

**MICROSTRUCTURES AND PROPERTIES OF Ti-51at.%Ni, Ti-23at.%Nb  
AND Ti-30at.%Ta SHAPE MEMORY ALLOYS FABRICATED BY  
MICROWAVE SINTERING FOR BIOMEDICAL APPLICATIONS**

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Ti-30at.%Ta SHAPE MEMORY ALLOYS FABRICATED BY MICROWAVE  
SINTERING FOR BIOMEDICAL APPLICATIONS

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***ALHAMDULILLAH***

*All Praise for Allah, Creator of This Universe  
Thanks for The Precious Iman & Islam You Blessed on Me  
Thanks for All the Strength and Knowledge You Granted on Me  
And, Peace Be Upon the Holy Prophet Muhammad SAW.  
Thanks*

I dedicated this work to,  
My mother, whose sacrifice,  
My Father, whose support and encouragement during his life,  
and  
All my family, whose love and patience  
led to achieving my doctoral degree

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## ABSTRACT

Titanium-nickel (Ti-Ni) shape memory alloys (SMAs) have been widely used for biomedical applications. However, Ni is recently known as a toxic element that can cause hypersensitivity on human body. Therefore, the development of Ni-free SMAs for biomedical applications is crucial. The best candidate to substitute Ti-Ni alloy is  $\beta$  type Ti alloys composed of nontoxic elements. The purpose of this research is to investigate the possibility of Ni-free Ti alloys, namely, titanium-niobium (Ti-Nb) and titanium-tantalum (Ti-Ta) to replace Ti-Ni. In the research, Ti-51at.%Ni, Ti-23at.%Nb and Ti-30at.%Ta SMAs were produced from elemental powders and fabricated by microwave sintering with addition of ternary elements namely, cerium, silver and tin. The microstructures of the sintered alloys were characterised by using differential scanning calorimetry (DSC) equipment, optical microscope, scanning electron microscope (SEM) and X-ray diffractometer (XRD). The mechanical and shape memory properties were determined using compressive test and specially designed equipment respectively, whereas corrosion and antibacterial behaviour were determined by using electrochemical test in simulated body fluid and agar disc diffusion technique with E.coli bacteria, respectively. Based on the experimental work on varying the sintering temperatures and times, it was found that 700°C for 15 min gave the least porosity of 20% for Ti-51at.%Ni alloy, whereas 900°C for 30 min gave the lowest porosity of 23% and 28.72% for Ti-23at.%Nb and Ti-30at.%Ta, respectively. It was observed that the microstructures of Ti-51at.%Ni alloys feature B2 austenite and B19' martensite phases, while Ti-23at.%Nb alloys exhibit  $\beta$  austenite,  $\alpha''$  martensite and  $\alpha$  phases. The binary Ti-51at.%Ni alloy gives the highest hardness of 152 Hv, whereas the ternary Ti-Ta-3Ag gives the lowest hardness of 43 Hv. It was also found that Ti-Ni-1Ce alloy has the lowest elastic modulus of 5.2 GPa indicating good biocompatibility. The addition of Ce, Ag and Sn elements to Ti-23at.%Nb and Ti-30at.%Ta SMAs improved the total strain recovery ( $\epsilon T$ ). The highest and lowest  $\epsilon T$  of 51.68% and 30.17% are shown by Ti-Ni-0.5Sn and Ti-Ni-3Ce alloys, respectively. The corrosion resistance was enhanced for all the ternary alloys due to the formation of passive layer on the surface and various phases within the material. The lowest corrosion rates observed in each type of the SMAs are 0.4076, 0.0155 and 0.0059 mm/year for Ti-Ni-0.5wt.%Sn, Ti-Nb-3wt.%Sn and Ti-Ta-0.5wt.%Sn alloys, respectively. Antibacterial property was improved after the addition of the alloying elements for all the ternary alloys indicated by the size of the inhibition zones against E. coli bacteria. It was found that Ti-Ta-3wt.%Ce alloy has the best anti-bacterial property with the largest inhibition zone of 7.75 mm compared with other SMAs. It can be concluded that the Ni-free SMAs, namely Ti-Nb and Ti-Ta alloys with the addition of alloying elements show promising candidates to be used as biomaterials due to their enhanced biocompatibility properties.

## ABSTRAK

Aloi memori bentuk, Titanium-Nikel (Ti-Ni) telah digunakan secara meluas untuk aplikasi bioperubatan. Walau bagaimanapun baru-baru ini Ni diketahui sebagai unsur toksik yang boleh menyebabkan hipersensitiviti pada tubuh manusia. Oleh itu, pembangunan aloi memori bentuk bebas Ni untuk aplikasi bioperubatan adalah penting. Calon terbaik untuk menggantikan aloi Ti-Ni adalah aloi jenis  $\beta$  Ti yang terdiri daripada unsur-unsur yang tidak bertoksik. Tujuan penyelidikan ini adalah untuk mengkaji kemungkinan Ti aloi tanpa Ni, iaitu, titanium-niobium (Ti-Nb) dan titanium-tantalum (Ti-Ta) sebagai pengganti Ti-Ni. Dalam kajian ini, aloi memori bentuk Ti-51at.% Ni, Ti-23at.%Nb dan Ti-30at.%Ta dihasilkan daripada unsur serbuk dan diperbuat dengan menggunakan alat gelombang mikro pensinteran dengan penambahan unsur pertigaan iaitu serium, perak dan timah. Mikrostruktur aloi yang telah melalui pensinteran dicirikan dengan menggunakan peralatan kalorimetri pengimbasan pembezaan (DSC), mikroskop optik, mikroskop elektron pengimbasan (SEM) dan meter pembelauan sinar-X (XRD). Sifat mekanikal dan memori bentuk masing-masing telah ditentukan dengan menggunakan ujian mampatan dan peralatan yang direka khas, manakala kelakuan kakisan dan antibakteria masing-masing ditentukan dengan menggunakan ujian elektrokimia di dalam cecair badan tiruan dan teknik serapan cakera agar dengan bakteria E.coli. Berdasarkan hasil eksperimen ke atas suhu dan masa pensinteran yang berbeza-beza, didapati bahawa suhu 700°C selama 15 minit memberikan keliangan paling kurang iaitu 20% bagi aloi Ti-51at.%Ni, manakala suhu 900°C selama 30 minit memberikan keliangan yang paling rendah, masing-masing 23% dan 28.72% bagi aloi Ti-23at.%Nb dan Ti-30at.%Ta. Hasil kajian menunjukkan bahawa mikrostruktur aloi Ti-51at.% Ni mempunyai fasa B2 austenit dan B19' martensit, manakala aloi Ti-23at.% Nb mempamerkan fasa  $\beta$  austenit,  $\alpha'$  martensit dan fasa  $\alpha$ . Aloi binary Ti-51at.%Ni memberikan kekerasan tertinggi iaitu 152 Hv, manakala aloi pertigaan Ti-Ta-3Ag memberikan kekerasan terendah iaitu 43 Hv. Hasil kajian juga mendapati bahawa aloi Ti-Ni-1Ce mempunyai modulus kenyal paling rendah iaitu 5.2 GPa yang menunjukkan bioserasi yang baik. Penambahan unsur Ce, Ag dan Sn kepada aloi Ti-23at.%Nb dan Ti-30at.%Ta telah menambah baik jumlah pemulihan terikan ( $\epsilon T$ ). Nilai tertinggi  $\epsilon T$  iaitu 51.68% dan terendah iaitu 30.17% masing-masing bagi aloi Ti-Ni-0.5Sn dan Ti-Ni-3Ce. Rintangan kakisan dipertingkatkan untuk semua aloi pertigaan disebabkan pembentukan lapisan pasif pada permukaan dan pelbagai fasa dalam bahan. Kadar kakisan yang paling rendah yang diperhatikan dalam setiap jenis aloi memori bentuk ialah 0.4076, 0.0155 dan 0.0059 mm/tahun masing-masing bagi aloi Ti-Ni-0.5wt.%Sn, Ti-Nb-3wt.%Sn dan Ti-Ta-0.5wt.%Sn. Sifat antibakteria telah bertambah baik selepas penambahan unsur-unsur pengaloiian bagi semua aloi pertigaan yang ditunjukkan dengan saiz zon perencatan terhadap bakteria E.coli. Kajian ini menunjukkan bahawa aloi Ti-Ta-3wt.%Ce mempunyai sifat anti-bakteria terbaik dengan zon perencatan terbesar iaitu 7.75mm berbanding dengan aloi memori bentuk yang lain. Ia dapat disimpulkan bahawa aloi memori bentuk bebas Ni, iaitu aloi Ti-Nb dan Ti-Ta dan dengan penambahan unsur pengaloiian menunjukkan calon yang terbaik untuk digunakan sebagai bahan-bio kerana sifat bioserasi yang dipertingkatkan.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	<b>DECLARATION</b>	<b>ii</b>
	<b>DEDICATION</b>	<b>iii</b>
	<b>ACKNOWLEDGEMENT</b>	<b>iv</b>
	<b>ABSTRACT</b>	<b>v</b>
	<b>ABSTRAK</b>	<b>vi</b>
	<b>TABLE OF CONTENTS</b>	<b>vii</b>
	<b>LIST OF TABLES</b>	<b>xv</b>
	<b>LIST OF FIGURES</b>	<b>xix</b>
	<b>LIST OF ABBREVIATIONS</b>	<b>xxxiv</b>
	<b>LIST OF SYMBOLS</b>	<b>xxxv</b>
	<b>LIST OF APPENDICES</b>	<b>xxxvi</b>
<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
	1.1 Background of the Research	1
	1.2 Problem Statement	3
	1.3 Objectives of this Research	4
	1.4 Scope of this Research	5
	1.5 Research Significance	5
<b>2</b>	<b>LITERATURE REVIEW</b>	<b>7</b>
	2.1 Introduction	7
	2.2 Shape Memory Mechanism	9
	2.3 Types of Shape Memory Alloys	11

