

CORROSION RESISTANCE ENHANCEMENT OF HYDROXYAPATITE AND
MAGNESIUM OXIDE MULTILAYER COATING ON MAGNESIUM ALLOY
AZ31 VIA ELECTROPHORETIC DEPOSITION

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ABSTRACT

Magnesium (Mg) and its alloys have recently gained attention among researchers due to their excellent biodegradable and mechanical properties. However, poor corrosion resistance of Mg and its alloys have limited their clinical application. Rapid corrosion of Mg and its alloys may cause an implant failed before the bone has fully restored. The aim of this research was to enhance corrosion resistance of biodegradable implant substrate that is suitable for biomedical applications. Multilayer coating of nano-powders HA/MgO were coated on AZ31 magnesium alloy substrate via electrophoretic deposition (EPD) technique. A coating was obtained by applying suitable EPD process parameters (applied voltage and deposition time) and coating approaches (single layer coating and multilayer coating). The results of coating behaviour were characterised by means of XRD, and SEM to examine the coating surface morphologies and their phases. Coating performances of HA, MgO, and HA/MgO coating were studied by immersion test, potentiodynamic test, and electrochemical impedance spectroscopy where all done *in-vitro*. Elemental analysis was carried out using EDS to verify that the composed elements are biodegradable and harmless to the human body. The results obtained in this research suggested that corrosion resistance of a coated sample was affected by its particles distribution structure. Particles distribution structure with higher compactness showed a homogeneous coating layer and smaller surface defects. In general, the multilayer coating approach has outperformed the single coating approach by demonstrating a higher compactness particle distribution structure. Corrosion results of each group were compared, and the optimum process parameters were determined. The optimum process parameters for single layer coating HA, MgO and HA/MgO were 2min/10V, 30V/1min, and 15V/1min, respectively. On the other hand, the optimum number of layers for multilayer coating HA, MgO and HA/MgO were 5 layers, 3 layers, and 2 layers, respectively. It was also found that composite coating of HA/MgO has successfully inherited the benefits and limitations of each coating powder. Furthermore, defects such as agglomeration and cracks were found significantly reduced to a lower degree in multilayer coating approach. Among all of the coated samples, Laco-HA/MgO 2 layers coated with 5V/10 min each layer showed the highest corrosion resistance. The significant improvement in inhibition efficiency achieved 99.76% against the uncoated AZ31. Based on these results, it was concluded that this sample has a great potential for biodegradable orthopaedic application. Lastly, it was recommended to conduct cell viability measurement, biological reaction, and cytotoxicity test on Laco-2 layers by biological field researchers in the future.

ABSTRAK

Aloi berasaskan magnesium (Mg) akhir-akhir ini mendapat perhatian penyelidik-penyelidik dengan sifat biodegradasi dan mekanikalnya yang sangat baik. Walau bagaimanapun, ketahanan kakisan yang lemah telah menghadkan penggunaan klinikalnya. Kakisan Mg yang cepat boleh menyebabkan kegagalan implan sebelum tulang pulih sepenuhnya. Tujuan penyelidikan ini adalah untuk meningkatkan rintangan kakisan aloi biodegradasi implan substrak untuk kegunaan bioperubatan. Komposit pelbagai lapisan serbuk nano HA / MgO telah disalut pada substrak aloi magnesium AZ31 dengan teknik pemendapan elektroforetik (EPD) untuk meningkatkan ketahanan kakisannya. Lapisan tersebut dihasilkan dengan menggunakan proses parameter yang sesuai (voltan dikenakan dan masa pemendapan) dan pendekatan salutan (lapisan tunggal dan lapisan pelbagai lapisan) menggunakan teknik EPD. Hasil tingkah laku salutan dicirikan dengan XRD, dan SEM untuk memeriksa morfologi permukaan lapisan dan analisis fasa. Kadar kakisan lapisan HA, MgO dan HA / MgO dikaji dengan ujian rendaman, ujian *potentiodynamic*, dan spektroskopi impedans elektrokimia secara *in-vitro*. Analisis unsur dijalankan menggunakan EDS untuk mengesahkan produk sampingan kakisan terbiodegradasi dan tidak berbahaya terhadap kepada manusia. Hasil kajian menunjukkan bahawa ketahanan kakisan sampel bersalut dipengaruhi oleh struktur taburan partikel. Struktur taburan partikel dengan kepadatan ketumpatan yang lebih tinggi menunjukkan lapisan yang sekata dan kecacatan permukaan yang lebih kecil. Secara umumnya, pendekatan salutan pelbagai lapisan menghasilkan struktur taburan partikel dengan kepadatan ketumpatan yang lebih tinggi berbanding dengan lapisan salutan tunggal. Hasil kadar kakisan setiap kumpulan dibandingkan, dan parameter proses optimum ditentukan. Parameter proses optimum salutan tunggal HA, MgO dan HA / MgO masing-masing adalah 2min / 10V, 30V / 1min, dan 15V / 1min. Sebaliknya, bilangan lapisan optimum dalam pendekatan lapisan pelbagai lapisan untuk HA, MgO dan HA / MgO adalah 5, 3, dan 2 lapisan. Selain itu, didapati juga salutan komposit HA / MgO telah berjaya mewarisi faedah dan batasan setiap salutan. Selanjutnya, kecacatan seperti penggumpalan dan retakan telah berkurang pada tahap pembentukan yang lebih rendah dengan pendekatan pelbagai lapisan. Di antara semua sampel yang disaluti, 2 lapisan Laco-HA/MgO yang tersalut pada 5V/10min setiap lapisan menunjukkan ketahanan kakisan tertinggi. Sampel ini telah menunjukkan peningkatan yang ketara dengan 99.76% perencatan kecekapan berbanding dengan AZ31 yang tidak disaluti. Berdasarkan hasil kajian ini, disimpulkan bahawa, Laco-komposit 2 lapisan berpotensi besar untuk aplikasi ortopedik terbiodegradasi. Pada masa hadapan, pengukuran daya maju sel, tindak balas biologi dan pengukuran ujian sitotoksiti disyorkan untuk dilakukan oleh penyelidik bidang biologi.

