PECVD-formed Polymer Coatings for the Corrosion Protection of Biocompatible Magnesium Alloy WE43

By

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Abstract

Magnesium (Mg) alloys have gained increasing attention for biomedical applications recently. Current permanently-implanted metallic implants for orthopaedic and cardiovascular applications could cause a range of complications, such as endothelial dysfunction, restenosis and local inflammation, which require subsequent surgical interventions. Magnesium and its alloys may be applied as potential biodegradable materials for such applications due to their good mechanical properties, biocompatibility and degradability. Mg alloy degrades *via* corrosion reaction in the body and should disappear once it finishes surgical fixation. However, the rapid degradation (corrosion) rate of Mg-based implants in the physiological environment poses challenge of their commercialization and widespread use. Formation of anti-corrosive coating is an effective technique to control the corrosion rate of Mg and its alloy.

This research focused on investigating the possibility of using biocompatible plasma polymer coatings fabricated by PECVD under various deposition condition, varying from pressure, deposition time and gas ratio to control degradation rate of a biocompatible Mg alloy WE43.

Preliminary measurements confirmed that a PECVD coating produced from 1,3-butadiene and ammonia (PPB:N) offered best anti-corrosive properties, and this coating was subsequently chosen for further optimization and characterization for its anti-corrosive properties. It was found that the anti-corrosive properties of the PPB:N depend on both the deposition time and deposition pressure. The optimum coating-formation conditions were determined to be at 100 Pa and 40 minutes of deposition. The coating produced under these conditions offered a protection efficiency of 99.7% after 20 hours of immersion in PBS. Long-term tests evidenced that the PPB:N coating offered a 92% of protection efficiency even after 10 days of immersion in corrosive PBS. Hence, this coating can be considered as a good candidate for control of corrosion rate of a biomedical grade Mg alloy WE43.

RÉSUMÉ

Magnésium (Mg) alliages ont obtenu une attention croissante pour les applications biomédicales récemment. Les implants métalliques qui sont actuellement implantés permanentement pour les applications orthopédiques et cardiovasculaires pourraient entraîner diverses complications, comme la dysfonction endothéliale, le resténose et l'inflammation locale, qui nécessitent des interventions chirurgicales ultérieures. Le magnésium et ses alliages peuvent être utilisés comme matériaux potentiellement biodégradables pour de telles applications en raison de leurs bonnes propriétés mécaniques, de leur biocompatibilité et de leur dégradabilité. L'alliage de magnésium se dégrade par réaction de corrosion dans le corps et devrait disparaître une fois la fixation chirurgicale terminée. Cependant, le taux de dégradation rapide (corrosion) des implants à base de Mg dans l'environnement physiologique pose un défi pour leur commercialisation et leur utilisation généralisée. La formation d'un revêtement anti-corrosif s'agit d'une technique efficace pour contrôler le taux de corrosion du Mg et de son alliage.

Cette recherche a porté sur la possibilité d'utiliser des revêtements de polymères plasmatiques biocompatibles fabriqués par PECVD sous diverses conditions de dépôt, variant de la pression, du temps de dépôt et du rapport de gaz pour contrôler le taux de dégradation d'un alliage biocompatible Mg WE43.

Selon les mesures préliminaires, un revêtement PECVD à base de 1,3-butadiène et d'ammoniac (PPB: N) est muni des meilleures propriétés anticorrosives, et ce revêtement a ensuite été sélectionné pour une optimisation et une caractérisation plus poussées de ses propriétés anticorrosives. Il a été constaté que les propriétés anticorrosives du PPB: N dépendent à la fois du temps de dépôt et de la pression de dépôt. Les conditions optimales de formation de revêtement ont été déterminées comme étant à 100 Pa et 40 minutes de dépôt. Le revêtement préparé dans ces conditions a fourni une efficacité de protection de 99,7% après une immersion dans du PBS

pendant 20 heures. Des essais à long terme ont montré que le revêtement PPB: N offre une efficacité de protection de 92% même après 10 jours d'immersion dans du PBS corrosif. Par conséquent, le revêtement peut être considéré comme un bon candidat pour contrôler le taux de corrosion de l'alliage biomédical Mg WE43.

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Chapter 1 Introduction

Magnesium alloys are considered to be engineered multi-purpose materials with promising applications in the aeronautic, electronic and in the medical field as implants, owing to their low density, high specific strength, excellent machinability and good biocompatibility[1]. As a new generation of medical metallic materials, magnesium (Mg) and its alloys have attracted a lot of attention and have been intensively studied since as early as 1878[2]. Magnesium and its alloys may be applied as degradable implant materials in cardiovascular and orthopedic applications due to properties similar to those of human bone and due to their good degradability and non-toxicity.