2.3.1	Fe-Based Shape Memory Alloys	11
2.3.2	Cu-Based Shape Memory Alloys	12
2.3.3	Co-Based Shape Memory Alloys	13
2.3.4	Ti-Based Shape Memory Alloys	14
2.3.4.1	Ti-Ni Shape Memory Alloys	14
2.3.4.2	Ti-Nb Shape Memory Alloys	17
2.3.4.3	Ti-Ta Shape Memory Alloys	18
2.4	Functional Properties of Ti-Based Shape Memory Alloys	20
2.4.1	Pseudo-Elasticity (PE) or Super-Elasticity (SE)	20
2.4.2	Shape Memory Effect (SME)	21
2.4.3	Biocompatibility	22
2.5	Fabrication Techniques	23
2.5.1	Convectional Casting	24
2.5.2	Melt Spinning	25
2.5.3	Powder Metallurgy	25
2.5.3.1	Conventional Sintering (CS)	26
2.5.3.2	Hot Isostatic Pressing (HIP)	27
2.5.3.3	Spark Plasma Sintering (SPS)	28
2.5.3.4	Microwave Sintering (MWS)	30
2.6	Effects of Alloying Elements on Ti-Ni, Ti-Nb and Ti-Ta SMAs	34
2.6.1	Microstructures, Shape Memory Characteristics and Mechanical Properties	34
2.6.2	Biocompatibility	56



	2.6.2.1 Bio-corrosion	59
	2.6.2.2 Antibacterial Effects	66
<b>3</b>	<b>RESEARCH METHODOLOGY</b>	<b>68</b>
3.1	Introduction	68
3.2	Materials	70
3.3	Sample Preparation by Powder Metallurgy	73
3.3.1	Mixing of Powder	73
3.3.2	Compaction by Cold Pressing	74
3.3.3	Microwave Sintering	75
3.4	Sample Preparation for Microstructural Studies	80
3.5	Sample Preparation for Mechanical, Shape Memory, Bio-Corrosion and Antibacterial Test	81
3.6	Material Characterization	81
3.6.1	Compositional Analysis	81
3.6.2	Phase Analysis by X-Ray Diffractometer XRD	82
3.6.3	Density and Image Analysis	82
3.6.4	Determination of Transformations Temperatures by DSC	83
3.7	Mechanical Tests	84
3.7.1	Hardness Test	84
3.7.2	Compressive Test	85
3.7.3	Shape Memory Test	85
3.8	Biocompatibility Tests	87
3.8.1	Bio-Corrosion Test/ Electrochemical Test	88
3.8.2	Antibacterial Test	89
<b>4</b>	<b>RESULTS AND DISCUSSION</b>	<b>90</b>
4.1	Introduction	90
4.2	Effect of Microwave Sintering Parameters on Ti-51at. %Ni Shape Memory Alloy	91
4.2.1	Microstructure Characteristics	91

4.2.2	Transformation Temperatures	100
4.2.3	Mechanical Properties	101
	4.2.3.1 Hardness Test	102
	4.2.3.2 Compressive Strength	102
	4.2.3.3 Shape Memory Test	103
4.2.4	Bio-Corrosion Test	104
4.2.5	Antibacterial Test	105
4.3	Effect of Alloying Elements on Ti-51at. %Ni Shape Memory Alloy	106
4.3.1	Cerium Addition	107
	4.3.1.1 Microstructure Characteristics	107
	4.3.1.2 Transformation Temperatures	111
	4.3.1.3 Mechanical Properties	113
	4.3.1.4 Bio-Corrosion Test	116
	4.3.1.5 Antibacterial Test	118
4.3.2	Effect of Silver Addition on Ti-51at. %Ni Shape Memory Alloy	120
	4.3.2.1 Microstructure Characteristics	120
	4.3.2.2 Transformation Temperatures	123
	4.3.2.3 Mechanical Properties	125
	4.3.2.4 Bio-Corrosion Test	129
	4.3.2.5 Antibacterial Test	130
4.3.3	Effect of Tin Addition on Ti-51at. %Ni Shape Memory Alloy	131
	4.3.3.1 Microstructure Characteristics	131
	4.3.3.2 Transformation Temperatures	135
	4.3.3.3 Mechanical Properties	137
	4.3.3.4 Bio-Corrosion Test	140

	4.3.3.5	Antibacterial Test	141
4.4		Effect of Microwave Sintering Parameters on Ti-23at. %Nb Shape Memory Alloy	142
	4.4.1	Microstructure Characteristics	143
	4.4.2	Transformation Temperatures	150
	4.4.3	Mechanical Properties	152
		4.4.3.1 Hardness Test	152
		4.4.3.2 Compressive Strength	153
		4.4.3.3 Shape Memory Test	155
	4.4.4	Bio-Corrosion Test	157
	4.4.5	Antibacterial Test	158
4.5		Effect of Alloying Elements on Ti-23at. %Nb Alloy	158
	4.5.1	Effect of Cerium Addition on Ti-23at. %Nb Shape Memory Alloy	159
		4.5.1.1 Microstructure Characteristics	159
		4.5.1.2 Transformation Temperatures	162
		4.5.1.3 Mechanical Properties	163
		4.5.1.4 Bio-Corrosion Test	166
		4.5.1.5 Antibacterial Test	168
	4.5.2	Effect of Silver Addition on Ti- 23at.%Nb Shape Memory Alloy	169
		4.5.2.1 Microstructure Characteristics	170
		4.5.2.2 Transformation Temperatures	173
		4.5.2.3 Mechanical Properties	174
		4.5.2.4 Bio-Corrosion Test	178
		4.5.2.5 Antibacterial Test	179
	4.5.3	Effect of Tin Addition on Ti-23at %Nb Shape Memory Alloy	180

