A STUDY ON NANOCOMPOSITE HYDROXYAPATITE COATINGS ON TI6AL4V FABRICATED BY ELECTROPHORETIC DEPOSITION AND LASER SURFACE TREATMENT

by

Zhang Bokai

M.Sc. in Electromechanical Engineering

2010/2011

Faculty of Science and Technology

University of Macau

A STUDY ON NANOCOMPOSITE HYDROXYAPATITE COATINGS ON TI6AL4V FABRICATED BY ELECTROPHORETIC DEPOSITION AND LASER SURFACE TREATMENT

by

Zhang Bokai

A thesis submitted in partial fulfillment of the
requirements for the degree of

M. Sc. In Electromechanical Engineering

Faculty of Science and Technology
University of Macau

2011

Approved by _____

Supervisor

_____

_____

_____

Date` _____

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at the University of Macau, I agree that the Library and the Faculty of Science and Technology shall make its copies freely available for inspection. However, reproduction of this thesis for any purposes or by any means shall not be allowed without my written permission. Authorization is sought by contacting the author at

Address: Room 903, Unit 4 of 7th Building, NanXiaFengZeYuan, No.161 Xiamei Road, Xiangzhou, Zhuhai, Guangdong, China.
519000
Telephone: 86-13232213136 or 853-62105340
Fax:
E-mail: Sonicgoboy@163.com

Signature _____

Date _____

UNIVERSIDADE DE MACAU
仁義禮知信
澳門大學

University of Macau

Abstract

A study on Nanocomposite hydroxyapatite Coatings on Ti6Al4V fabricated by Electrophoretic Deposition and Laser surface treatment

By Zhang Bokai

Thesis Supervisor:

Prof. Kwok Chi Tat

M.Sc. in Electromechanical Engineering

Due to their low density, high mechanical strength and corrosion resistance, titanium alloys are often used as implants in orthopedic surgery and dentistry. In order to improve the bone bioactivity and osteointergration of metallic implants, hydroxyapatite (HA) is often coated on their surface so that a real bond with the surrounding bone tissue can be formed. Plasma spraying is currently the only commercial process in service for fabricating HA coatings on the metallic implants, but long term stability of plasma sprayed coatings could be a problem because of high degree of porosities, poor bond strength, non–stoichiometric composition, non–uniformity and amorphous structure. In view of these shortcomings, electrophoretic deposition (EPD) and laser surface treatment (LST) have been attempted for fabricating HA–composite coatings. Different contents of HA and

multi-walled carbon nano-tube (CNT) nanoparticles were used to produce composite coatings on Ti6Al4V substrate and CNTs act as the reinforcement for enhancing hardness of the coating. Due to the good bonding ability to Ti6Al4V substrate, TiO_2 nanoparticles was also added to HA/CNT to serve as the interfacial bonding material. Moreover, hydrothermal treatment was also applied to pre–grow the TiO_2 layer on the Ti6Al4V substrate as an interfacial layer followed by subsequent EPD of HA/CNT coating. By laser surface treatment (LST), HA with Ti, TiO_2, and ZrO_2 were used to fabricate the composite coatings by a 2.3-kW diode laser for improving hardness and achieving strong metallurgical bond. Surface morphology, compositions and microstructure of the specimens fabricated by EPD and LST were investigated by scanning electron microscope, energy dispersive spectroscopy and X–ray diffractometry respectively. Moreover, the corrosion behavior of various coated specimens in Hanks' Solution at 37 ^{o}C was studied by means of open circuit potential measurement, and potentiodynamic polarization technique. Moreover, surface hardness and adhesion strength were evaluated, and the bioactivity was also determined by immersing the specimens in Hanks' Solution at 37 ^{o}C for 4 weeks. For both EPD and LST, the HA-composite coatings show higher corrosion resistance than that of the substrate as reflected by nobler open circuit potential and lower corrosion current density. The adhesion strength of HA-composite coatings fabricated by EPD was higher than that of plasma sprayed HA coating. The enhanced properties of coatings by EPD were attributed to the nanostructure of the coatings resulting in minimal imperfections. LST specimens possess strong metallurgical bond.