The use of Mg alloys in medical application has increased recently, with the aim of employing them as biodegradable materials, mostly as orthopaedic implants. Musculoskeletal disorders are one of the most common health problems in human that cause disability and subsequent lack of physical activity[3]. According to demographic changes, the number of elderly people who suffer from these diseases is increasing rapidly, and this problem will continue to increase, which also causes the increasing demand for metallic biomaterials. The most commonly used medical metal materials for bone fracture fixation are usually made of 316L stainless steel [1, 4]. However, its ferromagnetism and low density make it difficult to image. At the same time, the percentage of molybdenum, nickel, chromium in 316L stainless steel is 2.5%, 12% and 17% respectively[5]. The release of these harmful elements can cause allergic reaction and intimal hyperplasia, and chromium (VI) also cancirogenic, which means the biocompatibility of 316L is poor. In many situations the patients need only the temporary implant or device. However permanent implants could cause potential adverse effects or even local inflammation. Thus, one desirable characteristic of a temporary implant is its degradability. Magnesium alloys are the most promising materials for degradable biomaterials due to their biocompatibility, outstanding mechanical and physical properties. Thus, they have potential for avoiding the need for a second operation to remove the implant after the implant has assisted in surgical fixation. Screws and plates made of magnesium alloys that degraded *in vivo* have shown good biocompatibility, as observed in clinical studies[6, 7].

Nevertheless, the main drawback of Mg and its alloys as a temporary implant material is its rapid corrosion rate, which produces hydrogen gas during the corrosion process, which can be harmful to the surrounding tissue, especially in cardiovascular applications. The rapid degradation rate of Mg-based implants in the physiological environment poses challenges of their commercialization and widespread use.

Corrosion control technologies are possibly achieved by surface treatment, coatings, and inhibition[8]. Coatings are very widespread because of the simplicity and effectiveness of protecting the substrate by providing a barrier between the metal and corrosive environment[9]. In order to reduce the corrosion rate of magnesium alloys, various coating and coating technologies have been developed, with some reviews recently published[10, 11]. Within current coating technologies, there is a technology called plasma enhanced chemical vapor deposition (PECVD) appearing to be a promising approach for the corrosion protection of metals. PECVD can produce coatings at low temperature (below 350°C), and of high purity[12]. This technology has the ability to control the chemical composition and thickness of the produced coating layer using the process parameters (composition of power, working gases, time, temperature and pressure).

The goal of the project presented in this thesis was to form thin and potentially bio-compatible PECVD coatings on a Mg-alloy WE43 surface in order to decrease the initial corrosion rate of the alloy, and through this to contribute to the field of use of Mg-alloys as possible implant materials.

Chapter 2 Background and literature review

2.1 An overview of Mg biodegradable biomaterials

Metallic materials play an important role in biomedical engineering. A number of people lose their tissues or organs due to accidents or diseases. Using different kinds of biomaterials to repair the damaged tissues is the most promising way to treat the patients[13]. Biodegradable implants are of particular interest in medical applications [1]. Temporary implants using biodegradable materials have been proposed as an alternative to avoid complications caused by permanent implants. They provide temporary support (intended function) during tissue recovery and then can be gradually absorbed or dissolved by the body.[14, 15] In this respect, they are superior to permanent implants, which can lead to mismatches between the body and the implants as well as chronic inflammatory responses, thus requiring repeated surgery. Currently, most commonly used biodegradable implants are based on polymers, but metal implants have also gained much of interests[16].

In the human body, magnesium is the second most abundant intracellular positive ion. Among the metal ions in the entire human body, the content of magnesium is ranked fourth[17, 18]. It is mainly distributed in cells and participates in a series of human cell metabolism processes, including the formation of bone cells to accelerate bone healing. Magnesium plays an important role in the muscle, nerve and heart functions of the human body. Cardiovascular disease is one of the most serious diseases that can cause death, with an estimated increasing rate that will affect up to 23.6 million people by 2030. 70% of these deaths are caused by the blockage of the artery by cholesterol build-up[19]. In this process of the treatment to remove the blockage of the artery, a stent, which is a wire metal mesh device, is inserted into the narrowed site of artery and surround a balloon tip. Then, the balloon tip is inflated to expand the stent to keep the artery properly open (Figure 1). Currently, coronary stents made of 316L stainless steel, CoCr and CrPt are the mostcommonly used stents; however, these stents are permanently implanted, which causes a range of problems already mentioned before, and very often require removal and re-implantation. However, stents based on Mg-alloys have recently caught attention as possible biodegradable stents, and especially those made of Mg alloy WE43. These stents would be beneficial not only due to the fact they would eventually degrade and thus they would minimize long-term negative side effects of permanently-implanted stents, but dissolved Mg ions would also be beneficial to the surrounding tissue and the whole body. Namely, magnesium reduces blood flow resistance in blood vessels, reduces platelet aggregation, improves myocardial metabolic function, and reduces mortality from acute myocardial infarction. In addition, magnesium deficiency is one of the major etiological factors for some serious arrhythmias, hypertension, ischemic heart disease, especially myocardial infarction, arteriosclerosis, and sudden death. Therefore, magnesium plays an important role in preventing cardiovascular disease and sudden death. Magnesium supplementation has attracted enough attention in clinical medicine and plays an important role in disease prevention and treatment as well as health care[20].



Figure 1 An illustration of a coronary stent implantation. (A) Insertion of deflated balloon catheter with closed stent, (B) balloon inflation, stent expansion, (C) the catheter is removed and the stent remains to support the artery and restore the blood flow [21]

Biodegradable metals are expected to corrode gradually in vivo and the release of corrosion products can cause an appropriate host reactions, and then dissolve completely after assisting with tissue healing[22]. It can be seen that magnesium has a good medical safety foundation as a biomedical material, and especially it is suitable for the treatment of cardiovascular diseases. The densities of magnesium (1.749 g/cm³) and its alloys(1.75-1.85 g/cm³) are similar to the density of human bone (1.75 g/cm³) [23]. The Young's modulus of Mg is lower than those of aluminum and steel and closer to that of natural bone tissue, so it can effectively alleviate the stress shielding effect. Some of the important properties of Mg compared to other biomaterials and natural bone are listed in Table 1. The above characteristics of magnesium and magnesium alloys provide a broad space for their use as biological materials.