4.5.3.1	Microstructure Characteristics	180
4.5.3.2	Transformation Temperatures	183
4.5.3.3	Mechanical Properties	185
4.5.3.4	Bio-Corrosion Test	189
4.5.3.5	Antibacterial Test	191
4.6	Effect of Microwave Sintering Parameters on Ti-30at.%Ta Shape Memory Alloy	192
4.6.1	Microstructure Characteristics	192
4.6.2	Transformation Temperatures	198
4.6.3	Mechanical Properties	200
4.6.3.1	Hardness Test	201
4.6.3.2	Compressive Strength	201
4.6.3.3	Shape Memory Test	203
4.6.4	Bio-Corrosion Test	205
4.6.5	Antibacterial Test	205
4.7	Effect of Alloying Elements on Ti-30 at.%Ta Shape Memory Alloy	206
4.7.1	Effect of Cerium Addition on Ti-30 at.%Ta Shape Memory Alloy	207
4.7.1.1	Microstructure Characteristics	207
4.7.1.2	Transformation Temperatures	210
4.7.1.3	Mechanical Properties	212
4.7.1.4	Bio-Corrosion Test	215
4.7.1.5	Antibacterial Test	216
4.7.2	Effect of Silver Addition on Ti- 30at.%Ta Shape Memory Alloy	217
4.7.2.1	Microstructure Characteristics	218
4.7.2.2	Transformation Temperatures	221

4.7.2.3	Mechanical Properties	223
4.7.2.4	Bio-Corrosion Test	226
4.7.2.5	Antibacterial Test	228
4.7.3	Effect of Tin Addition on Ti-30at.%Ta Shape Memory Alloy	228
4.7.3.1	Microstructure Characteristics	229
4.7.3.2	Transformation Temperatures	232
4.7.3.3	Mechanical Properties	234
4.7.3.4	Bio-Corrosion Test	238
4.7.3.5	Antibacterial Test	240
4.8	Summary	240
4.8.1	Microstructures of Ti-51at.%Ni, Ti-23at.%Nb and Ti-30at.%Ta With and Without Alloying Elements	241
4.8.2	Hardness of Ti-51at.%Ni, Ti-23at.%Nb and Ti-30at.%Ta With and Without Alloying Elements	244
4.8.3	Compressive Strength of Ti-51at.%Ni, Ti-23at.%Nb and Ti-30at.%Ta With and Without Alloying Elements	246
4.8.4	Shape Memory Test of Ti-51at.%Ni, Ti-23at.%Nb and Ti-30at.%Ta With and Without Alloying Elements	248
4.8.5	Corrosion Behaviour of Ti-51at.%Ni, Ti-23at.%Nb and Ti-30at.%Ta With and Without Alloying Elements	250
4.8.6	Antibacterial Effect of Ti-51at.%Ni, Ti-23at.%Nb and Ti-30at.%Ta With and Without Alloying Elements	252

<b>5</b>	<b>CONCLUSIONS AND RECOMENDATIONS FOR FUTURE WORK</b>	<b>254</b>
5.1	Conclusions	254
5.2	Recommendations for Future Work	256
	<b>REFERENCES</b>	<b>257</b>
	<b>Appendix</b>	<b>278</b>

## LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Various sintering processes and their influence on the density of Ti-Ni, Ti-Nb and Ti-Ta powders	31
2.2	Effect of the elements as $\alpha$ and/or $\beta$ Ti-stabilizers	34
2.3	Biological effect of elements additions	58
3.1	Specifications of the elemental powders and mixtures	72
3.2	The compositions of the binary and ternary Ti-Ni alloys in terms of weight and atomic percentages	72
3.3	The compositions of the binary and ternary Ti-Nb alloys in terms of weight and atomic percentages	72
3.4	The compositions of the binary and ternary Ti-Ta alloys in terms of weight and atomic percentages	73
3.5	Microwave sintering of Ti-51at.%Ni	78
3.6	Microwave sintering of Ti-23at.%Nb	79
3.7	Microwave sintering conditions of Ti-30at.%Ta	80
4.1	Effect of sintering parameters on relative density, porosity of the Ti-51%Ni alloy	95
4.2	Phases and planes of Ti-51%Ni XRD patterns	99
4.3	Ti-51%Ni transformation temperatures	101
4.4	Effect of sintering parameters on mechanical properties of Ti-Ni alloys	103
4.5	The density of Ti-Ni-Ce	119
4.6	Phases and planes of Ti-51%Ni-Ce XRD patterns	111
4.7	Ti-Ni-Ce transformation temperatures	112

4.8	The effect of Ce addition on maximum stress and its strain and elastic modulus	115
4.9	The SME, residual strain, and total strain recovery of the Ti-Ni- $x$ Ce SMAs at 37°C	116
4.10	Electrochemical parameters of the Ti-Ni-Ce samples in SBF solution obtained with electrochemical polarization testing	118
4.11	The density of Ti-Ni-Ag	121
4.12	Phases and planes of Ti-51%Ni-Ag XRD patterns	123
4.13	Ti-Ni-Ag transformation temperatures	125
4.14	The effect of Ag addition on the maximum stress and its strain and elastic modulus	127
4.15	The SME, $\epsilon_R$ and total strain recovery of the Ti-Ni- $x$ Ag SMAs at 37°C	128
4.16	Electrochemical parameters of Ti-Ni-Ag samples in SBF solution obtained from the polarization test	130
4.17	The density of Ti-Ni-Sn	133
4.18	Phases and planes of Ti-51%Ni-Sn XRD patterns	135
4.19	Ti-Ni-Sn transformation temperatures	136
4.20	Effect of Sn addition on maximum strength, strain and elastic modulus	139
4.21	The SME, $\epsilon_R$ and $\epsilon_T$ of Ti-Ni- $x$ Sn SMAS at 37°C	140
4.22	Electrochemical parameters of Ti-Ni-Ag samples in SBF solution obtained from polarization testing	141
4.23	The relative density, porosity and average pore size of the Ti-23at.%Nb samples	145
4.24	Phases and planes of Ti-23%Nb XRD patterns	150
4.25	Ti-Nb transformation temperatures	152
4.26	The effect of sintering parameters on the maximum stress and its strain and elastic modulus	155
4.27	Maximum stress at 4% strain, SME, $\epsilon_R$ and $\epsilon_T$ at 37°C	156
4.28	The density of Ti-Nb-Ce	160
4.29	Phases and planes of Ti-23%Nb-Ce XRD patterns	161
4.30	Ti-Nb-Ce transformation temperatures	163



4.31	The effect of Ce addition on maximum stress and its strain and elastic modulus	165
4.32	The SME, $\epsilon_R$ and $\epsilon_T$ of Ti-Nb- $x$ Ce SMAs at 37°C	166
4.33	Electrochemical parameters of Ti-Nb- $x$ Ce samples in SBF solution obtained from polarization testing	168
4.34	The density of Ti-Nb-Ag	171
4.35	Phases and planes of Ti-23%Nb-Ag XRD patterns	172
4.36	Ti-Nb- $x$ Ag transformation temperatures	174
4.37	The effect of Ag addition on maximum stress and its strain and elastic modulus	176
4.38	The SME, $\epsilon_R$ and $\epsilon_T$ of Ti-Nb- $x$ Ag SMAs at 37°C	177
4.39	Electrochemical parameters of Ti-Nb- $x$ Ag samples in SBF solution obtained from polarization testing	178
4.40	The density of Ti-Nb-Sn	182
4.41	Phases and planes of Ti-23%Nb-Sn XRD patterns	183
4.42	Ti-Nb-Sn transformation temperatures	185
4.43	The effect of Sn addition on maximum stress and its strain and elastic modulus	187
4.44	The SME, $\epsilon_R$ and $\epsilon_T$ of Ti-Nb- $x$ Sn SMAs at 37°C	189
4.45	Electrochemical parameters of Ti-Nb-Sn samples in SBF solution obtained from polarization testing	190
4.46	The relative density, porosity and average pore size of the Ti-Ta samples	194
4.47	Phases and planes of Ti-30Ta XRD patterns	198
4.48	Ti-Ta transformation temperatures	200
4.49	The effect of MWS parameters on maximum stress and its strain and elastic modulus	203
4.50	SME, $\epsilon_R$ and $\epsilon_T$ of the Ti-Ta alloys	204
4.51	The density of Ti-Ta-Ce	209
4.52	Phases and planes of Ti-30Ta-Ce XRD patterns	210
4.53	Ti-Ta-Ce transformation temperatures	211
4.54	The effect of Ce additions on the maximum stress and its strain and elastic modulus	214
4.55	SME, $\epsilon_R$ and $\epsilon_T$ of the Ti-Ta- $x$ Ce SMAs at 37°C	215