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LIST OF ABBREVIATIONS

CT	-	Co-Deposition Various Deposition Time
CV	-	Co-Deposition Various Applied Voltage
DC	-	Direct Current
EDS	-	Energy Dispersive X-Ray Spectroscopy
EIS	-	Electrochemical Impedance Spectroscopy
ELD	-	Electroplating
EPD	-	Electrophoretic Deposition
FESEM	-	Field Emission Scanning Electron Microscope
HA	-	Hydroxyapatite
IE	-	Inhibition Efficiency
LACO	-	Layer by Layer Co-Deposition Various Number of Coating Layers
MgO	-	Magnesium Oxide
ML	-	Multi Layer Various Number of Coating Layers
OM	-	Optical Microscope
PDF	-	Powder Diffraction File
PDT	-	Potentiodynamic Test
SCE	-	Saturated Calomel Electrode
SEM	-	Scanning Electron Microscope
SHE	-	Standard Hydrogen Electrode
ST	-	Single Layer Various Deposition Time
SV	-	Single Layer Various Applied Voltage
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

ξ	-	zeta potential of the particles
ρ	-	Substrate Density
C	-	Concentration of the particle
C_1	-	Coating Capacitance
C_{dl}	-	Double Layer Capacitance
d	-	Distance between two electrodes
E	-	Applied potential
E_{corr}	-	Corrosion Potential
E_{oc}	-	Open Circuit Potential
I_{corr}	-	Corrosion Current Density
L	-	Distance between the electrodes
η	-	Viscosity of the solvent
R_{ct}	-	Polarization Resistance
R_{ct}	-	Charge Transfer Resistance
R_p	-	Resistance representing protectiveness of a coating
R_{pore}	-	Pore Resistance
R_s	-	Solution Resistance
SA	-	Surface Area
t	-	Deposition time
w	-	weight of charged particles deposited per unit area
β_a	-	Tafel Slope – Anode
β_c	-	Tafel Slope – Cathode
ϵ_0	-	Permittivity of vacuum
ϵ_r	-	Relative permittivity of the solvent

CHAPTER 1

INTRODUCTION

1.1 Background of Research

A massive number of orthopaedic implant surgeries were performed in worldwide each year [1]. In general, implant devices have been categorised as permanent implant or as a temporary fracture fixation [2]. Nowadays, the most common bioimplant metallic alloys used are titanium alloy, 316L stainless steel or cobalt-chromium alloys. However, the limitations of these materials are (i) it required second time of surgery to remove the implant as the bone has healed, (ii) relatively high stiffness caused bone shielding effect [3] and (iii) toxic level as if high concentration were used [4, 5].

