Laser surface processing of ultralight magnesium alloys

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**NANYANG
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UNIVERSITY**

**LASER SURFACE PROCESSING OF
ULTRALIGHT MAGNESIUM ALLOYS**

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Dedicated to my parents and family members

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Nomenclature

g	Gravitational acceleration
E_{corr}	Corrosion potential
i_{corr}	Cathodic current
z	Coordinate axis at the direction perpendicular to the surface
A	Surface transmission
C_e	Heat capacity of electron subsystem
C_l	Heat capacity of lattice subsystem
E	Activation energy
k	Thermal conductivity of the materials
$I(t)$	Laser intensity
K_e	Electric field vector electron thermal conductivity
L_R	Characteristic length taken as the liquid pool radius
L_b	Characteristic length for buoyancy force in the liquid pool
R	Gas constant
S	Laser heating source
T_e	Electron temperature
T_l	Lattice temperature
T_p	Peak temperature in DSC curve

FWHM	Full width at half maximum
α	Absorption coefficient
α_l	Thermal diffusivity, $\alpha_l=k/\rho C_p$
β	Thermal expansion coefficient
σ	Energy distribution parameter of the incident flux
ρ	Density of the materials
λ	Laser wavelength
A	Period of ripples
Λ_s	Wavelength of surface plasmons (SP)
C_p	Specific heat of the materials
ε_m	Dielectric constant of metal
ε_d	Dielectric constant of dielectric medium
τ_e	Electron cooling time
τ_l	Lattice heating time
τ_L	Laser pulse width
γ_{sv}	Solid-vapor interfacial energy
γ_{lv}	Liquid-vapor interfacial energy
γ_{sl}	Solid-liquid interfacial energy
$\partial\gamma/\partial T$	Temperature coefficient of surface tension
$\partial\gamma/\partial y$	Average temperature gradient (G) in the liquid pool
$\gamma_{sv}^{LW}, \gamma_{lv}^{LW}$	Lifshitz-van der Waals components
$\gamma_{sv}^{AB}, \gamma_{lv}^{AB}$	Lewis acid-base components

γ_{sv}^{+} , γ_{lv}^{+} Electron-acceptor parameters of acid-base surface free energy

component

γ_{sv}^{-} , γ_{lv}^{-} Electron-donor parameters of acid-base surface free energy

component

Abstract

Magnesium alloys have been increasingly used in the industries and biomaterial fields due to their low density, high specific strength and biodegradability. However, poor surface-related properties are major factors that limit their practical applications. Laser surface processing has been considered as an advanced technique to improve surface properties of materials. The present work investigates fundamental mechanisms of kinetics of phase transformation under non-equilibrium conditions, microstructural evolution and surface performance of laser-treated surfaces as well as laser-Mg interaction. This thesis demonstrates the capability of millisecond pulse laser in achieving the enhanced corrosion resistance and surface wettability of Mg alloy. It also analyzes heat flow and rapid solidification in the molten pool as well as material loss during laser irradiation. Furthermore, it explores theoretical study of nanosecond and femtosecond pulse laser processing on Mg alloy, and shows interesting results with potential applications.

Chapter 1

Introduction

1.1 Background Information

The need for lightweight structural as well as functional parts, particularly in the aerospace, automotive and electronic industries, has stimulated engineers to be more adventurous in their choice of materials. Magnesium (Mg) and its alloys, with one quarter of the density of steel and only two thirds that of aluminum, and a strength to weight ratio that far exceeds either, fulfills the role admirably as an “ultra light” alloy (Ambat *et al.* 2000; Kutz 2002). Moreover, Mg-based metal implants have attracted much attention in the fields of biomedical sciences nowadays due to their biodegradability (Heublein *et al.* 2003; Staigera *et al.* 2006). Witte (2010) claimed that this groundbreaking approach to temporary metallic implants was one of the latest developments in biomaterials science that was being rediscovered.