Comparing two fabrication methods (EPD and LST), the electrophoretically deposited HA coating with 10 wt% TiO_2 and 5 wt% CNT on Ti6Al4V shows no micro-cracks, high adhesion strength and corrosion resistance without compromising to bioactivity. LST can produce coatings with high hardness, improved corrosion resistance and strong metallurgical bond, but it compromises to decrease in bioactivity due to decomposition of HA. For the utility of HA composite coatings is in vivo implantation, so bioactivity is the most important factor, thus HA coating with 10 wt% TiO_2 and 5 wt% CNT on Ti6Al4V makes the best coating with good bioactivity and acceptable surface and mechanical properties.

UNIVERSIDADE DE MACAU
仁義禮知信
澳門大學

TABLE OF CONTENTS

LIST OF FIGURES……x

LIST OF TABLES……...……xvi

LIST OF ABBREVIATIONS…….xvii

LIST OF PUBLICATIONS……...xviii

ACKNOWLEGEMENTS……...xix

CHAPETER 1: INTRODUCTION

1.1 Introduction……...1

1.2 Objectives……...3

CHAPTER 2: LITERATURE REVIEW

2.1 Biomaterials……..5

2.1.1 Hydroxyapatite……..8

2.1.2 Biocompatibility…….9

2.1.3 Corrosion resistance……...9

2.1.4 Physiological environment of human body……..10

2.2 Carbon nanotubes……10

2.2.1 Types of CNTs……..11

2.2.2 Strength……12

2.2.3 Hardness……...13

2.2.4 Kinetic……..13

2.2.5 Thermal properties……...14

2.2.6 Toxicity…….14

2.3 Titanium dioxide (Titania)……...14

2.4 Zirconium Dioxide (Zirconia)…….15

2.5 Fabrication of HA coating……...17

2.5.1 Electrophoretic Deposition (EPD)……17

2.5.2 EPD process…….17

2.5.3 Factors affecting EPD……..18
2.5.4 EPD kinetics……19
2.5.5 Influence of gas during EPD……20
2.5.6 Key suspension parameters……..21
2.5.7 Particles arrangement and electric conditions……..23
2.5.8 Typical coatings fabricated by EPD……..…25
2.5.9 Nanostructured HA monolithic and composite coatings by EPD…26
2.6 Hydrothermal Treatment……28
2.6.1 Definition……28
2.6.2 Advantages……...28
2.6.2.1 Hydrothermal growth of rutile…….....28
2.6.2.2 Hydrothermal growth of anatase……..29
2.6.2.3 Hydrothermal growth of brookite……29
2.7 Laser surface treatment……...29
2.7.1 Laser surface melting and alloying……..29
2.7.2 Laser cladding……..31
2.7.3 Advantages of laser surface modification……31
2.7.4 Current research on laser surface treatment of bioactivity coatings……31
2.8 Evaluation of corrosion behavior in physiological environment……32
2.8.1 General theory……..32
2.8.2 Current……..34
2.8.3 DC techniques……..34
2.8.3.1 The anodic scan……35
2.8.3.2 The cathodic scan……37

CHAPTER 3: EXPERIMENTAL DETAILS

3.1 Substrate materials……..40
3.2 Coating materials……40
3.2.1 Nanocrystalling hydroxyapatite powder……..40

3.2.2 Multi – walled carbon nanotube powder……..40
3.2.3 Nano – sized titanium dioxide powder…….41
3.2.4 Zirconium dioxide powder……...41
3.2.5 Titanium powder……..41
3.3 Simulate body fluids……41
3.3.1 Co-deposition of HA/CNT coatings……..…41
3.3.2 Co-deposition of HA/TiO2/CNT coatings……...…42
3.3.3 Hydrothermal treatment of Ti and its alloys…….42
3.4 Sintering……..43
3.5 Laser surface modification……..43
3.6 Surface characterizations and phase present……...44
3.7 Simulated body fluid……...45
3.8 Corrosion behavior……..45
3.9 Hardness and bonding strength……...46
3.10 Bioactivity……...47

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Corrosion behaviour of hydrothermally treated titanium and its alloys…..48
4.2 Electrophoretically deposited HA/CNT coatings (sintered)……...50
4.2.1 Characterization of the coatings……...50
4.2.2 Composition analysis……...54
4.2.3 Phases identification……60
4.2.4 Corrosion behavior……..63
4.2.5 Hardness and adhesion strength……...66
4.2.6 Bioactivity……69
4.3 Electrophoretically deposited HA/TiO_2/CNT coatings (sintered)……..71
4.3.1 Characterization of the coatings……..72
4.3.2 Composition analysis……...75
4.3.3 Phases identification……79
4.3.4 Corrosion behavior……..82

