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**LASER SURFACE PROCESSING OF
MAGNESIUM ALLOYS**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2019

**LASER SURFACE PROCESSING OF
MAGNESIUM ALLOYS**

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School of Mechanical and Aerospace Engineering

**A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirement for the degree of Doctor of Philosophy**

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

26 March 2019

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Date

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Lam Yee Cheong

Authorship Attribution Statement

This thesis contains material from four papers published in the following peer-reviewed journals and from papers accepted at conferences in which I am listed as an author.

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The contributions of the co-authors are as follows:

- Prof. Sylvie Castagne, Dr. Wang Zhongke, and Dr. Zheng Hongyu provided the initial project direction.
- Dr. Wang Zhongke assisted in the laser experiments and provided guidance in selecting laser parameters.
- Dr. Zheng Hongyu provided suggestions regarding laser material processing.
- I prepared the manuscript drafts. All the manuscripts were revised by Prof. Sylvie Castagne. Prof. Sylvie Castagne provided technical contributions on all papers.
- Dr. Wang Zhongke provided suggestions during manuscripts revision.
- All the manuscripts were checked and approved by Dr. Wang Zhongke, Prof. Sylvie Castagne and Dr. Zheng Hongyu.
- I performed all the laboratory work at the School of Mechanical and Aerospace Engineering and at the Singapore Institute of Manufacturing and Technology. I also analyzed the data.

- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization and Testing.
- Shreyas Kuddannaya provided suggestions and guidance in cell culture experiments, in particular for the poster “Laser irradiation of WE54 surface through simulated body fluid layer”
- Shreyas Kuddannaya shared facilities for cell culture experiments at the biological lab of the School of Mechanical and Aerospace engineering.

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Abstract

Magnesium and its alloys are promising biomaterials for temporary implants. They have superior properties compared to other metallic biomaterials such as high specific strength, biodegradability and physiological compatibility. However, Mg has the inconvenience of rapid degradation at the initial stage prior to the formation of magnesium oxide under an environment of pH ranging from 7.4 to 7.6, which may cause its failure. For Mg and its alloys to be used as a biomaterial, surface properties and morphology should be modified properly to achieve a slow degradation rate as well as biocompatibility.

Laser surface engineering is a promising approach for the surface modification of different materials. The rapidly heating and cooling process during laser-material interactions results in a change in the surface properties with or without changing the properties of the bulk material. As such, laser surface treatment is investigated for the modification of the surface properties of rare earth-Mg alloys to improve the degradation resistance and wettability properties. In particular, the research focuses on the surface modification of WE54 Mg alloy for bio-applications. This alloy is commonly used for aerospace and automobile industry. However, its potential usage for bio-application has not been explored.

Different types of lasers, namely femtosecond, picosecond, and Nd: YAG lasers were employed to gain an understanding of the ultrafast laser-material interaction with WE54 Mg alloy. In particular, the resulting laser irradiated surface structure of WE54 was analyzed. A random microstructure was observed when the surface was irradiated by the femtosecond laser with a pulse energy of 84 μJ . The surface consisted of buds like microstructure, which appeared grey and slightly yellowish. Selective vaporization and change in optical properties of the surface was observed.

A periodic surface structure was observed when the surface was irradiated by the picosecond laser with a pulse energy of 50.2 μJ . This periodic structure can act as a diffraction grating. The initial single scanning observation suggested a change in optical properties of WE54 alloy. Formation of clusters and particles distribution was higher in picosecond laser than that of femtosecond laser. More particles were deposited on the surface during the picosecond laser irradiation process.

Using the Nd: YAG laser, surface irradiation of WE54 was studied at different laser power parameters. Granular, cellular and ripple surface structures were observed with the laser power density of 1.307×10^5 , 2.770×10^5 , and $3.901 \times 10^5 \text{ W/cm}^2$, respectively. Less protruded particles were observed at high laser power density. High power Nd: YAG laser irradiation resulted in the formation of variable surface structures including granular, coarse, flower as well as ripple structures.

The optimized Nd: YAG laser parameters of frequency 10 kHz, 20 mm/s scanning speed, 50% overlapping and 0.001 mm hatching density were used for further treatment and characterization of WE54 alloy. For the degradation behavior in simulated body fluid of WE54 alloy, the surface was irradiated with a laser power density of $2.770 \times 10^5 \text{ W/cm}^2$ (at laser power of 100 W and focal length 152.5 mm). Dissolution of the $\alpha\text{-Mg}$ matrix, as well as melting of second phase particles and their redistribution on the surface, was observed on the laser irradiated surface. The concentration of the Y element was increased from 5% to 12.15 %. The corrosion potential was reduced to less negative values from -1.810 V to -1.503 V. The two weeks immersion test in SBF resulted in weight loss improvement by 30%, namely from 11.43 mg without laser treatment to 7.952 mg after laser treatment.

In addition, Nd: YAG laser treatment had a significant effect on the wetting behavior of the WE54 alloy due to the changes of surface microstructure, surface roughness and oxygen content. With the laser power density ranging from 1.307 to 3.901×10^5 W/cm², the concentration of rare earth elements Y and Nd along the grain boundaries was increased and the overall concentration of Mg was reduced. The changes in the surface structure and chemical elements of WE54 alloy reduced the contact angle from 60.84° before laser treatment to 23.13° after laser treatment. The reduction of contact angle is an indication of better wettability of WE54 after laser irradiation.

Furthermore, to study cell viability on the WE54 alloy, surface irradiation with Nd: YAG laser power density of 3.901×10^5 W/cm² was carried out with SBF solution covering the WE54 surface. During the laser irradiation process, deposition of calcium and phosphate elements, originating from the SBF solution, was obtained on the WE54 surface. The deposited Ca/P layer on the surface of WE54 alloy can act as hydroxyapatite layer for the cells activity. The cells propagation rates on the laser modified surface with SBF solution were faster than for the untreated surface which was verified by the PrestoBlue test for cell viability. The reduction of PrestoBlue reagent changed from 46.83 % in as-received WE54 to 61.34 % in the laser treated surface with SBF. This indicates that the activity of the cells was high for the laser modified surface of WE54 in the presence of SBF solution.

In summary, the interaction of WE54 with different lasers was explored. The Nd: YAG laser was chosen to study the degradation, wettability and cell viability characteristics of WE54 alloy. The laser modified surface of WE54 alloy showed improvement in surface properties by controlling its degradation properties. The laser treatment method with the SBF solution generated a surface with Ca and P ions on WE54 surface and this surface resulted in an improvement in the cells activity.

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Nomenclature

CR	Corrosion rate
I_{corr}	Corrosion current
E_{corr}	Corrosion potential
S_q	Root mean square height
F	Force
f	Frequency
P	Power
Pw	Pulse width
γ	Surface tension
θ	Contact angle
EW	Equivalent weight
γ_{sl}	Interfacial energy between solid and liquid
γ_{sv}	Interfacial energy between solid and vapor
γ_{lv}	Interfacial energy between liquid and vapor
SCE	Saturated calomel electrode
OCP	Open circuit potential
TCL	Tissue culture plates
β	Coefficient of thermal expansion
K	Thermal conductivity
As	Surface area
t	time

CHAPTER 1

INTRODUCTION

1.1 Background information

Magnesium and its alloys are lightweight and high specific strength materials. Their use is well established in automotive, structural, and electronic applications. Self-degradability characteristics of Mg alloys indicate that they can be a potential biomaterial for temporary implant applications. They have a broad range of potential applications in bio-implants; these include dental, bone replacement, joints, human arteries, orthopedic, endovascular and cardiovascular stents. Ceramics, metals, polymers and their composites are used for bio-implants. The fabrication process and embedding of bio-properties in a composite are challenging, whereas a polymer has the disadvantage of low stiffness [1]. Ceramics are brittle and have low toughness. Metals are good for load bearing applications because of their high strength and fracture toughness. Although titanium, cobalt-chromium, and steel bio-implants have a wide range of applications, their corrosion byproducts are harmful to human health [2, 3]. Mg as bio-implant has drawn attention of the researchers because of its physiological benefits [4, 5]. According to the US Department of Health and Human Services, an adult human body contains 24-25 gram of Mg [6, 7]. Unlike titanium and cobalt, byproducts of Mg cause no problem to the human health and moreover, it is excreted by urine [8].

Mg and its alloys have gained popularity in the biomedical field. Mg alloys are recognized for their high compatibility with human tissues due to their mechanical characteristics: Young's modulus and specific density (41-45 GPa, 1.74–2 g/cm³) of Mg alloy are close to those (1.8–2.1 g/cm³, 3–20 GPa) of human bone [9]. Although Mg alloys provide very good properties for

bio-application regarding their low density, high specific strength, and biocompatibility, they suffer from poor corrosion resistance and high reactivity [10, 11].

Kirkland et al. [12] has concluded that Mg alloy is useful as bio-implant because of its unique ability to act as a load bearing implant as well as safely degrade itself in vivo. To consider Mg as bio-implant, it needs to have: appropriate mechanical characteristics to heal the injured tissues, uniform degradation rate during the healing process and good biocompatibility, which is the most important requirement [13]. Previous researches had shown that Mg, and its alloys are bio-degradable. However, their intense degradation rate limits their use in a wide range of applications. Many researchers have been working to control corrosion in Mg and its alloy. Dutta et al. [14] used the laser surface melting technique to improve the pitting corrosion resistance of commercial Mg alloy, which results in grain refinement and redistribution of intermetallic phases of Mg alloy.

Surface topography greatly influences cell behaviors such as adhesion, migration, orientation, guidance, profiling, protein synthesis and segregation, and gene expression, which are essential for tissue formation. By using laser technology, the substrate can be modified to achieve the desired surface topography, which positively supports the growth of tissue and cell behavior. Laser processing is an advanced technology, which has a very simple set up, easy processing and yet a very relevant method for surface treatment. Laser treatment increases the surface hardness and wear resistance of Mg alloy due to grain refinement and solid solution strengthening [15] and can be used for the selective modification of the surfaces.

Under a controlled environment, laser technology can be used to improve the corrosion resistance of Mg alloys. Studies have shown that laser surface melting process enhances corrosion resistance of Mg alloys in NaCl as well as in SBF solutions [16, 17]. By using optimized laser parameters,

the complex structure of a Mg alloy can be generated by laser treatment in the range of micrometer and nanometer. Laser surface micromachining technique utilizes high laser power density available from a focused and localized laser source to melt, heat or modify the material surface. Besides ease of use and flexibility, the laser technique also has the advantage of precise control, which is attractive for laser surface irradiation of potential biomaterials.

1.2 Research Objectives

The goals of this investigation are as follows:

1. To achieve controlled surface properties of the rare earth-Mg alloy by laser surface modification method for potential bioapplication.
2. To study the behavior of rare earth-Mg alloy during ultrafast laser material processing.
3. To study the degradation mechanism and compatibility of laser melted surface of rare earth-Mg alloy in SBF environment.

1.3 Research Scope

The research work includes the following main stages:

1. Modification of microstructure of rare earth-Mg alloy using laser surface melting technique
 - Analyze the laser melted Mg alloys morphologies by using SEM, EDS, and XRD.
 - Wettability analysis of laser melted surface through contact angle measurements.
2. Study and explore the degradation process of Mg alloys under simulated body fluid.
 - Immersion test in the simulated body fluid before and after laser modification.
 - Corrosion rate measurement by potentiodynamic polarization before and after laser treatment.

3. Characterization of material surface properties of rare earth-Mg alloy before and after laser treatment.
 - Characterization of wettability and surface energy of Mg alloys.
 - Characterization of surface morphology and cell viability.
 - Ultrafast laser-material interaction and ablation. Surface structure, morphology, ablation depth, and threshold value measurement.

1.4 Motivation

Literature shows that Mg and its alloy have been used primarily in the automobile and aerospace applications. Apart from this, Mg alloy has also been considered as a potential bio-material because of its bio-degradability, Young's modulus close to the human bone, non-toxicity and physiological benefits as discussed earlier. Recent trends show that Mg alloys fit well as a temporary implant for osteosynthesis. As the injuries heal, Mg alloy degrades, and surgery is not required to remove the implants. The patient is benefitted by not requiring a second surgery, which also saves the cost of surgery [2, 18]. As stated earlier, the degradation property of Mg alloy helps to accelerate bone growth and also possesses anti-bacterial function [19]. The major problem of using Mg and its alloy is its rapid degradation behavior. Several research works have been performed in AZ series Mg alloy. Although these alloys are used as implants, recent studies showed that Al contained bio-implants harm human health because of the toxicity of Al.

Our project aims to investigate the rare earth-Mg alloy as a potential material for bio-implantation, motivated by the initial research of rare earth-Mg alloy as a bio-implant. WE54 alloy with rare earth elements is a new material for bio-implant application though it was developed initially for

aerospace applications. Preliminary research suggested that a Mg alloy containing yttrium and rare earth element enhances corrosion resistance [20-23]. Corrosion resistance in these materials can be improved by various techniques, which are described in chapter 2. Degradation, compatibility and ultrafast laser interaction of WE54 alloy are investigated for a better understanding of the behavior of this alloy. Degradation observation was made in a simulated body fluid (SBF) environment. Evaluation of WE54 as a promising biomaterial was examined by cell viability and wetting characteristics in SBF.

Various types of lasers, namely femtosecond, picosecond and Nd: YAG lasers were employed for surface treatments of WE54. Laser technology is an advanced technique. It is a precise, non-contact, fast and flexible process. It gives clear and uniform structure unlike sandblasting and ion beam processing. A laser has the ability to melt, harden, ablate, and structured the surface as well as changes the phase of the material. Laser technology has been explained in detail in chapter 2.

1.5 Thesis Outline

This dissertation consists of eight chapters. In chapter 1, background information, objective, scope and contributions are presented. Literature review of magnesium alloys, rare earth-Mg alloys, corrosion mechanisms, laser technology, and surface properties improvement methods, are discussed in chapter 2. Chapter 3 presents the materials, methods, and technologies used in this investigation. Chapter 4 describes the behavior of Mg alloys treated with ultrafast lasers. Surface geometry and structure, as well as ablation, were studied. Chapter 5 reports on corrosion behavior of as-received and laser treated Mg alloys. The changes in the surface properties of the rare earth-Mg alloy after laser treatments are discussed. Chapter 6 discusses the biocompatibility behavior of

WE54 alloys as analyzed by their wetting behavior, adhesion behavior and surface energy. Chapter 7 presents the cell attachment behavior in laser treated Mg alloys in SBF environment. Chapter 8 contains conclusions and recommendation for possible future works.

CHAPTER 2

LITERATURE REVIEW

This chapter consists of a literature review on the following topics: introduction of magnesium alloys, the potential of WE series Mg alloy, corrosion mechanisms and corrosion behavior of Mg alloys, bio-application of magnesium alloy, laser fundamentals, laser processing techniques, and laser irradiation in a liquid environment.

2.1 Magnesium alloys

Magnesium is a light weight metal having a density of two-third of aluminum. Besides the low density, Mg possesses high specific strength, good castability and good machinability which make it an attractive material for a wide range of applications. Al, Mn, and Zn containing Mg alloys are commonly used in automotive, structural, and electronic fields. They also have potential for biomedical applications. Pure magnesium itself has limited applications due to its poor corrosion properties. It is commonly alloyed with different alloying elements to improve its corrosion, mechanical and electrochemical properties. In past decades, several Mg alloys were developed based on these requirements. Figure 2.1 shows the trends of Mg alloys developed for surface properties improvement. Al, Mn, Zn, Li, Cu alloying elements are used to improve the specific strength. Al alloying element also plays an important role in the improvement of corrosion resistance. Additions of rare earth elements improve the creep resistance of Mg as well. Mg is reinforced with Al_2O_3 , SiC or C to improve its elastic modulus as well as wear resistance /creep-resistance [24, 25]. In recent years, different Mg alloys are in the developing stage to meet the changing requirements.

Figure 2.1: Trends of Mg alloy development [24]

2.2.1 Properties of Mg and Mg alloys

Mg is the 8th most abundant element in the earth crust. Magnesium is very chemically active. Mg and its alloys are highly flammable, especially in the form of powder. The physical properties of Mg and its alloys used in the current investigation are listed in table 2.1.

Table 2.1: Physical properties of Mg alloys

Property	Mg	AZ31	AZ91	WE54
Melting point (°C)	650±2	566-630	470-595	545-640
Thermal conductivity W/(KgK)	155	96	84	52
Coefficient of thermal expansion (K ⁻¹)	25.2*10 ⁻⁶	26*10 ⁻⁶	27*10 ⁻⁶	27*10 ⁻⁶
Specific heat (J/(kgK))	1030	1040	1000	960
Specific density g/cm ³	1.738	1.78	1.81	1.85

2.3 Mg as a potential biomaterial

Mg as a bio-material was introduced in the first half of 20th century. The first use of Mg in a medical setting was in trauma surgery where a plate of pure Mg with gold plated steel nails was applied to secure the fracture involving the bones of lower legs [26]. However, it was not too successful because pure Mg corroded too rapidly.

