite with different HA content	81

Table 4.3	Water contact angles and surface energy of Ti-Nb-HA incorporated with (a) 0 wt.% HA (b) 5 wt.% HA (c) 10 wt.% HA and (d) 15 wt.% HA. The data are presented as mean values \pm standard deviation	114
Table 4.4	HA/Ti ratio of Ti-Nb-HA composite with different Nb content	123
Table 4.5	Phase percentage of α and β in Ti-Nb-HA composite with different Nb content	124
Table 4.6	Summary of result for Ti-Nb-HA with various Nb content	160

LIST OF FIGURES

		Page
Figure 2.1	Bone classification depending on the structure	15
Figure 2.2	Orthopaedic implant devices: (a) hip implant, (b) knee implant, (c) shoulder implant and (d) elbow implant (Paital & Dahotre, 2009)	16
Figure 2.3	Stress shielding phenomenon (Arifin et al., 2014)	20
Figure 2.4	Crystalline structure of Ti (Prasad et al., 2015)	22
Figure 2.5	Effect of alloying elements on phase diagrams of titanium alloys (a) neutral, (b) α -stabilizing, (c) β -stabilizing (isomorphous) and (d) β -stabilizing (eutectoid) (Campbell, 2016)	23
Figure 2.6	Ti-Nb phase diagram and the metastable ω - β phase diagram (Bönisch, 2016)	26
Figure 2.7	Schematic illustration of the α - β phase diagram in a β isomorphous Ti-x alloy (x = Nb, V, Ta, Mo) (Long and Rack, 1998)	27
Figure 2.8	Distortion of crystal lattice substitutional solid solution (a) Large solute atom distorts to increase the lattice constant, (b) Small solute atoms distorts to decrease the lattice constant	28
Figure 2.9	Morphological observation on Ti-35Nb alloy sintered at 1600°C (Roberto et al., 2005)	35
Figure 2.10	Back scattered image of Ti-40Nb alloy (Sharma et al., 2015)	36
Figure 2.11	Scanning electron microscope-back scattered electron (SEM-BSE) of (a) Ti-35Nb-7Zr alloy, (b) Ti-35Nb-7Zr-5CPP, (c) Ti-35Nb-7Zr-10CPP, (d) Ti-35Nb-7Zr-15CPP and (e) Ti-35Nb-7Zr-20CPP (He et al., 2016)	37
Figure 2.12	Ball-powder-ball collision of powder mixture during mechanical alloying (Suryanarayana, 2019)	40
Figure 2.13	Deformation characteristics of representative constituents of starting powder in mechanical alloying (Suryanarayana, 2019)	40

Figure 2.14	Schematic of stages involve in uniaxial pressing	43
Figure 2.15	Illustration of stage in sintering (Prakasam et al., 2015)	45
Figure 2.16	Stress shielding in locking compression hip joint fracture (Surin, 2005)	49
Figure 2.17	Weight gain of metal/HA composite with different HA contents (Soon et al., 2016)	50
Figure 3.1	Flow chart of overall experimental work	54
Figure 3.2	Sintering profile of Ti-Nb-HA biocomposite	60
Figure 3.3	Schematic diagram on fabrication of Ti-Nb-HA	60
Figure 3.4	Schematic of indentation mark in Vickers microhardness test	65
Figure 3.5	A sessile drop to the left is an example of poor wetting ($\theta > 90^\circ$) and the sessile drop to the right is an example of good wetting ($\theta < 90^\circ$) (Aziz et al., 2015)	67
Figure 3.6	Schematic diagram of sample being soaked in HBSS solution	70
Figure 4.1	XRD spectra of raw powder : a) Ti, b) Nb and c) HA	75
Figure 4.2	FESEM photograph of starting materials (a) Ti, (b) Nb and (c) HA at magnification of 100x	76
Figure 4.3	Presence of α and β in Ti-Nb-HA composite with different HA content (a) 0 wt.% HA, (b) 5 wt.% HA, (c) 10 wt.% HA and (d) 15 wt.% HA	77
Figure 4.4	Oxygen contents in Ti	82
Figure 4.5	Oxygen contents in Ti-Nb-HA incorporated with 0 wt.% HA	82
Figure 4.6	Oxygen contents in Ti-Nb-HA incorporated with 5 wt.% HA	83
Figure 4.7	Oxygen contents in Ti-Nb-HA incorporated with 10 wt.% HA	83
Figure 4.8	Oxygen contents in Ti-Nb-HA incorporated with 15 wt.% HA	83
Figure 4.9	Particle size of Ti-Nb-HA after mechanical alloying as a function of various HA content	84
Figure 4.10	FESEM of as-milled Ti-Nb-HA incorporated with 0 wt.% HA. The magnification is 500x	85
Figure 4.11	FESEM of as-milled Ti-Nb-HA incorporated with 5 wt.% HA. The magnification is 500x	86
Figure 4.12	FESEM of as-milled Ti-Nb-HA incorporated with 10 wt.% HA. The magnification is 500x	86