Unfortunately, although a wide variety of applications can be envisaged for Mg alloys, the actual use at present is limited mainly due to their inferior corrosion properties (Ambat *et al.* 2000; Ghali *et al.* 2004; Ballerini *et al.* 2005). It is known that the standard electrochemical potential of Mg is -2.4 V (NHE), even though in aqueous solutions it shows a potential of -1.5 V due to the formation of Mg(OH)_2 film. Therefore, Mg dissolves rapidly in aqueous solutions by evolving hydrogen below pH 11.0, which is the equilibrium pH value for Mg(OH)_2 . Similarly, Mg alloy implants corrode very quickly in the pH level of 7.4-7.6 and high chloride environment of the physiological systems. Consequently, the implant will lose its mechanical integrity before the tissues sufficiently heal (Kannan and Raman 2008). As a result, researchers all over the world have shown much interest to study the corrosion behaviour of Mg alloys and to develop protective methods.

Laser surface processing has been considered as an advanced alternative over conventional counterparts to improve the surface properties of materials (Silfvast 2004; Steen 2010). It has been recognized that laser surface engineering can produce surface layers with a fine microstructure that reduce the size of galvanic couples and expand the solid solution range of alloying elements (Majumdar *et al.* 2003; Liu *et al.* 2006; Mondal 2008). Such factors can potentially improve surface performance of laser-treated metallic alloys. Moreover, short processing time, flexibility in operation, economy in time/energy/material consumption, shallow heat affected zone, and precision are the important advantages of laser processing methods (Lugomer 1990; Steen and William 1991).

In the previous studies, most of researchers worked to improve wear and corrosion resistances of Mg alloys after various laser treatments methods, but little literature is available in the public domain on the kinetics of phase transformation under non equilibrium conditions and the interaction between laser and Mg as well as its alloys (Majumdar *et al.* 2003; Silfvast 2004; Liu *et al.* 2006; Mondal 2008; Steen 2010). Therefore, a good understanding of Mg alloy and its response to laser treatment is required. This thesis demonstrates the rapid melting and solidification of Mg alloy by direct laser treatment, and analyzes its response to phase transformation, microstructural evolution and surface performance in the molten pool. Moreover, short pulse laser, including nanosecond and femtosecond, was also used in order to further exploration of laser-Mg interaction.

1.2 Thesis Objectives and Scope

(1) Objectives

(a) To study kinetics of phase transformation and microstructural evolution of Mg alloy under non-equilibrium conditions

The most widely used Mg alloy AZ91D was studied in this part. Calorimetric analysis of as-received material was investigated to discuss the kinetics of β -Mg₁₇Al₁₂ phase and eutectic structure transformation. Solidification microstructure and phase transformation of laser-treated layer was studied following millisecond pulse Nd:YAG laser irradiation. Moreover, heat transfer and liquid flow in the molten pool was estimated based on numerical simulation from classic thermal models. Furthermore, microstructure in-homogeneities is discussed due to laser multiple pulses effect for large surface components in real engineering applications.

(b) To study surface properties of Mg alloy before and after laser surface processing

First, degradation behaviour of as-received and laser-treated AZ91D Mg alloy was analyzed in modified body simulated fluid, and electrochemical behaviour of laser-treated layer was also studied in 3.5 wt. % NaCl solution to investigate the effect of microstructure in-homogeneities on corrosion resistance. Second, surface energy and surface wettability of AZ91D Mg alloy before and after laser treatment is examined based upon the acid-base theory. Lastly, material loss including selective vaporization of Mg and Al alloying elements during laser irradiation is analyzed to understand the effect of Al enrichment on the improved surface properties of laser-treated AZ91D Mg alloy.

(c) To explore interaction between short pulse laser and Mg

For nanosecond pulse laser, including Nd:YAG laser and Excimer laser, boiling effect and superheating phenomena as well as oxidation companied by material redeposition on the irradiated surface were studied. For femtosecond pulse laser, formation of periodical surface structures was investigated. Meanwhile, laser-

induced darken effect and structure color at the surface of AZ31B Mg alloy was further explored for potential applications.