Witte et al. [27] used Mg and AZ91 for the subchondral bone replacement. Mg scaffolds was degraded in vivo. The initial high corrosion rate must be reduced to allow the formation of appropriate cartilage tissue. AZ31, AZ91, AM60 were also studied under in vivo experiments to investigate reaction in the human body. Xu et al. [28] studied Mg alloy by implanting Mg in rats to investigate the in vivo degradation behavior of Mg. In this experiment, blood biochemical examination showed that the degradation of Mg does not cause an increase in serum Mg or any disorders of the kidney. Investigation to control corrosion on these Mg alloys based on surface properties had been conducted. AZ (aluminum and zinc) series Mg alloys were widely studied for several years [29-36]. Though AZ Mg alloys have potential as bio-implants, Al contained in Mg is a curse to human health. Al affects the immune system of living beings [37-39]. Experiments on rats showed that Al induced allergic responses and disordered humor immune responses [39]. This limitation promotes further investigation in other types of Mg alloys. In recent years, interest has been growing on rare earth-Mg alloys to explore their potential bio-application. This is promising especially if appropriate improvement in surface properties can be achieved. Rare earth containing Mg alloys have emerged for different applications, due to their good properties such as; creep, temperature and corrosion resistance [40-43].

The advantages and disadvantages of Mg alloy as a biomaterial are summarised below:

- Advantages of Mg alloys

Stress shielding effect: Compared to the other metallic biomaterials, polymers and degradable ceramics, Mg has a good resemblance to human bone in terms of density and elastic modulus. Uneven stress distribution between implant and bone can cause failure of orthopedic devices, which is one of the biggest concerns for biomaterial implants. Stainless steel and Co-Cr alloys have elastic modulus ten times greater than natural bone. Ti and its alloys have their elastic modulus five times greater than human bone. This difference in elastic modulus can be the problem for load-bearing applications because of the mechanical and structural incompatibility between an the implant and a host tissue. Therefore, the use of Mg alloys which has suitable mechanical properties minimizes the stress shielding effect.

Degradability: Mg is biodegradable and can be used in temporary implants. As the injuries heal, Mg alloys biodegrade and they disappear finally. The use of Mg alloys prevents the necessity for a second surgery, as there is no need to remove the implants from the body. This reduces the costs as well as save the patient from the side effects of surgery. Mg ions are essential for the human body. Excessive Mg ions can be excreted through urine. Unlike Mg alloys, other metallic biomaterials are degradation resistant and they are suitable for permanent implant applications. Biodegradability is an essential characteristic which is important for temporary application. In a biological environment, biomaterial should have the ability to withstand corrosion depending upon the applications.

Density and specific strength: Mg and its alloys are light weight metals with density ranging from 1.74 to 2.0 g/cm³, which is much less than that of the biomedical Ti alloy (4.4–4.5 g/cm³) and

close to that of the bone ($1.8\text{--}2.1\text{ g/cm}^3$) [44]. Pure Mg has a strength to weight ratio of approximately 130 kN m/kg; however rapidly cooled Mg alloys can reach 490 kN m/kg.

In addition, Mg and its alloys are biocompatible. It can be defined as the ability of biomaterials to perform the desired functions without any rejection, inflammation, and irritation with the host tissues, i.e. acceptance of artificial implant by the surrounding tissues and the whole body as a part of it. The surface of biomaterials should provide channels for blood supply and help in biochemical and biological processes for tissue generation. It should not be toxic to tissues. Summing up, Mg biomaterials are nontoxic, non-immunogenic, supportive and bio-stable.

- Disadvantages of Mg alloys

Rapid degradation: Although Mg alloys are biodegradable; they degrade too quickly at pH ranges from 7.4 to 7.6, which is the major problem for implant performance. Mg and its alloys can corrode too quickly under physiological conditions, resulting in early loosening or disintegration of the implants before the tissue has sufficiently healed. The degradation behavior of Mg alloys should be improved to establish them as a biomaterial. Rapid degradation of Mg alloys releases corresponding ions quickly, which can cause adverse effects in biological system. The unnecessary and excess ions of alloying elements such as Zn, Ca and Mn can be toxic, causing respiratory and neurological problems.

Hydrogen evolution: Degradation of Mg releases hydrogen gas. The release of hydrogen gas is proportional to the degradation rate of Mg. In the human body, the evolved hydrogen bubbles from a corroding magnesium implant can be accumulated around the implant, which will delay healing of surgery region and lead to necrosis of tissues. The accumulated hydrogen gas pocket can cause separation of tissues and tissue layers. Rapid degradation of Mg can release a large

number of hydrogen bubbles. The bubbles can be present in the blood circulating system; there will be a risk that the bubbles may block the blood stream.

2.3.1 Rare earth Mg alloys

Research on AZ series of Mg alloys has been conducted for decades. The problems of instability of AZ Mg alloys and effects of corrosion products are big challenges. The potential toxic effect of Al on human body leads to the alternative search of Al-free Mg alloys. Recently, different types of Mg alloys containing Ca, Zn, Mn as well as rare earth elements have been explored. WE series of Mg alloys are of great interest. They contain Y, Nd, Ce and Gd rare earth elements, i.e. WE43 and WE54. For aerospace and automobile applications of Mg alloys, rare earth elements were used to develop new Mg alloys which enhance their creep resistance [45].

Reports have shown that in a chloride environment, the corrosion resistance of Mg alloys was enhanced by their rare earth elements. Yttrium containing WE54 and WE43 alloys have good corrosion properties. Due to the presence of rare earth elements, a passive thin layer, which acts as a temporary protective layer against corrosion, is formed in the surface. This passive layer helps to reduce corrosion to a certain extent [22, 46-48]. Studies indicated that by using surface modification techniques, the surface properties of alloys could be improved and so does their biocompatibility. Davenport [49] showed that Nd-rich intermetallic particles and Y-rich regions of the matrix could reduce the corrosion rate of as-cast WE43. Heat treatment of WE43 to homogenize the Y distribution improves its corrosion resistance. Passivation behavior of rare earth-Mg alloys was reported in several literatures [20, 23, 42, 50-52].

He et al. [23] found that the Y content above 0.36% in Mg-2Zn-1 Mn caused the formation of a Y_2O_3 protective surface film under Hank's solution at 37 °C; the cathodic current of Mg alloy was

decreased, which improved corrosion resistance. It was reported that phytic acid coated WE43 alloy showed improved corrosion resistance when the sample was tested by hydrogen evolution test and potentiodynamic polarization test in SBF environment [53]. When WE43 was tested in phosphate buffered solution, the weight loss rate of WE43 increased gradually up to 48 hours, and after 48 hours the weight loss rate was decreased up to 96 hours. After 96 hours, the mass loss rate was stable and constant [54]. This is beneficial for potential bio-application.

In isotonic saline and in simulated body fluid environments, the presence of rare earth elements in WE54 alloy increases corrosion resistance when compared to that of pure Mg [21, 55, 56]. Somla et al. [21] experimented on T4 and T6 heat treated WE54 alloy in isotonic saline (9 gm/l NaCl, H₂O) for 24 hours. It was found that the corrosion rate was 80 times lower than that of commercial Mg alloy.

Wang et al. [57] studied the biodegradability and biocompatibility of WE series alloys in different concentrations of yttrium and neodymium elements. They found that an addition of rare earth (RE) elements reduced the corrosion resistance and increased cell viability and hemocompatibility [57]. Investigation showed that an increased percentage of Y and Nd increased the tensile and yield strength as well. Therefore, literature suggested that a rare earth-containing Mg alloys can be a potential candidate for bio-applications.

2.4 Corrosion of Mg and Mg alloys

Corrosion is the degradation of the material by reaction with its environment. All corrosion processes have electrochemical reactions. Mg is chemically unstable and starts to corrode with the release of hydrogen gas. Corrosion rate of Mg alloys depends on various factors such as

microstructure, porosity, alloying elements, pH level, temperature, manufacturing processes, albumin, grain size etc.

2.4.1 Corrosion mechanism

The standard electrode potential of Mg is -2.37V but it is less in an aqueous solution. Mg is used as the sacrificial anode [58]. When Mg reacts with the solution, it starts to corrode by leaving hydrogen gas and Mg hydroxide as its byproducts. In an aqueous environment, the corrosion of Mg may be described by the following reaction :

Anodic reaction

Cathodic reaction

Product formation

General reaction

Figure 2.2: Electrochemical corrosion on Mg surface [59]

In figure 2.2, Mg reacts with water and forms Mg hydroxide with the generation of hydrogen gas. Different types of corrosions occur in Mg and its alloys. Mg alloys are highly susceptible to galvanic corrosion. When pure Mg is coupled with a large cathode, the current density increases at the anode and the corrosion rate also increases. Galvanic corrosion can be significantly reduced by selecting proper material, design, and use of coating and insulation. Figure 2.3 (a) shows that the external galvanic corrosion occurs due to dust, contamination, and exposure to a corrosion environment. Figure 2.3 (b) shows internal galvanic corrosion. Internal galvanic corrosion is due to impurities and poor design.

Mg is also susceptible to pitting corrosion. Pitting corrosion is a form of localized corrosion. The attack is confined to the numerous small cavities (pits) on a metal surface. Generally, corrosion pits initiate at the flaws adjacent to a fraction of secondary phase particles such as $Mg_{17}Al_{12}$, $AlMn$, $Mg-Y$, as a result of the breakdown of passivity. Usually, precipitation and segregation occur at the grain boundaries, and intergranular corrosion occurs in the grain boundaries of Mg alloys.

Figure 2.3: (a) External Galvanic Corrosion, (b) Internal Galvanic Corrosion [59]

Intergranular corrosion attack in Mg and its alloys at the grain boundaries was observed [11]. Crevice corrosion can occur in a confined space due to oxygen depletion. Any layer of solid matter or deposit on the surface of a metal can cause crevice corrosion. Crevice corrosion is very destructive since the damage is much localized. Stress corrosion cracking of Mg alloy can occur in moist air, high purity water, NaCl+K₂CrO₄ solution, NaBr, Na₂SO₄, NaCl, NaNO₃, Na₂CO₃, H₂SO₄, KF, KCl, NaI, MgCO₃, NaOH, H₂SO₄, HNO₃, and hydrogen chloride solutions. Hydrogen reduces the cohesive strength of Mg alloy, hence resulting in hydrogen embrittlement [60]. There are many factors that affect corrosion of Mg alloys. The influencing factors are described below:

- Alloying element:

In recent years, studies indicate that the presence of rare earth element in Mg alloy contributes to good corrosion resistance [23, 61-66]. Extruded Mg-Zn-Mn alloy with Y element was tested in Hank's solution at 37°C. XPS results showed the formation of passive layer Y₂O₃ after 360 seconds of ion etching [23], see figure 2.4.

Figure 2.4: (a) XPS analysis of Mg-Zn-Mn-Y alloy, (b) binding energy showing passive layer

Addition of 0.7 - 0.8 % Nd in AM50 and AZ91D alloy reduced corrosion rate by 90 %. Addition of Nd reduces surface potential and formation of intermetallic compound and thus suppressed micro galvanic couples [67]. The general and pitting corrosion resistances of calcium-containing Mg alloy in modified-simulated body fluid was significantly improved as compared to a pure Mg alloy [68]. Hence, it was observed that the alloying element helps to refine grain structure, promote intermetallic phases and can enhance corrosion resistance. WE54 alloy has 5% yttrium and 4% rare earth elements. The corrosion resistance of Mg-*x*Gd-3Y-0.4Zr alloys decreases with an increase of Gd content from 6% to 10% and then increase from 10% to 12%. [69]. The presence of these alloying elements is believed to increase corrosion resistance.

- Microstructure

Microstructure of a metallic material plays an effective role in corrosion. There are fine grain (uniform) and coarse (random) grain structures. Grain with random size promotes corrosion. Intergranular corrosion attacks grain boundaries and degrades material from the surface. In

chloride media, it was discovered that fine lamellar microstructure of AZ80 alloy formed a wall to block the attack of corrosion [70]. In post degradation analysis, the micro structural difference between a fine-grained die-cast and a coarse-grained sand-cast Mg-based alloys has a significant effect. Experiment on coarse microstructure revealed degradation rate could be controlled by ageing Mg alloys [71]. Extruded Mg alloy of grain size 15 μ m has lower corrosion resistance than as cast Mg alloy with 100 μ m grain size [72]. In Mg-Y-RE_Zr alloys, it was found that the central zirconium-rich areas within the grains of the alloys were more corrosion resistant than the outer zirconium-depleted areas of the grains [73].

- Phase

Mg has a different phases which influences corrosion behavior. High aluminum content alloy like AZ91 has an appreciable amount of beta phase ($Mg_{17}Al_{12}$ along α grain boundaries). Corrosion attacks the Al depleted region between the beta phase lamellae along the grain boundary but passivates after a few minutes of propagation [36, 74]. When tested on 5% NaCl solution, a significant effect of β phase was found [75]. β phase provides a barrier for corrosion. Hydrogen surface potential of Mg alloy [76]. This ultimately helps to prevent corrosion.

The observation of phases of WE54 on corrosion presented an attractive but challenging avenue to control the corrosion rate. In Mg-Y binary alloy, the Y contained intermetallic has an effective role in the corrosion process. In 0.1 M NaCl environment, the corrosion rate increases with increasing Y content attributed to increasing amounts of the Y-containing intermetallic [77]. Further, corrosion propagated by filiform corrosion following corrosion initiation locally due to the presence of the second phase.

- Manufacturing process and heat treatment

Production process also influences the corrosion behavior of Mg alloys. The rapid solidification process can refine the microstructure which is beneficial to the corrosion properties. Production technique has an effect on the properties of the material. Zhang [64] showed the properties difference between as-cast and extruded alloy and Wang et al. [78] showed the effect of alloying elements produced from the extrusion process.

Heat treatment is another factor which affects the microstructure of Mg alloys. Aging allows Al atoms diffuse towards grain boundaries and form precipitation of γ phase. This reduces the aluminum concentration in an α -Mg matrix of Mg-9Al alloy from 9% to 3% [59, 79]. Zheng [80] mentioned that aging reduced the corrosion rate of Mg-Al alloys in chloride solution. Effective heat treatment leads to a lower corrosion rate. Mg–Y–RE–Zr after 3 h of aging (grain centers, rich of zirconium) exhibits better corrosion resistance than the zirconium-depleted edge areas of the grains [73]. Kannan et al. [55] reported that heat-treatment procedure enhanced the passivity in WE54 alloy but the pseudo-passive film resistance was inferior to that of AZ91 alloy. Therefore, the heat treatment of those alloys highly influences their corrosion behavior.

- Albumin and influence of pH value

Albumin is another factor which affects the degradation behavior of Mg alloys. Bio-implants react with the proteins in our body and alter the corrosion process and properties. In the presence of albumin, the range of passivation region of Mg alloy AZ31 and LAE442 was extended [81]. When a magnesium surface was exposed, magnesium oxide was formed. In the presence of moisture, magnesium hydroxide was produced. At pH value between 8.5 and 11.5, it can form a thin oxide

protective layer. Above pH 11.5, the protective qualities of magnesium hydroxide layer dominate the corrosion behavior.

2.5 Laser technology and laser processing of materials

2.5.1 Laser fundamentals

A laser (beam) is a light generated from the stimulated emission of radiation. Laser light has unique properties viz; high monochromaticity, a high degree of both spatial and temporal coherence, capability of continuous power output and capability of being focused to a small diffraction limited spot size. When the electron drops down from an excited state to a lower energy state, it releases energy which is equivalent to the energy of the photon. This phenomenon is called spontaneous emission. Photon has a particular wavelength, direction, and phase. By population inversion when electrons are excited and shift to the higher level, then this photon emits another equivalent photon which is called stimulated emission. *“An optical resonator causes the light generated by the active medium, parallel to its axis, to be reflected back and forth through the medium”* [82]. Ultimately, this action of stimulated emission and amplification generates highly monochromatic, coherent and unidirectional light as an output. During the operation of laser, atoms are energized from the ground state to the excited state by pumping.

A laser system consists of three main components: (1) amplifying medium, (2) means of exciting the medium to its amplifying state or pump source and (3) an optical resonator. The active medium comprises of materials that produce energy-carrying photons of specific wavelengths when excited. The pump source is determined by the type of active medium used. Examples of pump sources include flash lamps and electrical discharges for Nd: YAG and CO₂ media, respectively. The optical resonator, in its simplest form, is composed of two parallel mirrors, one fully and one

partially reflective, placed around the active medium to filter and transmit photons that fully satisfy specific conditions for oscillation.