4.3.5 Hardness and adhesion strength……...86
4.3.6 Bioactivity……89
4.4 Laser fabricated coatings…….……91
4.4.1 Characterization of the coatings……...91
4.4.1.1 Surface morphology…….....95
4.4.1.2 Cross-sectioned microstructure.....95
4.4.2 Composition analysis…….100
4.4.2.1 EDS analysis of the surface……..……..100
4.4.2.2 EDS analysis of cross-section……109
4.4.3 Phases identification…….……..115
4.4.4 Corrosion behavior……118
4.4.4.1 OCP……..……..……..118
4.4.4.2 Cyclic potentiodynamic polarization……119
4.4.5 Hardness…….124
4.4.6 Bioactivity……..126

CHAPTER 5: CONCLUSIONS

5.1 HA/CNT coatings fabricated by EPD……..136
5.2 HA/CNT/TiO_2 coatings fabricated by EPD…….136
5.3 Laser surface treated coatings……..137
5.4 Comparison of EPD and LST ……..137
5.5 Suggestions for further work……...….138

References

Chapter 1……139
Chapter 2……141
Chapter 3……150
Chapter 4……151

APPENDIX.....155

LIST OF FIGURES

Fig. 2.1 Examples of biomaterials……..7

Fig. 2.2 A stable nanobud structure……..12

Fig. 2.3 Scheme of particles dispersed electrostatically (a), distorted doublelayers due to the shear action of the fluid during the electrophoretic motion of particles in the bulk suspension (b), and change of the ionic and particles concentration in the electrode boundary (c)……23

Fig. 2.4 Potential energy evolution vs. particles distance for surfaces dispersed by an electrostatic mechanism, (a) High energy barrier and (b) low energy barrier……..25

Fig. 2.5 Hydro–dynamic forces developed over the particles close to the surface electrode……..25

Fig. 2.6 Morphologies of laser remelted coating: (a) bonding state between surface layer and transitional layer; (b) bonding state between transitional layer and substrate ……...30

Fig. 2.7 Experimental configuration for galvanic corrosion testing…….……35

Fig. 2.8 Theoretical anodic polarization scan……...37

Fig. 2.9 Anodic polarization scan of Ti6Al4V, heat treated Ti6Al4V, HA coated Ti6Al4V and HA/CNT coated Ti6Al4V by EPD in Hanks' solution at 37 ^{o}C…….38

Fig. 2.10 Theoretical cathodic polarization scan……38

Fig. 3.1 SEM micrograph of needle shaped nano-sized HA powder……40

Fig. 3.2 SEM micrograph of multi – walled carbon nanotube powder……41

Fig. 3.3 Schematic of laser surface processing……44

Fig. 3.4 A flat cell for corrosion test……..……..46

Fig. 4.1 Polarization curves of pure Ti before and after hydrothermal treatment……..49

Fig. 4.2 Polarization curves of β Ti before and after hydrothermal treatment….49

Fig. 4.3 Polarization curves of Ti6Al4V before and after hydrothermal treatment……..50

Fig. 4.4 SEM micrographs of various coated specimens after sintering: (a) nHA, (b) nHA4CNT, (c) nHA10CNT, (d) nHA20CNT, (e) nHA25CNT at different magnifications……..53
Fig. 4.5 Cross-sectional appearance of nHA20CNT……53
Fig. 4.6 EDS analysis of nHA on (a) coating region and (b) crack region……...54
Fig. 4.7 EDS analysis of nHA4CNT on (a) coating region and (b) crack region.55
Fig. 4.8 EDS analysis of nHA10CNT on (a)coating region and (b)crack region.56
Fig. 4.9 EDS analysis of nHA20CNT on (a) coating region and (b) agglomeration region……...57
Fig. 4.10 EDS analysis of nHA25CNT on (a)coating region and, (b) agglomeration region, and (c)pin shape regain……...59
Fig. 4.11 XRD pattern of HA monolithic coating after sintering (H = HA, R = Rutile)……..60
Fig. 4.12 XRD pattern of nHA4CNT coating after sintering (H = HA, C = CNT, R = Rutile)……...61
Fig. 4.13 XRD pattern of nHA10CNT coating after sintering (H = HA, C = CNT, R = Rutile)……...61
Fig. 4.14 XRD pattern of nHA20CNT coating after sintering (H = HA, C = CNT, R = Rutile)……...62
Fig. 4.15 XRD pattern of nHA25CNT coating after sintering (H = HA, C = CNT, R = Rutile)……...62
Fig. 4.16 XRD pattern of multi – walled CNTs (C = CNT)……...63
Fig. 4.17 XRD pattern of HA monolithic and HA/CNT composite coatings after sintering (H = HA, C = CNT, R = Rutile)……..……..…63
Fig. 4.18 (a) Plot of OCP vs time and (b) polarization curves of Ti6Al4V substrate and HA/CNT coated specimens in Hanks' solution at 37 ^{o}C……..66
Fig. 4.19 Plots of (a) I_{corr} vs CNT content, (b) hardness vs CNT content, (c) adhesion strength vs CNT content……...69