Despite the many advantages, magnesium and its alloys are largely limited as biomaterial (implant) materials. This is mainly because magnesium is electrochemically extremely active (standard electrode potential is $.2.36 V_{\text{NHE}}$) and dissolves readily in aqueous solutions[24]. The oxide film formed on its surface in the corrosive medium (the human body is a very corrosive medium) is porous and does not provide good protection to the substrate. The corrosion process is accompanied by generation of a large amounts of hydrogen. Especially in corrosive media containing chloride ions (like in the human body), the integrity of the surface film of magnesium oxide is destroyed, resulting in increased corrosion.

At present, the development of biodegradable materials mainly focuses on two applications: biodegradable stents for cardiovascular therapy and biodegradable implants for bone tissue repair[25, 26]. Improving the corrosion resistance of magnesium and its alloys has become the key to solving the application of magnesium and its alloys in the field of biomaterials.

 Table 1 Summary of the physical and mechanical properties of various implant materials in comparison to natural bone[27-29]

	Density (g/cm ³)	Elastic modulus (GPa)	Compressive yield strength (MPa)	Fracture toughness (MPam ^{1/2})
Natural bone	1.8-2.1	3-20	130-180	3-6
Ti alloy	4.4-4.5	110-117	758-1117	55-115
Magnesium	1.74-2.0	41-45	65-100	15-40
Stainless steel	7.9-8.1	189-205	170-310	50-200
Co–Cr alloy	8.3-9.2	230	450-1000	N/A
Synthetic	3.1	73-117	600	0.7
hydroxyapatite				

2.2 Corrosion of Mg and Mg alloys

The main drawback of Mg as a biodegradable material is its high susceptibility to corrosion and fast corrosion rate. Therefore, understanding the corrosion mechanism and the corrosion behavior of Mg and its alloys are important to overcome this deficiency when used as an implant material in order to achieve the desired corrosion rate for specific applications.

Mg has low corrosion resistance in the presence of corrosive electrolyte and metallic impurities[30]. The corrosion performance of Mg alloy is due to (1) the high dissolution tendency of Mg alloy and weak inhibition ability of the corrosion product film and due to (2) the occurrence of internal galvanic corrosion caused by a second phase or impurities which act as local cathodes impeding the stability of the protective film. Magnesium and its alloys usually degrade in aqueous environments by electrochemical reactions, which produces Mg (OH)₂ and H₂. It has been shown that there is no significant influence of oxygen concentration on magnesium corrosion [31-33]. The overall corrosion reaction of magnesium in aqueous solutions at the corrosion potential is as follows[32]:

$$Mg_{(s)} + 2H_2O_{(aq)} \to Mg(OH)_{2(s)} + H_{2(g)}$$
 (2.1)

However, the corrosion process of Mg is rather complex, and different mechanisms have been proposed[34]. The above expression can be expressed as the sum of the following partial reactions defining respectively, the anodic, cathodic and product formation reactions:

$$Mg_{(s)} \rightarrow Mg_{(aq)}^{2+} + 2e^{-}$$
 (anodic reaction) (2.2)

$$2H_2O_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^- \text{ (cathodic reaction)}$$
(2.3)

$$Mg_{(aq)}^{2+} + 20H_{(aq)}^{-} \rightarrow Mg(OH)_{2(s)}$$
 (product formation) (2.4)

and it has been proposed that the anodic reaction can also produce Mg^+ which is further oxidized to Mg^{2+} through the following chemical reaction:

$$2Mg^{+}_{(aq)} + 2H_2O_{(aq)} \to 2Mg^{2+}_{(aq)} + H_{2(g)} + 2OH^{-}_{(aq)} \text{ (chemical reaction)}$$
(2.5)

Based on this mechanism, corrosion of Mg involves the formation of Mg⁺ intermediates at the substrate with a short lifetime[35]. Reaction (2.2) is Mg dissolution that produces electrons consumed at the cathode (2.3) resulting in the production of hydrogen gas. Here are two different relationships between the production of hydrogen and dissolution of Mg. (a) An electrochemical reaction (2.3) accompanies Mg dissolution reaction (2.2). (b) The reaction of Mg⁺ with water also directly produces H₂ (2.5). The accumulation of OH⁻ species (2.3), and the corresponding increase in pH near the metal surface result in the formation of an Mg-oxide/hydroxide insulating layer.

Magnesium hydroxide accumulates on the magnesium substrate as a corrosion protective layer in water, but when the concentration of chloride ion (Cl⁻) in the corrosive environment reaches above 30 mmol/l[36] Mg (OH)₂ begins to convert to highly soluble magnesium chloride. Therefore, since the chloride content in the body is about 150 mmol/L, a continuous corrosion of Mg can be observed [37-39]. Both the anodic and cathodic reactions occur on the surface of Mg. The detailed reaction steps that are involved in the anodic and cathodic processes have been demonstrated by Song (2011) and are schematically illustrated in Figure 2.