4.56	Electrochemical parameters of the Ti-Ta-Ce samples in SBF solution obtained from polarization testing	216
4.57	The density of Ti-Ta-Ag	220
4.58	Phases and planes of Ti-30Ta-Ag XRD patterns	221
4.59	Ti-Ta-Ag transformation temperatures	222
4.60	The effect of Ag additions on the maximum stress and its strain and elastic modulus	225
4.61	The SME, $\epsilon_R$ and $\epsilon_T$ of the Ti-Ta-xAg SMAs at 37°C	226
4.62	Electrochemical parameters of the Ti-Ta-Ag samples in SBF solution obtained from polarization testing	227
4.63	The density of Ti-Ta-Sn	230
4.64	Phases and planes of Ti-30Ta-Sn XRD patterns	231
4.65	Ti-Ta-Sn transformation temperatures	234
4.66	The effect of Sn addition on maximum stress and its strain, elastic modulus and Vickers hardness	236
4.67	The SME, $\epsilon_R$ and $\epsilon_T$ of the Ti-Ta-xSn SMAs at 37°C	238
4.68	Electrochemical parameters of the Ti-Ta-Sn samples in SBF solution obtained from polarization testing	239
4.69	Phase transformations after microwave sintering for the Ti-51at.%Ni, Ti-23at.%Nb and Ti-30at.%Ta SMAs with and without alloying elements	242

**LIST OF FIGURES**

<b>FIGURE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Development cycle of Ti-based shape memory alloys fabricated by powder metallurgy	9
2.2	Austenite to twinned-martensite transformation	10
2.3	Illustration of martensitic de-twinning at low temperatures	11
2.4	Ti-Ni phase diagram featuring an enlarged region for the metastable inter-metallic phases	15
2.5	Common transformation sequences in near-equiatomic Ti-Ni SMA	16
2.6	Ti-Nb phase diagram	18
2.7	Ti-Ta phase diagram	19
2.8	Schematic diagram depicting stress-induced martensitic transformation	21
2.9	Stress, strain and temperature variation of a Ti-Ni SMA exhibiting SME	22
2.10	Classification of fabrication techniques of Ti-based alloy	24
2.11	Schematic of hot isostatic pressing unit	28
2.12	Components of a SPS system	29
2.13	Schematic diagram of microwave sintering vacuum pot containing the insulation barrel	31
2.14	Compressive stress-strain curves of SPS-sintered (a) 50Ti50Ni and (b) 50Ti-30Ni-20Cu alloy specimens	35

2.15	Microstructures of the shape-memory-treated alloys (a) Ti-50.2mol%Ni and (b) Ti-30.2mol%Ni-20mol%Cu	36
2.16	Stress–strain curves of the Ti–45.2Ni–5Cu and Ti–35.2Ni–15Cu alloys during thermo-mechanical training	36
2.17	XRD patterns of the PM alloys with various Cu content at 27°C	37
2.18	Compressive stress–strain curves of (a) 50Ti-49Ni-0.1Mo and (b) 50Ti-49Ni-0.3Mo porous specimens	37
2.19	DSC curves of (a) 50Ti-49Ni-0.1Mo powders and spark plasma sintering (SPS) specimens and (b) 50Ti-49Ni-0.3Mo powders and SPS specimens	38
2.20	SEM micrographs of as-milled (a) Ti-Ni powder and (b) 0.5 vol.% CNT/Ti-Ni composite powder with insets of low magnification micrographs	38
2.21	Microstructural and EDS elemental analyses of the various regions of the (a) Ti-Ni and (b) 0.5 vol.% CNT/Ti-Ni. Red circles signify the lighter phase and black circles represent the dark phase	39
2.22	Shape-memory tests performed by sequential loading and unloading of the (a) Ti-Ni and (b) 0.5vol%CNT/Ti-Ni	39
2.23	Stress–strain curves of the Ti-Ni and CNT/Ti-Ni composites	40
2.24	CNTs observed at the fracture surface of the 0.5 vol.% CNT/Ti-Ni composite; (a) low magnification and (b) high magnification	40
2.25	The microstructures of as-sintered and HIP 51Ti-49Ni compacts at (a, b) low magnification and (c, d) high magnification, which exhibit significant grain growth after HIP and a network-like Ti <sub>2</sub> -Ni at the grain boundaries	41
2.26	The stress–strain curves of as-sintered and HIP 51Ti-49Ni compacts tested at 25°C	42

2.27	Cross-section of the microstructure and fracture surface of (a, b) as-sintered and (c, d) HIP 51Ti-49Ni compacts	42
2.28	The tensile stress–strain curves of (a) as-sintered and (b) HIP 51Ti-49Ni compacts with and without 964 °C and 1004 °C annealing treatment	43
2.29	Effects of annealing and HIP on the martensitic transformation behaviour of 51Ti-49Ni compacts	43
2.30	Effect of annealing and HIP on the shape recovery rate of Ti51-Ni49 compacts as a function of (a) different bending strains and (b) training cycles at a constant bending strain of 6.25%	44
2.31	Transformation temperatures for the master alloy with various (a) compacting pressures, (b) addition of Cr, pressed at 800 MPa, (c) addition of Cr, pressed at 800 MPa and (d) addition of Al, pressed at 800 MPa and sintered at 950 °C for 9 hour	45
2.32	Hardness values for the master alloy with various additions (a), (b) of Cr (low and high) and (c) Al, pressed at 800 MPa and sintered at 950 °C for 9 hours	46
2.33	Porosity percentages for the master alloy with various (a) compacting pressures and (b), (c) addition of Cr (low and high) and (d) Al, pressed at 800 MPa and sintered at 950 °C for 9 hours	46
2.34	Corrosion rate for the master alloy with various (a), (b) additions of Cr (low and high) and (c) Al, pressed at 800 MPa and sintered at 950 °C for 9 hour	47
2.35	SEM micrographs of a Ti–26Nb–5Ag alloy after vacuum sintering at (a) low and (b) high magnifications	48
2.36	SEM micrographs of a Ti–26Nb–5Ag alloy after SPS at (a) low and (b) high magnifications	48
2.37	(a) Compression curves of a Ti–Nb–Ag alloy fabricated via different sintering routes, (b) fracture surface of vacuum-sintered sample and (c) fracture surface of SPS-sintered sample	49

2.38	XRD patterns: (a) powders before and after ball milling for 2 and 20 h, and (b) Ti-26Nb-5Ag alloys after vacuum furnace sintering and SPS	49
2.39	Stress-strain curves of the solution-treated alloys tested at 250 K (a) Ti-22at.%Nb, (b) Ti-22at.%Nb-4at.%Ta, (c) Ti-22at.%Nb-4at.%Al and (d) Ti-22at.%Nb-4at.%Sn	50
2.40	Variations in SE strain of the solution-treated alloys as a function of tensile strain	51
2.41	Fracture surface of the cyclic-tensile tested Ti-22at.%Nb alloy	51
2.42	The tensile stress-strain curves for Ti-Nb alloys	52
2.43	Stress-strain curves of Ti-(20-28)at.%Nb alloys obtained at room temperature after solution treatment at 1173K for 1.8 kilosec	52
2.44	Optical micrographs of porous Ti-Ni alloys prepared by MWS with different contents of $\text{NH}_4\text{HCO}_3$ : (a) 0; (b) 10 wt.%; (c) 20 wt.%; and (d) 30 wt.%	53
2.45	Compressive stress-strain curves of porous Ti-Ni alloys with different porosities	54
2.46	Relationship between porosity and (a) Rockwell hardness, (b) compressive strength and elastic modulus and (c) bending strength of porous Ti-Ni alloys	54
2.47	XRD patterns of porous Ti-Ni alloys produced via MWS with different porosities	55
2.48	Potentiodynamic polarization curves for Ni-Ti and 316L stainless steel in de-aerated Hank's physiological solution at 37°C	59
2.49	Anodic polarization curves in Hank's solution at 37°C of the Ni-Ti, Ti6Al4V and AISI 316 LVM samples	60
2.50	Tafel curves (a, b) of Ti-Ag sintered alloys with different Ag contents (a) for S75 (the size of Ag particles are 75 u) alloys and (b) for S10 (the size of Ag particles are 10 u) alloys	61