(2) Scope

(a) Microstructure development of AZ91D Mg alloy under non-equilibrium conditions

Activation energies for β -Mg₁₇Al₁₂ phase and eutectic structure dissolution/precipitation as well as microstructural evolution in as-received microstructure using DSC tests;

Solidification microstructure and phase transformation after millisecond pulse Nd:YAG laser irradiation using XRD, SEM/EDS, and TEM/EDS;

Heat transfer and liquid flow in the molten pool during laser irradiation;

Microstructure in-homogeneities after laser irradiation using OM, SEM, and thermal models.

(b) Surface properties of AZ91D Mg alloy before and after laser treatment

Corrosion resistance before and after millisecond pulse Nd:YAG laser irradiation, including degradation behaviour in modified-simulated body fluid and electrochemical analysis in 3.5% NaCl solution;

Effect of microstructure in-homogeneities on the corrosion behaviour;

Surface energy and surface wettability before and after millisecond pulse Nd:YAG laser irradiation based upon the acid-base theory;

Material loss, including selective vaporization of alloying elements and liquid matter ejection, during laser irradiation processing.

(c) Interaction between short pulse laser and Mg

Solidification microstructural evolution of AZ91D Mg alloy after nanosecond pulse Nd:YAG laser irradiation;

Local boiling and superheating phenomena on AZ91D Mg alloy during nanosecond pulse Nd:YAG laser irradiation;

Oxidation and material redeposition on AZ31B Mg alloy during nanosecond pulse Nd:YAG laser and Excimer laser irradiation;

Periodical surface structures on pure Mg induced by femtosecond pulse laser irradiation;

Surface coloration of AZ31B Mg alloy after nanosecond pulse Nd:YAG laser, Excimer laser, and femtosecond laser irradiation, respectively.

1.3 Thesis Outline

This dissertation is organized into eight chapters. A brief background on Mg alloys and objectives of current study are presented in Chapter 1. Chapter 2 provides review of the literature on fundamental mechanism of Mg corrosion and laser surface processing of Mg alloys. Chapter 3 presents details of three types of Mg and Mg alloys studied, four types of lasers used, and more than ten types of equipments used for surface characterization and surface properties tests work. Chapter 4 focuses on kinetics of AZ91D Mg alloy under non-equilibrium conditions. Calorimetric analysis using DSC tests is discussed. Solidification microstructure evolution in the molten pool after millisecond

pulse Nd:YAG laser processing is also examined. Chapter 5 describes corrosion resistance of AZ91D Mg alloy before and after laser irradiation, including electrochemical and degradation behaviour in modified-simulated body fluid and 3.5% NaCl solution. Effect of microstructure in-homogeneities on corrosion resistance is also analyzed. Chapter 6 discusses surface energy of AZ91D Mg alloy before and after laser irradiation based upon the acid-base theory. Effect of material loss during laser irradiation on Al enrichment in the laser-irradiated layer is further analyzed. Chapter 7 reports the results and discussion of effect of nanosecond and femtosecond pulse laser on Mg and AZ91D/AZ31B Mg alloys. Surface coloration and structure color is also studied. Lastly, Chapter 8 summarizes the results of current study with a brief outline of possible further researches.

Chapter 2

Literature Review

2.1 Introduction

In this chapter, relevant background work of Mg and Mg alloys as well as their corrosion mechanism, techniques for improving properties including rapid solidification, surface engineering and laser surface processing is presented.

2.2 Mg and Mg Alloys

Magnesium (Mg), with a specific gravity of 1.74, is the lowest-density structural metal available for engineering use. Pure Mg is rarely used for practical applications without being alloyed with other elements due to its poor properties. It is well known that the requirement for structural uses can be achieved by alloying different elements, such as Al, Zn, Mn, rare earths, Zr, Ag, and Th. The physical properties of Mg alloy are largely influenced by these individual alloying elements added to it (Avedesian and Baker 1999; Erickson 2002).

The application of Mg and Mg alloys has been successful owing to their attractive properties. Today, more than 200 years after the first production of metallic Mg by Sir Humphry Davy in 1808, Mg and Mg alloys have been increasingly used in the industries due to the low density, high specific strength and excellent damping capacity (Mordike and Ebert 2001). Particularly, in the transport industry, Mg alloys have become promising materials for the reduction of component weight to reduce both greenhouse gas emissions and the fuel cost of transport. For example, it is reported that Mg use in the automotive industry has grown by 10-15 percent per annum over the past two decades (Mordike and Ebert 2001; Easton *et al.* 2008).