Figure 2 Schematic illustration of anodic and cathodic reactions involved in the self-corrosion of Mg[40]

Mg and its alloys form a surface hydroxide and oxide layer when they are exposed to the moist environment. This layer is stable at high pH but it is not in the neutral or acid environment, as shown in the Pourbaix diagram in Figure 3. As can be seen from the figure, when the pH value is above 11.5, a stable and self-healing passive layer is generated, which is responsible for the corrosion resistance.

As mentioned above, the corrosion rate of magnesium alloys is affected by pH of the surrounding medium and it also depends on state of the metal surface, the dependence of surface films on the alloy-composition, and the distribution and type of intermetallic phases. If the pH value is above 11.5, a stable and self-healing passive layer is produced, which is responsible for the corrosion resistance. For pH in the range of 8–10, the layer changes between a stable and an unstable state. In this range, reaction layers consisting of loosely adhering corrosion products are developed. The rate of corrosion is controlled by diffusion through the layer and depends primarily

on the layer thickness. During the dissolution and hydrogen evolution, the pH of the near surface region increases. As a result, the formation of the reaction layer changes to achive higher stability.



Figure 3 Potential-pH (Pourbaix) diagram for the system of magnesium and water at 25°C[41]

2.3 Corrosion Protection

2.3.1 Alloying

Magnesium alloys are currently being investigated as biodegradable materials, which are usually considered as alloys developed to meet the needs in the transportation industry[42]. The excellent corrosion performance of these alloys observed in industrial applications is related to the use of alloying elements such as aluminum (Al), zirconium (Zr), zinc (Zn), calcium (Ca), yttrium (Y), lithium (Li) and rare earth (RE). Theoretically, alloying can improve corrosion resistance of Mg by producing a stable, repairable, protective passive film. Magnesium alloys have also been investigated for orthopaedic applications. They can be used in various designs e.g. as plates, screws, stents or other fixture devices. An open porous scaffold made of magnesium alloys AZ91D was introduced as a substitute for subchondral bone in cartilage tissue engineering[43]. In recent years, more and more attention has been paid to the application of magnesium implants in orthopedics. In particular, WE43 magnesium alloy has been employed for stents. This alloy comprises of rare earth element (REE) mixtures based on cerium or neodymium as hardeners. For biomedical applications, the alloy composition is a crucial issue in biocompatibility. As showed in Table 2, various Mg alloys have been studied as biodegradable materials and some of them have shown biocompatibility.

Table 2 The nominal chemical compositions of Mg alloys researched as degradable biomaterials[44]

Alloy type	Aluminum (wt.%)	Rare earth element	Zinc (wt.%)	Other
AE21	2	1 wt.% (Ce, Pr, Nd)		
AZ31	3		1	
AZ91	9		1	
WE43		3 wt.% (Nd, Ce, Dy), 4 wt.% (Y)		
LAE442	4	2 wt.% (Ce, La, Nd, Pr)		4 wt.% Li
AM60B	6		0.07	0.33 wt.% Mn
Mg-Ca				<2 wt.% Ca
Mg–Zn–Y		~0.36–1.54 wt.% Y	2	
Mg–Mn–Zn			1	1.2 wt.% Mn

Although some alloying elements have shown good effects on improving alloy performance, their toxicity limits the use of alloy use as implant materials. Aluminum is associated to nerve damage, osteoblasts, dementia and Alzheimer's disease[45-48]. Some rare earth elements (Pr, Y, Ce, etc.) could lead to hepatotoxicity[49-51]. Excessive yttrium ions can alter the expression of certain rat genes and adversely affect DNA transcription factors[52]. Some rare earth elements have been clinically applied: neodymium is applied in magnetic prosthetic devices[53]. Lanthanum is proposed as a phosphate binder [54]. In addition, there is growing evidence that many rare earths have anticancer properties[55, 56].

2.3.2 Protective coating

The development of surface treatments and protective coatings is an efficient way to control the corrosion rate of biodegradable Mg implants. Coatings can protect a substrate by establishing a barrier between the metal and its environment. In order to provide adequate corrosion protection, the coating must be uniform, pore free and well adhered to the substrate surface. For biomedical applications, coatings should also possess other properties such as improvement of biocompatibility, antibiotic ability, nontoxicity, local drug delivery ability and, they should enable biodegradation at a desired rate. Ideally, they should offer only a limited barrier function[57]. There are a number of different coatings that could be employed for control of corrosion of Mg and its alloys, and some of them are presented in the following text.

2.3.1.1 Conversion coatings

Conversion coatings are produced by electrochemical or chemical treatment of a metal surface to produce a layer to protect the substrate from corrosion[58]. On magnesium, these

coatings act as an insulating barrier of low solubility between magnesium and the environment. There are several different types of conversion coatings, including calcium, phosphate chromate, fluorozirconate and permanganate.

Calcium phosphate coatings

Calcium phosphate-containing layers are the most widely studied for biomedical application in bone replacement and orthopedic materials. The bone-like apatite deposit formed by calcium phosphate is similar to the hydroxyapatite (HA) layer and is the mineral phase of bone[59]. One method to prepare calcium phosphate-containing coatings is by immersing in simulated-body-fluid (SBF). The resulting layers are usually predominantly amorphous, but they contain some crystalline HA and other calcium phosphate phases[60]. Mg compounds can be detected in conversion coatings because these coatings are formed by direct reaction with the substrate. Chen et al.[61]used a sodium phosphate solution and calcium nitrate to obtain a stable HA coating. Asdeposited samples were post-treated in alkaline solution to form a HA component in the coating. The result showed that the prepared HA–Mg(OH)₂ coating improved the corrosion resistance of the Mg matrix.