2.51	Comparison of anodic polarization curves. (a) The Ti-35Nb alloy and the Ti-Ni alloy; (b) the Ti-52Nb alloy and the Ti-Ni alloy; (c) the Ti-35Nb alloy and the Ti-52Nb alloy in Hank's solution and artificial saliva	61
2.52	Tafel plots obtained for CPT and TNZT in Hank's solution	62
2.53	Anodic polarization curves of Ti-Nb-Sn alloys in (a) Hank's solution (pH 7.4) and (b) NaCl solution (pH = 7.4)	63
2.54	Tafel plots of the TNT (A00), TNTO (A01) and TNTFO (A11) alloys in the ST condition and Ti-6Al-4V in Ringer's solution at room temperature	64
2.55	Comparison of anodic curves for pure Ti, Ti-6Al-4V ELI and Ti-Ta alloys in 5% HCl solution at 310K	65
2.56	The potential dynamic polarization curves of Ti-Ta-based alloys after immersion for 3.6 kilosec in 0.9% NaCl solution	66
3.1	Flow chart outlining the research methodology	69
3.2	(a) As-received powder materials used for the research and SEM micrographs of (b) Ti, (c) Ni, (d) Nb, (e) Ta, (f) Sn, (g) Ag and (h) Ce powders	71
3.3	(a) Planetary ball mill (PM100), (b) internal view of the planetary ball mill (PM100), (c) milling jar and balls	74
3.4	Hydraulic press mould (on the left hand) and hydraulic pressing machine (on the right hand)	75
3.5	The microwave sintering equipment consist the microwave sintering vacuum pot. (a) Schematic diagram of the microwave sintering vacuum pot featuring the insulation barrel (outer cylindrical insulator). The alumina crucible is in the left panel portraying the (b) outer cylindrical insulator and (c) alumina crucible	77

3.6	The microwave sintering screen shows the graph of the adjusted parameters for the Ti-51at.%Ni sample, which was sintered at 700°C for 15 min	78
3.7	The microwave sintering screen shows the graph of the adjusted parameters for the Ti-23at.%Nb sample, which was sintered at 900°C for 30 min	79
3.8	Scheme of a typical differential scanning calorimeter curve showing the critical transformation temperatures, ( $\gamma$ : austenite; M: martensite)	84
3.9	Instron Universal Tensile Testing Machine	85
3.10	Shape memory effect test. (a, b) Experimental; (c) Schematic includes (1) undeformed sample, (2) deformed sample, (3) preheating the deformed samples above $A_f$ and (4) the sample following recovery	86
3.11	(a) Three electrode potentiodynamic polarization cell and (b) Schematic diagram of the electrochemical polarization cell with the electrodes.	89
3.12	Agar-disc with bacteria and sample, (1, 2, 3 and 4), respectively refers to the sequence of adding the agar into the disc, and then rubbing the bacteria on the agar and then placing the sample.	90
4.1	Optical micrographs of Ti-51%Ni samples sintered at (a) 800°C for 5 min, (b) 800°C for 30 min, (c) 900°C for 5 min, (d) 900°C for 30 min, (e) 1000°C for 5 min and (f) 1000°C for 30 min	93
4.2	(a) Swelling of the sample sintered at 800°C for 5 min, (b) non-uniform shrinkage of the sintered sample at 800°C for 30 min, (c) sample sintered at 900°C for 30 min, (d) cross-section of partially melted Ti-51%Ni sample after MWS at a temperature of 1200°C for 5 min and (e) sample sintered at 700°C for 15 min	94
4.3	Optical micrographs of Ti-51%Ni sample sintered at 700°C for 15 min	95



4.4	SEM micrographs of Ti-Ni sample: (a) sintering at 700°C for 15 min with EDS analysis at spots 1, 2, 3 and 4 (■ Ti and ■ Ni), and (b and c) elemental mapping of sintered Ti-51%Ni SMA at 700°C for 15 min	97
4.5	(a) SEM micrograph, (b) and (c) EDS results (■ Ti, ■ Ni and ■ O) of Ti-51%Ni SMA sintered at 700°C for 15 min at low magnification	98
4.6	XRD pattern of Ti-51%Ni MWS sample sintered at 700°C for 15 min	99
4.7	DSC curves of the Ti-Ni alloys sintered at 700°C for 15 min	101
4.8	Compressive stress-strain curves of Ti-Ni samples	103
4.9	Shape memory effect test of Ti-Ni alloy sintered at 700°C for 15 min	104
4.10	Electrochemical polarization curves of Ti-Ni in the simulated body fluid (SBF)	105
4.11	Inhibition zone around the sample (sintered at 700°C) against <i>E. coli</i> for Ti-Ni	106
4.12	SEM micrographs of Ti-Ni-Ce at (a) 0.5wt. %Ce, (b) 1wt. %Ce with EDS analysis at spots 1, 2, 3 and 4 (■ Ti, ■ Ni and ■ Ce) and (c) 3wt. %Ce	108
4.13	(a) SEM micrograph, (b) and (c) EDS of Ti-Ni-1wt.%Ce SMA sintered at 700°C for 15 min at low magnification, For (b) ■ Ti, ■ Ni, ■ Ce and ■ O while for (c) ■ Ti, ■ Ni, ■ Ce and ■ O	109
4.14	XRD of the Ti-Ni-Ce samples sintered at 700°C for 15 min	110
4.15	DSC curves of the Ti-Ni-Ce samples with addition of Ce (a) 0.5wt.%Ce, (b) 1wt.%Ce and (c) 3wt.%Ce	112
4.16	Vickers hardness of Ti-Ni-Ce SMAs	113
4.17	Compressive stress-strain curves of Ti-Ni-Ce with varying amounts of Ce	115
4.18	Shape memory test of Ti-Ni-Ce	116

4.19	Electrochemical polarization curves of the Ti-Ni-Ce alloys in SBF solution	118
4.20	Inhibition zones around the Ti-Ni-Ce samples against <i>E. coli</i> at (1) 0.5wt. %Ce, (2) 1wt. %Ce and (3) 3wt. %Ce	119
4.21	SEM micrographs of Ti-Ni-Ag at (a) 0.5wt. %Ag, (b) 1wt. %Ag and (c) 3wt. %Ag	121
4.22	(a) SEM micrograph, (b) and (c) EDS of Ti-Ni-0.5wt.%Ag SMA (■ Ti, ■ Ni, ■ Ag and ■ O) at low magnification	122
4.23	XRD of Ti-Ni-Ag samples sintered at 700°C for 15 min	123
4.24	DSC curves of the Ti-Ni-Ag samples with addition of Ag (a) 0.5at. %Ag, (b) 1at. %Ag and (c) 3at. %Ag	124
4.25	Vickers hardness of Ti-Ni-Ag SMAs	126
4.26	Compressive stress-strain curves of Ti-Ni-Ag with varying amounts of Ag	127
4.27	Shape memory effect test of Ti-Ni-Ag	128
4.28	Electrochemical polarization curves of Ti-Ni-Ag in SBF solution	129
4.29	Inhibition zones around the Ti-Ni-Ag samples against <i>E. coli</i> at (1) 0.5wt. %Ag, (2) 1wt. %Ag and (3) 3wt. %Ag	131
4.30	SEM micrographs of Ti-51%Ni-Sn at (a) 0.5wt. %Sn, (b) 1wt. %Sn and (c) 3wt. %Sn	132
4.31	(a) SEM micrograph, (b), (c), (d) and (e) EDS of Ti-51%Ni-0.5wt.%Sn SMA at low magnification, For (b) and (e) ■ Ti, ■ Ni, ■ Sn and ■ O while for (c) ■ Ti, ■ Ni, ■ Sn and ■ O and For (d) ■ Ti, ■ Ni, ■ Sn and ■ O	133
4.32	XRD of Ti-Ni-Sn samples sintered at 700°C for 15 min	134
4.33	DSC curves of the Ti-Ni-Sn samples with addition of Sn (a) 0.5wt. %Sn, (b) 1wt. %Sn and (c) 3wt. %Sn	136
4.34	Vickers hardness of Ti-Ni-Sn SMAs	137
4.35	Compressive stress-strain curves of Ti-Ni-Sn samples with varying amounts of Sn	138