Fig. 4.20 SEM micrographs of monolithic HA and HA/CNT composite coated specimens after immersed in Hanks' solution at 37 ^{o}C for 4 weeks: (a) nHA, (b) nHA4CNT, (c) nHA10CNT (d) nHA20CNT and (e) nHA25CNT…….70

Fig. 4.21 Typical XRD patterns of nHA25CNT compared with nHA25CNT immersed in Hanks' solution at 37 ^{o}C for 3 weeks…….71

Fig. 4.22 SEM micrographs of various HA/CNT/TiO_2 composite coated specimens after sintering: (a) nHA10TiO, (b) nHA10TiO5CNT, (c) nHA5TiO10CNT, (d) nHA5TiO5CNT and (e) nHA10CNT(TiO layer) at different magnifications……..74

Fig. 4.23 Cross – sectional appearance of nHA10TiO5CNT (continued)……..75

Fig. 4.24 EDS analysis (line scan) from the surface of the coating to the substrate of nHA10TiO5CNT……76

Fig. 4.25 EDS analysis of nHA10TiO5CNT…….…….77

Fig. 4.26 EDS analysis of nHA5TiO10CNT……..77

Fig. 4.27 EDS analysis of nHA5TiO5CNT……78

Fig. 4.28 EDS analysis of nHA10CNT(TiO layer)……79

Fig. 4.29 XRD pattern of nHA10TiO5CNT after sintering (A = anatase, C = CNT, H = HA, R = rutile)…….80

Fig. 4.30 XRD pattern of nHA5TiO10CNT after sintering (A = anatase, C = CNT, H = HA, R = rutile)…….81

Fig. 4.31 XRD pattern of nHA5TiO5CNT after sintering (A = anatase, C = CNT, H = HA, R = rutile)…….81

Fig. 4.32 XRD pattern of nHA10CNT (TiO layer) after sintering (A = anatase, C = CNT, H = HA, R = rutile)……...82

Fig. 4.33 XRD patterns of HA/CNT/TiO_2 composite coatings after sintering and multi – walled CNTs (A = anatase, C = CNT, H = HA, R = rutile)……82

Fig. 4.34 (a) Plot of OCP vs time and (b) polarization curves of HA/CNT/TiO, HA/TiO, HA coated specimens and Ti6Al4V substrate in Hanks' solution at 37 ^{o}C……86

Fig. 4.35 Morphology of failed surface of (a) nHA10TiO5CNT, (b) nHA5TiO10CNT, (c) nHA5TiO5CNT and (d) nHA showing the coatings peeled off from the substrate after adhesion test……..89

Fig. 4.36 SEM micrographs of various coated specimens after immersing in Hanks' solution for 4 weeks: (a) Ti6Al4V, (b) nHA10TiO, (c) nHA10TiO5CNT, (d) nHA5TiO10CNT, (e) nHA5TiO5CNT, (f) nHA10CNT (TiO layer)……..90

Fig. 4.37 SEM micrographs of various laser treated surface, (a)L-nHA, (b) L-nHA25TiO, (c) L-nHA25ZrO, (d) L-TiO, (e) ZrO.....93

Fig. 4.38 SEM micrographs of various laser treated surface, (a) L-nHA5Ti, (b)L-nHA30Ti and (c)L-nHA50Ti.....95

Fig. 4.39 SEM micrographs of cross-sectional (a) L-nHA(b)L-nHA25TiO, (c) L-nHA30Ti, (d) L-nHA50Ti ,(e) laser melted Ti6Al4V……...…….98