Fluorozirconate conversion coatings

Fluorozirconate treatment has also shown potential as a pretreatment for magnesium and magnesium alloys, and it has been used to remove surface contamination. The coating procedure typically involves immersing the Mg alloy matrix in 40% or 48% hydrofluoric acid[62]. Since the surface has a fluorine-containing coating, it is generally observed that the corrosion resistance of the magnesium alloy and the magnesium alloy sample is remarkably improved. However, the coating protective effect is temporary. Although the low solubility of MgF₂ can be of a benefit to form conversion layer containing MgF₂ on the substrate, fluoride-containing coatings will dissolve when the sample is removed from concentrated HF[63].

2.3.1.2 Hydride coating

Electrochemical methods are used to prepare hydride coatings on the surface of magnesium and its alloys, which can be an alternative to Cr-based conversion coating[64]. The process of preparing a magnesium hydride coating comprises of treating the Mg substrate in an alkaline solution prepared by adding alkali metal hydroxide, similar alkaline materials or ammonium salts [65]. It is also possible to reduce the resistance of the solution by adding a supporting electrolyte. The hydride coating has been found to reduce the corrosion rate of AZ91D alloy by 1/3. The protective performance is comparable to the dichromate treatment.

2.3.1.3 Organic coating

Organic coatings have attracted a lot of attention in biomedical application due to their great properties such as drug delivery capabilities and their ability to be functionalized with organic biomolecules. The organic coating can be applied to the substrate by a variety of methods, including dip coating, painting, plasma polymerization and electrochemical coating (for conducting polymers). In recent years, plasma technologies have been wildly used to change the surface properties of synthetic plasma polymers, so as to induce expected reactions with the biological environment. Plasma polymers are described as compact, smooth and pinhole free[66]. There is a growing interest in the possibility of preparing nanostructures and nanostructured plasma polymer coatings that can be used for a wide range of applications. In this study, we introduce the strategy that utilizes plasma enhanced chemical vapor deposition (PECVD) for production of protective plasma polymer coating of Mg alloy.

2.4 PECVD Technology for Metal Protection

To develop a new anti-corrosion coating to protect the magnesium part, a clean and environmentally friendly process is used due to health and economic considerations. There is a strong demand to replace hazardous coating technologies currently used and to improve the use of lightweight materials. In this case, thin-film technology for surface modification of nonequilibrium materials is becoming popular, because it allows the modification of the substrate by application of surface coatings without altering the disirable bulk properties. The PECVD technology has received much attention in the biomedical field. It is a sub-method of the Chemical vapor deposition (CVD) method, which is a common and effective thin film deposition method. In a CVD device, a solid product is formed by reactions of a gas mixture and is deposited as a coating on the surface of a substrate. Conventionally, the CVD process is initiated and controlled by heat as an energy source. In the CVD reaction, the decomposition of gas molecules requires high deposition temperature as excitation energy, which limits the types of coating materials that can be deposited and substrates that can be used [67]. However, as alternatives to thermal energy, plasma and photons are also widely used as energy source in CVD processes. Plasma Enhanced Chemical Vapor Deposition (PECVD), or plasma-assisted CVD, is a CVD technique that uses plasmas, ionized gasses generated by electrical discharges. instead of heat. Energy is primarily used to activate ions and free radicals that initiate chemical reactions.

Lower temperatures in PECVD allow the use of temperature sensitive substrates and deposition of layers that cannot withstand high temperatures. Furthermore, the deposition rate in PECVD is generally higher and it is easier to control coating properties because the precursor activated by the plasma is more reactive and the rate of arrival of the ionizing precursor can be controlled by a bias voltage[68]. Moreover, PECVD coatings tend to adhere strongly to a wide range of substrates, including metals. One of the most important technical achievements of the PECVD technology is the ability to deposit a variety of void-free, well-bonded films with

thickenesses ranging between 10-1000 nm. In the PECVD system, the films generally have a high packing density (~98%) making them hard and environmentally stable. By adjusting the thickness of the film, its characteristics change constantly. PECVD is suitable for the preparation of films with different compositions and microstructures. This can be utilized to fabricate a tough protective coatings and biomedical materials [69]. Such coatings have been considered as good candidates for protective coatings for metals and other substrates. PECVD has been applied to deposit a number of protective coatings, including organic coatings, silicon carbide, silicon nitride, silicon dioxide, amorphous silicon, diamond-like carbon and titanium nitride.

Chapter 3 Objectives

The major problem of magnesium alloys for biomedical applications is their low corrosion resistance, especially at physiological pH (7.4–7.6) and in a high chloride-containing environment of the physiological system [70]. The control of the implant degradation rate is crucial, since the resorption capacity of the tissue is limited and the implant could lose mechanical integrity before tissue has healed[71]. To improve the (bio)corrosion stability of Mg alloys, several coating technologies have been studied[9]. For biomedical application, these protective coatings must be composed of a non-toxic, biologically compatible material. Plasma polymerization is considered as a promising technique for producing such coatings. It allows the deposition of thin organic polymer coatings on top of the original metal substrate surface without affecting the intrinsic properties of the substrates.