4.36	Shape memory test of Ti-Ni-Sn	139
4.37	Electrochemical polarization curves of Ti-Ni-Sn in the SBF solution	141
4.38	Inhibition zones around the Ti-Ni-Sn samples against <i>E. coli</i> at (1) 0.5wt. %Sn, (2) 1wt. %Sn and (3) 3wt. %Sn	142
4.39	Optical micrographs of Ti-23%Nb samples sintered at (a) 900°C for 10 min, (b) 900°C for 30 min, (c) 1000°C for 10 min, (d) 1000°C for 30 min, (e) 1200°C for 10 min and (f) 1200°C for 30 min	144
4.40	Ti-23%Nb samples (a) before MWS (b) during sintering in a MWS pot, (c) after sintering at 1200°C for 30 min and (d) after grinding and polishing	145
4.41	SEM micrographs portraying the microstructure of Ti-23%Nb SMAs sintered at (a) 900°C for 10 min, (b) 900°C for 30 min, (c) 1000°C for 10 min, (d) 1000°C for 30 min, (e) 1200°C for 10 min, (f) 1200°C for 30 min; (g) EDS of the Ti-Nb samples sintered at 900°C for 30 min, where 1 and 2 (■ Ti, ■ Nb and ■ O) refer to points on the micrograph in Figure 4.34 (b)	147
4.42	Elemental mapping of samples from the micrograph (b) in Figure 4.41 sintered at 900°C for 30 min of (with dotted yellow box), where (a) Ti, (b) Nb and (c) Oxygen	148
4.43	XRD patterns of MWS Ti-23%Nb alloys at (a) 900°C for 10 min, (b) 900°C for 30 min, (c) 1000°C for 10 min, (d) 1000°C for 30 min, (e) 1200°C for 10 min and (f) 1200°C for 30 min	149
4.44	DSC data with the Ti-Nb samples sintered at (a) 900°C for 10 min, (b) 900°C for 30 min, (c) 1000°C for 10 min, (d) 1000°C for 30 min, (e) 1200°C for 10 min and (f) 1200°C for 30 min	151
4.45	Vickers hardness of Ti-Nb SMAs	153

4.46	Compressive stress-strain curves of Ti-23at. %Nb alloys for various MWS parameters at (a) 10 min and (b) 30 min. (c) Illustration of the three main regions of the stress-strain curve of sample sintered at 900°C for 30 min	154
4.47	Shape memory effect test of the Ti-Nb alloys of different sintering parameters at room temperature 37°C and sintering at different temperatures for (a) 10 min and (b) 30 min	156
4.48	Electrochemical polarization curve of the Ti-Nb SMA sintered at 900°C for 30 min in SBF	157
4.49	Inhibition zones around the Ti-Nb samples against <i>E. coli</i> sintered at 900°C for 30 min	158
4.50	SEM micrographs of Ti-23%Nb-Ce at (a) 0.5wt %Ce via EDS analysis at spots 1 (■ Ti, ■ Nb, ■ Ce and ■ O) and 2 (■ Ti, ■ Nb, ■ Ce and ■ O); (b) 1wt.%Ce and (c) 3wt.%Ce	160
4.51	XRD of Ti-Nb-Ce samples sintered at 900°C for 30 min	161
4.52	DSC curves of the Ti-Nb-Ce samples with addition of Ce (a) 0.5wt. %Ce, (b) 1wt. %Ce and (c) 3wt. %Ce	162
4.53	Vickers hardness of Ti-Nb-Ce SMAs	164
4.54	Compressive stress-strain curves of Ti-Nb-Ce with varying amounts of Ce	165
4.55	Shape memory test of Ti-Nb-(0.5-3wt.%)Ce	166
4.56	Electrochemical polarization curves of Ti-Nb-xCe alloys in SBF solution	167
4.57	Inhibition zones around the Ti-Nb-Ce samples against <i>E. coli</i> at (1) 0.5wt.%Ce, (2) 1wt.%Ce and (3) 3wt.%Ce	169
4.58	SEM micrographs of Ti-23%Nb-Ag at (a) 0.5wt.%Ag with EDS analysis at spots 1 and 2 (■ Ti, ■ Nb, ■ Ag and ■ O), (b) 1wt.%Ag and (c) 3wt.%Ag	171
4.59	XRD of Ti-Nb-xAg samples sintered at 900°C for 30 min	172

4.60	DSC curves of the Ti-Nb-Ag samples with addition of Ag (a) 0.5at.%Ag, (b) 1at.%Ag and (c) 3at.%Ag	173
4.61	Vickers hardness values of Ti-Nb-Ag SMAs	175
4.62	Compressive stress-strain curves of Ti-Nb-Ag with varying amounts of Ag	176
4.63	Shape memory test of Ti-Nb-Ag	177
4.64	Electrochemical polarization curves of Ti-Nb-xAg in SBF solution	178
4.65	Inhibition zones around the Ti-Nb-Ag samples against <i>E. coli</i> at (1) 0.5wt.%Ag, (2) 1wt.%Ag and (3) 3wt.%Ag	179
4.66	SEM micrographs of Ti-Nb-Sn at (a) 0.5wt.%Sn with EDS analysis at spots 1 and 2 (■ Ti, ■ Nb, ■ Sn and ■ O); (b) 1wt.%Sn and (c) 3wt.%Sn	181
4.67	XRD of Ti-Nb-Sn samples sintered at 900°C for 30 min	182
4.68	DSC curves of the Ti-Nb-Sn samples with addition of Sn (a) 0.5wt.%Sn, (b) 1wt.%Sn and (c) 3wt.%Sn	184
4.69	Vickers hardness of Ti-Nb-Sn SMAs	186
4.70	Compressive stress-strain curves of Ti-Nb-xSn with varying amounts of Sn	187
4.71	Shape memory test of Ti-Nb-Sn	189
4.72	Electrochemical polarization curves of Ti-Nb-Sn in SBF solution	190
4.73	Inhibition zones around the Ti-Nb-Sn samples against <i>E. coli</i> at (1) 0.5wt.%Sn, (2) 1wt.%Sn and (3) 3wt.%Sn	191
4.74	Optical micrographs of the Ti-30%Ta samples sintered at (a) 900°C for 10 min, (b) 900°C for 30 min, (c) 1000°C for 10 min, (d) 1000°C for 30 min, (e) 1200°C for 10 min and (f) 1200°C for 30 min	193
4.75	SEM micrographs showing the microstructure of the Ti-30%Ta SMAs sintered at (a) 900°C for 10 min, (b) 900°C for 30 min, (c) 1000°C for 10 min, (d) 1000°C for 30 min, (e) 1200°C for 10 min, (f) 1200°C for 30 min and the (g) EDS data of the Ti-Nb samples sintered	