2.5.2 Laser surface processing

Laser surface engineering is a promising approach for surface modification of different materials. A high energy laser beam is capable to generate rapid rates of heating and cooling. This process can lead to non- equilibrium cooling resulting in grain refinement, morphology change, phase transformation and change in chemical composition of surface without changing the properties of the bulk material. Compared to other surface modification techniques such as sand blasting and machining, laser surface processing is a direct process which can provide uniform surface structure. Photolithography has well-controlled feature, but it is a multistage process. Electron and ion beam processes require vacuum. Laser has overcome the problems of these conventional techniques and laser is a fast and non-contact process. The characteristics of these processes are summarized in table 2.2. Unlike the coating method, laser processing does not have issue of poor adherence of surface with bulk material.

In the past, laser technology has been used to improve surface properties such as mechanical, corrosion, wear and wettability properties of materials. There are reports on the efficiency of laser material processing to achieve better surface properties [83-85]. Laser micromachining is very fast, so it is good for mass production. Different patterns can be formed according to the applications. Laser is capable of producing complex 3D structures and uniform grooves. Laser machining is advanced and has more advantages than the conventional one.

Table 2.2: Surface modification techniques [86].

Process	Characteristics
Sandblasting	Random surface textures, Messy process Difficulty in controlling regularity of features
Photolithography	Well-controlled features Problems with multistage process
Electron beam processing	Precise control, up to nanofeatures Requires vacuum
Ion beam processing	Charged ions bombarding surface for texturing Requires vacuum
Laser micromachining	Precisely controlled complex features Fast, clean, non-contact process

There are various types of laser treatment processes for magnesium alloys surface as shown in figure 2.5. Laser surface melting is a process of melting the surface of the material with high laser energy density without changing physical topography. After melting, resolidification occurs within a very small timeframe and refines the grain structure. Many researches have provided data on improving the corrosion resistance of Mg alloy by laser surface melting [14, 87-90]. Walid et al. [91] performed laser treatment on ZE41 Mg alloy and they found that the melted Mg alloy presented a homogenous distribution of the alloying elements in the Mg matrix. The laser surface melting treatment increased the micro hardness of the ZE41 Mg alloy and also improved its corrosion resistance.

Figure 2.5: Overview of laser surface engineering of Mg

For Mg alloys, high power CO₂ and Nd: YAG lasers are generally used . Mg is highly reactive in nature. As such, experiments of Mg and Mg alloys should be performed under shielding inert gas to avoid the surface oxidation.

Laser surface alloying is a process of adding another element in a molten pool of bulk material. Processing parameters should be carefully optimized so that there is significant melting of alloying elements and formation of new modified surface. In laser composite surfacing, hard ceramics particles are introduced in the melted surface of bulk material which resolidifies to form a new surface. A drawback of this process is the undesirable effect of interfacial reaction between the reinforced particles and matrix which needs to be minimized. In laser surface cladding, chemically different materials are fused with the melted bulk material. For magnesium alloys, it is also one of the potential techniques to improve surface properties.

2.5.3 Surface morphology

Surface morphology is also one of the crucial factors which determine surface functionality. Investigation suggested that surface texture of tissues, joints, and bones varies from nanometers to micrometers. Protein adsorption and cell attachment are directly related to surface topography. Grid, chaotic, dimpling, honeycomb, troughs, porous, an array of pits, craters, dendrite, square, wavy, grooved surfaces were studied [90-98]. Micro-grooves, pores and array patterns are found in dental implants [99]. Creased, roughened and smooth textured surfaces were obtained by laser surface melting with a defocusing laser beam. Laser parameters highly influence the formation of surface geometry of Mg alloys. Flat energy intensity distribution was obtained by lowering the laser energy and defocusing which also had an effect on surface geometry [93].

Figure 2.6: Titanium surface textured with femtosecond laser (a) Peaks and troughs
(b) ridges superimposed on the surface [100].

By laser nitriding, dendrite and needle-like structures were obtained with a pulse frequency of 2000Hz CO₂ laser, whereas it also damaged the surface due to the deposition of materials on the surface [97]. Cone, porous, groove and ridge structures were found in titanium implants created by laser [92, 94, 100]. Figure 2.6 (a) shows peaks and troughs that measure ~250 nm in width, 10

μm in height and $15\ \mu\text{m}$ at the base, tapering to $\sim 1\ \mu\text{m}$ at the peak. Figure 2.6 (b) shows $250\ \text{nm}$ ridge texture across both pillars and troughs [100].

Most of the comparative studies were conducted on ridge and groove types topography. Bones are porous ranging from 6 % to 30%. Porosity and pores interconnectivity are important as they control the level of oxygen and nutrient transport through the scaffold and they influence the proliferation of functional cells. Some literature suggest that movement of a cell in a scaffold was effective above $100\ \mu\text{m}$ [101, 102]. The range of pore sizes which promotes bone growth is $100\text{-}500\ \mu\text{m}$. This range supports capillaries growth and allows the bone cell to bridge pores [102].

ZE41 Mg alloy was textured by Excimer laser to increase corrosion resistance. Material was lost by evaporation with the high power density ($160\ \text{MW cm}^{-2}$). There was formation of wavy surface morphology with successive hollows and hills as shown in figure 2.7. The maximum laser melted depth was $70\ \mu\text{m}$ [91]. This investigation was succeeded to improve corrosion resistance.

Figure 2.7: Excimer laser textured ZE41 Mg alloy with hills and hollows geometry [91].

2.5.4 Ultrafast laser interaction

Ultrafast lasers have provided significant contributions in various fields such as surface cleaning, micro-structuring, thin film deposition, ablation, cutting, drilling etc. Surface functionalization of a wide range of materials can be achieved by modifying tribological, chemical, mechanical,

wetting, optical and electrical properties of materials by ultrafast lasers. The unique micro/nano surface structures produced by femtosecond laser have potential applications in the different fields. Studies have also been conducted on various metals, e.g., aluminum, zinc, copper, titanium, steel, Mg with laser parameters such as laser ablation threshold, the effect of pulses and ablation efficiency. Random / periodic / groove / columnar structures were observed on these metals [103, 104].

Ultrafast laser structures can be categorized as laser irradiated structures and self-organized structures [105]. Laser-irradiated structures can consist of micro/nano structures. Nanostructures have random and periodic patterns whereas microstructures have undulating grooves, columnar, hole and maze structures. Barada et al. [106] have reported self-organized conical micro/nano structures on Ti sheets by direct laser texturing. They showed that the conical microstructure and the inter cone distance was highly dependent on the laser fluence.

The optical, hydrodynamic and plasmonic effects could be the key factors for creating the conical surface structure. Laser-induced periodic surface structures (LIPSS) can be classified into two main types: low spatial frequency LIPSS (LSFL) and high spatial frequency LIPSS (HSFL). The LSFL periodic surface structures, which are perpendicular to the polarization of the incident laser beam, have a spatial period close to the laser wavelength. The HSFL periodic surface structures, which are either perpendicular or parallel to the polarization of the beam polarization, have a spatial period much smaller than the laser wavelength. The formation of periodic structures depends upon the spatial energy distribution. The interference between the incident laser beam and scattered optical wave at the metal surface leads to a periodic distribution [107, 108]. Metal colorization in different metals as a result of femtosecond laser structuring has been reported [109,

110]. Vorobyev et al. [110] reported that highly reflective metals can be changed to highly absorptive due to the color change induced by laser irradiation.

Laser surface melting of magnesium alloys by continuous wave Nd: YAG, excimer and CO₂ lasers [16, 111] have been widely reported. However, little research has been reported on ultrafast laser structuring of magnesium alloys [35, 112]. Guan et al. [109] reported nano and micro ripples formation on femtosecond laser irradiation on AZ31B Mg alloy. The formation of micro ripples was attributed to the combined effect of surface roughness and near field interference. The formation of the nano ripples on the AZ31 surface was due to the interference between incident light and surface plasmons. The structured Mg alloys can be useful for structural and implant applications.

2.6 Surface modification techniques and laser

Corrosion can be prevented by coating, ion implantation, thermal spraying, sputtering etc. For coating, the coating material degrades after a certain time. Fluoride and alkaline coatings on Mg alloys surface decreased corrosion rate by 50% to 80% respectively [113]. However, a major challenge for coating is the lack of perfect adhesion between bulk material and coating substrate [114]. Another disadvantage is crack formation on the coating surface of Mg alloys. These are not desirable for medical applications. From the viewpoint of a bio-implant, analyses of surface chemistry, coating morphology, adhesion, wear, and corrosion rate are necessary.

An alternative to coating is surface modification of the bulk materials to obtain the required properties. This avoids the difficulties of cracking and the lack of perfect adhesion between coating the bulk materials. Laser surface modification methods are versatile, fast and direct. When the

surface structure is designed which is compatible with the tissue, the surface can be irradiated with laser by controlling the appropriate laser parameters.

CO₂ laser, Nd: YAG laser, excimer laser, diode laser, and time bandwidth ultrafast laser are available for surface texturing of biomaterials. CO₂ laser has disadvantages in that it can cause surface oxidation and brittle rim which reduce the lifetime of surface geometry. Wettability properties could be influenced also by surface oxidation [86, 115].

Ultrafast lasers directly vaporize the material, therefore less heat is generated. The relatively small amount of heat produced by each pulse has plenty of time to disappear before the next pulse arrives. Ultrafast lasers (femtosecond and picosecond) have advantages of consistency, precision, reduce thermal loading and quality products [61, 116-119].

2.7 Degradation improvement through laser surface modification

A laser is an effective tool for surface modification of biomaterials [120]. By microstructure modification, phase transformation, melting and solidification, and surface texturing, the properties of the material can be improved for various applications. Laser surface melting (LSM) enhanced wear and degradation resistance of biomaterials [14, 15, 36]. By laser surface modification, the corrosion properties of Mg alloys could be improved [43, 91, 99, 106, 121-126]. The corrosion resistance of Mg alloy can also be improved by laser surface melting [14, 87-90]. Walid et al. [120] discovered that the laser melted ZE41Mg-alloy contained a homogenous distribution of the alloying elements in the Mg matrix.

Uniform microstructure and distribution of phases were obtained in AZ31, AZ61, and WE43 by LSM. 1mm depth WE43 surface was melted by CO₂ continuous wave laser. Laser modified WE43 showed better corrosion resistance, reducing weight loss by 87%. Studies on these alloys suggest

that a uniform distribution of β phase acts as a barrier for corrosion [88]. Microstructure of as-received commercial AZ Mg alloy was coarse-grained and precipitate along grain boundaries. After LSM, grain refinement was obtained with crack and defect free microstructure [14]. Laser surface treatment can also change the chemical composition on the surface [14, 111].

Laser parameters play a vital role to obtain effective surface properties of Mg alloys. At different combination of the laser parameters, different degradation behavior and rate can be obtained. Surface morphology highly affects the degradation behavior of Mg alloys. Therefore, these present opportunity of using laser surface treatment to improve degradation behavior of material by modifying its surface properties viz: microstructure, phase, grain size, chemical composition, and surface morphology.

2.8 Laser and wettability characteristics

Few investigations have been reported on Mg-Al alloys on the improvement of wetting characteristics after laser irradiation. Guan et al. [127] have reported a significant improvement in surface energy (from 25.80 to 40.76 mJ/m²) of laser melted AZ91D. The formation of a continuous network of β phase at the dendrite / cellular structure and the enrichment of Al resulted in the improvement in the corrosion and wettability properties. Demir et al. [128] studied the wettability of laser structured AZ31 Mg alloy in water. They concluded that the oxidized surface has a tendency to reduce the contact angle. A laser structured surface with entrapped air has a tendency to increase the contact angle.

Ho et al. [129] have reported the bio-wettability of AZ31B Mg alloy under SBF solution. The enhancement of bio-wettability was due to the combined effect of surface roughness, grain size,

surface morphology, and surface chemistry. A surface with low roughness and homogenous chemical compositions provides better bio-wettability.

Enhancement in bio-wettability is necessary for the growth and activities of the cell. Nie et al. [130] have reported corrosion and biocompatibility of rare earth Mg alloy (Mg-6Gd-0.6Ca) by using continuous wave fiber laser and pulsed Nd: YAG laser. They have reported that corrosion resistance of alloy was improved by LSM. After surface texturing on melting surface, corrosion resistance was decreased. However, biocompatibility properties have been enhanced by surface texturing. Cell adhesion and proliferation highly depend upon the wetting characteristics of a biomaterial.

Lawrence et al. studied the wettability characteristics of laser modified surfaces of different materials such as Mg alloys, titanium, and mild steel [83, 131]. The effective changes on wetting properties of Mg alloys and mild steel were achieved with lasers of different wavelengths, namely CO₂, Nd: YAG, excimer and high power diode lasers [83, 130].

2.9 Laser surface irradiation of metals through liquids

Laser irradiation in a liquid medium is one of the effective methods to obtain the desired surface morphology and deposition of thin films on the surface. Ouyang et al. [132] have studied Nd: YAG laser treated Al alloys in air, isopropanol, distilled water and glycerin respectively. Laser ablation of Al in liquids resulted in the formation of porous surface structures in the craters of Al. Generation of the porous surface was due to the phase explosion mechanism. With femtosecond laser irradiation of Ti surface through a confined layer of supersaturated HA suspension, Yang et al. [133] observed the deposition of Ca/P elements on the microstructure surfaces. In contrast, the deposition of ions was not observed on the surface when the surface was irradiated through an

unsaturated solution of CaCl_2 and Na_3PO_4 [133]. With femtosecond laser ablation through simulated body fluid (SBF), Wang et al. [134] also reported micro-patterns with deposited calcium/phosphorus (Ca/P) elements on pure titanium (Ti) surface. They concluded that the femtosecond laser ablated surface could grow cell faster than the sand blasting and acid etching surfaces. In vitro cell culture of osteoblasts in Ca/P deposited femtosecond irradiated surface showed a positive response [133].

Hayat et al. [135] studied laser ablation in ethanol with an excimer laser. Cavities and less debris depositions were observed at both low (2.8 J/cm^2) and higher (4 J/cm^2) laser fluences. With 200 fs pulse laser irradiated through water, Katayama et al. [136] observed ring pattern from 500 nm to 10 μm in a laser-treated silicon surface. The reason for the ring pattern was water bubble oscillation, and deformation occurs by acoustic pressure.

CHAPTER 3

MATERIAL AND METHODS

In this chapter, types of materials and methodologies used are presented. Different types of lasers employed for surface modification of Mg alloys are introduced. Corrosion behavior of Mg alloy was observed in simulated body fluid by different corrosion test techniques. Different characterization techniques used to identify the surface structure and properties are described.

3.1 Materials

The materials studied under are: WE54, AZ91 and AZ31. Their chemical compositions are listed in tables 3.1 and 3.2.

Table 3.1: Chemical composition of AZ series alloys (wt. %)

Mg alloys	Al	Zn	Mn	Si	Fe	Ni	Cu	Ca	Other	Mg
AZ91	8.9	0.7	0.2	0.02	0.003	0.001	0.005	-	<0.3	balance
AZ31	2.8	0.72	0.24	0.01	0.003	0.001	<0.0005	<0.005	-	balance

Table 3.2: Chemical composition of WE54 (wt. %)

WE54 element	Y	Nd	Mn	La	Li	Zr	Zn	HR	Mg
WE54	5.5	1.7	0.01	0.05	0.05	0.4	0.08	1.2	balance

WE54 contains 1.2 % heavy rare earth elements (HR), and 2.96% in total for rare earth (TR) elements, with 0.3% for total other elements (TO). AZ91, AZ31 and WE54 alloys were extruded

with dimensions of 31.75 mm in diameter and 1000 mm in length. These materials were supplied by Magnesium Elektron, UK. They were cut into small circular disk of 31.75mm in diameter and 3mm thick for the purpose of laser modification after polishing and etching.

3.2 Laser

Three types of lasers were used for surface treatment, namely a Rofin Nd: YAG laser, picosecond laser and femtosecond laser. The specifications of these lasers are shown in table 3.3. A Rofin Nd: YAG 500 watt nanosecond pulsed laser, having a wavelength of 1064 nm and pulse duration of 38ns was used for laser surface melting of Mg alloys. This laser is also suitable for laser alloying, laser hardening as well as laser ablation. Time bandwidth duetto picosecond laser having a wavelength of 1064 nm and power 10 W was used for surface structuring of Mg alloys. Quantronix Integra C, a femtosecond laser, having power of 1.5 W was used for surface irradiation study.