This thesis hypothesizes that depositing an organic polymer coating on WE43 alloy by using plasma enhanced chemical vapor deposition will increase its initial corrosion resistance under physiological environments.

The goals of our research were:

- Improve initial corrosion resistance of WE43 alloy by forming a surface plasma polymer coating.
- Investigate the influence of plasma polymer coating fabricated under different deposition condition (deposition time, pressure, gas ratio) on the resulting corrosion behavior of WE43 alloy.

Chapter 4: Experimental and Methods

4.1 Sample Preparation

A WE 43 alloy rod was supplied by Magnesium Elektron, USA, with the nominal composition given in Table 3. The Mg alloy rod of a diameter of 1.59 cm was cut into coins with thickness of 3mm. Before the polymer deposition, both sides of the Mg alloy coin were polished with 600-grit SiC papers to remove the surface oxide layer and then the electrode surface that was subsequently coated was polished by 1200-grit SiC paper. Ethanol was used as a lubricant during the polishing process. After the second polishing, samples were rinsed with ethanol to remove the polishing residue and then they were degreased with ethanol again, followed by ultrasonic cleaning in acetone bath for 10 minutes. The samples were then dried with argon. This was done to avoid corroding the sample by moist air as much as possible.

Element	Mass Fraction (%)
Yttrium, Y	3.7-4.3
Rare Earths	2.4-4.4
Zirconium	0.4
Magnesium, Mg	Remainder

Table 3 Nominal composition of WE43 magnesium alloys in wt.%

4.2 Coating Deposition

The plasma polymer coatings were deposited on Mg alloy samples using a radio frequency (RF,13.56 MHz) plasma enhanced chemical vapor deposition (PECVD) system. A schematic of a PECVD system used to deposit organic coatings is presented in Table 4. The PECVD chamber was evacuated by turbo-molecular pumps to reach a high vacuum. Deposition is achieved by introducing reactant gases between parallel electrodes—a grounded electrode and an RF-energized electrode. The capacitive coupling between the electrodes activates the reactant gases into a plasma, which induces a chemical reaction and leads to the product being deposited on the substrate. The plasma in PECVD is triggered and maintained by radio frequency (RF).

The system used electronic mass flow controllers (Brooks Instrument) to introduce highpurity gases (ammonia 99.99% and1,3-butadiene 99.8%, Megs, Inc.) to the chamber. The operating pressure, during plasma deposition varied from 30Pa to 120Pa and the deposition time varied from 10mins to 40 mins (experimental parameters), while the power was set at 20W. Gas flowrate were fixed at 20 sccm (standard cubic centimeters per minute) for the 1,3-butadiene and ammonia mixture with N/C=1 ratio. These coatings are termed as "PPB:N" coatings.



Figure 4 Schematic diagram of PECVD reactor used for depositing thin organic coatings[72].

4.3 Corrosion immersion experiments

In order to investigate the resulting longer-term (up to 10 days) corrosion behavior of the samples, immersion experiments were carried out in phosphate-buffered saline (PBS), which simulates the human body fluid. The composition of PBS shown in Table 4. The PBS solution was prepared by diluting these reagent-grade chemicals in nano-pure water of resistivity of 18.2 M Ω cm. The pH of the PBS solution was adjusted to 7.4 using hydrochloric acid or sodium hydroxide before immersing the samples. Immersion experiments were performed for a time period up to 10 days. The ratio of PBS buffer to the surface area of the sample exposed to the electrolyte was kept at 127.3 ml/cm² in all experiments, and the electrolyte was in contact with air. All the experiments were done in triplicates. At the end of each immersion experiment, the Mg alloy samples were

removed from the electrochemical cell and then rinsed with deionized water and dried with argon for further characterization.

Reagents -	Mass .	Molarity .
NaCl	8g.~	0.137M
KCL	200mg.~	0.0027M °
Na ₂ HPO ₄ ,	1.44g.,	0.01M e
KH ₂ PO ₄ ,	240mg	0.0018M °

Table 4 Amounts of reagents used to prepare 1000 ml of PBS

4.4 Electrochemical test

Electrochemical tests were conducted in a standard three- electrode electrochemical cell. A commercial saturated calomel electrode (SCE) was used as reference electrode (RE), a graphite rod as counter electrode (CE), and WE43 Mg alloy samples as working electrode (WE). All potentials reported in this work are quoted with reference to the SCE. As an electrolyte, PBS solution of the composition listed in Table 4 was used. Electrochemical measurements were performed using an AUTOLAB potentiostat. The WE43 sample was assembled in the Teflon holder, exposing 1 cm² of the sample to the corrosive electrolyte. The holder was then immersed

in 100 ml of PBS electrolyte for 1 h at open circuit potential (OCP) to reach the steady state of the redox reactions. After this step, an electrochemical impedance spectroscopy (EIS) measurement was carried out at OCP with AC amplitude of ± 10 mV, over the frequency range from 50 kHz to 10^{-2} Hz.