In addition, Mg alloys have been investigated as implant materials for a long time. During the last two centuries, Mg alloys for clinical use were explored mainly by surgeons with various clinical backgrounds. Nearly all patients benefited from the treatment with Mg implants. Although most patients experienced subcutaneous gas cavities caused by rapid implant corrosion, most patients had no pain and almost no infections were observed during the postoperative followup (Staigera *et al.* 2006; Witte 2010).

The selection of Mg alloys as structural materials as well as implants on the basis of both surface and bulk properties severely limits engineering and economic considerations. According to the most common failure analysis of corrosion and wear in Mg alloys, it has been found that most of the failures are affected and initiated by surface conditions, such as environment, contact stress and other physical as well as chemical stimuli (Woodruff and Delchar 1994).

2.3 Corrosion Behaviour of Mg and Mg Alloys

2.3.1 Fundamental Mechanism of Mg Corrosion

There is a lot of information in the literature on corrosion mechanism of Mg. Most of the researches are experimental studies, in which the corrosion mechanism was defined as all physical and chemical features and processes involved when metallic Mg was exposed to an environment (Ahmad 2006; Song 2006; Edward 2010). In this section, we will review these experimental studies that have been carried out by many investigators to understand the fundamental mechanism of Mg and Mg alloys corrosion.

In a review article, Makar and Kruger (1993) found that Mg alloys followed a corrosion mechanism different from other engineering metallic materials such as steel, aluminum alloys, and zinc. Based on this study, Song and Atrens (1999 and 2003) reviewed previous work on the corrosion of Mg alloys, and pointed

out that some fundamental questions were still not clear, such as mechanisms of the effect of impurities, electrochemical behavior of second phases, and role of all phases and microstructures in the corrosion process. Ghali *et al.* (2004) summarized the influence of alloying elements and the different casting processes on the microstructure and performance of Mg alloys, especially for general and localized corrosion. Zeng *et al.* (2006) also presented basic study of different types of Mg corrosion, such as galvanic corrosion, pitting corrosion, intergranular corrosion, filiform corrosion, crevice corrosion, stress corrosion cracking, and corrosion fatigue. Additionally, Chang *et al.* (2008) and Pardo *et al.* (2008) provided detailed experimental work on the influence of alloying element on corrosion behaviour of Mg alloys in chloride environment.

In order to better understand the fundamental mechanism of Mg corrosion, detailed anodic and cathodic reactions on pure Mg or Mg alloy under a steady corrosion condition will be giving in the following, according to previous extensive work (Makar and Kruger 1993; Song and Atrens 2003; Song 2010):

First, the overall corrosion reaction can be written as:

Or

This overall corrosion can be decomposed into anodic and cathodic reaction:

The cathodic process is

Or

And the anodic process

(in a neutral or basic solution) (2.6)

where y is the ratio of Mg^+ turning into Mg^{2+} over reacting with H_2O to produce H_2 .

Finally, the product formation is

In general, the anodic dissolution occurs mainly in a film-free area, where in a film covered area the anodic dissolution is negligible. The cathodic reaction, which is mainly a hydrogen evolution process, can take place in both film-free and film-covered areas, but the reaction rate in a film-free area is much faster than the rate in film-covered area, particularly if impurity particles are present here. The process is schematically illustrated in Figure 2.1 (Song and Atrens 2003).

Besides these works on electrochemical reactions in Mg alloy, studies have also been carried out on the other aspects, such as the environmental factors including temperature, relative humidity, solution pH values and concentration on corrosion in the literature. Ambat *et al.* (2000) carried out the study on influence of chloride ion and pH on the electrochemical behaviour of AZ91D Mg alloy, and they found that corrosion rate increased with the chloride ion concentration. Ghali *et al.* (2004) have been reported that exposure to humid air with ~65% relative humidity during 4 days gives 100-150 nm thickness, and the film is amorphous and has an oxidation rate less than 0.01 $\mu m/y$. Moreover, they found that pH values between 8.5 and 11.5 corresponded to a relatively protective oxide or hydroxide film; however when pH was above 11.5, a passive stable layer was observed.