Table 3.3: Specification of lasers

Laser Types	Model	Average energy (W)	Pulse duration (s)	Wavelength (nm)	Repetition rate (kHz)
Rofin_Nd:YAG laser	AVIA Diode Pumped Solid State UV laser	500	38×10^{-9}	1064	6-15
Duetto_Picosecond laser	Time-Bandwidth PS _Duetto laser	15	12×10^{-12}	1064	50-750
Femtosecond laser	Quantronix Integra C	1.5	130×10^{-15}	795	1.0

3.3 Sample preparation

All the Mg alloys specimens were polished with abrasive SiC papers from 320 to 4000 grade followed by 3µm diamond polishing, ethanol cleaning and drying. All the consumables for polishing were supplied by Struers. Subsequently, fine polish was achieved using Md mol and Mol disc, followed by diamond suspended particles and Md chem disc polishing. Finally, the surface was etched to reveal its microstructure before and after laser surface treatment of the Mg alloys. To observe clean and clear microstructure, selection of etchant is important. The specifications of the etchants used are as follows:

- 19ml water, 60ml ethylene glycol, 20ml acetic acid and 1ml nitric acid
- Acetic picral: 5ml acetic acid, 6g picric acid, 10ml water and 100ml ethanol (95%)

Both etchants were tested and acetic picral showed better result for all AZ31, AZ91 and WE54 alloys.

3.4 Corrosion experiments

Corrosion experiments were performed by potentiodynamic polarization (PDP) and immersion method under simulated body fluid environment and sodium chloride solution. Their results were cross checked and analyzed. Experiments were performed before and after the laser surface treatments. Corrosion experiments methods are described in section 3.4.2 and 3.4.3.

3.4.1 Sodium chloride and simulated body fluid (SBF)

Sodium chloride and simulated body fluid (SBF) were used as a solvent in the corrosion experiments. 3.5% NaCl solution was used to examine the corrosion density and corrosion susceptibility. Simulated body fluid (SBF) was used for in-vitro degradation test in which ion

concentration is equivalent to human body plasma. This allows the degradation behavior to be predicated for potential biomaterial. The SBF chemicals concentrations [137] are listed in table 3.4.

Table 3.4: Simulated body fluid reagents concentration

Order	Reagent	SBF	1.5SBF
0	Total volume	1000ml	1000ml
1	Ultra-pure water	750 mL	750 mL
2	NaCl	7.996 g	11.994 g
3	NaHCO ₃	0.350 g	0.525 g
4	KCl	0.224 g	0.336 g
5	K ₂ HPO ₄ • 3H ₂ O	0.228 g	0.342 g
6	MgCl ₂ • 6H ₂ O	0.305 g	0.458 g
7	1 kmol/m ³ HCl	40 cm ³	60 cm ³
8	CaCl ₂	0.278 g	0.417 g
9	Na ₂ SO ₄	0.071 g	0.107 g
10	(CH ₂ OH) ₃ CNH ₂	6.057 g	9.086 g
11	1 kmol/m ³ HCl	Appropriate amount for adjusting pH	

3.4.2 Potentiodynamic polarization

Potentiodynamic polarization was used to study the in-vitro degradation behavior of Mg alloys. Potentiodynamic polarization can provide significant information on corrosion mechanisms, corrosion rates, and susceptibility of specific materials to corrosion in designated environments. It

provides information on the kinetic and thermodynamic differences between various alloys and solutions.

Solarton 1287 potentiostat was used to measure potentiodynamic polarization. It is a three - electrode system; the Mg alloy of interest act as a working electrode, silver chloride (AgCl_2/Ag) as a reference electrode and graphite as a counter electrode. Figure 3.1 shows a schematic diagram of the potentiodynamic corrosion set up for the experiments.

Figure 3.1: Schematic experimental set up for potentiodynamic polarization test

Before potentiodynamic polarization, open circuit potential (OCP), i.e. without connecting the counter electrode with the reference electrode, was run to stabilize the potential of the working electrode, and the value of the stabilized OCP was recorded. Subsequently, the counter electrode is connected to the reference electrode for carrying out the potentiodynamic experiment to obtain the corrosion current between the reference electrode and the working electrode (Mg alloy of interest). This current was used to calculate the corrosion rate. Corrosion potential between these

two electrodes could also be obtained. Both corrosion current and potential were measured for Mg alloys of interest before and after laser surface treatment. Based on the Faraday's Law the corrosion rate equation is [138]:

$$\text{Corrosion rate, CR} = K_1 (\rho_{\text{corr}}/\rho) \text{ EW} \quad (3.1)$$

$$\text{Weight loss rate, MR} = K_2 i_{\text{corr}} \text{ EW} \quad (3.2)$$

Where CR is given in mm/y, i_{corr} in $\mu\text{A}/\text{cm}^2$, K_1 in $3.2710 \cdot 10^{-3} \text{ mmg}/\mu\text{Acm}^2\text{y}$, MR in g/m^2 , K_2 in $(8.954 \cdot 10^{-3}) \text{ gcm}^2/\mu\text{Acm}^2\text{d}$ and EW is equivalent weight in gram

3.5% NaCl solution and SBF were prepared and corrosion studies were carried out in a Model K0235 Flat cell kit using three electrodes. The scan rate in the potentiodynamic polarization was set as 0.5mV/s and 1mV/s. Two variables are used to determine the corrosion rates i.e. current i_{corr} (A/cm^2) and voltage E_{corr} (V_{SCE}). The experiment was conducted in SBF solution and the corrosion rates were calculated for different laser treated substrates.

3.4.3 Immersion test

AZ31, AZ91 and WE54 were immersed in SBF and their weight degradation was noted in different time intervals. i.e.: 8, 24, 48, 72 and 96 hours. Weight loss was measured by subtracting the weight of Mg alloy after the immersion test from the weight before the immersion test. Corrosion rate was calculated by weight loss and the surface area exposed to SBF. Immersion test reveals how much corrosion occurred but it does not reveal the corrosion mechanism.

Weight of sample before immersion = M_a (g)

Weight of sample after immersion (without corrosion products) = M_b (g)

Surface area of Sample= A_s (cm²)

Immersion time = t (hrs.)

Corrosion weight loss rate = C (mm/yr) and it is calculated as follows:

$$C = (M_a - M_b)/(A_s t) \quad (3.3)$$

3.5 Cell culture

Mesenchymal stem cells were obtained from the National University Hospital (Singapore) under an Institution Review Board (IRB) approved protocol. The isolated cells were cultured in a medium (DMEM based expansion medium supplemented with 10% Fetal Bovine Serum (FBS)), 100 µg/ml penicillin, 100 µg/ml streptomycin and 2 mM Glutamax™ prior to seeding them into a culture flask. MSCs were cultured at 37 °C under a humidified atmosphere with 5% CO₂. After 24 h, the non-adherent cells were washed away by rinsing the flask with sterile 1x PBS and fresh medium was added. The adhered MSCs were further expanded until reaching confluence with medium changes during alternate days. The cells were finally harvested and seeded on three different substrates: the native (unmodified Mg), SBF treated and control substrates. These were used in cell culture with a seeding density of 10,000 cells/cm² in 6-well plates.

3.6 PrestoBlue analysis and cell viability

PrestoBlue® cell viability reagent was used to estimate the relative levels of proliferation activity of hMSCs on Mg substrates. Mg substrates were placed in 6 well plates for cell culture. Cell cultures were performed for 3 hours and 8 hours interval in a Dulbecco's Modified Eagle Medium (DMEM) at 23° C in an incubator. In general, DMEM is the most suitable medium for many

adherent cell phenotypes among the defined media for cell and tissue cultures. After cell culture, DMEM medium was removed and the cells were washed twice with 1x PBS solution.

Subsequently, cells were incubated with 10 vol % PrestoBlue reagent diluted in DMEM cell expansion medium for 1 h at 37 °C in an incubator. Following the incubation, equal volume of reacted medium were collected from each well of the respective culture plates.

The absorbance of the reduced PrestoBlue reagent was read at 570 nm (excitation wavelength) and 600 nm (emission and reference wavelength) with a Multiskan Spectrum microplate reader (Thermo Scientific, Singapore). The reduction percentage of PrestoBlue reagent is proportional to the viable cells.

3.7 Optical Microscope and Scanning Electron Microscope (SEM)

Optical and scanning electron microscopes were used for microstructure imaging. JEOL 5600 LV scanning electron microscope was used in this study. In SEM, when electrons penetrate into the sample within a very short distance, active signal is generated. These signals lead to the formation of an image. It can also be used for the identification of the chemical composition of the sample's surface since the brightness of the image formed by backscattered electrons increases with the atomic number of the elements. Mg samples were etched to visualize the microstructure in SEM. In the SEM, a EDS system is attached, which is used for the quantitative elemental analysis. It consists of an excitation source (electron beam or x-ray beam), the X-ray detector, the pulse processor and the analyzer. The EDS is facilitated with point X-ray mapping, elemental mapping and phase mapping. The accuracy of EDS can be affected by various factors such as, overlapping peaks, nature of sample and direction of emission.

3.8 X-Ray Diffraction (XRD)

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. This phenomenon is called X-ray diffraction. XRD is a non-destructive technique. It is used to identify crystalline phases and orientation of materials, determine structural and chemical properties, identification of fine grained minerals and determination of unit cell dimensions.

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge the inner shell electrons of the target material, characteristic X-ray spectra are produced. Different phases of Mg were detected from XRD before and after laser treatment. The majority of phases in a surface were detected before and after corrosion test. The corrosion product should be removed and clean before performing XRD.

3. 9 Wettability and contact angle

Contact angle measurement was used to evaluate the wetting characteristics of Mg alloys before and after laser surface treatment. Contact angle measurement quantifies the wettability of a solid surface by a liquid via the Young equation. Basically, this system includes a CCD camera, a dosing system, a stage for sample placement and a light source, see figure 3.2. Liquid droplet is released from the syringe to the material surface. The contact angle between a substrate and a liquid is recorded by a CCD Camera. The wetting characteristics are highly influenced by surface

roughness, oxygen content, surface microstructure and surface energy. In this study, SBF was used to investigate the bio-wettability of laser treated surface of rare earth Mg alloy. A three liquid method was used to determine the surface energy of WE54. An Attension THETA AUTO-D tensiometer was used for the wetting measurements.

Figure 3.2: Schematic diagram of contact angle measurement system

Figure 3.3 illustrates the contact angle between solid, liquid and gas, with θ equal to 90° indicating neutral wettability.. The interfacial energy can be calculated based on the Young's equation.

γ_{sl} = interfacial energy between solid and liquid, dyne/cm

γ_{sv} = interfacial energy between solid and vapor, dyne/cm

γ_{lv} = interfacial energy between liquid and vapor, dyne/cm

θ = contact angle

Figure 3.3: Schematic illustration of contact angle measurement [139]

3.10 Surface profilometer

Taylor Hobson profilometer is used to measure surface profiles of Mg alloys, namely surface roughness and geometry. The stylus profilometer, with stylus of diameter 2 μm was used to contact the surface. The profilometer has a movable stage in the ZX direction, and the stylus moves vertically to maintain surface height and to detect the surface. It operates based on force feedback and physically touching the sample surface.

CHAPTER 4

LASER INTERACTION WITH Mg ALLOY

This chapter details the ultrafast laser-material interaction with WE54 Mg alloy. Femtosecond, picosecond and nanosecond laser surface irradiation of WE54 Mg alloy were investigated. In particular, the effective response of rare earth elements during laser structuring and the surface structure formation mechanisms were studied. The investigation of ultrafast laser structuring suggests that the surface properties created by laser structuring of WE54 can be controlled with proper laser processing.

4.1 Laser parameters

Laser interaction with WE54 alloy was studied by using a 1.5-watt QUANTRONIX Integra-C femtosecond laser, 10 watt DUETTO time bandwidth picosecond laser and a 500-watt pulsed nanosecond laser. Various laser pulse repetition rates and scanning speeds were used in Nd: YAG laser material processing.

For the femtosecond laser, 100 to 1500 pulses were used progressively to create a single and multiple craters in WE54 Mg alloy. To scan a (10 x 10) mm² surface area in open atmosphere environment, the following femtosecond laser parameters were employed: 795 nm wavelength, pulse duration 130 fs, repetition rate 5 kHz, scanning speed 200 mm/s, focal length 163 mm and hatching density 0.01 mm. The laser focus was maintained by using a camera.

Similar procedure was applied for picosecond laser texturing. The picosecond laser textured a (10 x 10) mm² surface area of WE54 alloy with the following laser parameters: 1064 nm wavelength, pulse energy 50.2 μJ, repetition rate 50 kHz, pulse duration 10 ps, focal length 100 mm, scanning

speed 200 mm/s and hatching density 0.01 mm. The picosecond laser experiments were performed in a closed chamber with a vacuum machine to remove dust.

Both femtosecond and picosecond laser surface irradiations were performed at focused beam condition. Single and multiple craters were created at different pulse energy with different number of pulses to obtain a ablation threshold fluence. Cross section profile of laser textured surface, surface roughness and particle size distribution were obtained with a profilometer.

Various repetition rate and scanning speed were used in the 500-watt pulsed nanosecond laser (Nd: YAG laser) material processing. The threshold pulse energy was calculated by using a craters diameter and a pulse energy relationship from equation 4.1. The calculated ablation threshold fluence was used to scan the WE54 surface. The experimental details are further described in sections 4.6.1 and 4.6.2.

4.2 Crater Formation

The single and multiple row craters were created by the femtosecond laser to understand the relation between the crater depth and laser fluence. The ablation threshold fluence is the minimum amount of laser energy required to ablate the material from the surface. The single pulse threshold fluence was investigated by single shot crater formation, known as the D^2 method. The single pulse ablation threshold can be obtained from the linear relationship between the square of the crater diameter and the logarithm of the laser fluence. The threshold energy was analytically calculated by using the following equation [140]:

$$D^2 = 2W_0^2 \ln(E/E_{th}) \quad (4.1)$$

where D is the diameter of the crater which can be measured by a profilometer. W_0 is the radius of beam measured at $(1/e^2)$ intensity. E is the applied laser energy during the experiment. E_{th} is the threshold energy which is the energy required to form the crater.

Different laser pulse energies were applied to ablate the material. 100 to 1500 laser pulses were applied to observe the effect of pulses on the surface of WE54. The affected area increased with an increased number of pulses. Figure 4.1 (a) shows the effect of a single laser pulses at 28 μJ with no ablation. The crater in figure 4.1 (b) resulted from ablation by 500 laser pulses with a pulse energy of 84 μJ . There was deposition of ablated material around the crater surface. The deposited material was highly enriched with MgO. Figure 4.1 (c) shows the effect 1500 pulses on the surface of WE54, resulting in the formation of a larger circular crater than that from the 500 pulses. The ablation depth can be measured by the surface profilometer or it can be calculated by the following equation [141]:

$$d = 1/\alpha_{eff} \ln (E/E_{th}) \quad (4.2)$$

α_{eff} represents the effective absorption coefficient. The linear relationship between the ablation depth and the logarithm of laser energy provides the multi-pulse ablation threshold. When the surface is in the laser focused plane, the threshold pulse energy and threshold fluence for the 500 laser pulses used in this study were (84 μJ , 11.39 J/cm^2), respectively. The crater depth at the multi pulse threshold fluence is nearly 1.1 μm . Figure 4.1 (d) shows the multiple craters created at the 500 multi pulse threshold pulse energy demonstrating the consistent ablation of craters.

Figure 4.1. Crater formation by femtosecond laser: (a) Single laser pulse at energy (28 μJ) lower than the threshold value (84 μJ). (b) at 500 pulses, and laser pulse energy and threshold fluence (84 μJ , 11.39 J/cm² respectively). (c) at 1500 laser pulses, showing larger affected area, d) multiple craters at laser pulse energy 84 μJ , showing consistent crater formation.

Similarly, if the surface is in the laser-focused plane, the threshold pulse energy and threshold fluence were (50.2 μJ , 13.21 J/cm²) respectively, employed for the picosecond laser. Using a similar procedure, the crater depth of picosecond laser ablated surface was found to be approximately 2 μm . Picosecond and femtosecond lasers have entirely different specifications and they provide different results when texturing on the same material. Multiple craters were created at the threshold energy and the variation in depth was analyzed.

4.3 Surface Structuring with Femtosecond / Picosecond Laser

Single pass scan was performed on WE54 Mg alloy surface. Random micro structure was observed when the surface was textured by the femtosecond laser at the 500 multi pulse threshold energy of 84 μJ . The surface consists of buds like structure when viewed in low magnification (400x) as shown in figure 4.2 (a). Grey and slightly yellowish colors were seen when the surface was viewed from different angles (visually and through a microscope). Guan et al. [109] reported the term iridescent effect which occurs because of the nano ripples caused by laser irradiation act as a diffraction grating and eventually induces color on the surface. The grey color surface indicates that the optical properties of the surface have changed after texturing. In addition, oxidation was induced during laser material processing. The oxidation layer can also cause color change on the surface. 6.7% oxygen content was observed on the surface. Similarly, the change in the concentration of Y element from 5.5% to 8% was observed in femtosecond laser texturing. Selective vaporization occurred during laser-material interaction. The Mg element vaporized directly whereas yttrium element was gradually ablated with an increasing number of laser scanning.