Chapter 5: Results and Discussion

5.3 Effect of the plasma polymer coating on OCP

Figure 5 and Figure 6 show the open circuit potential (OCP) variations with time curves of bare WE43 alloy and selected PPB:N coated samples in PBS solution in 1 hour. The first graph shows the effect of pressure at constant time of deposition (20 min) while the second graphs shows the effect to deposition time at constant deposition pressure (100 Pa). It should be noted that a range of coating chemistries had previously been tested by the thesis author, under different deposition conditions, and the PPB:N samples were selected as best ones (most resistant to corrosion) – only results related to PPB:N samples are presented in this thesis. Although the electrochemical experiments were operated under room temperature, the Pourbaix diagram could still be considered as a good source to compare the control sample and coated samples. The diagram indicates that Mg²⁺ is the stable species favoured up to a pH of 10, above which the formation of Mg(OH)₂ starts. Figure 5 below, shows that Eoc fluctuates between ca. -1.77V and -1.86V for the control sample (naked sample, without the plasma polymer coating). The shape of the curve indicates that the sample first starts passivating, indicated by the positive shift in OCP, but then after ca. 600s, OCP starts decreasing. This indicates that a Mg(OH)₂ might initially be formed on the surface, and then it breaks down exposing the fresh surface that starts corroding, yielding a more negative OCP value. However, when the plasma polymer coating is introduced, the potential constantly increased which indicates the coatings contributed to the protection of the sample against corrosion. The initial rapid increase in the potential is most likely due to the buildup of a corrosion layer within the coating's pores, resulting in an increasing protective properties that blocks the surface and reduce the corrosion rate over time. Unlike on the bare samples, the increase of pH within the pores is faster and larger, enabling the formation of a better-quality Mg(OH)₂ film that 'plugs' the pores and minimizes access of PBS to the WE43 surface. After 20min of duration,

the OCP increase rate slows down, indicating stabilization of the film (polymer + $Mg(OH)_2$). As the deposition pressure of PPB:N coating increases, the potential was seen to also increase. This increase could be related to the increase in thickness of the of coating and, possibly, also to the decrease in its porosity.

Similarly, as the deposition time of PPB:N film increased (Figure 6), an increase in OCP was measured, indicating improvement in corrosion properties of the coating. However, it was found that at 40 min of deposition, OCP was below that one for the coating deposited for 20 min. In conclusion, the results in Figure 5 and Figure 6 indicate that the PPB:N plasma polymer film works as a protective layer to slow down the initial corrosion rate of WE 43. Other measurements were performed to further verify this assumption.



Figure 5 Open circuit potential (V) vs time (s) for PPB:N samples deposited at 20min in PBS solution



Figure 6 Open circuit potential (V) vs time (s) for PPB:N samples deposited under the pressure of 100Pa with different deposition time in PBS solution

5.4 Corrosion rate measurements by electrochemical impedance spectroscopy (EIS)

To better understand the interaction between the plasma polymer coating with the WE43 Mg alloy samples and evaluate the protective performance of the coating, electrochemical impedance spectroscopy (EIS) measurements was made to investigate the corrosion resistance of bare WE43 and PPB:N/WE43 Mg alloys. EIS tests were performed int a frequency range from 50 kHz to 10⁻ ² Hz to make sure a complete characterization of the electrode/electrolyte interface and the corresponding charge transfer processes is done. The resulting EIS spectra recorded on the control (coating-free) WE43 surface at different immersion times are presented in Figure 7 in the form of Nyquist plot. The spectra recorded at short times show the presence of three time constants, namely they exhibit characteristics of two capacitive loops at high and intermediate frequencies (HF and MF), which can be attributed to charge transfer reactions during magnesium corrosion and are typical for Mg alloys and to the properties of the surface corrosion film[73, 74]. At low frequency, an inductive behavior can be seen, and this behavior can be related to the response of corrosion intermediates adsorbed on the substrate surface, namely to Mg⁺_{ads}, which subsequently react to produce Mg²⁺. Both the HF and MF capacitive loops increased with the immersion time, evidencing an increase in corrosion resistance of the electrode; as a general rule, the difference between the real impedance values (Z') at low and high frequency (intersection of the spectrum with the abscissa) can be taken to be proportional to corrosion resistance, R_{corr}. In addition, the three-time-constant response is not visible at 15h and 20h of immersion, but rather the HF and MF regions could poorly be distinguished, indicating the presence of two time constants. Thus, the increase in impedance with time in Figure 7 and the conversion of the three- to two-time-constant behaviour could be related to the increase in the corrosion Mg(OH)₂ layer protective performance over time. Also, it is likely that a more protective MgO layer is formed between the Mg(OH)2 layer and WE43 substrate surface, as reported in the literature[75-77]. Past 15h of immersion, the

corrosion resistance decreased, probably due to the rupture of the semi-protective MgO/Mg(OH)₂ film.



Figure 7 Electrochemical impedance response of WE43 Mg alloy in PBS solution after different immersion time

Figure 8 shows the Nyquist plots of coated WE43 Mg alloys recorded after 20h of immersion in PBS; each plot represents the response of the coating deposited during the specified time. The shape of the spectra is different than that for the naked (control) sample (Figure 7) recorded at short times – only one time constant can clearly be seen, characterized by the presence of one

semi-circle. This also indicates the good protective properties of the formed surface coating (better 'blocking' properties).