As the most widely used Mg alloy in industries, a lot of effort has been made to understand corrosion behaviour of AZ91D. Ambat *et al.* (2000) observed that size and morphology of intermetallic β -Mg₁₇Al₁₂ phase had significant influence on corrosion behavior of AZ91D alloy. Similar results have been reported by Song *et al.* (2004), Zhang *et al.* (2006), and Jonsson *et al.* (2007) for the role of β phase on the corrosion performance. Ballerini *et al.* (2005) showed that the corrosion resistance of AZ91D depended on composition, presence of several impurity elements, total amount of impurity elements, and production process. Therefore, in order to enhance corrosion resistance of AZ91D Mg alloy more significantly, a modification of microstructure and alloying concentration in the substrate is needed.

Figure 2.1 Corrosion mechanisms for all types of corrosion of Mg alloys. (a) when potential E is more negative than E_p , a protective film covers the surface. (b) when potential E is above E_p , the film is partially protective. Corrosion starts at breaks in the surface film. Corrosion occurs by means of electrochemical partial reaction (Eqs. (2.3)-(2.6)) and chemical reaction (Eq. (2.2)). (c) the chance development of areas of localized corrosion leads to (d) the undermining and (e) the falling out of particles of Mg, even in the corrosion of pure Mg (Song and Atrens 2003).

2.3.2 Biodegradation Behaviour of Mg Alloys

Compared with traditional implants such as stainless steels, titanium alloys, and cobalt-chromium-based alloys, Mg alloys are much more attractive mainly due to their degradation behaviour in the human body (Staiger *et al.* 2006). Significant progress of research on bioabsorbable Mg stents and orthopaedic bones has been achieved in recent years due to their advantages and obvious benefits (Heublein *et al.* 2003; Zeng *et al.* 2008; Witte *et al.* 2005; Witte 2010). Witte *et al.* (2005) reported that there was a strong rationale for Mg as a future implant material in bone surgery. However, they also pointed out that even though Mg and its alloys have been investigated as implants for almost two centuries, commercial implants containing Mg and its alloys are still not available (2008).

It is generally known that Mg and its alloys are degraded in aqueous environments via an electrochemical reaction (corrosion) which produces $Mg(OH)_2$ and hydrogen gas, and the fundamental corrosion reactions follows Eqs. (2.1)-(2.7). Unfortunately, rapid corrosion is an intrinsic response of Mg alloys to chloride containing solutions, including the human body fluid or blood plasma. Consequently, the implant will lose its mechanical integrity before the tissues sufficiently heal (Staiger *et al.* 2006; Liu *et al.* 2007; Kannan and

Raman 2008). In order to control biodegradation of Mg alloys, Song (2007) found that it was possible to develop biodegradable biocompatible Mg-based implants with specific biodegradation process and tolerable hydrogen evolution rate by utilizing its rapid corrosion reaction and controlling its degradation process through adding alloying elements, purification and anodization.

Apart from in vitro studies on the biodegradable behaviour of Mg alloy, the results of corrosion tests in vivo has also been challenging by researchers due to the complexity relationship between Mg-based implants and biological host response. Witte *et al.* (2006) found that current ASTM standards cannot be used to predict corrosion rates of magnesium alloys in vivo. Staiger *et al.* (2006) and Kirkland *et al.* (2010) claimed that consideration must be given to the following critical factors which would dictate the corrosion and suitability of a given Mg alloy as a bio-implant, including corrosion mode, corrosion products and solubility, corrosion rate variation with temperature, toxicity of metal ions released where relevantly large doses are evolved, and proliferation and formation of a mineralized matrix and studies of bone apposition and tissue in-growth in vivo. Further effort is needed to elucidate surface functionalization of Mg alloy for host-implant interactions.