	at 900°C for 30 min, where 1 (■ Ti, ■ Ta and ■ O), 2 (■ Ti, ■ Ta and ■ O) and 3 (■ Ti, ■ Ta and ■ O) refer to points on the micrograph in (b)	195
4.76	Elemental mapping of the samples sintered at 900°C for 30 min at low magnification; (a) Ti, (b) Ta and (c) Oxygen	197
4.77	XRD patterns of the Ti-30%Ta samples with different MWS parameters of temperatures and times at (a) 900°C for 10 min, (b) 900°C for 30 min, (c) 1000°C for 10 min, (d) 1000°C for 30 min, (e) 1200°C for 10 min and (f) 1200°C for 30 min	198
4.78	DSC data of the Ti-Ta samples sintered at (a) 900°C for 10 min, (b) 900°C for 30 min, (c) 1000°C for 10 min, (d) 1000 °C for 30 min, (e) 1200°C for 10 min and (f) 1200°C for 30 min	199
4.79	Vickers hardness of Ti-Ta SMAs	201
4.80	Compressive stress-strain curves of Ti-30%Ta alloys for different MWS parameters at (a) 10 min and (b) 30 min	203
4.81	Shape memory effect test of the Ti-Ta alloys of various sintering parameters at different temperatures for (a) 10 min and (b) 30 min	204
4.82	Electrochemical polarization curves of the Ti-Ta samples sintered at 900°C for 30 min in SBF solution	205
4.83	Inhibition zones around the Ti-Ta samples against <i>E. coli</i> sintered at 900°C for 30 min	206
4.84	SEM micrographs of the Ti-Ta-Ce alloys with additions of (a) 0.5wt.%Ce with EDS analysis at spots 1 (■ Ti, ■ Ta, ■ Ce and ■ O), 2 (■ Ti, ■ Ta, ■ Ce and ■ O) and 3 (■ Ti, ■ Ta, ■ Ce and ■ O); (b) 1wt.%Ce and (c) 3wt.%Ce	208
4.85	XRD of the Ti-Ta-Ce samples sintered at 900°C for 30 min	209

4.86	DSC curves of the Ti-Ta-Ce samples with addition of Ce (a) 0.5wt.%Ce, (b) 1wt.%Ce and (c) 3wt.%Ce	211
4.87	Vickers hardness of Ti-Ta-Ce SMAs	212
4.88	Compressive stress-strain curves of the Ti-Ta-Ce samples with varying amounts of Ce	213
4.89	Shape memory test of the Ti-Ta-Ce samples	214
4.90	Electrochemical polarization curves of the Ti-Ta-Ce samples in SBF solution	216
4.91	Inhibition zones around the Ti-Ta-Ce samples against <i>E. coli</i> at (1) 0.5wt.%Ce, (2) 1wt.%Ce and (3) 3wt.%Ce	217
4.92	SEM micrographs of the Ti-Ta-Ag samples with additions of (a) 0.5wt. %Ag with EDS analysis at spots 1 (■ Ti, ■ Ta, ■ Ag and ■ O), 2 (■ Ti, ■ Ta, ■ Ag and ■ O) and 3 (■ Ti, ■ Ta, ■ Ag and ■ O), (b) 1wt.%Ag and (c) 3wt.%Ag	219
4.93	XRD of the Ti-Ta-Ag samples sintered at 900°C for 30 min	220
4.94	DSC curves of the Ti-Ta-Ag samples with addition of Ag (a) 0.5wt.%Ag, (b) 1wt. %Ag and (c) 3wt.%Ag	222
4.95	Vickers hardness of Ti-Ta-Ag SMAs	223
4.96	Compressive stress-strain curves of the Ti-Ta-Ag samples with varying amounts of Ag	224
4.97	Shape memory test of Ti-Ta-Ag	226
4.98	Electrochemical polarization curves of the Ti-Ta-Ag samples in SBF solution	227
4.99	Inhibition zones around the Ti-Ta-Ag samples against <i>E. coli</i> at (1) 0.5wt.%Ag, (2) 1wt.%Ag and (3) 3wt.%Ag	228
4.100	SEM micrographs of the Ti-Ta-Sn samples at (a) 0.5wt.%Sn, (b) 1wt. %Sn and (c) 3wt.%Sn with EDS analysis at spots 1 (■ Ti, ■ Ta, ■ Sn and ■ O) and 2 (■ Ti, ■ Ta, ■ Sn and ■ O)	230
4.101	XRD data of the Ti-Ta-Sn samples sintered at 900°C for 30 min	231

4.102	DSC curves of the Ti-Ta-Sn samples with addition of Sn (a) 0.5wt.%Sn, (b) 1wt.%Sn and (c) 3wt.%Sn	233
4.103	Vickers hardness of Ti-Ta-Sn SMAs	235
4.104	Compressive stress-strain curves of Ti-Ta-Sn with varying amount of Sn	236
4.105	Shape memory test of Ti-Ta-Sn	237
4.106	Electrochemical polarization curves of the Ti-Ta-Sn SMAS in SBF solution	239
4.107	Inhibition zones around the Ti-Ta-Sn samples against <i>E. coli</i> at (1) 0.5wt.%Sn, (2) 1wt.%Sn and (3) 3wt.%Sn	240
4.108	Optical micrographs of (a) Ti-Ni SMA sintered at 700 °C for 15 min, (b) Ti-Nb SMA sintered at 900°C for 30 min and (c) Ti-Ta SMA sintered at 900°C for 30 min	242
4.109	SEM micrographs of (a) Ti-Ni SMA sintered at 700°C for 15 min, (b) Ti-Nb SMA sintered at 900°C for 30 min and (c) Ti-Ta SMA sintered at 900°C for 30 min	243
4.110	Hardness of Ti-51Ni sintered at 700°C for 15 min, Ti-23Nb sintered 900°C for 30 min and Ti-30Ta sintered 900°C for 30 min SMAs before and after adding 3wt.% of Ce, Ag and Sn	245
4.111	Elastic modulus of Ti-51Ni sintered at 700°C for 15 min, Ti-23Nb sintered 900°C for 30 min and Ti-30Ta sintered 900°C for 30 min SMAs before and after adding 3wt.% of Ce, Ag and Sn	246
4.112	Compressive strength of Ti-51Ni sintered at 700°C for 15 min, Ti-23Nb sintered 900°C for 30 min and Ti-30Ta sintered 900°C for 30 min SMAs before and after adding Ce, Ag and Sn	247
4.113	Compressive strain of Ti-51Ni sintered at 700°C for 15 min, Ti-23Nb sintered 900°C for 30 min and Ti-30Ta sintered 900°C for 30 min SMAs before and after adding Ce, Ag and Sn	248
4.114	Shape memory effect test (loading-unloading) of Ti-51Ni, Ti-23Nb and Ti-30Ta SMAs (a) without alloying	



	elements, (b) after adding Ce, (c) after adding Ag and (d) after adding Sn	249
4.115	Total strain recovery ( $\epsilon_T$ ) of Ti-Ni, Ti-Nb and Ti-Ta SMAs before and after adding alloying elements (Ce, Ag and Sn)	250
4.116	Electrochemical polarization curves of the Ti-Ni, Ti-Nb and Ti-Ta SMAs (a) without alloying elements, (b) after adding Ce, (c) after adding Ag and (d) after adding Sn	251
4.117	Corrosion rate ( $R_i$ ) of the Ti-Ni, Ti-Nb and Ti-Ta SMAs before and after adding alloying elements (Ce, Ag and Sn)	252
4.118	Antibacterial effects in terms of inhibition zones against E. coli of the Ti-Ni, Ti-Nb and Ti-Ta SMAs before and after adding 3wt.% of the alloying elements (Ce, Ag and Sn)	253

**LIST OF ABBREVIATIONS**

Ti – Ni	-	Titanium Nickel
Ti – Nb	-	Titanium Niobium
Ti – Ta	-	Titanium Tantalum
Ce	-	Cerium
Sn	-	Tin
Ag	-	Silver
SMAS	-	Shape Memory Alloys
SME	-	Shape Memory Effect
SE	-	Superelasticity
bcc	-	Body Centered Cubic
FCC	-	Face Centered Cubic
SEM	-	Scanning Electron Microscope
OM	-	Optical Microscope
SEM	-	Scanning Electron Microscope
XRD	-	X-ray Diffraction
EDS	-	Energy Dispersive Spectroscopy
DSC	-	Differential Scanning Calorimetry
ASTM	-	American Society for Testing and Materials
EDM	-	Electro-discharged Machining
SPS	-	Spark plasma sintering
GA	-	Gas atomization

