



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS AND CHARACTERIZATION OF TITANIUM-BASED METALLIC
GLASS BIOCOMPOSITE FILM FOR SURFACE MODIFICATION OF 316L
STAINLESS STEEL IMPLANT**

MOHSEN SARAF BIDABAD

ITMA 2012 2

**SYNTHESIS AND CHARACTERIZATION OF TITANIUM-
BASED METALLIC GLASS BIOCOMPOSITE FILM FOR
SURFACE MODIFICATION OF 316L STAINLESS STEEL
IMPLANT**

By

MOHSEN SARAF BIDABAD

**Thesis Submitted to the School of Graduate Study, Universiti Putra Malaysia,
In Fulfilment of the Requirements of the Degree of Doctor of Philosophy**

January 2012

DEDICATION

To

*Presence of Imam zaman and My Beloved Leader
and
My family: Wife, Mother, and Father
For their endless support and love*



Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of requirements for the degree of Doctor of Philosophy

SYNTHESIS AND CHARACTERIZATION OF TITANIUM-BASED METALLIC GLASS BIOCOMPOSITE FILM FOR SURFACE MODIFICATION OF 316L STAINLESS STEEL IMPLANT

By

MOHSEN SARAF BIDABAD

January 2012

Chairman: Prof. Ir. Barkawi Sahari, PhD

Faculty: Institute of Advanced Technology

This work is a study to show applicability of a new class of amorphous metallic material that are called metallic glass (MG) or glassy metal in biomedical application as a biofilm. Superior properties of these alloys designate them as a new age of biomaterial in biomedical applications, but thickness limitation in bulk form is the main problem for their production. Presented idea in this study intends to fabricate and implement them in composite thin film form for surface modification of a biomedical grade of stainless steel (316L) with weak surface properties that is widely applied as bone implant. This type of coating can solve production constraints of MG materials to be implemented in wide range of biomedical or other industrial applications.

For depositing these alloys, PLAD technique was used as a versatile technique to make amorphous film so that stoichiometry and other excellent properties were

preserved in deposited film and related source in PLAD target. PLAD vacuum chamber was designed according to the research requirements. The target was composed of two parts. First is a Ti-based MG matrix obtained in Ti-Cu-Zr-Si system by mechanical alloying and second is tricalcium phosphate (TCP), which is a bioceramic phase for improving film biocompatibility and osseointegration.

Before deposition and sample making, laser-target interaction was simulated by COMSOL Multiphysics computer software to predict cooling rate and maximum temperature in irradiated zone on surface target. Relationship between them and process parameters was estimated and the optimum amount of process parameters was predicted. Regarding to simulation results, PLAD was done to deposit MG composite films on 316L SS. Finally, physical characteristics of synthesized as-deposited films were evaluated and biological assays in vitro and in vivo were performed for selected samples successfully.

Performed biological results confirmed that connectivity between as-deposited TCP/Ti-based MG composite film and osteoblast like cells (MG63) was desirable and cytotoxicity in presence of these films was in low level in contrast with uncoated 316L SS. The composite films with 15 wt.%, TCP additive in $Ti_{40}Cu_{30}Zr_5Si_{25}$ MG matrix were the best composition both in physical and biological film characteristics.

According to the predicted PLAD process parameters and practical experiments based on them, obtained results had a particular agreement with our hypothesis.

Based on physical and structural properties it was found that by using a Gaussian Nd:YAG pulsed laser at second harmonic wavelength equivalent to 532nm and pulse duration about 140 ns, a Ti-based MG thin film is deposited on heated 316L SS successfully.

Numerical calculations indicate that cooling rate in irradiated zone reaches to about 10^6 K/s as atoms have no chance to order in crystalline structure and have to form an amorphous structure. Film characterization techniques such as XRD and DSC confirm this and show full amorphicity in as-deposited film structure when process parameters including vacuum pressure, target rotation speed and substrate temperature set at 10^{-5} Torr, 2000 rpm, (450-500°C) respectively as predicted in the modeling. It reveals that experimental results are in good agreement with the modeling and it is proven that PLAD is capable to form a thin MG film on metallic substrate as was desirable in hypothesis.