2.4 Techniques for Improving Properties

2.4.1 Rapid Solidification

Rapid solidification from the liquid state is an important non-equilibrium processing technique, and has been frequently employed to improve the properties and performance of existing alloys. Compared to conventional methods, rapid solidification processes can create a fine dispersion of intermetallic phases, produce a homogeneous distribution of elements and extended solid solutions. These microstructural features, obtained far from equilibrium conditions, usually led to stronger and harder alloys with better

material properties (Flemings 1974). Furthermore, Pol Duwez (1960) and his colleagues obtained metallic glasses by the innovation of rapid quenching methods to suppress the nucleation and growth of competing crystalline phases, and a lot of researchers have been studies on the widespread investigations of bulk metallic glasses (Harimkar *et al.* 2006).

However, it may not be practical or economic for industry application. Therefore, a more significant improvement is desired selectively on the surface of materials.

2.4.2 Surface Engineering

Surface engineering is the sub-discipline of materials science which deals with the surface of solid matter which involves altering the properties of the surface phase in order to reduce the degradation over time. This is accomplished by making the surface robust to the environment in which it will be used. The techniques of surface engineering covered may be divided broadly into three categories: (1) Techniques to prepare a surface for subsequent treatment; (2) Techniques to cover a surface with a material of different composition or structure; (3) Techniques to modify an existing surface topographically, chemically, or microstructurally to enhance its properties (Rastogi 2003; Bull 2005).

Surface engineering techniques can be used to develop a wide range of functional properties, including physical, chemical, electrical, electronic, magnetic, mechanical, wear-resistant and corrosion-resistant properties at the required substrate surfaces (Woodruff and Delchar 1994; Cotell *et al.* 2002). Gray and Luan (2002) reviews that there were many techniques can be applied to surface protection of Mg alloys, including but were not limited to conversion coatings, hydride coating, organic/polymer coatings, electroplating, noble metal

plating, immersion plating, gas-phase deposition processes, and laser surface engineering.

In recent years, there has been a paradigm shift in surface engineering from age-old electroplating to processes such as vapor phase deposition, diffusion, thermal spray & welding using advanced heat sources like laser, plasma, ion, electron, microwave, solar beams, pulsed arc, pulsed combustion, spark, friction and induction (Chattopadhyay 2004). These tools of improving surface characteristics have greatly increased opportunity to utilize advantages of many materials. Additionally, it has improved design parameters, manufacturability, component performance, life and reliability and economy.

2.4.3 Laser Surface Processing

Laser is acronym for “Light Amplification by Stimulated Emission of Radiation”, because it is an optical oscillator in which the oscillating radiation is amplified by a process of simulated emission (Steen 2010). The principle of a laser is to excite atoms to a high-energy state level and to get an inversion in population with respect to an intermediate level. When radiation interacts with the excited atom with a frequency that corresponding to the energy difference between the higher energy state of the atoms and the intermediate state with inverted population, it produces an emission of radiation with the same phase as the incidental radiation. It is possible to amplify this radiation by using a resonance, in order to get a beam of coherent light. Besides its coherence, the emitted light is highly monochromatic which enables efficient focusing (Feynman 1986; Silfvast 2004).

The medium used for laser determines the wavelength and quality of laser. The primary lasers available in market for high power applications are continuous CO₂ laser, Nd:YAG laser (active entity Nd⁺³ with wavelength 1.06 μm) and

Excimer laser (lasing medium dimmer a compound between is one inert gas atom and an halide atom, wavelength in ArF:193 nm, KrF:248 nm, XeCl:308 nm, and Aef:351 nm) (Cunningham 1964; Lugomer1990). As suggested by Steen and William (1991), the first attempt at laser surface processing was reported in 1964. However, the application of lasers in surface engineering technology has developed rapidly only after 1980. Availability of various types of laser, such as CO₂, Nd:YAG, Excimer, and femtosecond, in adequate power level and optical fiber delivery system has extended usability of laser in surface engineering and many other manufacturing process. Today, the reliability and the robustness have made laser as one of most other machine tools. Moreover, the cost of ownership and operation has fallen significantly. The main industrial lasers are listed in Table 2.1 (Steen 2010).