Magnesium and its alloy (Mg) have gained significant attention in biodegradable implant as a temporary fixation to solve the stated problems. Mg possesses with superior mechanical properties, bioactivity and lightweight (density of 1.77 g/cm^3 which closer to natural bone $1.8\text{-}2.1 \text{ g/cm}^3$). Mg^{2+} ion is the fourth most abundant cation in human body to helps metabolism activities in human body [6, 7] and to stimulate new bone growth [8, 9]. In the meantime, the decomposition element of Mg^{2+} is harmless to human body [10]. AZ31 is one of the most potential based material that performed a biodegradable, non-toxic, excellent strength materials. Details of AZ31 is stated at section 2.3.

However, Mg degrade rapidly in physiological environment (pH 7.4-7.6) has limited the use of Mg in orthopaedic applications. High degradation rate of the implant causes mechanical failure by losing its mechanical strength before bone has fully restored [7]. For decades, researchers has been trying to study the variable methods and solutions to fulfil the requirement for biomedical applications [11].

Clinical concern is ambivalent on a biodegradable implant degradation rate [12]. On one hand, a slow degradation rate is preferred in the initial stage to maintain the mechanical strength and biological favour [13, 14]. On the other hand, fast degradation is preferred after the bone has been consolidated. In principle, an implant shall not remain inside a human body for unnecessary long period of time [12]. Therefore, surface coating has become an interesting option where it could effectively to achieve ambivalent implant requirements [12].

In this research, an AZ31 Mg alloy is coated by using electrophoretic deposition (EPD). Other coating methods such as thermal spray, pulsed laser deposition, dip coating has the limitations of controlling the thickness, and high temperature coating process. Therefore, EPD comes out as relatively outstanding nano powder ceramic coating technique, easy fabricate, cost effective, and an excellent choice for ceramic nano powders colloid deposition as compared to other coating methods [15]. Besides, EPD is a coating process that allow the coating at room temperature, and with flexible coating thickness which suitable for low melting point Mg substrate. Many studies of EPD are relates to its kinetic movement of charged particles motion [16-19]. However, the studies on coating approach such as the effects of multilayer coating, the particles distribution of multilayer approach, the corrosion resistance by applying various layers have not been reported.

Hence, the aim of this research was to study the effects on suitable coating parameters of single layer approach and effectiveness of multilayer coating approach on HA and MgO coating powder. Nano powders size is used to enhance the fine dispersion of HA and MgO in the suspension. HA is one of the most common coating powders applied on implant to increase it biological favour while MgO natural protectiveness of Mg based alloy. A synthetic compact MgO coated on AZ31 with the purpose of increase it corrosion resistance. Through studies, MgO not commonly applied by using wet coating method such as EPD due to its hygroscopic character. In this research, the aim is not only applying MgO but also applying composite HA/MgO.

Composite coating of HA/MgO with co-deposition and layer by layer with co-deposition method (named as Laco) was introduced to performance on HA/MgO.

HA/MgO composite coating is coated to enhancing implant corrosion resistance and maintaining the biological stability at the same time. Multilayer coating of HA/MgO is to increase the coating compactness of the composite. Composite of HA/MgO with the advantages of enhancing biological favour and increase the corrosion resistance of the implant.

In this research, the focus on corrosion of biodegradable implant. Adhesion and substrate roughness of biodegradable coating are unlike permanent implant coating where the features of coating adhesion or roughness of substrate implant are not critical. A biodegradable coating is meant to be dissolved during the process and bonded with the new bone growth.

1.2 Problem Statement

A permanent implant is an implant that used to serve patient for the life span of the implant such as non-loading implant at joint. A biodegradable implant material it is expected to exist in human body, as a load bearing implant until the bone fully recover.

However, rapid corrosion behaviour of Mg in physiological environment has limited its clinical application. It reacts with high concentration of chloride (Cl^-) in aqueous environment, and form soluble MgCl_2 and hydrogen gas, H_2 as the by-products. Hydrogen gas evolved is harmless to human body but with a rapid corrosion, and considerable amount of H_2 might resulting undesired inflammation and creates an empty space weaken the adhesion between the substrate with adjacent bone.

Rapid corrosion also results the risk of implant failure. Implant may lose its mechanical integrity before the bone has fully healed. Patient might face unnecessary pain and cost due to implant failure and extend the healing time.

Current coating methods are limited by low melting point substrate of magnesium in the range of 500-650°C. In general, the ceramic coating powder

requires a sintering process around 1300-1500°C. Coating such as HA on titanium are eligible to perform a high sintering process but it is not applicable on magnesium-based material. Room temperature coating methods without sintering process caused coating powder in a loosen and less compactness condition.