Fig. 4.40 SEM micrographs of cross-sectional view (a) L-nHA25TiO (etched), (b) L-nHA25ZrO (etched), (c) L-nHA5Ti (etched) and (d) laser melted Ti6Al4V (etched)……..100

Fig. 4.41 EDS analysis of L-nHA…….101

Fig. 4.42 EDS analysis of L-nHA25TiO……..102

Fig. 4.43 EDS analysis of L-nHA25ZrO……..104

Fig. 4.44 EDS analysis of L-nHA5Ti……...105

Fig. 4.45 EDS analysis of L-nHA30Ti…….106

Fig. 4.46 EDS analysis of L-nHA50Ti…….107

Fig. 4.47 EDS analysis of L-TiO……..108

Fig. 4.48 EDS analysis ofL-ZrO……...109

Fig. 4.49 EDS analysis of L-nHA25TiO (cross–sectioned, etched)…….110

Fig. 4.50 EDS analysis of L-nHA25ZrO (cross–sectioned, etched)…….111

Fig. 4.51 EDS analysis of L-nHA5Ti (cross–sectioned, etched)……..……112

Fig. 4.52 EDS analysis of L-nHA30Ti (cross–sectioned)……114

Fig. 4.53 EDS analysis of L-nHA50Ti (cross–sectioned)……115

Fig. 4.54 XRD pattern of L-nHA25TiO after laser surface treatment (A = anatase,

H = HA, R = rutile, T = TTCP)…….115

Fig. 4.55 XRD pattern of L-nHA30Ti after laser surface treatment (A = anatase, H = HA, R = rutile, T = TTCP)…….116

Fig. 4.56 XRD pattern of L-nHA50Ti after laser surface treatment (A = anatase, H = HA, R = rutile, T = TTCP)…….116

Fig. 4.57 XRD pattern of L-nHA25TiO, L-nHA30Ti and L-nHA50Ti after laser surface treatment (A = anatase, H = HA, R = rutile, T = TTCP)……..117

Fig. 4.58 (a) Plot of OCP vs time and (b) polarization curves of Ti6Al4V substrate and all laser treated specimens in Hanks' solution at 37 ^{o}C……..123

Fig. 4.59 Hardness profile of L-nHA25TiO…….126

Fig. 4.60 SEM micrographs of HA composite and oxide coated specimens after immersed in Hanks' solution at 37 ^{o}C for 4 weeks: (a) L-nHA, (b) L-nHA25TiO, (c) L-nHA25ZrO, (d) L-nHA5Ti, (e) L-nHA30Ti, (f) L-nHA50Ti, (g) L-TiO, (h) L-ZrO, and (i) Ti6Al4V substrate……130

Fig. 4.61 XRD pattern of L-nHA immersed in Hanks' solution at 37 ^{o}C for 4 weeks. (A = anatase, H = HA, R = rutile, T = TTCP)……...131

Fig. 4.62 XRD pattern of L-nHA25TiO immersed in Hanks' solution at 37 ^{o}C for 4 weeks. (A = anatase, H = HA, R = rutile, T = TTCP)……...131

Fig. 4.63 XRD pattern of L-nHA25ZrO immersed in Hanks' solution at 37 ^{o}C for 4 weeks. (A = anatase, H = HA, R = rutile, T = TTCP)……132

Fig 4.64 XRD pattern of L-nHA5Ti immersed in Hanks' solution at 37 ^{o}C for 4 weeks. (A = anatase, H = HA, R = rutile, T = TTCP)……...132

Fig 4.65 XRD pattern of L-TiO immersed in Hanks' solution at 37 ^{o}C for 4 weeks. (A = anatase, H = HA, R = rutile, T = TTCP)……...133

Fig 4.66 XRD pattern of L-ZrO immersed in Hanks' solution at 37 ^{o}C for 4 weeks. (A = anatase, H = HA, R = rutile, T = TTCP)……...133

Fig 4.67 XRD pattern of L-nHA, L-nHA25TiO, L-nHA25ZrO, L-nHA5Ti, L-TiO and L-ZrO immersed in Hanks' solution at 37 ^{o}C for 4 weeks. (A = anatase, H = HA, R = rutile, T = TTCP)……...134

Fig 4.68 Typical XRD pattern of L-nHA25TiO compared with L-nHA25TiO

immersed in Hanks' solution at 37 ^{o}C for 4 weeks. (A = anatase, H = HA, R = rutile, T = TTCP)……134