Similarly, picosecond laser was used to single pass scan on WE54 Mg alloy surface. Figure 4.2 (b) shows the micro-structure on the surface by picosecond laser. A periodic structure was observed at the micro scale with a grey appearance when viewed by a naked eye. The surface was seen to have an arrangement of crests and troughs. The enlarged view, which represents the white portion of figure 4.2 (b), was enriched with Y element. The element was detected by the EDS analysis. The major elements identified on the laser textured surface were Y, Nd, and Mg. These elements can form different stages of $(\text{Mg}_a\text{Y}_b, \text{Nd}_c)$ phase, where a, b and c are variables. It has been reported that evaporation of Mg occurs due to its low melting and boiling points compared to other elements

in Mg alloy during laser surface melting [111]. The melting and boiling points of Mg are 650 °C and 1090 °C whereas the melting and boiling points of (Y and Nd) are (1523 °C and 1010 °C) and (3337 °C and 3127 °C), respectively.

In picosecond laser texturing, a change in element concentration has been observed. The concentration of Y was increased from 5.5% to 11% after texturing with picosecond laser whereas the concentration of Nd was increased by only 0.5%. Mg element of WE54 was vaporized quickly as compared to the Y element of WE54. The thermal conductivity of Mg is $156 \text{ Wm}^{-1} \text{ K}^{-1}$ at room temperature whereas the thermal conductivity of yttrium is $17.2 \text{ Wm}^{-1} \text{ K}^{-1}$. It indicates that the thermal properties of the material such as heat capacity, heat of vaporization, heat of fusion and optical properties play an important role during ultrafast laser irradiation.

When 5 times line scanning was performed on the WE54 surface, the surface was changed into a dark color when viewed by a naked eye. This color change is due to the light trapping properties of metal [106]. The active interaction of rare earth elements has been observed. The white portion was minimized, with a reduction of Y element concentration as the number of scanning was increased from 1 to 5 times.

The micro/nano structure with colored appearance can be used in photovoltaics, artificial colorization, and bio-optical devices. The single and multi-colors surface can be obtained by the use of proper laser parameters [142]. The periodic structure formed by laser texturing can act as diffraction grating. The single scanning observation demonstrated the change in optical properties of WE54 alloy by both femtosecond and picosecond lasers.

Figure 4.2. Single scan laser texturing by (a) femtosecond laser at 84 μJ (500 pulse threshold energy), (b) picosecond laser texturing of WE54 at 50.2 μJ (500 pulse threshold energy)

4.4 Surface Morphology

A profilometer was used for the quantitative analysis of the textured surface. A random (buds like) structure was found in the micro scale by femtosecond laser texturing. The linearly polarized laser was incident on the surface of WE54. The polarization of the laser was horizontal. It was observed that the structure formed on the surface was parallel to the laser polarization direction. Figure 4.3 (a) shows the 3D view of laser textured surface by femtosecond laser. The ridges on the

femtosecond laser textured surface of WE54 ranged from $0.3\ \mu\text{m}$ to $1\ \mu\text{m}$. The cross section profile of ridges is shown in figure 4.3 (c).

A periodic surface structure was created by picosecond laser texturing on the WE54 surface. Figure 4.3 (b) shows the 3D view of laser textured surface by picosecond laser. The ridges on the picosecond laser textured surface of WE54 ranged from $0.3\ \mu\text{m}$ to $2\ \mu\text{m}$ as shown in figure 4.3 (d).

Figure 4.3: Representative surface morphology by (a) femtosecond laser, $84\ \mu\text{J}$ and (b) picosecond laser, $50.2\ \mu\text{J}$, respectively. Cross-section profile of textured surface (c) by femtosecond laser, (d) by picosecond laser.

The surface roughness (S_a) of as-received WE54 used for laser texturing was $37.82 \pm 2.182\ \text{nm}$. The average three-dimensional surface roughness (S_a) of femtosecond laser textured surface were $0.535 \pm 0.034\ \mu\text{m}$. Figure 4.4 (a) shows the cluster distribution on the femtosecond laser textured surface. The particle size of protruded particles was $8\ \mu\text{m}$ in femtosecond laser textured surface at

threshold fluence of 84 μJ . The maximum number of cluster distribution in femtosecond laser textured surface was 800/ mm^2 as shown in figures 4.4 (a).

The average three-dimensional surface roughness (S_a) of picosecond laser textured surface were $0.858 \pm 0.145 \mu\text{m}$ respectively. Figure 4.4 (b) shows the cluster distribution on the picosecond laser textured surface. The structure is highly dependent upon the laser wavelength (1064 nm) and laser fluence (50.2 μJ) of the picosecond laser. The particle size of protruded particles was 3 μm in picosecond laser textured surface at threshold fluence of 50.2 μJ . The cluster distribution can be dense as 1800 / mm^2 in picosecond laser.

Figure 4.4: Size distribution of protruded particles of irradiated structure of laser textured surface at threshold pulse energy with 500 laser pulses: (a) femtosecond laser at 84 μJ , b) picosecond laser at 50.2 μJ

4.5 X-ray Diffraction Analysis

In as-received WE54 alloy, the grain boundaries were enriched in Y and Nd elements as observed by electron dispersive spectroscopy (EDS). Generally, compounds are formed from the precipitates of Nd and Y along the grain boundaries. The microstructure of WE54 consists of α -

Mg matrix and secondary phase as Y and Nd precipitates. Figure 4.5 shows the X-ray diffraction graphs of as-received and laser textured surface of WE54 alloy.

In figure 4.6, **A** represents the α -Mg phase, **B** represents $Mg_{24}Y_5$ and **C** represents $Mg_{41}Nd_5$ phase which were analyzed by Panalytical X'Pert HIGHSCORE Plus software and compared with the standard data. X-ray diffraction analysis showed that the intensity of peaks decreased after laser surface texturing. The elements present in the WE54 also play a vital role during laser texturing. The intensity ratio of Mg- α phase decreased significantly to 0.075 after laser irradiation of WE54 alloy. The Mg- α phase was eliminated from some portion of the surface, which was shown in figure 4.5 XRD pattern of as received, femtosecond and picosecond textured surfaces.

Figure 4.5 (a) demonstrates the XRD pattern of as received WE54 alloy. **A**, **B** and **C** represent α Mg, $Mg_{24}Y_5$ and $Mg_{41}Nd_5$, respectively. Figure 4.5 (b) represents the XRD patterns of femtosecond laser textured surface and peaks are named accordingly. Figure 4.5 (c) represents the XRD peaks of picosecond laser textured surface.

Figure 4.5: X-ray diffraction pattern showing different phases of WE54 Mg alloy, a) as-received, b) femtosecond laser textured surface (84 μ J) and c) picosecond laser textured surface (50.2 μ J).

4.6 Nano second pulsed Nd: YAG laser interaction with rare earth Mg alloy

A 500 watt pulsed nanosecond Nd: YAG laser has very high energy delivery. In 100% power, the 3mm thickness WE54 was totally converted from solid metal into powder. Power of 100 W to 250 W is better suited to study melted, textured and ablated surface of rare earth-Mg alloy. When the pulse repetition rate is high, the energy delivery is less or vice versa.

4.6.1 Nd: YAG laser interaction: repetition rate and laser fluence

Various pulse repetition rates, namely 6, 8, 10, 12 and 15 kHz were studied. Figures 4.6 (a) and (b) at different magnifications (700x and 2000x) show the granular surface structure of the WE54 surface irradiated with a laser fluence of 4.63 J/cm² and 6 kHz repetition rate. Protruded particles were observed. Granular surface structure with some oxide particles were observed in the magnified image shown in figure 4.6 (b). Oxide and yttrium elements were observed on the WE54 surface from energy dispersive spectroscopy (EDS). Uneven surface structure was observed with laser energy of 3.47 J/cm² energy and 8 kHz repetition rate as shown in figures 4.6 (c) and (d).

With a laser energy density of 2.78 J/cm² and 10 kHz repetition rate, large particles as well as uneven surface, were formed, see figures 4.6 (e) and (f). The thermal conductivity of magnesium is very high. The Mg element will therefore response first to the thermal effect of the laser pulse. Other elements, such as yttrium and neodymium, will respond subsequently. The surface will melt when the surface temperature reaches its melting point. This is followed by vaporization (ablation), with Mg the first element to vaporize. The interaction of laser pulses with the other elements and their ablation caused their ejection from the surface and later re-deposition on the surface.

This process resulted in the formation of protruded particles on the surface. An oxide layer was formed on the laser irradiated surface of WE54. Figures 4.6 (g), (h) show the irradiated surface by 12 kHz repetition rate and laser energy density of 2.31 J/cm². Overlapping zones can be seen in these images. A flower structure was observed with a magnified view (1500x) in figure 4.6 (h). Similar results were observed when WE54 surface was irradiated with laser parameters of 15 kHz and 1.85 J/cm² as shown in figures 4.6 (i) and (j).

Figure 4.6: Nd: YAG laser irradiation of WE54 with 100 W power and various repetition rates, (a) and (b) 6 kHz, (c) and (d) 8 kHz, (e) and (f) 10 kHz, (g) and (h) 12 kHz, (i) and (j) 15 kHz

Figure 4.7 represents the 3D surface topography of the laser irradiated surface of WE54 Mg alloy at various repetition rates and laser energy densities. Figure 4.7 (a), shows an irregular surface and few ridges on the surface. The maximum depth of the Nd: YAG laser irradiated surface is $10 \pm 2.836 \mu\text{m}$. Figure 4.7 (b) shows a very rough surface with an average surface roughness of

$3.08 \pm 1.263 \text{ } \mu\text{m}$; the particles sizes on the surface were approximately $22 \pm 3.12 \text{ } \mu\text{m per mm}^2$. The maximum valley of the surface measured was $12.9 \text{ } \mu\text{m}$. Figure 4.7 (c) shows a very wavy surface with clear ridges formed. The material was deposited on the overlapping zone. Surfaces created by laser fluence of 2.78 J/cm^2 and 2.31 J/cm^2 have similar surface topography, but with particles sizes of $25 \pm 3.14 \text{ } \mu\text{m}$ and $32 \pm 3.784 \text{ } \mu\text{m}$ respectively, see figures 4.8 (c) and (d). Figure 4.7 (e) shows the 3D topography of 1.85 J/cm^2 laser modified surface with protruded particles.

Figure 4.7: 3D surface topography of Nd: YAG laser irradiated surface of WE54 Mg alloy (laser pulse repetition rate is indicated in each figure)

Figure 4.8 (a) shows the peak count distribution of protruded particles in 1mm x 1mm area. The sizes of the particles were $12 \mu\text{m}$ per mm^2 . When the laser energy density was $1.85 \text{ J}/\text{cm}^2$, the size of the particles was $35 \pm 3.067 \mu\text{m}$, see figure 4.8 (e). When the surface was at the defocused plane of 2.5 mm and laser pulse repetition rate of 10kHz, the protruded particles sizes were around $0.9 \pm 0.023 \mu\text{m}$, see figure 4.8 (f). The surface was very smooth with less deposited particles.

Figure 4.8: Particle size distribution of the laser-irradiated surface of WE54 Mg alloy at defocus plane of 2.5mm with laser pulse repetition rates of a) 6 kHz, b) 8 kHz, c) 10 kHz, d) 12 kHz, e) 15 kHz, f) 10 kHz

4.6.2 Effect of a scanning speed of nanosecond pulsed Nd: YAG laser

Rare earth Mg alloy surface was irradiated with 100 W, 13 kHz repetition rate with various scanning speeds. For the 100 W Nd: YAG laser, the resulting surface was almost covered with an oxide layer with a scanning speed of 5 mm/s; there was significant formation of oxide, see figure 4.9 (a). At 100 W laser power and 5 mm/s scanning speed, a very round granular structure was

created with a surface oxide layer, see figure 4.9 (b). At lower speed, the heat accumulation on the surface is very high resulting in larger irradiation depth.

Figure 4.9: Nd: YAG laser irradiation of WE54 with (100W, 13 kHz) at different scanning speeds. (a) and (b) 5mm/s. (c), (d) and (e) 10mm/s. (f), (g) and (h) 20mm/s. (i) and (j) 100mm/s.

Figure 4.9 (c), (d), and (e) represent different parts of the WE54 surface irradiated with a scanning speed of 10 mm /s. The surface was less oxidized but the material was deposited at the laser scanning end area and the starting corner of the surface as shown in figure 4.9 (d). Some parts of the surface were melted, see figure 4.9 (e). The surface was uneven with melting. Figure 4.9 (f), (g), and (h) represent the laser irradiated structure with 20mm/s scanning speed. Dendrite/cellular structure was observed in 20 mm/s scanning speed. When the laser was defocused at the 2.5 mm plane, melted surface was observed as shown in figure 4.9 (h). At scanning speed of 100mm/s, the surface was hardly ablated as shown in figures 4.9 (i) and (j). When as received WE54 surface was polished and cleaned before laser irradiation, the surface was very shiny. This leads to the reflection of some laser energy and in very high speed the surface was less irradiated.

4.7 Conclusion

Different types of lasers, namely femtosecond, picosecond, and Nd: YAG lasers have been employed to gain an understanding on the ultrafast laser-material interaction with WE54 Mg alloy, in particular the laser irradiated surface structure of WE54. Random micro structure was observed when the surface was irradiated by the femtosecond laser with a pulse energy of 84 μJ . The laser irradiated surface consisted of buds like micro structure, which appeared grey and slightly yellowish. Selective vaporization and change in surface optical properties were observed. A periodic surface structure was observed when the surface was irradiated by the picosecond laser with a pulse energy of 50.2 μJ . This periodic structure can act as a diffraction grating. With single scanning, a change in optical properties of WE54 alloy was observed.

With Nd: YAG laser, surface irradiation of WE54 was studied with laser energy from 1.85 J/cm^2 to 4.63 J/cm^2 . Granular, uneven (coarse) and flower surface structures were observed with laser energies of 4.63 J/cm^2 , 3.47 J/cm^2 and 2.31 J/cm^2 , respectively. Less protruded particles were observed when the surface was at the laser defocused plane of 2.5 mm with laser repetition rate of 10 kHz and power of 100W.

CHAPTER 5

CORROSION BEHAVIOR STUDY OF MAGNESIUM ALLOYS

Corrosion behavior of WE54, AZ91, and AZ31 Mg alloys was studied in 3.5% NaCl and simulated body fluid (SBF) solutions by using immersion and electrochemical tests. The microstructure and weight loss of Mg alloys and laser melted WE54 Mg alloy were studied during the two-week of immersion test.

5.1 Corrosion conditions

The compositions of AZ31, AZ91, and WE54 are described in chapter 3, section 3.1. Specimens were cold mounted to expose an area of 1cm x 1cm. The polished surface was exposed to 100 ml 3.5% NaCl and SBF solutions respectively. The study of corrosion behavior under sodium chloride provides an indication of the general corrosion behavior for engineering applications. SBF solution was used to understand the bio-degradation process of Mg alloys.

Electrochemical polarization was carried out using Solartron 1287 potentiostat. The standard three electrode system was adopted to conduct the polarization test; AgCl₂/Ag was used as the reference electrode, graphite as the counter electrode and Mg alloys as the working electrode. Open circuit potential (OCP) was conducted for 30 minutes to stabilize the potential before the polarization experiments. Potentiodynamic polarization (PDP) was carried out at a scanning rate of 1mV/s and 90 minutes experiment running time. Data were recorded and analyzed by CorrWare® and CView™ Software. The microstructure and corrosion morphology of the specimens were characterized by an optical microscope (OM) and JEOL 5600LV scanning electron microscope (SEM). The corrosion products were identified by energy dispersive spectroscopy (EDS).

For the immersion test, the weight loss was measured at different time intervals. Finally, corrosion products were removed in a solution of 10% chromium oxide and 1% silver chromate in 100 ml of water. The specimens were dipped into the solution for 5 minutes, followed by ethanol cleaning and drying by flowing air. The room temperature for NaCl immersion test was 21⁰C whereas corrosion performance in SBF solution was studied at 37⁰ C, close to human body temperature. The composition of SBF has been presented in chapter 3.

