



**UNIVERSITI PUTRA MALAYSIA**

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

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**ITMA 2012 2**

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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**

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**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  $\text{Ti}_{40}\text{Cu}_{30}\text{Zr}_{5}\text{Si}_{25}$  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

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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.

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## 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.

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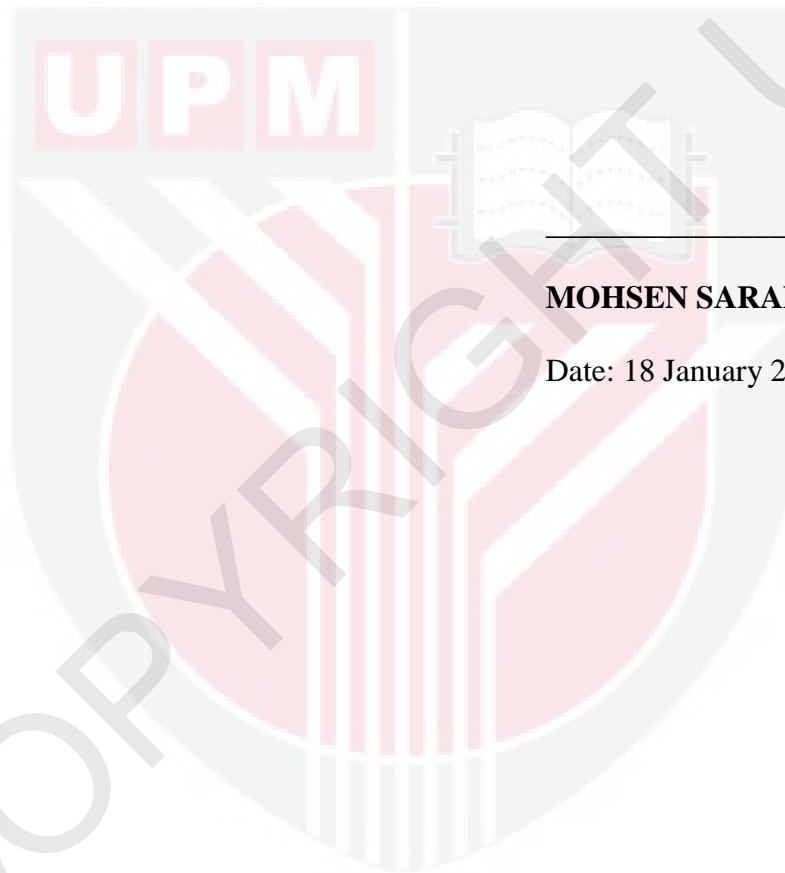
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## DECLARATION

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.



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**MOHSEN SARAF BIDABAD**

Date: 18 January 2012

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