Both performed surface characterization (topography, morphology, hardness and wettability) and short-term biocompatibility assay (MTS, hemolytic and acute systemic toxicity) for coated and uncoated 316L SS samples illustrated that coated samples with this synthesized composite film were enhanced significantly in comparison with uncoated 316L SS and these new synthesized films meet essential requirements for an implant coating in biomedical applications.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**SINTESIS DAN PENCIRIAN TITANIUM BERASASKAN FILEM
BIOKOMPOSIT LOGAM KACA UNTUK PENGUBAHSUAIAN
PERMUKAAN IMPLAN BESI TAHAN KARAT 316L SS**

Oleh

MOHSEN SARAF BIDABAD

January 2012

Pengerusi: Prof. Ir. Barkawi Sahari, PhD

Fakulti : Institut Teknologi Maju

Hasil kerja ini adalah suatu penyelidikan yang menunjukkan kebolehpayaan kelas baharu bahan logam amorfus yang dipanggil logam kaca (MG) atau sebagai biofilem logam berkaca dalam aplikasi bioperubatan. Ciri-ciri unggul aloi ini dicipta sebagai generasi baru biobahan dalam aplikasi bioperubatan, tetapi keterbatasan ketebalan dalam bentuk pukal adalah masalah utama untuk penghasilan. Idea yang ditonjolkan dalam penyelidikan ini ialah untuk fabrikasi dan menggunakan ia dalam bentuk filem nipis komposit untuk pengubahsuaian permukaan gred besi kalis karat bioperubatan (316L) dengan ciri struktur yang lemah dimana ia digunakan secara meluas sebagai implan tulang. Jenis salutan ini boleh menyelesaikan kekangan pengeluaran bahan-bahan MG yang akan digunakan dalam pelbagai aplikasi bioperubatan atau lain-lain industri.

Untuk menghasilkan aloi-aloi ini, teknik PLAD telah digunakan sebagai teknik yang serba boleh untuk membuat filem amorfus, supaya stoikiometri dan ciri-ciri terbaik yang lain terpelihara dalam filem yang didepositkan dan sumber yang berkaitan dalam sasaran PLAD. Kebuk vakum PLAD direka bentuk mengikut keperluan penyelidikan. Sasaran tersebut terdiri daripada dua bahagian. Pertama adalah matrik yang berasaskan Ti-MG yang diperolehi dalam sistem Ti-Cu-Zr-Si oleh pengaloi mekanikal dan yang kedua adalah trikalsium fosfat (TCP) yang merupakan fasa bioseamik untuk meningkatkan keserasian biologi filem dan osseointegration. Sebelum pendepositan dan penghasilan filem, interaksi laser-sasaran disimulasikan oleh perisian komputer "COMSOL Multiphysics" untuk meramalkan kadar penyejukan dan suhu tertinggi dalam zon pemancaran terhadap permukaan sasaran. Keterkaitan antara mereka dan parameter proses-proses telah dianggarkan dan jumlah optimum parameter proses telah diramalkan. Mengikut keputusan simulasi, PLAD dilakukan untuk mendepositkan komposit filem MG keatas 316L SS. Akhirnya, ciri-ciri fizikal filem yang disintesis sebagai filem terdeposit dinilai dan ujian biologi secara in vitro dan in vivo telah dilakukan bagi sampel yang berjaya terpilih.

Hasil ujian biologi yang dilakukan disahkan bahawa hubungan antara TCP/Ti terdeposit berasaskan filem komposit MG dan osteoblast menyerupai sel (MG63) adalah wajar dan sitotoksik hadir dalam filem dalam paras yang rendah berlawanan dengan 316L SS tanpa salutan. Filem komposit dengan berat 15%, penambahan TCP dalam matrik $Ti_{40}Cu_{30}Zr_5Si_{25}$ MG adalah komposisi yang terbaik dalam kedua-dua ciri filem fizikal dan biologi.