5.2 Laser surface treatment

Before laser surface melting, the specimens were grounded from 320 to 2400 grit SiC paper followed by ethanol cleaning and airflow drying. LSM was carried out with a 500-watt nanosecond pulsed Nd: YAG laser; it has a wavelength of 1064 nm, repetition rate of 12,000Hz and pulse duration of 38ns. The laser parameters employed were: power density 2.77×10^5 W/cm², repetition rate 10,000Hz, scanning speed 20mm/s, and overlap 50%. The flat top hat beam (focal length 152.5mm) was defocused to 2.5mm. 1 cm by 1cm surface was irradiated in a closed chamber nitrogen gas environment. After laser surface irradiation, the surface was slightly polished and etched with an acetic-glycol solution (20 ml acetic acid, 1 ml HNO₃, 60ml ethylene glycol, and 20 ml water), followed by ultrasonic ethanol cleaning for 5 minutes.

5.3 Microstructure

Figures 5.1 and 5.2 represent the microstructure of extruded AZ91 and AZ31 alloys respectively before the corrosion test. In figure 5.1, the black portion on the grain boundaries represents the β -

Mg₁₇Al₁₂ phase. The extruded AZ91 and AZ31 Mg alloys have primary α -Mg matrix, eutectic Mg phase, and β -Mg₁₇Al₁₂ phase. The concentration of Al is higher in AZ91 and exists in the form of β phase. The grains were not uniform in all Mg alloys. The presence of Mn elements on grain boundaries was observed by EDS, indicating the presence of AlMn precipitates. Discontinuous intermetallic β -Mg₁₇Al₁₂ was observed in both AZ91 and AZ31 alloys by OM and SEM. As measured by the Heyn lineal intercept method according to the ASTM standards, the average grain sizes of as-received AZ91 and AZ31 were approximately $10.32 \pm 4.16 \mu\text{m}$ and $8.53 \pm 3.49 \mu\text{m}$ respectively.

Figure 5.3, shows the microstructure of WE54 alloy. The extruded WE54 has an α -Mg matrix separated by grain boundaries consisting of secondary phases. The compounds were formed from the precipitates of Nd and Y along the grain boundaries in the WE54 alloy, which may contain Mg₁₂Nd/Mg_aNd_b and Mg₂₄Y₅/Mg_aY_b [143-145] where **a** and **b** are variables. EDS showed the presence of Nd elements in the grain boundaries. The average grain size of as-received WE54 was approximately $25.5 \pm 3.17 \mu\text{m}$.

Figure 5.1: Optical micrographs of AZ91 before corrosion test.

Figure 5.2: Optical micrographs of AZ31 before corrosion test.

Figure 5.3: Optical micrographs of WE54 before corrosion test.

5.4 Electrochemical test (potentiodynamic polarization test)

The potentiodynamic polarization curve for the three Mg alloys under 3.5% NaCl solution is shown in figure 5.4. It provides information on corrosion potential E_{corr} (V)/AgCl₂/Ag and corrosion current density (I_{corr} (mA / cm²)). From figure 5.4, the corrosion potential of AZ91, AZ31, and WE54 in 3.5% NaCl solution are -1.458, -1.438 and -1.736 V, respectively. The corresponding value of I_{corr} of AZ91, AZ31, and WE54 are 1.497, 2.528 and 0.655 mA/cm², respectively. In a

3.5 % NaCl solution, WE54 has a current density less than that of AZ31 and AZ91 alloys. However, the susceptibility of WE54 alloy towards corrosion is high according to the corrosion potential. It has been reported that the corrosion potential of WE54 was -1.8 V, which was 64 mV higher than our results [146]. The differences in reference electrode and temperature might be the reasons for this 64 mV difference in corrosion potential value. From the potentiodynamic curves, both AZ alloyed Mg alloy, and WE alloyed Mg alloy did not show high passivity in NaCl solution. In a 3.5 % NaCl solution, WE54 has a current density less than that of AZ31 and AZ91 alloys. However, the susceptibility of WE54 alloy towards corrosion is high according to the corrosion potential.

The polarization curve of figure 5.5 provides the electrochemical data for AZ91, AZ31 and WE54 alloys in a SBF corrosive medium. The corresponding corrosion potential V vs (AgCl₂/Ag) of AZ91, AZ31 and WE54 are -1.483, -1.577 and -1.810, respectively, whereas the corrosion current densities (mA/cm²) are: 0.349, 0.962 and 0.401, respectively. The instantaneous corrosion rate of WE54 alloy is lower than that of AZ91 and AZ31 alloys under SBF environment at 37°C temperature. As indicated above, the difference between corrosion current density of AZ91 and WE54 is noticeable under similar conditions. Cathodic current gradually increases in WE54 alloy whereas in AZ91 and AZ31 alloys, the current flow is higher. The anodic curve of AZ91 is quite stable in the beginning as compared to that of AZ31 and WE54. In WE54 alloy the dissolution of α -Mg matrix also occurs gradually as shown by the anodic potentiodynamic curves in figure 5.5.

Figure 5.4: Polarization curves of AZ31, AZ91, and WE54 alloys in 3.5% NaCl solution at room temperature.

Figure 5.5: Polarization curves of AZ31, AZ91 and WE54 alloys in the SBF solution at 37°C

In the tested samples of AZ91, AZ31, and WE54, there was heterogeneous distribution of phases with a major portion as α phase as shown in figures 5.1, 5.2 and 5.3. The distribution of phases (α phase, β phase, and eutectic α) on the surface highly depends upon the manufacturing process and solidification rate. Corrosion behavior depends upon alloying elements of Mg alloys. Yttrium and aluminum elements are the main corrosion resistance elements in WE54 and AZ Mg alloys

respectively. The locations and distributions of micro-constituents on the sample surfaces are responsible for corrosion.

5.5 Immersion test

5.5.1 Corrosive media: 3.5% NaCl solution

Figure 5.6 shows the surface morphology of corroded Mg alloys which were exposed to 3.5% NaCl solution. Chloride ions are very corrosive towards Mg alloys. The surface oxide film is converted into $\text{Mg}(\text{OH})_2$ at the initial stage of the corrosion process. The dissolution of Mg further increases because of the presence of Cl^- ions which react with $\text{Mg}(\text{OH})_2$, forming more soluble MgCl_2 [18]. Therefore, the presence of Cl^- ions further promotes the corrosion of Mg. Hydrogen bubbles could be observed visually when the Mg alloys were immersed in the NaCl solution. Due to surface tension, the bubbles were retained on the metallic surface [32]. At 1 hour, AZ91 and AZ31 showed a thread/cross-linked structure in some locations of the exposed surface as shown in figures 5.6 (a) and (b) while other parts have a negligible reaction with the corrosive solution. The attacked surface was the Mg- α matrix around the intermetallic phase. After 2 days, AZ91 was corroded on some parts of its surface and its material loss increased gradually as shown in figure 5.7. The corrosion morphology of AZ91 in 3.5% NaCl was similar to the morphology caused by 5% NaCl reported in [147]. Figures 5.6 (d) and (e) represent the corrosion morphology of AZ91 and AZ31 after 14 days of immersion. A massive loss of material was observed on the surface of AZ91 as shown in figure 5.6 (d). In figure 5.6 (e), several pits were observed on the AZ31 surface.

Raman et al. [30] described that the die cast AZ91D showed a steady decrease in corrosion rate up to 6 days, except for the initial 24 hours of a slight increase in corrosion rate. In this study, steady

decrease in corrosion rate of AZ91 was not observed. Extruded AZ91 and AZ31 alloys have no continuous and uniform distributions of $Mg_{17}Al_{12}$ phase which promotes the corrosion rate.

A passive film was observed on the surface of WE54 after 1 hour, and the initiation of the corrosion process was subsequently observed as shown in figure 5.6 (c). Figure 5.6 (f) represents the corrosion morphology of WE54 after 14 days of immersion. Grain boundaries were corroded, and materials started to corrode from the surface as shown in figure 5.6 (f). A yellowish-grey color partial protective film was observed visually after 1 hour. Corrosion attack on grain boundaries and α matrix were not visible due to the partial protective film. The film started to break out from the grain boundaries, and the corrosion process was increased gradually in the NaCl medium [146]. These observations are consistent with that of Li et al. [146]. They mentioned that the corrosion potential of the β phase was 420 mV higher than that of α -Mg matrix and that the β phase was highly cathodic during the corrosion process. The β phase has enough resistance to act as a cathode until the matrix around the β phase corrodes out.

Deeper groove and pits were observed in AZ91 and AZ31 (see figure 5.6, (d) and (e)) as compared to that of WE54 (see figure 5.6 f). The weight reduction of WE54 was less as compared to AZ31 and AZ91. The observed corrosion rate for the extruded WE54 in this investigation did not increased monotonously respect to exposure of time, in contrast to the reported corrosion rate for as-cast WE54, which increased monotonously [148].

Figure 5.6: Optical and SEM images of corrosion morphology exposed in 3.5% NaCl solution: after 1 hour of immersion, (a) AZ91, (b) AZ31, (c) WE54; after 14 days of immersion (d) AZ91, (e) AZ31, (f) WE54

5.5.2 Corrosive media: SBF solution

Figure 5.7 shows the corrosion rate of Mg alloys in NaCl and SBF environments respectively. In SBF solution, it was observed that WE54 shows a similar passive layer as in the NaCl solution during the initial stage of immersion. Due to the passive film formation, the corrosion attack could not be clearly observed in figure 5.8 (c). During the corrosion process, several ions were active in SBF solution such as sulphate, phosphate and chloride ions. Despite of the lack of clear observation of corrosion attack in figure 5.8 (c), these ions were detected by EDS during corrosion products identification.

The weight loss rate was $0.6696 \text{ mg cm}^{-2}\text{day}^{-1}$ in NaCl solution and $1.3580 \text{ mg cm}^{-2}\text{day}^{-1}$ in SBF solution for WE54 alloy as shown in figure 5.7. The standard deviation in the duplicate immersion experiments was a maximum of $\pm 0.0015 \text{ mg cm}^{-2}\text{day}^{-1}$ and $\pm 0.00295 \text{ mg cm}^{-2}\text{day}^{-1}$ in NaCl and SBF solutions respectively. After immersion for 14 days, the corrosion rate of WE54 was approximately double in the SBF solution as compared to that in NaCl solution.

Figure 5.7: Weight loss rate of AZ31, AZ91, and WE54 with respect to exposure time in 3.5% NaCl and SBF solutions

Figures 5.8 (a) and (b) show the corrosion morphology of AZ91 and AZ31 after 1 hour of immersion. In the SBF solution, AZ91 showed a slight passive nature around the β phase, but AZ31 showed initiation of pits and uniform corrosion. In AZ91 and AZ31, the α -matrix started to corrode and later converted into pitting. The observed results were similar to Xin and Witte [149, 150]. Xin et al. [32] mentioned that the first 2 hours of immersion showed high hydrogen activity but the evolution rate of hydrogen gradually reduced after 6 hours of immersion in the SBF solution.

Figure 5.8: Optical and SEM images of corrosion morphology exposed in SBF solution, after 1 hour of immersion, (a) AZ91, (b) AZ31, (c) WE54. After 14 days of immersion (d) AZ91, (e) AZ31, (f) WE54, Mg- α matrix corroded from the surface, leaving the surrounding β phase

Figures 5.8, (d) and (e) represent the surface morphology of AZ91 and AZ31 after 14 days of immersion test. In figure 5.8 (d), the α matrix around the β phase was completely removed.

Figure 5.8 (f) represents the surface morphology of WE54 after 14 days of immersion test. WE54 alloy has weight loss of $1.3580 \text{ mgcm}^{-2}\text{day}^{-1}$ at the later stage of the immersion test.

5.6 Laser melted surface of WE54

The microstructure of extruded WE54 mainly consists of α - Mg matrix, and a secondary phase as Y and Nd precipitates along the grain boundaries. As measured by Heyn lineal intercept method according to the ASTM standards, the average grain size of as- received WE54 was $25.5 \text{ }\mu\text{m}$. Figure 5.9 (a) is the enlarged view of figure of 5.9 (b), which shows the microstructure and phases of as-received WE54. From the electron dispersive spectroscopy (EDS), it was shown that the grain boundaries were enriched in Y and Nd elements. Generally, the compounds are formed from the precipitates of Nd and Y along the grain boundaries which may contain $\text{Mg}_{12}\text{Nd}/\text{Mg}_a\text{Nd}_b$ and $\text{Mg}_{24}\text{Y}_5/\text{Mg}_a\text{Y}_b$ [143, 144] where **a** and **b** are variables. Heavy rare earth element Gd was also found in the grain boundaries from the EDS analysis.

Figure 5.9: SEM image of WE54, (a) shows phases of WE54, (b) general microstructure as-received WE54, (c) laser melted surface of WE54, d) laser melted and as-received surface, and (e) enlarged view of laser irradiated surface.

In WE54/ WE43 Mg alloys, eutectic compounds of Mg_{12}Nd and Mg_{24}Y_5 have a similar role as the $\text{Mg}_{17}\text{Al}_{12}$ phase in AZ Mg alloy [151]. These phases act as a corrosion barrier if they have a

continuous network. The second phase Mg_{12}Nd acts as a cathode with respect to Mg matrix as demonstrated by Guo [151]. When a droplet of NaCl solution was used on the surface, hydrogen bubbles were observed at the second phase particles (Mg_{12}Nd); later on, micro-cells appeared between the second phase and Mg matrix. Figure 5.9 (c) is the surface morphology of the laser melted layer where laser melted tracks can be seen. Figure 5.9 (d) shows both the laser melted zone and the as-received surface of WE54. Figure 5.9 (e) shows a magnified view of the laser melted surface of WE54 in which dendrites and cellular structures can be observed. An elemental analysis was conducted on the laser melted surface.

It was observed that Mg had evaporated from the surface and enrichment of Y occurred. Y element was increased from 5% to 12.15%, Nd increased from 1.7% to 5.16%, whereas the concentration of Mg on the laser melted surface was 81.15%. Therefore, the concentration of rare earth elements on the surface had increased after laser surface treatment. The elemental mapping of the laser treated surface was performed by EDS system. The concentration and location of the Mg, Y and Nd elements after the laser surface treatment was observed. The concentration of Y along the grain boundaries was higher in the laser melted surface. The combination of Mg and Y elements were also seen on some parts of the surface. Nd element was found together with Mg and Y element. 8-11% of oxides/nitrides were also observed in the melted surface.

Figure 5.10 shows the X-ray diffraction graphs of as received and laser melted surface of WE54 alloy. In figure 5.10, **A**, **B** and **C** represent the α -Mg, Mg_{24}Y_5 and $\text{Mg}_{41}\text{Nd}_5$ phases respectively as analyzed by Panalytical X'Pert HIGHSCORE Plus software and compared with the standard data. In some parts of the laser melted surface, the presence of Mg, Y, and Nd elements was found which can be considered as a form of the β phase ($\text{Mg}_{14}\text{Nd}_2\text{Y}$). In the laser melted surface, the decrease

of intensity peaks of the α -Mg phase indicates the dissolution of α -Mg matrix in solid solution after the LSM process. Both XRD patterns of WE54 before and after LSM process consists of α and secondary phases.

Figure 5.10: X-Ray Diffraction graphs of as-received and laser treated surface of WE54 Mg alloy

5.7 Corrosion behavior of laser treated WE54 alloy

a) Electrochemical corrosion behavior

Potentiodynamic polarization (PDP) was performed to observe the electrochemical behavior of as-received and laser melted surface of WE54. Open circuit potential (OCP) test showed that the laser treated surface was more stable. OCP values for the as received and laser treated surface of WE54 were -1.874V and -1.623V respectively. The polarization curves obtained by potentiodynamic corrosion test under the SBF solution are shown in figure 5.11. The corrosion potential increased after laser treatment from -1.810V to -1.503V (i.e. less negative). Uniform corrosion can be observed over the whole laser treated surface. As such, uniform corrosion and reduced corrosion rate were observed through the electrochemical analysis of a substrate. The absence of pitting corrosion was verified by the PDP curves.

Figure 5.11: Potentiodynamic polarization curve of WE54 Mg alloy

Cathodic curves show a decrease in cathodic current. This means that the laser melted surface provides lower corrosion rates. The dissolution of an α phase, as well as uniform distribution of

alloying elements in solid solution, are the reasons for the reduction of corrosion rate as well as the uniform corrosion behavior.

b) Immersion test

Figure 5.12 represents the weight loss with exposure of time of WE54 alloy in SBF solution before and after laser treatment. When the surface was immersed in SBF, initially a passive layer was observed visually on the surface of as-received as well as in laser treated surface within half an hour. Material loss with the exposure of time increased from the as-received substrate as compared to the laser treated substrate. After one week, more pits were seen on the surface of the as-received Mg alloys. α -Mg matrix started to be removed because of the second particles around it causing galvanic reaction. Less material removal was observed on the laser melted surface. Within ten days, 4.21 mg material was corroded from the laser melted surface, whereas 6.45 mg material was corroded from the as-received surface. After two weeks, the as-received surface corroded rapidly, and the material loss reached to 11.4 mg. In contrast, uniform corrosion was found on the laser treated surface. 30% less weight loss was measured for the laser melted surface as compared to that of the as-received surface. This indicates that the LSM process had improved the corrosion resistance of WE54.