The most important feature of laser surface processing is localized melting for substrate materials. The coherent nature of laser beam allows it to be focused to a small spot 0.1-1.0 mm, leading to high energy density (up to 10^{10} W/m²). The input of laser energy into the near-surface regions of substrate materials involves electronic excitation and de-excitation within an extremely short period of time. This allows the near-surface region of substrate to be processed under extreme conditions without altering or affecting bulk properties. Therefore, CO₂ and Nd:YAG laser are successfully applied for materials processing such as welding, cutting, and to a lesser extent for heat treatment, melting and alloying (Steen 2003).

High laser energy density when scanned over a surface (if coupled), it can melt only a confined volume of laser-material interaction. Simultaneously, the rest of the component is at lower temperature and thus acts as an infinite heat sink (chill). Busk (2002) reported that high power density as 10^5 - 10^7 W/cm² could produce a temperature gradient of the order of 10^6 K/cm and a very high cooling rate or rapid self quench, sometime exceeding 10^9 K/s. Such high

temperature gradient and cooling rates induces rapid solidification of molten metal on the surface once the laser has moved away from the previous spot, and the achieved rapid solidification could produce novel microstructure that is far-from equilibrium (Lugomer 1990).

Table 2.1 The main industrial lasers

Type of laser	Wavelength (nm)	Wall plug efficiency	Approx market value %
CO ₂	10600	12	36
CO	5400	19	-
Nd:YAG lamp pumped	1064	4	33
Nd:YAG diode pumped	1064	8-12	4
Nd:glass	1064	4	
Yb fibre	1034	20	
Er fibre	1540	20	
Diode GaAs	750-870	80	
Diode GaP	540	80	
Excimer KrF	248	0.5-2	

Wall plug efficiency is the ratio of optical energy output divided by the electrical energy input.

Laser-induced rapid solidification from liquid state is an important non-equilibrium processing technique for surface property development of substrate materials. Compared to conventional methods, laser-induced rapid solidification can create a fine dispersion of intermetallic phases, produce a homogeneous distribution of elements and extended solid solutions, leading to enhance corrosion protection as well as other surface properties of irradiated

materials. Moreover, laser-processing parameters can be controlled to optimize the melting and re-solidification process, thus design performance of the irradiated surface. Mazumder and his co-works (1991 and 1993) described the improvement of laser-cladding process for Mg alloys using CO₂ laser, and an investigation of the effect of the laser-cladding technique upon the microstructure and the corrosion resistance of Mg alloys. They found that corrosion properties of the laser claddings had been improved significantly compared with that of the commercially used Mg alloy. Cadek and Sustek (1996) found that the improvement in mechanical and electrochemical properties through microstructure refinements roughly translated into better surface-related, in particular, friction, tribological and corrosion resistance properties of Mg alloys.

As a chemically clean source of heating with unique optical properties, laser offers a wide range of surface engineering methods to improve surface properties of various metallic alloys (Lugomer 1990; Allmen and Blatter 1986; Steen 2003). The typical laser surface processing techniques for corrosion protection purpose is listed in Figure 2.2.

Figure 2.2 Typical laser surface processing techniques for corrosion protection (Liu *et al.* 2006)

In this thesis, we focus on laser surface melting technique, because it is the fundamental process and is involved in most of other laser methods. Laser irradiation of material surface initiates a complex sequence of events, which occur both during and after the laser pulse, and the processes occurring between the melted volume and the plasma can lead to important chemical and physical modifications of the surface properties (Rubahn 1999; Steen 2003; Tillack *et al.* 2004). We aim to discuss the effect of laser surface processing on solidification microstructure and on corrosion resistance as well as surface energy improvement of Mg alloy. Moreover, we explore further theoretical understanding on the interaction of laser and Mg and Mg alloys, including long pulse laser (millisecond) and short pulse laser (nanosecond and femtosecond). The emphasis of current study is to understand the kinetics of phase transformation and microstructural evolution under non-equilibrium conditions, the surface-related performance of laser-treated regions, and the fundamental mechanisms of laser-Mg interaction. It should be noted here that the specific literature review for each study on basis of these objectives will be further discussed in the following chapters.