Berhubung kepada parameter proses PLAD yang diramalkan dan kajian praktikal berdasarkan kepada mereka, keputusan yang diperolehi mempunyai persetujuan

tertentu dengan hipotesis kami. Berdasarkan ciri-ciri fizikal dan struktur, didapati bahawa dengan menggunakan Gaussian denyutan laser Nd:YAG pada panjang gelombang harmonik kedua bersamaan 532nm dan jangkamasa denyutan kira-kira 140 ns, filem nipis MG berasaskan Ti terdeposit dengan jayanya kepada 316L SS yang dipanaskan.

Pengiraan berangka menunjukkan bahawa kadar penyejukan dalam zon terradiasi mencapai kira-kira 10^6 K/s sebagai atom-atom yang tidak mempunyai peluang untuk bertindak dalam struktur kristal dan perlu membentuk struktur amorfus. Teknik pencirian filem seperti XRD and DSC mengesahkan perkara ini dan menunjukkan darjah amorfus penuh dalam struktur filem yang di depositkan apabila parameter proses termasuk tekanan vakum, kelajuan putaran sasaran dan suhu substrat ditetapkan pada 10^{-5} Torr, 2000 rpm, (450-500 °C) masing-masing seperti diramalkan dalam permodelan. Terbukti bahawa keputusan ujikaji adalah dalam kedudukan yang diyakini dengan permodelan dan ia dibuktikan bahawa PLAD mampu untuk membentuk filem nipis MG keatas substrat logam seperti yang dihasratkan dalam hipotesis.

Kedua-dua menunjukkan pencirian permukaan (topografi, kekerasan morfologi dan kebolehbasahan) dan esei jangka pendek keserasian bio (MTS, hemolitik, dan ketoksikan sistem akut) untuk sampel-sampel 316L SS yang bersalut dan tidak bersalut diilustrasikan bahawa sampel bersalut dengan komposit filem tersintesis telah dipertingkatkan dengan ketara sekali berbanding 316L SS tidak bersalut dan sintesis filem baru ini memenuhi keperluan untuk salutan implan dalam aplikasi bioperubatan.

ACKNOWLEDGEMENTS

First of all, great thanks to the Most Gracious and Most Merciful ALLAH (S.W.T) without his wish and help this work would not have been possible. I also would like to express the most sincere appreciation to those who made this work possible: Advisory members and Family.

I would like to thank Prof. Dr. Barkawi Sahari for providing me with the opportunity to complete my Ph.D studies under his valuable guidance, for the many useful advices, discussions and financial support, for his constant encouragement and guidance. Also special thanks extend to the supervisory committee members; Prof. Dr. Azmi Zakaria and Dr. Fatemeh Jahanshiri. I am grateful for their willingness to serve on my supervisory committee, constant encouragement, helpful advice and many fruitful discussions. I would like to thank all my colleagues and science officers, in special brother Kadri Masaud in Advanced Materials and Nanotechnology Laboratory of ITMA Institute of Advanced Technology for their kindness, support and for providing help whenever needed. Very special thanks to Dr. Farid Azizi for his help in performing of biological experiments in Virology Laboratory of Medicine and Health Sciences Faculty, UPM.

I would like to express my appreciation and thanks to all who have taught me during my life in special, my ledears, martyrs, teachers and friends.

Thanks and acknowledgements are meaningless if not extended to my parents who deserve my deepest appreciation. Not all praise and thanks words said to them will be enough. Lastly but not least, very special thanks to my wife, confidante, faithful and true love. Her love and encouragement along with her efforts in preparing of my thesis are behind my success.

APPROVAL

I certify that a Thesis Examination Committee has met on 18 Jan 2012 to conduct the final examination of Mohsen Saraf Bidabad on his thesis entitled " Synthesis and Characterization of a Titanium-based Metallic Glass Biocomposite Film for Surface Modification of 316L Stainless Steel Implant " in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

ABDUL RAHMAN B. RAMLI, PhD

Assoc. Professor
Institute of Advanced Technology, ITMA
Universiti Putra Malaysia
(Chairman)

Mohd Zobir B. Hussein, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Abdul Halim B. Abdullah, PhD

Assoc. Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

SHAKER A. MEGUID, PhD

Professor
Mechanical and Industrial Engineering
University of Toronto
(External Examiner)