UNIVERSIDADE DE MACAU
仁義禮知信
澳門大學

LIST OF TABLES

Table 2.1 Materials and their Medical Uses……7

Table 2.2 Properties of orthopaedic alloys……..8

Table 2.3 Comparison of mechanical properties of CNTs and different materials...13

Table 2.4 Mechanical properties of zirconia……16

Table 2.5 Comparison of EPD, LST and hydrothermal treatment……32

Table 4.1 E_{corr} and I_{corr} of Ti and its alloys before and after hydrothermal treatment……..50

Table 4.2 Compositions, corrosion parameters of Ti6Al4V substrate and HA/CNT coatings in Hanks' Solution at 37 ^{o}C……65

Table 4.3 Average hardness and adhesion strength of Ti6Al4V substrate and HA/CNT coatings……...……...67

Table 4.4 Corrosion parameters of HA/CNT/TiO, HA/TiO, HA coated specimens and Ti6Al4V substrate in Hanks' Solution at 37 ^{o}C……..86

Table 4.5 Average hardness and adhesion strength of Ti6Al4V substrate, monolithic HA, HA/TiO and HA/CNT/TiO coatings……..88

Table 4.6 Designations of the coated specimens for laser surface treatment……91

Table 4.7 PDF card number for different phases……118

Table 4.8 Summary of phases have been identified in the various laser-treated specimens……..……..118

Table 4.9 Lattice and system of TiO_2……..118

Table 4.10 Corrosion parameters of Ti6Al4V substrate and all laser treated specimens in Hanks' Solution at 37 ^{o}C……123

Table 4.11 Average hardness and apatite forming abiligy of Ti6Al4V and all laser treated specimens……125

LIST OF ABBREVIATIONS

ASTM	America Society of Testing and Materials
CNT	Carbon Nanotubes
DC	Direct Current
EDS	Energy Dispersive Spectroscopy
EPD	Electrophoretic Deposition
E_{corr}	Corrosion Potential
HA	Hydroxyapatite
ISO	International Organization for Standardization
I_{corr}	Corrosion Current Density
I_{pass}	Passive Ccurrent Density
OCP	Open Circuit Potential
SBF	Stimulated Body Fluid
SEM	Scanning Electron Microscope
XRD	X–ray Diffractometry

UNIVERSIDADE DE MACAU
仁義禮知信
澳門大學

LIST OF PUBLICATIONS

Journal paper

B.K. Zhang, C.T. Kwok, F.T. Cheng, H.C. Man, 'Fabrication of Nano-structured HA/CNT Coatings on Ti6Al4V by Electrophoretic Deposition for Biomedical Applications,' Journal of Nanoscience and Nanotechnology, 11 (2011) 1-6 doi:10.1166/jnn.2011.3939 (full version).

Conference paper

B.K. Zhang, C.T. Kwok, F.T. Cheng, H.C. Man, 'Fabrication of Nano-structured HA/CNT Coatings on Ti6Al4V by Electrophoretic Deposition for Biomedical Applications', 2010 3rd IEEE International Nanoelectronics Conference Proceedings (INEC 2010), January 3-8, City University, Hong Kong, (2010) 813 – 814.

UNIVERSIDADE DE MACAU
仁義禮知信
澳門大學

ACKNOWLEDGMENTS

My study in University of Macau will soon come to an end, at the completion of my master thesis, I wish to express my sincere appreciation to all those who have offered me invaluable help during the three years of my graduate study.

Firstly, I would like to express my heartfelt gratitude to my supervisor, Professor Kwok Chi Tat, for his constant encouragement and guidance. He has led me through all the stages of the experiments and the writing of this thesis. Without his consistent and illuminating instructions, this thesis could not reach to present form.

Secondly, I would like to thank the technician Miss Ivy Wong, for her provding me inspiration on the EPD experiments and thesis writing, and also her help in the conducting SEM works.

Thirdly, I would like to thank the master student Mr Eric Chan, for his help in conducting a lot of experiments for laser processing.

Fourthly, I should give my hearty thanks to all the other faculty members of the Department of Electromechanical Engineering for their patient instructions in various courses and their precious suggestions for my MSc study.

Lastly, my thanks would go to my beloved family for their loving considerations and great confidence in me all through these years. I also owe my sincere gratitude to my friends who listen to me and gave me help to fix the problems encountered in conducting experiments and writing thesis.