**LIST OF SYMBOLS**

$M_s$	-	Martensitic start temperature
$M_f$	-	Martensitic finish temperature
$A_s$	-	Austenite start temperature
$A_f$	-	Austenite finish temperature
$\sigma_s$	-	Slip deformation
$\varepsilon_y$	-	Yield strain
$\varepsilon_T$	-	Total strain recovery
$\varepsilon_R$	-	Residual strain

**APPENDIX**

<b>APPENDIX</b>	<b>TITLE</b>	<b>PAGE</b>
A	Publications	263

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of the Research

Among the various classes of smart materials, there is a unique class of these materials known as Shape memory alloys (SMAs). SMAs have a unique characteristic in that when temperature is applied on them, they recover their shapes. Additionally, the application of cyclic mechanical load on SMA makes them undergo a reversible hysteresis change of form and thus absorbing or dissipating mechanical energy. Due to these unique characteristics, SMAs have found broad application in vibration and damping, sensing and actuation and impact absorption. Furthermore, the functional characteristics of SMA are attributed to thermoelastic martensitic transformation which usually takes place at a temperature of between -100 and 200 °C depending on the applied heat treatment and the composition of the alloy [1].

Intermetallic compounds, Such as Ti-Ni, with shape memory effects (SMEs), are an interesting group of materials. They are used in a wide range of industries, namely electronics, robotics, telecommunications, as well as in medicine and optics. For commercial alloys made from Ti and Ni, their martensitic transformation start temperature ( $M_s$ ) falls below a temperature of 373K [1], and for this reason, the

alloys of Ti-Ni are used in applications requiring temperatures below 373K. Due to this limitation of Ti-Ni based alloys, scientists have extensively pursued the development of high-temperature SMAs (HTSMAs) such as Ni–Al, Ni–Mn, and Ti–Ni–X (X = Zr, Hf, Pd, Pt, Au) based HTSMAs [2]. However, the actual application of the existing HTSMAs is hindered by their poor cold workability which makes it difficult for thin plates and fine wires to be fabricated from them. Nonetheless, there has been a lot of investigation recently on the  $\beta$ -type Ti-based SMAs which have better cold workability. For example, a lot of findings on shape memory behaviour of  $\beta$ -type Ti-base alloys have been reported recently. The excellent cold workability of  $\beta$ -type Ti-based SMAs has increased the interest of researchers and users in these SMAs, and they are currently being explored for practical applications due to their ease of fabrication into wires and plates that can be used for various purposes.

Nickel-free Ti-based alloys, such as Ti-Nb and Ti-Ta, are good candidate materials to replace Ti-Ni alloys for biomedical applications because it was recently demonstrated that nickel is toxic to human beings. Additionally, the application of these alloys has increased with the advancement of other methods of processing such as powder metallurgy (PM) and mechanical alloying (MA) which have allowed the control of composition and grain size of alloys [2, 3]. These processes make use of solid-state powder techniques which are widely applied in the production of dispersion-strengthen alloys, refractory metals, nanocrystalline materials, and amorphous composite materials [4-6].

The transformation characteristics of Ti-based alloys made using PM have been investigated by several researchers followed by application of sintering using different techniques [7-10]. Despite the advantages of these alloys, studies have shown that a majority of them consume a lot of time during fabrication, and secondly, they develop cracks which reduce their mechanical properties. In sintering, a new technique for sintering referred to as microwave sintering is applied to heat the green compacts until they attain a temperature close to that suitable for sintering to allow densifying and alloying of ceramics, metals, and composites. Microwave sintering integrates pre-alloyed elements and absorbs electromagnetic energy using

volumetric means and leading to transformation into heat [11-13]. Microwave sintering is different from other sintering technologies and provides the following benefits; it has a rapid rate of heating, uses less amount of energy, reduces the time used for sintering, enhances mechanical and physical properties of the materials being sintered and results in the improvement of element diffusion process [11].

## **1.2 Problem Statement**

Ti-based alloys are good candidates for biomedical applications compared to other biocompatible metals due to their enhanced biocompatibility and superior mechanical properties. However, it is found that Ti-Ni is detrimental to human health due to the presence of nickel element. Therefore it is important to investigate and search for new nickel-free Ti-based alloys, such as Ti-Nb and Ti-Ta. Both alloys are known to have great potential to replace Ti-Ni alloys for biomedical applications.

Recently many researches have been done to develop ternary Ti-based alloys in order to obtain better properties. Selection of alloying elements are important because they affect the microstructures and properties of the alloys. There are many alloying elements which can be added to binary Ti-based alloys, however, very few will give the required properties such as excellent biocompatibility and enhanced mechanical properties. The elements which have these attributes include cerium (Ce), silver (Ag) and tin (Sn).

Powder metallurgy (PM) is a method of production used for the production of components with a near-net shape and is aimed at reducing the cost of machining and finishing of parts as in the case of casting method. The PM method is simple, versatile and inexpensive, and the sintering process occurs at much lower temperatures than the melting point of the constituent elements. As compared to

other sintering techniques, microwave sintering has several advantages that include rapid rate of heating, use less energy, reduced times for sintering and produce porous alloys which are suitable for biomedical purpose. Hence, variations in sintering time and temperature with the PM process are essential for producing porous alloys. On the other hand, the pore size, shape, distribution and density during sintering is also important because it affects the stiffness of the materials and reduce the density as well as the elastic modulus. Thus, the main purpose of this research was to develop Ni-free Ti-based shape memory alloys for biomedical applications in order to prevent the toxicity of Ni.

### **1.3 Objectives of this Research**

The objectives of this research are as follows:

1. To determine the effect of sintering temperature and time on density, microstructure and transformation temperatures of Ti-Ni, Ti-Nb and Ti-Ta shape memory alloys fabricated by microwave sintering;
2. To examine the microstructure and phase variations of Ti-Ni, Ti-Nb and Ti-Ta shape-memory alloys produced by the powder metallurgy method;
3. To investigate the effect of a third element addition Ce, Ag and Sn on the microstructure, mechanical properties and shape memory behaviour as well as biocompatibility of Ti-Ni, Ti-Nb and Ti-Ta based shape memory alloys.



## 1.4 Scope of this Research

The scopes of this research are as follows:

1. Preparation of samples by powder metallurgy method which includes mechanical mixing of Ti, Ni, Ta, Nb and alloying element powders. This was followed by compaction using hydraulic press. The final fabricating method was sintering process using microwave sintering technique.
2. Characterization of the sintered materials by optical microscopy, scanning electron microscopy, energy dispersive spectrometry, and x-ray diffractometry to determine the porosity content, microstructures and phases formed.
3. Determination of phase transformation temperatures of the sintered materials using differential scanning calorimetry equipment.
4. Performing the compression test of pre-alloyed powder samples in order to establish the compressive stress and strain with an Instron 600 DX-type universal testing machine.
5. Conduct shape-memory test on the fabricated samples using specially designed compression test machine.
6. Perform electrochemical polarization test to evaluate the bio-corrosion properties on all fabricated samples.
7. Perform the antibacterial test using ager disc diffusion technique on the fabricated sample.

## 1.5 Significance of Research

The main aim of this research was to improve the mechanical properties and shape memory behaviour of Ti-51%Ni, Ti-23%Nb and Ti-30%Ta SMAs produced by powder metallurgy methods. This work provided significant information on the behaviour of these binary shape-memory alloys and on the influence of third elemental additions on their properties. Detailed investigation into phase transformation and microstructural variation is significant for determining the

optimum powder metallurgy parameters that can yield Ti-based alloys with the desired properties. The findings of this research will benefit the biomedical field in terms of applications such as dental implants, joint replacement systems, mechanical heart valves and stents based on the materials improve mechanical properties, shape memory behaviour and bio-corrosion properties.

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