Figure 5.12: Weight loss of as received and laser melted WE54 in SBF solution at 37 °C.

5.8 Conclusion

This study analyzed the corrosion behavior of extruded WE54, AZ31 and AZ91 alloys in NaCl and SBF solutions. The corrosion behavior of these Mg alloys is dependent upon the presence of intermetallic compounds on the surface. In AZ91 and AZ31 alloys, Al plays a special role, and β - $Mg_{17}Al_{12}$ is the key phase for corrosion performance. WE54 shows galvanic corrosion starting from the grain boundaries after the break down of the passive layer. The formation of a Y_2O_3 passive layer prevents corrosion at the initial stage. The rare earth contained phases $Mg(Y, Nd)$ are responsible to slow down the corrosion process because of their protective layer as well as corrosion resistance properties. From the potentiodynamic tests, it was found that WE54 has a high susceptibility to corrosion.

Nanosecond pulsed Nd: YAG laser was suitable to melt the surface of the WE54 alloy. Mg concentration was reduced because Mg was evaporated during the melting process, resulting in the enrichment of rare earth elements on the surface. The concentration of Y increased from 5.5% to 12.15%. Dendrites and cellular microstructures were observed on the surface of melted WE54. Dissolution of the α -Mg matrix, as well as melting of second phase particles and their redistribution on the surface, resulted in a reduction of corrosion current. This resulted in a decrease of corrosion rate after laser surface melting. The immersion test in SBF solution after two weeks showed that the weight loss of the laser treated surface was less by 30% as compared to that of as-received WE54.

CHAPTER 6

WETTING AND COMPATIBILITY CHARACTERISTICS OF WE54 Mg ALLOY

Wetting properties of WE54 alloy was studied. The effective change on wettability properties of WE54 after LSM process was measured under deionized water (DI) and simulated body fluid (SBF). The bio-wettability of WE54 at various laser power of nanosecond Nd: YAG laser was analyzed. The surface energy of as received and laser treated surfaces of WE54 were analyzed.

6.1 Contact angle and wettability

Thomas Young (in 1805) introduced a correlation between contact angle and interfacial tensions between solid, liquid and vapor at the three-phase equilibrium condition [152, 153], namely the Young's equation as follows:

$$\bullet \quad \gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl} \quad (6.1)$$

Where, γ_{lv} , γ_{sv} , and γ_{sl} represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and θ is Young's contact angle. When a liquid drop is in contact with a solid surface, the interfacial tensions and contact angle are linked through this equation. The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface, whereas the wettability is the ability of a solid surface to be in contact with the liquid. The contact angle formed by a sessile drop on a smooth surface is shown in figure 6.1. A contact angle $\theta < 90^\circ$ indicates a hydrophilic surface, i.e. good wetting properties, whereas $\theta > 90^\circ$ indicates a hydrophobic surface. A surface having a contact angle larger than 150° is referred as a super hydrophobic surface.

Figure 6.1: Contact angles formed by sessile liquid drops on a smooth surface, adapted from ref. [152]

The adhesion intensity of a liquid surface to a solid surface is known as the work of adhesion, W_{ad} , and it can be calculated by the Young–Dupré equation:

$$\bullet \quad W_{ad} = \gamma_{lv} (1 + \cos\theta) \quad (6.2)$$

With equation (2), the adhesion intensity of DI water and SBF solution can be calculated.

Surface roughness is one of the factors that greatly influence the wetting contact angle [6]. The correlation between the roughness factor and contact angle θ can be described by Wenzel's equation. Wenzel's model represents the relationship between surface roughness and contact angle for a homogenous surface. If the surface is heterogeneous, a more appropriate model is the Cassie/Baxter's model; it explains that the gas entrapped in the surface increase the contact angle. Cassie's model is mostly used for complex surfaces and super hydrophobic surface structures.

Contact angle is employed here as the major parameter for the quantification of surface wettability. Surface roughness, chemical composition, oxygen content as well as surface chemistry are key factors that influence wettability.

6.2 Laser irradiation condition and contact angle measurement

The as-received WE54 bar of 3 cm diameter was cut into 3 mm thick disks. The samples were polished with SiC papers ranging from 320 to 2400 grit before being subjected to ethanol cleaning and airflow drying. An etchant composed of 19 ml water, 60ml ethylene glycol, 20 ml acetic acid, 1 ml HNO₃ was used to etch the as-received and the laser melted surface of WE54 to reveal the microstructures. The etching time was 60 seconds.

Laser irradiation was carried out using a Rofin pulsed Nd: YAG laser with laser parameters listed in table 6.1. (10 x 10) mm² surface of WE54 alloy was irradiated. The position of the laser spot was aligned with the Rofin control system. The experiments were performed in a closed chamber with a supply of nitrogen gas to reduce oxygen formation on the surface of WE54 during the melting process.

Table 6.1: Laser processing parameters used in the study

Laser parameters (units)	Symbol	Value
Power density (x 10 ⁵ W/cm ²)	Pd	1.307, 2.770, 3.901
Frequency (Hz)	f	10000
Scanning speed (mm/s)	v	20
Overlap (%)	O	50
Hatching density (mm)	H	0.001
Pulse width (μs)	Pw	10
Focal length (mm)	F	152.5

The liquids used for the contact angle measurements are SBF (simulated body fluid) and deionized water. The chemical composition of SBF was described in chapter 3, section 3.5 . The pH value

of SBF was 7.4 at room temperature. After laser surface melting, the contact angle measurement was performed at room temperature with “Attension THETA AUTO-D” Tensiometer. 500 μl volume of liquid was filled in the micropipette, and 2 μl volume was set for the sessile liquid droplet. The contact angle was measured 10 seconds after the liquid was dropped on the sample’s surface. Five sets of contact angle were measured for each sample at different locations to validate the consistency of the data.

Laser irradiated surfaces were examined by JEOL 5600 LV Scanning Electron Microscope (SEM) and optical microscope (OM). Electron dispersive spectroscopy (EDS) was used to investigate the concentration of alloying elements on the laser irradiated surface. Taylor Hobson Profilometer was used to observe the surface morphology. 2 mm² surfaces were scanned with 2000 $\mu\text{m/s}$ stylus speed. Cross section profile of laser irradiated surface and surface roughness were obtained from the profilometer. Commonly used roughness parameters are Sa and its 2D counterpart Ra, which give the standard deviation of height.

6.3 Microstructure

Figure 6.2 (a) shows the general microstructure of as-received WE54 observed by an optical microscope. The as-received WE54 Mg alloy consists of α -Mg matrix and secondary phases including Y and Nd formed by precipitates along the grain boundaries as indicated by the EDS and XRD observations. Analysis by Panalytical X’Pert HIGHSCORE Plus XRD analysis software showed that the secondary phases were Mg_{24}Y_5 and $\text{Mg}_{41}\text{Nd}_5$ phases.

Figures 6.2 (b) and (c) show the general surface structure before and after laser surface irradiation of WE54. The chemical composition of the laser irradiated surface was changed as compared to the as-received WE54. The variation in the evaporation of Mg and enrichment of Y were obtained depending on the laser process parameters. When the laser power density of $1.307 \times 10^5 \text{ W/cm}^2$ was used, there was no significant change in the chemical composition of the laser irradiated surface. Figure 6.2 (d) represents the surface structure created using a laser power density of $1.307 \times 10^5 \text{ W/cm}^2$.

Figure 6.2: (a) Microstructure of as-received WE54, (b) and (c) show the surface structure of WE54 Mg alloy before and after laser irradiation. (d), (e) and (f) show the laser irradiated surface with power density of $1.307 \times 10^5 \text{ W/cm}^2$, $2.77 \times 10^5 \text{ W/cm}^2$ and $3.90 \times 10^5 \text{ W/cm}^2$, respectively.

Figures 6.2 (e) and (f) show the cellular microstructure melted by laser power density of $2.77 \times 10^5 \text{ W/cm}^2$ and $3.90 \times 10^5 \text{ W/cm}^2$ respectively. Y element was increased from 5% to 12.15% and 13.43%, whereas the concentration of Mg was reduced from 91.05% to 81.15% and 80.97% for a

laser power density of $2.77 \times 10^5 \text{ W/cm}^2$ and $3.90 \times 10^5 \text{ W/cm}^2$ respectively. The distribution of rare earth element along the grain boundaries was modified after the laser surface irradiation.

6.4 Surface morphology

The surface roughness S_a of as-received and laser treated surface of WE54 with power density of $1.307 \times 10^5 \text{ W/cm}^2$, $2.77 \times 10^5 \text{ W/cm}^2$ and $3.90 \times 10^5 \text{ W/cm}^2$ were 0.170, 0.332, 0.241 and 0.532 μm respectively. The roughness value along with the standard deviation is listed in table 6.2. Before measuring the roughness parameter, the as-received WE54 was polished by 2400 SiC paper, whereas the laser treated samples were cleaned with ethanol ultrasonic bath.

It has been reported that the higher surface roughness with smaller grain size provides poor wettability [129]. The optimal combination of surface roughness, grain size and homogenous chemical composition of surface improves the wettability. When a laser power of 50 W was used, the surface was not melted properly because of insufficient power. Therefore the roughness of the surface was 0.332 μm which was high as compared to as-received and 100 W laser power irradiated surface.

It was observed that the surface roughness of the 100 W laser irradiated surface was lower than that of the 150 W laser-irradiated surface (data table 6.2). This indicated that with sufficient laser power in melting the surface, the surface roughness increased with a further increase in the laser power. Ho et al. [129] mentioned that the surface roughness of laser treated samples increased with an increase in the laser energy density, which is in agreement with our observations.

6.5 Wetting characteristics

The contact angle measurement was performed to observe the wetting behavior of laser treated WE54 alloy. Figure 6.3 represents the contact angle photographs of as-received WE54, 50 W, 100 W and 150 W laser treated surface of WE54 under DI water and SBF solution. The variations of contact angle are listed in table 6.2. By optimizing the laser processing parameters, the contact angle could be reduced from 81° to 43.10° and 41.03° in DI water and from 60.84° to 33.20° and 23.13° in SBF solution.

Laser processing parameters affect the contact angle. Laser irradiated surfaces with 50W, 100W and 150W laser power have lower contact angle than that of the as-received WE54. At a laser power density of $2.77 \times 10^5 \text{ W/cm}^2$ (namely at laser power of 100W), the minimum contact angles of 41.03° and 23.13° were observed for DI water and SBF respectively.

Contact angle in SBF solution was smaller as compared to the contact angle of DI water. SBF solution consists of several ions representative of the composition of the human blood. These ions could play a role by reacting with the surface of the substrate. The surface roughness and microstructure influence cell bioactivity [154]. In this investigation, the moderate laser power density of $2.77 \times 10^5 \text{ W/cm}^2$ leading to a surface roughness of $0.241 \pm 0.033 \mu\text{m}$ produces a surface with better bio-wettability.

Figure 6.3: Wet angle measurement of as-received and laser treated surface at various laser powers

Figure 6.4: Adhesion intensities of DI water and SBF solution at various laser powers.

Table 6.2: Summary of laser process parameters, adhesion energy, surface roughness and CA

Laser power density (10 ⁵ W/cm ²)	Roughness (Sa) μ m	Adhesion energy (mJ/m ²)		Contact angle		Variation in contact angle ($\pm$)	
		DI water	SBF	DI water	SBF	DI water	SBF
As-received	0.170 $\pm$ 0.002	81.18	107.87	81.00°	60.84°	3.00°	3.14°
1.307	0.332 $\pm$ 0.031	110.27	129.59	59.02°	38.12°	2.56°	3.65°
2.770	0.241 $\pm$ 0.033	127.71	139.22	41.03°	23.13°	4.15°	3.90°
3.901	0.532 $\pm$ 0.047	125.95	133.22	43.10°	33.20°	5.50°	4.71°

Figure 6.4 represents the adhesion energies of DI water and SBF which were calculated by the Young–Dupré equation (6.2). The surface tension (γ_{lv}) value of SBF was taken as 72.53 $\pm$ 0.11 mJ/m² as reported elsewhere [155]. The work of adhesion of as-received WE54 was 81.18 mJ/m² and 107.87 mJ/m² in DI water and SBF solution respectively.

The types of liquids used have an effect on adhesion energies. The bio-wettability of the material under SBF solution is very complex as there are several ions which are taking part during the process. The work of adhesion on laser treated WE54 50, 100 and 150W were respectively 129.59, 139.22 and 139.22 mJ/m² for SBF solution, and 110.27, 127.71, 125.95 mJ/m² for DI water. The maximum adhesion energy of SBF was obtained when the contact angle was small. Small contact angle provides high surface and adhesion energy; these improves the bio-wettability of WE54. Comparing the adhesion energy of SBF with that of DI water, SBF has significantly better adhesion energy. The adhesion energy, contact angle and surface roughness data are summarized in table 6.2.

6.6 Surface energy of LSM treated WE54 Mg alloy

Surface energy is one of the important factors which influence the wetting characteristics. The total surface energy is a combination of polar and disperses components. The total work of adhesion can be described as $W_{ad}=W^p+W^d$.

$$W_{ad} = 2\sqrt{(\gamma_{sv}^d + \gamma_{lv}^d)} + 2\sqrt{(\gamma_{sv}^p + \gamma_{lv}^p)} \quad 6.3$$

$$\cos\theta = \frac{2\sqrt{(\gamma_{sv}^d + \gamma_{lv}^d)} + 2\sqrt{(\gamma_{sv}^p + \gamma_{lv}^p)}}{\gamma_{lv}} - 1 \quad 6.4$$

γ_{sv}^d and γ_{sv}^p can be obtained from the values of θ measured with the testing liquids whose surface tension components are known. γ^+ is the Lewis acidic or the electron-acceptor component, γ^- is the Lewis basic or the electron-donor component, subscripts s, l, v represent solid, liquid and vapor, respectively, and θ is the contact angle.

The powder density of $2.77 \times 10^5 \text{ W/cm}^2$ was chosen for the surface energy calculation. Water, ethylene glycol and formamide were chosen, whose interfacial tension was known. The interfacial tension values of these liquid are listed in table 6.3. The contact angle values of water, ethylene glycol and formamide measured are listed in table 6.4., and are shown in figures 6.5, 6.6 and 6.7 respectively.

Table 6.3: The values of surface energy components used in this study (units mJ/m²)

Liquid	γ^{LW}	γ^+	γ^-	γ^p	γ
Water	21.8	25.5	25.5	25.5	72.8
Ethylene glycol	29	1.9	47.0	18.9	47.9
Formamide	39	2.28	39.6	19	58

Table 6.4: Contact angle values for the three liquids (DI water, Ethylene glycol, Formamide)

Laser power density (10^5W/cm^2)	Contact angle		
	DI water	Ethylene glycol	Formamide
As-received	81.00°	57.90°	111.10°
2.770	41.03°	21.96°	39.71°

Figure 6.5: Contact angle in DI water. As-received (left), LSM (right)

Figure 6.6: Contact angle in ethylene glycol. As-received (left), LSM (right)

Figure 6.7: Contact angle in formamide. As-received (left), LSM (right)

From equation 6.4, the surface energy was calculated. The surface energy of as received and laser treated WE54 alloy is listed in table 6.5.

Table 6.5: Surface energy component and total surface energy, (mJ/m^2)

Sample	Dispersive comp.	Polar comp.	Total surface energy
As-received	16.49	6.77	23.26
Laser treated	28.00	14.13	42.13

The total surface energy of laser treated WE54 is $42.13 \text{ mJ}/\text{m}^2$. The polar component increases from 6.77 to $14.13 \text{ mJ}/\text{m}^2$. Surface energy was highly enhanced in laser melted surface than that of the as-received WE54. The changes in microstructure and phases by LSM process lead to the improvement of wetting behavior. Chemical composition, surface roughness and oxygen content on the surface also influence wetting characteristics.

6.7 Conclusion

The lowest contact angle of 23.13° in SBF solution was measured for laser treated WE54 Mg surface with laser power density of $2.770 \times 10^5 \text{ W/cm}^2$. This surface had a measured roughness of $0.241 \pm 0.033 \text{ }\mu\text{m}$. In SBF solution, it also demonstrated significant adhesion intensity of 139.22 mJ/cm^2 . Changes in the concentration of elements of WE54 alloy were observed by EDS. In the LSM process, Mg was evaporated during the melting process, and the concentration of Y and Nd were increased. The changes in the laser treated surface chemical composition, microstructure, and surface morphology were responsible for the improvement of wetting behavior. Indeed, wetting properties of WE54 Mg alloy in SBF solution was significantly improved after Nd: YAG laser surface irradiation.