Figure 4.13	FESEM of as-milled Ti-Nb-HA incorporated with 15 wt.% HA. The magnification is 500x	87
Figure 4.14	FESEM of as-milled Ti-Nb-HA incorporated with 0 wt.% HA. The magnification is 500x	88
Figure 4.15	FESEM of as-sintered of Ti-Nb-HA incorporated with 5 wt.% HA. The magnification is 500x	88
Figure 4.16	FESEM of as-sintered of Ti-Nb-HA incorporated with 10 wt.% HA. The magnification is 500x	89
Figure 4.17	FESEM of as-sintered of Ti-Nb-HA incorporated with 15 wt.% HA. The magnification is 500x	89
Figure 4.18	EDX-SEM observation of as-sintered Ti-Nb-HA incorporated with 0 wt.% HA	91
Figure 4.19	EDX-SEM observation of as-sintered Ti-Nb-HA incorporated with 5 wt.% HA	91
Figure 4.20	EDX-SEM observation of as-sintered Ti-Nb-HA incorporated with 10 wt.% HA	92
Figure 4.21	EDX-SEM observation of as-sintered Ti-Nb-HA incorporated with 15 wt.% HA	92
Figure 4.22	Experimental density and theoretical density of Ti-Nb-HA composite with various content of HA	94
Figure 4.23	The relative density and porosity of Ti-Nb-HA with various HA content	95
Figure 4.24	The hardness plot of Ti-Nb-HA fabricated by mechanical alloying as a function of different HA content	96
Figure 4.25	Compressive strength and elastic modulus of Ti-Nb-HA composite with various HA content	97
Figure 4.26	Fractography of Ti-Nb-HA incorporated with 0 wt.% HA after subjected to compression test. The magnification is 50x and 500x	101
Figure 4.27	Fractography of Ti-Nb-HA incorporated with 5 wt.% HA after subjected to compression test. The magnification is 50x and 500x	102

Figure 4.28	Fractography of Ti-Nb-HA incorporated with 10 wt.% HA after subjected to compression test. The magnification is 50x and 500x	102
Figure 4.29	Fractography of Ti-Nb-HA incorporated with 15 wt.% HA after subjected to compression test. The magnification is 50x and 500x	103
Figure 4.30	Distribution of Ca, P and O on the surface of Ti, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	104
Figure 4.31	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 0 wt.% HA, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	104
Figure 4.32	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 5 wt.% HA, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	105
Figure 4.33	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 10 wt.% HA, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	105
Figure 4.34	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 15 wt.% HA, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	106
Figure 4.35	FESEM images of the surfaces of pure Ti, after immersion in HBSS for 30 days. The magnification is 100x and 500x	108
Figure 4.36	FESEM images of the surfaces of Ti-Nb-HA incorporated with 0 wt.% HA, after immersion in HBSS for 30 days. The magnification is 100x and 500x	108
Figure 4.37	FESEM images of the surfaces of Ti-Nb-HA incorporated with 5 wt.% HA, after immersion in HBSS for 30 days. The magnification is 100x and 500x	109

Figure 4.38	FESEM images of the surfaces of Ti-Nb-HA incorporated with 10 wt.% HA, after immersion in HBSS for 30 days. The magnification is 100x and 500x	109
Figure 4.39	FESEM images of the surfaces of Ti-Nb-HA incorporated with 15 wt.% HA, after immersion in HBSS for 30 days. The magnification is 100x and 500x	110
Figure 4.40	FTIR spectrum of precipitates formed in HBSS solution for Ti-Nb-HA incorporated with (b) 0 wt.% HA (c) 5 wt.% HA (d) 10 wt.% HA and (e) 15 wt.% HA	113
Figure 4.41	Optical image of drop profiles of Ti-Nb-HA incorporated with (a) 0 wt.% HA (b) 5 wt.% HA (c) 10 wt.% HA and (d) 15 wt.% HA	114
Figure 4.42	Measured pH of HBSS solution related to different content of HA in Ti-Nb-HA composite	117
Figure 4.43	Measured weight gain after immersion in HBSS solution for 30 days related to the different content of HA in Ti-Nb-HA composite	119
Figure 4.44	Presence of α and β in Ti-Nb-HA composite with different Nb content (a) 0 wt.% Nb, (b) 10 wt.% Nb, (c) 20 wt.% Nb, (d) 30 wt.% Nb and (e) 40 wt.% Nb	123
Figure 4.45	Particle size of Ti-Nb-HA fabricated by mechanical alloying as a function of various Nb content	126
Figure 4.46	FESEM of as-milled Ti-Nb-HA incorporated with 0 wt.% Nb. The magnification is 500x	127
Figure 4.47	FESEM of as-milled Ti-Nb-HA incorporated with 10 wt.% Nb. The magnification is 500x	127
Figure 4.48	FESEM of as-milled Ti-Nb-HA incorporated with 20 wt.% Nb. The magnification is 500x	128
Figure 4.49	FESEM of as-milled Ti-Nb-HA incorporated with 30 wt.% Nb. The magnification is 500x	128
Figure 4.50	FESEM of as-milled Ti-Nb-HA incorporated with 40 wt.% Nb. The magnification is 500x	129