SEOW HENG FONG, PhD

Professor/ Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 18 March 2012

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment on the requirement for the degree of Doctor of Philosophy. The members of the supervisory committee were as follows:

BARKAWI B. SAHARI, PhD

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

AZMI B. ZAKARIA, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

FATEMEH JAHANSHIRI, PhD

Assoc. Professor
Faculty of Biotechnology and Biomolecular Sciences
Universiti Putra Malaysia
(Member)

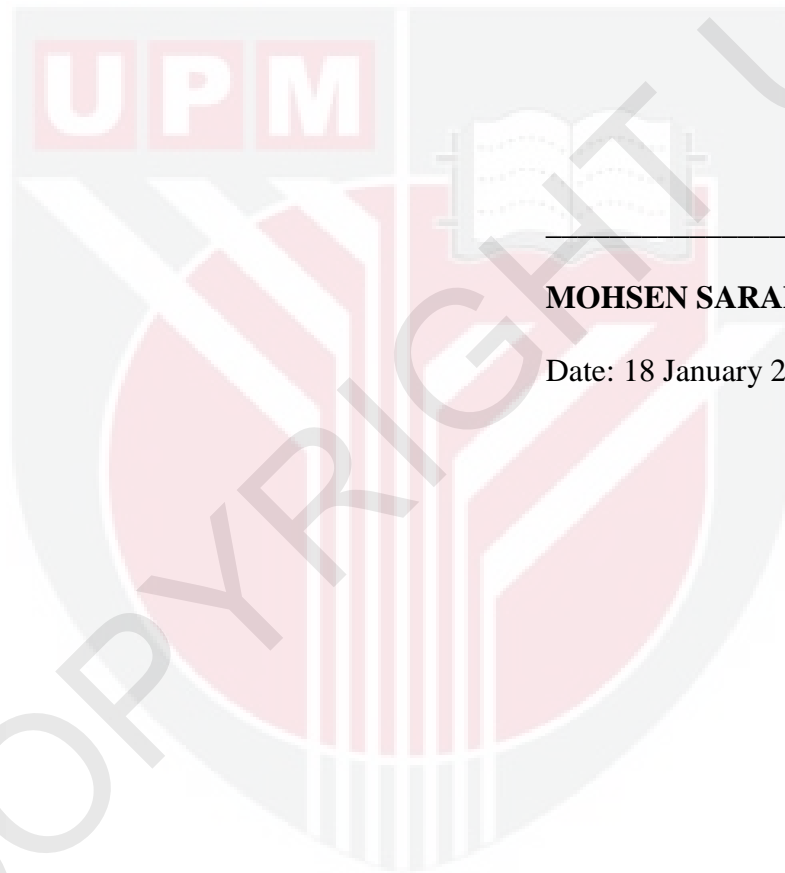
BUJANG BIN KIM HUAT, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 19 March 2012

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



MOHSEN SARAF BIDABAD

Date: 18 January 2012

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
APPROVAL	x
DECLARATION	xii
LIST OF TABLE	xvii
LIST OF FIGURES	xviii
LIST OF ABBREVIATION/NOTATION	xxiii
CHAPTER	
1. INTRODUCTION	1
1.1 Background	1
1.2 Surface Modification of 316L SS by Ceramic/Metallic Glass Composite Coating	3
1.3 Pulsed Laser Ablation Deposition	4
1.4 The problem and Its Settings	6
1.4.1 The Statement of Problem	6
1.4.2 The Hypotheses	7
1.4.3 The Limitation	8
1.4.4 Assumptions	8
1.5 The Importance of the Study	9
1.6 The Main Objectives and Specific Aims of Research	9
1.7 Overview of Research	10
2 LITERATURE REVIEW	11
2.1 Biomaterial Implants and Their Requirements	11
2.1.1 Mechanical Properties	11
2.1.2 Biocompatibility	12
2.1.3 Corrosion and Wear Resistance	12
2.1.4 Osseointegration	13
2.2 Bone	13