CHAPTER 7

LASER IRRADIATION OF WE54 ALLOY SURFACE UNDER SBF CONFINING LAYER

7.1 Laser irradiation in a liquid medium

Laser irradiation in air is commonly used in a wide range of processes, including machining and surface texturing. However, laser irradiation in liquid medium can be advantageous for specific applications as it is one of the effective techniques to obtain the desired surface morphology and to deposit thin films on the surface of components. One of such application examples is the surface treatment of biomaterials to be used in implantable devices or components.

For implantable materials, the biocompatibility of the final product is crucial for their successful integration and performance. It is important to characterize cell-material interactions after adequate surface treatment to understand the effects induced by foreign materials at the cellular and tissue level. Mesenchymal stem cells (MSCs) have been extensively used in biomaterial driven regeneration due to their potential for self-renewal with minimal immunogenicity as confirmed by several previous studies. Since most of the differentiated cells originate from stem cells, and their behavior is closely affected by the contacting materials, evaluation of the biocompatibility of materials with stem cells can provide insights on their potential usage as an implant material.

In this investigation, laser irradiation through simulated body fluid (SBF) has been studied. The MSC cytocompatibility on SBF treated substrates was evaluated. The laser modified WE54 alloy was used for the cell culture, and cell viability was studied by using PrestoBlue™ assay test. The cell adhesion in WE54 alloy was observed after laser irradiation through SBF.

7.2 Laser conditions

5 mm thick and 30 mm diameter WE54 sample were immersed in SBF contained in the beaker. The distance between the WE54 sample surface and SBF solution surface were 2 mm. The beaker was placed on the sample stage of Nd: YAG laser system. A nanosecond pulsed Nd: YAG laser, having a wavelength of 1064 nm, was used to irradiate WE54 surface. The power density of $3.901 \times 10^5 \text{ W/cm}^2$, overlap 50%, repetition rate 10 kHz and pulse duration 38 ns were employed.

Laser modified microstructures were examined by JEOL 5600 LV Scanning electron microscope (SEM) and optical microscope (OM). Energy dispersive spectrometry (EDS) was used to analyze the elemental concentrations of the samples. The bio-activity of the laser treated samples was measured by cell culture with MSC stem cells. The cell viability was measured by the PrestoBlue™ assay test after 3 and 8 hours of cell culture. The experimental details of cell culture and PrestoBlue™ assay test were explained in chapter 3 sections 3.5 and 3.6.

7.3 Laser irradiation

The laser beam was directed towards the WE54 Mg alloy surface, passing through the SBF solution. Laser fluence was the major parameter to control ablation of the surface and creation of new surface structures. Ejection of particles occurred when the laser fluence was higher than the threshold fluence. Lower energy laser fluences normally lead to the formation of micro-holes because of the microbubbles produced from the plasma and liquid environment [156]. It was reported that the generation of hot plasma at the higher laser fluence causes the vaporization of water molecules [133]. During laser material processing in the liquid environment, plasma vaporized water molecules at the specific laser irradiated region and the concentration of other

ions in liquids increases. As the water molecules decreases, other ions increases and a supersaturated condition is reached after some time. These supersaturated ions will deposit on the surface after the laser irradiation process.

7.4 SEM analysis

Figure 7.1 represents as-received WE54 before laser irradiation. The surface was clean and smooth.

Figure 7.1: As-received WE54 alloy

WE54 mainly consists of α -Mg matrix, secondary phase as Y and Nd precipitates along the grain boundaries. Figure 7.2 (a) represents the direct laser irradiation of WE54 alloy, where the surface of WE54 was melted. The overlapping surface was visible after direct laser irradiation of WE54. In contrast, after laser irradiated through the SBF layer, figure 7.2 (b) shows a WE54 surface with formation of surface morphology with deposition of calcium and phosphate ions. White parts in figure 7.2 (b) contained Ca/P ion and oxide which were detected by Energy Dispersive Spectroscopy (EDS). Figures 7.3 and 7.4 show the deposition of calcium and phosphate ions on the surface of WE54. Both Ca and P ions were observed as shown in figure 7.4. Red and green

color on the surface of WE54 represents the presence of phosphorus ions and calcium ions respectively (see figure 7.4).

Figure 7.2: (a) Direct laser irradiation of WE54, (b) laser irradiation of WE54 under 2 mm SBF layer.

Figure 7.3: Elemental mapping of calcium and phosphorous (a) Ca and (b) P ions.

Figure 7.4: Elemental Mapping of laser treated WE54 alloy in SBF showing a), red color is phosphorus ions and b) green color is calcium ions.

7.4.1 SEM after 3 hours of cell culture

Pure Mg substrate was used in the cell culture experiments to compare with WE54 alloy. Figure 7.5 (a) presents the Mg surface after 3 hours of cell culture. Black dots on the surface were dead cells. A number of cells were very few, and the base surface was prone to corrode in figure 7.5. Thin lines were observed on the surface due to the corrosion of substrate. Enlarge view of the cell in white color is shown in figure 7.5 (b). Cell reproducibility was not observed on this surface.

Figure 7.5: (a) Pure Mg surface after 3 hours of cell culture. (b) enlarged view of cell

Figure 7.6: As-received WE54 after 3 hours of cell culture

Figure 7.6 shows the number of cells in the as-received WE54 surface. As compared to the Mg surface, the number of cells attached on the surface is high. After 3 hours of cell culture, the surface appeared to be compatible and no corrosion products were observed.

Figure 7.7 presents the cell cultured surface of nanosecond Nd: YAG laser treated WE54 surface without and with a SBF layer. Cells were very active in the laser irradiated WE54 with SBF layer. Cells grow were observed from 3 hours of cell culture. The coated calcium and phosphate layer has a positive influence on cell attachment. Figure 7.8 represents the detailed view of the cells present in the SBF coated surface.

In a similar investigation, Wang et al. [134], through femtosecond laser ablation, also reported micro-patterns on a pure titanium (Ti) surface in SBF with deposited calcium/phosphorus (Ca/P) elements. They concluded that the femtosecond laser ablated surface could grow cell faster than the sandblasting and acid etching surface.

Figure 7.7: After 3 hours of cell culture (a) laser treated WE54 and (b) laser irradiated WE54 with SBF.

Figure 7.8: (a) and (b) SEM image after 3 hours of cell culture of laser irradiated WE54 surface with SBF.

7.4.2 SEM after 8 hours of cell culture

Figure 7.9 presents the Mg surface after 8 hours of cell culture. The white portions on the surface were cells as well as corrosion products. Surface of Mg substrate was corroded, and corrosion byproducts were observed. A corrosion product mainly consists of Mg ion and oxide layer. Enlarge view (1700x) of the cell is shown in figure 7.9 (b), which was almost covered by the corrosion products. Cell reproducibility decreased after the formation of corrosion byproducts.

Figure 7.9: (a) Pure Mg surface after 8 hours of cell culture, (b) enlarged view Mg surface after 8 hours of cell culture.

The cell cultured surface after 8 hours of laser treated WE54 surface is shown in figure 7.10 and the laser irradiated WE54 surface with SBF layer in figure 7.11. Cells were very active in the laser irradiated WE54 with SBF layer. An enlarged view of SBF coated surface shows in figure 7.11 (b) that the cell was dividing and reproducing new cells. The number of cells had increased. Cells were properly attached on the surface, which is visible in figure 7.11.

Figure 7.10: (a) 8 hours of cell culture of laser treated WE54 and (b) magnified view of cell culture surface of laser treated WE54.

Figure 7.11: (a) SEM image of laser treated WE54 with SBF layer after 8 hours of cell culture, (b) magnified view of cells on SBF coated laser treated surface

7.5 Cell viability after 3 hours and 8 hours

MSC stem cells were used for cell viability. Surfaces of as-received WE54, laser treated WE54, pure Mg, and laser treated WE54 through SBF, were used to examine the cell viability. Tissue culture plate (TCP) was used as controls in the cell culture test. After 3 hours of cell incubation, cells were fixed in 4% paraformaldehyde and dried by washing in PBS (Phosphate-buffered saline) and ethanol. After cell incubation and fixation, cells were placed in PrestoBlue containing well plate (500μl per well) for cell viability test: In the well plate, a color change from blue to purple indicates the degree of cell metabolism/viability on the material surfaces. The viable cells were measured by absorbance of PrestoBlue™ reagent. The cell viability test shows increase in cell number in laser treated sample with SBF solution as compared to the other samples as shown in figure 7.12.

Figure 7.12: Cell viability measurement in Presto Blue in 3 hours

After 8 hours of cell culture, the PrestoBlue™ cell assay test showed better cells attachment in laser treated WE54 in SBF environment with $61.34 \pm 0.22\%$ reduction of PrestoBlue™ reagent. Mg^{2+} ions were released from the surface resulted in the formation of compounds such as $Mg_aCa_b(PO_4)$ on the surface of WE54 surface. This indicates that the presence of Ca/P ions has a positive influence during cell culture, and significant cell viability was observed in the WE54 surface irradiated with SBF layer. Cells were attached on laser modified WE54, while as-received WE54 surfaces did not show any changes in cell attachment during SEM observation as shown in figure 7.10. It indicates that the micro-patterns formed during the laser treatment are favorable for cell attachment.

The cell propagation rates on laser treated with SBF WE54 surfaces were faster than those on as-received Mg and WE54 surfaces as shown in figures 7.12 and 7.13. In the laser treated WE54 surface under SBF, the blue color was converted into purple indicating the high cell activity. The SEM image after 8-hours of cell culture shows the micropattern and cell attachment, see figure 7.11. The activity of the cell could not be observed because of the corrosion products (appear black in color). Table 7.1 summarizes the % reduction of PrestoBlue with time.

Figure 7.13: Cell viability measurement in Presto Blue in 8 hours

Table 7.1: % reduction of PrestoBlue™ reagent with time.

WE54 surface	3h (%)	8h (%)
As-received	46.22 ± 5.64	46.83±4.46
Laser treated in air	50.93±4.39	55.02±5.79
Laser treated under SBF	55.4±2.32	61.34±0.22

7.6 Conclusion

For Nd: YAG pulsed laser treated WE54 surface in a SBF environment, deposition of calcium and phosphate elements on the surface was obtained. Water evaporation occurred due to plasma generation, leaving saturated ions. Bubbles burst near the surface helped to embed the Ca and P ions deeper into the surface. In laser treated WE54 surface in SBF environment, the PrestoBlue™ cell assay test showed better cells attachment with $61.34 \pm 0.22\%$ reduction of PrestoBlue™ reagent after 8 hours of cell culture. The amount of Ca/P ions deposited on the WE54 surface was beneficial for cell viability.

CHAPTER 8: CONCLUSIONS

In this chapter, the investigation is summarized with major conclusions. Recommendations for future work are presented to extend this investigation.

8.1. Conclusions

Laser interaction with WE54 alloy was studied by using a 1.5-watt QUANTRONIX Integra-C femtosecond laser, 10 watt DUETTO time bandwidth picosecond laser and a 500-watt pulsed nanosecond Nd: YAG laser. Random micro structure was observed when the surface was irradiated by the femtosecond laser with a pulse energy of 84 μJ . The laser irradiated surface consisted of buds like microstructure, which appeared grey and slightly yellowish. Selective vaporization and change in surface optical properties were observed.

A periodic surface structure was observed when the surface was irradiated by the picosecond laser with a pulse energy of 50.2 μJ . This periodic structure can act as a diffraction grating. With single scanning, a change in optical properties of WE54 alloy was observed.

With Nd: YAG laser, surface irradiation of WE54 was studied with laser energy from 1.85 J/cm^2 to 4.63 J/cm^2 . Granular, uneven (coarse) and flower surface structures were observed with laser energies of 4.63 J/cm^2 , 3.47 J/cm^2 , and 2.31 J/cm^2 , respectively. Less protruded particles were observed when the surface was at the defocused laser plane of 2.5 mm with a laser repetition rate of 10 kHz and power of 100W.

The corrosion behavior of Mg alloys was studied. This study analyzed the corrosion behavior of extruded WE54, AZ31 and AZ91 alloys in NaCl and SBF solutions. The corrosion behavior of these Mg alloys is dependent upon the presence of intermetallic compounds on the surface. In

AZ91 and AZ31 alloys, Al plays a special role, and $\beta\text{-Mg}_{17}\text{Al}_{12}$ is the key phase for corrosion performance. WE54 shows galvanic corrosion starting from the grain boundaries after the breakdown of the passive layer. The formation of a Y_2O_3 passive layer prevents corrosion at the initial stage. The rare earth contained phases $\text{Mg}(\text{Y}, \text{Nd})$ are responsible for slowing down the corrosion process because of their protective layer as well as corrosion resistance properties.

WE54 alloy was irradiated with the optimized Nd: YAG laser parameters of laser power density of $2.77 \times 10^5 \text{ W/cm}^2$, repetition rate 10 kHz, scanning speed 20 mm/s, overlap 50% and pulse duration 38 ns. Mg concentration was reduced from 90.05% to 81.15% as Mg was evaporated during the melting process, resulting in the enrichment of rare earth elements on the surface. The concentration of Y increased from 5.5% to 12.15%. Dendrites and cellular microstructures were observed on the surface of melted WE54. This laser treated WE54 was subsequently used to study the corrosion behavior under simulated body fluid (SBF) environment.

Dissolution of the $\alpha\text{-Mg}$ matrix, as well as melting of second phase particles and their redistribution on the surface, resulted in a reduction of corrosion current. This resulted in a decrease of corrosion rate after laser surface melting. The immersion test in SBF solution after two weeks showed that the weight loss of the laser treated surface (7.952 mg) was less by 30% compared to that of as-received WE54 (11.43 mg).

In addition, the wetting characteristics of laser irradiated WE54 alloy were studied at different powers of Nd: YAG laser, namely 50 W, 100 W and 150 W. Rough, granular and cellular structures were observed on the laser melted surface of WE54 at laser powers of 50 W, 100 W and 150 W respectively. The contact angle was reduced from 81° to 59.02° , 43.10° and 41.03° in DI water, and from 60.84° to 38.12° , 23.13° and 33.23° in SBF solution with the laser power density

of $1.307 \times 10^5 \text{ W/cm}^2$, $2.77 \times 10^5 \text{ W/cm}^2$ and $3.90 \times 10^5 \text{ W/cm}^2$, respectively. The lowest contact angle of 23.13° in SBF solution was obtained for laser treated WE54 Mg surface with a laser power density of $2.770 \times 10^5 \text{ W/cm}^2$. As such, the wetting properties of WE54 in SBF solution were significantly improved. The change in microstructure and phases by LSM process leads to the improvement of wetting behavior.

Laser irradiation of WE54 with 2 mm SBF layer covering its surface was conducted by using a pulse Nd: YAG laser with a power density of $3.901 \times 10^5 \text{ W/cm}^2$. A laser beam was focused on the specimen through a 2mm layer of SBF. A new surface was created with Ca/P ions deposited on it. The PrestoBlue™ cell assay test showed better cells attachment in laser treated WE54 in SBF environment with $61.34 \pm 0.22\%$ reduction of PrestoBlue™ reagent after 8 hours of cell culture. Cell adhesion could be observed by SEM for the laser treated WE54 alloy surface through SBF. This indicates that with a single step laser irradiation on WE54 surface under SBF, a bio-compatible surface for cell attachment and growth can be obtained.

8.2 Recommendations for Future works

The followings are recommended to extend the current investigation:

1. Investigation of multiple scanning of Mg alloys. Detailed study of multiple scanned surfaces could provide different surface structures beneficial to cell attachment and growth.
2. A comparison between surface formation on WE54 alloy by continuous wave laser and pulse laser can be further studied. Laser surface irradiation by continuous wave laser could result in less surface roughness as it helps to melt a substrate surface at a very fine level. It

could also have a different effect on the deposition of rare earth elements on the surface, which is an important consideration for cell attachment and growth.

3. The thermodynamic phenomena during laser processing could be further studied. Heat affected zone is a major concern during laser material processing. Heat transfer from laser to material can be studied through simulation and this could provide a good understanding on the formation of microstructures for WE54 Mg alloy. This could result in a correlation model between heat transfer and microstructures formation of WE54 Mg alloy.
4. Further study is to be conducted on laser treated rare earth Mg alloys (e.g. containing yttrium and neodymium elements) as biomaterials; the potential has been demonstrated by this preliminary investigation.

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