Figure 4.51	FESEM of as-sintered of Ti-Nb-HA incorporated with 0 wt.% Nb. The magnification is 500x	130
Figure 4.52	FESEM of as-sintered of Ti-Nb-HA incorporated with 10 wt.% Nb. The magnification is 500x	130
Figure 4.53	FESEM of as-sintered of Ti-Nb-HA incorporated with 20 wt.% Nb. The magnification is 500x	131
Figure 4.54	FESEM of as-sintered of Ti-Nb-HA incorporated with 30 wt.% Nb. The magnification is 500x	131
Figure 4.55	FESEM of as-sintered of Ti-Nb-HA incorporated with 40 wt.% Nb. The magnification is 500x	132
Figure 4.56	Microstructure of Ti-Nb-HA incorporated with 0 wt.% Nb	133
Figure 4.57	Microstructure of Ti-Nb-HA incorporated with 10 wt.% Nb	133
Figure 4.58	Microstructure of Ti-Nb-HA incorporated with 20 wt.% Nb	134
Figure 4.59	Microstructure of Ti-Nb-HA incorporated with 30 wt.% Nb	134
Figure 4.60	Microstructure of Ti-Nb-HA incorporated with 40 wt.% Nb	135
Figure 4.61	Experimental density and theoretical density of Ti-Nb-HA with various content of Nb	136
Figure 4.62	The relative density and porosity of Ti-Nb-HA with various Nb content	137
Figure 4.63	The hardness plot of Ti-Nb-HA fabricated by mechanical alloying as a function of different Nb content	139
Figure 4.64	Compressive strength and elastic modulus of Ti-Nb-HA composite with various Nb content	140
Figure 4.65	Fractography of Ti-Nb-HA incorporated with 0 wt.% Nb, after subjected to compression test. The magnification is 50x and 500x	145
Figure 4.66	Fractography of Ti-Nb-HA incorporated with 10 wt.% Nb, after subjected to compression test. The magnification is 50x and 500x	145
Figure 4.67	Fractography of Ti-Nb-HA incorporated with 20 wt.% Nb, after subjected to compression test. The magnification is 50x and 500x	145

Figure 4.68	Fractography of Ti-Nb-HA incorporated with 30 wt.% Nb, after subjected to compression test. The magnification is 50x and 500x	146
Figure 4.69	Fractography of Ti-Nb-HA incorporated with 40 wt.% Nb, after subjected to compression test. The magnification is 50x and 500x	146
Figure 4.70	Distribution of Ca, P and O on the surface of Ti, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	148
Figure 4.71	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 0 wt.% Nb, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	148
Figure 4.72	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 10 wt.% Nb, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	149
Figure 4.73	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 20 wt.% Nb, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	149
Figure 4.74	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 30 wt.% Nb, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	150
Figure 4.75	Distribution of Ca, P and O on the surface of Ti-Nb-HA incorporated with 40 wt.% Nb, after immerse in HBSS solution for 30 days. It is noted that calcium (red), phosphorus (green) and oxygen (blue)	150
Figure 4.76	FESEM images of the surfaces of Ti, after immersion in HBSS for 30 days. The magnification is 100x and 500x	151

Figure 4.77	FESEM images of the surfaces of Ti-Nb-HA incorporated with 0 wt.% Nb, after immersion in HBSS for 30 days. The magnification is 100x and 500x	151
Figure 4.78	FESEM images of the surfaces of Ti-Nb-HA incorporated with 10 wt.% Nb, after immersion in HBSS for 30 days. The magnification is 100x and 500x	152
Figure 4.79	FESEM images of the surfaces of Ti-Nb-HA incorporated with 20 wt.% Nb, after immersion in HBSS for 30 days. The magnification is 100x and 500x	152
Figure 4.80	FESEM images of the surfaces of Ti-Nb-HA incorporated with 30 wt.% Nb, after immersion in HBSS for 30 days. The magnification is 100x and 500x	153
Figure 4.81	FESEM images of the surfaces of Ti-Nb-HA incorporated with 40 wt.% Nb, after immersion in HBSS for 30 days. The magnification is 100x and 500x	153
Figure 4.82	FTIR spectrum of precipitates formed in HBSS solution for Ti-Nb-HA incorporated with (a) 0 wt.% Nb (b) 10 wt.% Nb (c) 20 wt.% Nb (d) 30 wt.% Nb and (e) 40 wt.% Nb	156
Figure 4.83	Measured pH of HBSS solution related to different content of Nb in Ti-Nb-HA composite	157
Figure 4.84	Measured weight gain after immersion in HBSS solution for 30 days related to different content of Nb in Ti-Nb-HA composite	158

LIST OF SYMBOLS

α	Alpha phase
β	Beta phase
θ	Bragg angle
$^{\circ}\text{C}$	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 pengaloiian 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 keamanan kalsium lalu mempercepat 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 CaTiO₃. As a result, the presence of these Ca²⁺ 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