2.2.1	Bone Structure	13
2.2.2	Bone cells	15
2.2.3	Bone Remodelling	16
2.2.4	Bone Healing around Implants	17
2.3	Metallic Implants and Their Limitations	18
2.4	Host Response to Metallic Implants	20
2.5	Previous Failures in Applying Metallic Alloy as a Biomaterial	23
2.5.1	316L Stainless Steel	24
2.6	Surface of Metallic Implants	24
2.7	Surface Modification for Metallic Implants	26
2.8	Surface Modification by PLAD in Biomedical Applications	29
2.9	Metallic Glass as a New Age of Biomaterial	30
2.10	Ti-Based Metallic Glass	33
2.11	Implant Coating	36
2.12	Metallic Glass Coatings	39
2.13	Metallic Glass Matrix Composite	40
2.14	Pulsed Laser Ablation Deposition	40
2.15	Pulsed Laser Ablation Deposition in Biomedical Applications	43
2.16	Properties and Fundamental Characteristics of Bio-Films	44
2.17	Metallic Glass Characteristics	46
2.17.1	Atomic Structure (X-Ray Diffraction)	46
2.17.2	Glass Forming Ability	49
2.17.3	Differential Scanning Calorimetry	50
2.17.4	Electron Microscopy	51
2.17.5	Biological and Biocompatibility Behaviors of BMGs	52
2.18	Summary	58
2.19	Motivations and Approaches	61
	METHODOLOGY	62
3.1	Introduction	62
3.2	Thermal Modeling	65
3.2.1	Defining the Geometry	68
3.2.2	Meshing	68
3.2.3	Physical Settings and Governing Equations	69

3.2.4	Material Properties	75
3.2.5	Boundary conditions settings	78
3.2.6	COMSOL Fulfillment	79
3.3	Experimental Film Deposition Technique	80
3.3.1	PLAD System Setup	81
3.3.2	Deposition Procedure for Ti-based MG Films	88
3.4	Film Characterization Techniques	94
3.4.1	Film Atomic Structure and Phase Analysis	94
3.4.2	Thermal Properties	97
3.4.3	Nanoindentation Test	98
3.4.4	Wettability	99
3.4.5	Contact Angle Measurement	100
3.5	Biological Experiments	101
3.5.1	In Vitro and in Vivo Biocompatibility Assays	101
3.5.2	In Vitro Cell Culture Tests	102
3.5.3	Indirect Cytotoxicity Test	107
3.5.4	Cell Morphology Observation by SEM	108
3.5.5	Hemolysis Assay	109
3.5.6	In Vivo Test	110
3.5.7	Metal Element Concentration in SBF	112
3.6	Statistical Analysis	113
3.7	Data to be Determined	114
3.8	Summary	115
4	PLAD RESULTS AND DISCUSSIONS	117
4.1	Thermal Modeling of Laser-Target Interaction Results	117
4.1.1	Temperature Behavior in on Target Surface	118
4.1.2	Thermal Profile in Surface Target	118
4.1.3	Prediction of Cooling Rate in Targets	121
4.1.4	Relative Laser-beam Intensity in Target	127
4.1.5	Summary of Thermal Modeling	129
4.2	Film Deposition Results	130
4.2.1	Film Atomic Structure and Phase Analysis	130
4.2.2	Surface Characterization of Coated Samples	140

4.2.3	Film Particle Size and Morphology	159
4.2.4	Transmission Electron Microscopy	160
4.2.5	Thermal Properties of Deposited Films	166
4.2.6	Film Hardness	174
4.2.7	Wettability	178
5	BIOLOGICAL COMPATIBILITY RESULTS	183
5.1	In vitro Biocompatibility Test Results	183
5.1.1	Cytotoxicity Test (MTS Assay)	183
5.1.2	Cell Morphology Observation	197
5.1.3	Hemolysis Assay	204
5.2	In Vivo Test	208
5.2.1	Acute Toxicity Test Results	208
6	CONCLUSION AND RECOMENDATION	213
6.1	Conclusion	213
6.2	Recommendation for Future Work	218
	REFERENCES	220
	APPENDICES	233
	BIODATA OF STUDENT	236
	PUBLICATIONS	237