Currently, a permanent implant material is applied with a biological favour coating material to increase its biological favour. However, a single coating as such is insufficient for a biodegradable material to act as a biological favour and increase the corrosion resistance at the same time. A biodegradable implant is unlike the permanent implant which possesses with high corrosion resistance. Hence, it may lead to implant failure during the healing process.

Besides, the stress shielding effect remains the issue of permanent implant materials. Stress shielding effect is the effect that caused the low density of new bone growth as the implant is relatively too stiff to human bone. The healed new bone growth with low density may cause the bone too weak as compared to a healthy healing bone and without the strength that is supposed to support human activities.

1.3 Purpose of Research

This research addressed the problems described above namely, to increase the corrosion resistance of the magnesium alloy to synchronize between degradation rate of a magnesium alloy biodegradable implant and restoration period of a fracture bone. Firstly, to obtain a successful coated suspension parameters nano powders hydroxyapatite (HA), magnesium oxide (MgO) and nano composite HA/MgO respectively. Secondly, to investigate the effects of various process parameters of EPD coating on HA, MgO and HA/MgO for single coating layers approach for the corrosion protection of on bare material magnesium alloy (AZ31). Thirdly, to determine the multilayer coating approach of HA, MgO and HA/MgO to demonstrate enhancement of corrosion resistance of AZ31. Forth, to investigate the composite deposition of HA/MgO coating has influenced to the coating layer by complementary the limitation

embodied by each coating behaviour to increase the corrosion resistance by using multilayer coating approach.

1.4 Objectives of the Research

The principal objective of the research to increase corrosion resistance of magnesium alloy AZ31 by using electrophoretic deposition (EPD) with nano hydroxyapatite (HA), nano magnesium (MgO) and nano HA/MgO composite coatings with single layer and multilayer approaches for biomedical applications. Specific objectives include:

- (a) To study the effects EPD coating process parameters of applied voltage and deposition time of nano powders HA and MgO in terms of its surface morphologies relates to particles mobility rate, agglomeration, and particles distribution structures.
- (b) To investigate the effects of EPD multilayer coating approach of HA nano powders HA and MgO coating behaviour (surface morphologies examination, deposition yield measurement, and coating thickness measurement) and corrosion resistivity (evaluated by immersion test, potentiodynamic test, and electrochemical impedance spectroscopy).
- (c) To investigate the effects of co-deposition HA/MgO and Laco-deposition HA/MgO composite coating behaviour (surface morphologies examination, deposition yield measurement, and coating thickness measurement) and corrosion resistivity (evaluated by immersion test, potentiodynamic test, and electrochemical impedance spectroscopy).

1.5 Significance of the Research

The significant study of the research is to enhance the corrosion resistance of Mg base alloys with easy fabricate, and cost saving method. The experimental works

have undertaken, particularly in investigate the potential used of Mg biodegradable implant in extending knowledge and greater understanding level of electrophoretic deposition (EPD) and its possibility to increase the corrosion resistance.

This research also intended to extend the possible solution for biodegradable implant to apply practically. An extending of multilayer coating approach to produce a high compact density and corrosion resistance of Mg implant to replace permanent implant in temporary bone fixation applications. Hence, cost saving, and less suffering would have been borne by patients to conduct second time surgery all around the world.

The quantitative analysing data that have accumulated in depth with effects process parameters would provide valuable information for future research. An extensive study on Laco coating approach of HA/MgO extend the possibility to coat on Mg and provide the solution of Mg rapid corrosion.

1.6 Scope of the Research

The powder using are limited to nano hydroxyapatite (HA) at the length of 40 nm and nano magnesium oxide (MgO) is limited at the radius of 20 nm. Substrate of the research of Mg alloy AZ31 with the size of 30 x 10 x 3 mm and coated with 3.0 cm² effective surface area. Electrophoretic deposition (EPD) as the only coating method in this research by the process parameters limit with voltage and deposition time.

The responses on the effect of the coating protection on AZ31 were limited to the coating characterizations (microstructure, deposition yield, phase, and coating thickness), and corrosion behaviour (immersion test, potentiodynamic test, and electrochemical impedance spectrometry test). Machines that used to investigate coating behaviours are including optical microscope, X-ray diffraction, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and potentiostat. In addition, all corrosion performance of coated samples were investigated in *in vitro* condition only.

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