As the deposition pressure increases (starting from 30Pa), the diameter of the semi-circles changes significantly indicating change in corrosion resistance of the sample. Also, Figure 8 shows that the resistance of the plasma polymer coated specimens is much greater than that of the bare WE43 alloy (Figure 7) after 20 h of immersion in PBS solution, evidencing good barrier properties of the coating. The highest corrosion resistance of the coated sample (100Pa, 40min,20W) is about 340 times that of the corrosion resistance of bare WE43 Mg alloy (1.5 G Ω vs. 4.4 k Ω), which represents the 99.7% protection efficiency against corrosion.





Figure 8 Nyquist diagrams of the plasma polymer coated WE43 Mg alloy with different deposition time: (a) 10min, (b) 20min, (c) 40min immersed in PBS solution after 20h

In order to better present the trend in corrosion resistance with pressure for the three deposition times, the corrosion resistance values from the spectra in Figure 8 were determined (as the difference between the real impedance values (Z') at low and high frequency) and are presented in Figure 9. For the deposition time of 10 min, as the deposition pressure increased from 30 to 60 Pa, the corrosion resistance also increased, but with further increase in pressure, the corrosion resistance decreased. This shows that the best 'blocking' (anti-corrosive) properties of coating at 10min of deposition are obtained at 60 Pa. The trend of the corrosion resistance with pressure at the other two deposition times is different; the maximum is achieved at 100 Pa. However, the resistance at 80 Pa is lower than at 60 and 100 Pa, and it is not currently clear what is the origin of this behaviour. The maximum corrosion resistance was measured to reach 1.5 G Ω , and this is obtained at deposition conditions of 100 Pa and 40 min. However, even when the lowest-resistance coating is considered (30 Pa, 10 min), the corrosion protection efficiency of this coating is 85%.



Figure 9 Corrosion resistance for the plasma polymer coated specimen in PBS after 20h of immersion, determined for coatings formed at different pressures and times.

After immersion of plasma polymer coated samples in PBS for 20h, the sample with highest resistance (100Pa, 40min) was chosen as the best one to continue with long-term immersion tests (up to 10 days) to investigate the effect of immersion time on anti-corrosive behavior of the coating. The resulting spectra are presented in Figure 10. The resulting Nyquist plots are characterized by one time constant, i.e. a semi-circular capacitive loop, whose diameter, and thus the corrosion resistance, depends on the immersion time. The plots evidence a marked decrease of corrosion resistance with immersion time; after 10 days of immersion, the corrosion resistance of the sample decreased from 1357 k Ω cm² to 57.36 k Ω cm². Nevertheless, even after 10 days of constant immersion, the corrosion protection efficiency of the coating is 92%.





Figure 10 Electrochemical impedance of WE43 Mg alloy in PBS during the immersion test, recorded as a function of immersion time.

Chapter 6: Conclusions

An investigation of the corrosion behavior of plasma polymer coated WE43 Mg alloy in PBS was conducted over a time period of 10 days using electrochemical impedance spectroscopy. In this work, the PECVD technique is used to modify the surface of biodegradable WE43 alloy by deposition of a polymer coating.

The main conclusions of this work can be as follows:

- The PECVD was demonstrated to be a good technique for the formation of PPB:N polymer coatings on a WE43 surface
- ii. These polymer coatings were found to significantly affect the corrosion behavior of WE43, by imposing a diffusion barrier for corrosive ions
- iii. With an increase in deposition pressure, the open circuit potential increased towards more noble values, indicating improvement in corrosion resistance of the coating.
- iv. The anti-corrosive properties of the coatings were found to depend on both the deposition time and deposition pressure.
- v. The optimum coating-formation conditions were determined to be at 100 Pa and 40 minutes of deposition; this coating gave a protection efficiency of 99.7% after 20 hours of immersion in PBS.
- vi. Long-term tests evidenced that the PPB:N polymer coating formed on the WE43 substrate can offer 92% of protection efficiency even after 10 days of immersion of the sample in corrosive PBS.

Chapter 7: Future Work

From this work, it was found that the PPB:N plasma polymer coating formed on WE43 performs very well as a corrosion protective layer in PBS at room temperature and over a period of 10 days. However, more work is required to be done to further investigate various properties of the coating under different conditions. The following is a set of suggestions:

- i. All the testing in this study was performed in the PBS solution, which contains only part of the inorganic portion of the body fluid. However, it would be important to evaluate the influence of other inorganic and bio-organic components present in the biological fluid on the anti-corrosion behavior of the coating.
- ii. Analysis of ion release into the solution as a consequence of corrosion can also be performed.
- iii. Change in pH of the electrolyte during long-term immersion of the sample can be monitored since corrosion of Mg is accompanied by a pH increase, which contributes towards formation of more protective Mg(OH)₂ corrosion layer. Since the measurements presented here were done in a static electrolyte, neither the pH could not be controlled nor the concentration of dissolved Mg² ions (both influencing OCP and the corrosion behaviour). Thus, it would be interesting to investigate the anti-corrosive behavior of the coating under continuous electrolyte flow.
- iv. The anti-corrosive properties of the coating should be investigated at physiological temperature (37°C).
- v. The surface and chemical characterization of the PPB:N plasma polymer should be performed using scanning electron microscopy, IR spectroscopy, X-Ray Photoelectron Spectroscopy. Wetting properties of the coating should also be determined, as this plays an important role in anti-corrosive behaviour.

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