2.5 Summary

From the survey of the literature in this Chapter as well as in the following Chapters 4-7 based on the objectives and scope of current thesis, following are issues need to be addressed:

1. For kinetics study of phase transformation and microstructure development under non-equilibrium conditions, AZ91D Mg alloy is used due to its wide application:

- (1) β -Mg₁₇Al₁₂ phase plays a very important role in optimizing the microstructure and properties of AZ91D Mg alloy. Activation energies of β -

Mg₁₇Al₁₂ phase and eutectic structure transformation as well as microstructure evolution will be discussed using calorimetric analysis method based on DSC tests.

(2) Microstructural evolution of β -Mg₁₇Al₁₂ phase and α -Mg matrix before and after laser processing will be investigated using material characterization techniques. Special attention will be made to understand the effect of rapid solidification on phase transformation induced by laser irradiation.

(3) Microstructure development in the molten pool is very complicated, and it profoundly affects solidification microstructure evolution. Heat transfer and fluid flow will be analyzed to investigate heat transport mechanism and thermal aspects of solidification following laser irradiation. Much attention will be given to study the effect of laser multiple pulses on the microstructure in-homogeneities.

2. For surface-related properties of AZ91D Mg alloy before and after millisecond pulse Nd:YAG laser irradiation, corrosion behaviour and surface energy as well as material loss will be examined:

(1) Degradation behaviour will be studied in modified-simulated body fluid to study the effect of laser treatment on corrosion resistance of Mg alloy as implants. Moreover, electrochemical behaviour will be studied in 3.5 wt. % NaCl solution to investigate the effect of microstructure in-homogeneities on corrosion resistance.

(2) The understanding of surface energy and wettability characteristics of Mg alloy is of great interest in both engineering and scientific fields. Surface energy of AZ91D Mg alloy before and after laser irradiation will be calculated using contact angle measurement based upon acid-base theory.

(3) Material loss plays a significant role in determining the surface properties of laser-treated layer, especially for expanding solid solution range in the molten pool. In this study, we will investigate the evolution of craters on laser-irradiated surface and plumes above the substrate surface. Particularly, the selective vaporization of Mg and Al alloying elements during laser irradiation will be analyzed to understand Al enrichment effect.

3. For interaction between short pulse laser and Mg as well as Mg alloys, boiling effect and superheating phenomena, surface coloration, periodical surface structure and structure color will be studied:

(1) Compared with millisecond pulse Nd:YAG laser irradiation, microstructure evolution of AZ91D Mg alloy induced by nanosecond pulse Nd:YAG laser will be analyzed. Local boiling effect and superheating phenomena will also be investigated.

(2) Surface coloration on AZ31B Mg alloy will be observed following both nanosecond pulse Nd:YAG laser and Excimer laser irradiation. The study will attempt to characterize morphological evolution and chemical composition of irradiated areas in different environment, with the aim of furthering engineering applications in product identification and biocompatible implants.

(3) Periodical surface structures on pure Mg as well as AZ91D/AZ31B Mg alloys will be reported following femtosecond pulse laser irradiation. We demonstrate structure color on AZ31B Mg alloy by scanning laser beam with multiply pluses at the near damage threshold fluence, in order to explore potential applications.

Chapter 3

Materials and Experimental Procedures

3.1 Introduction

In this chapter, the materials studied and lasers used for surface treatment are specified. The laser processing parameters are omitted from this chapter but are presented later in Chapters 4-6. Corrosion study is an important part of the project, so techniques used for the study are described in detail. The extensive range of characterization techniques used is classified into two broad categories: characterization of materials and characterization of surfaces.

3.2 Materials

Three materials were studied. They were pure Mg ingot, as-cast AZ91D Mg alloy ingot, and wrought AZ31B Mg alloy plate. Pure Mg was used to study the interaction of laser and material, while two commercial widely used alloys AZ91D and AZ31B were used to study the effect of laser process on the microstructure and the surface properties. Their chemical compositions are listed in Table 3.1.

Table 3.1 Chemical compositions of materials used in this study (wt%)

Mg and Mg alloys	Al	Zn	Mn	Si	Cu	Ni	Mg
Pure Mg	-	-	-	-	-	-	99.99
AZ91D	8.97	0.78	0.31	0.023	0.002	0.0005	Balance
AZ31B	2.89	0.87	0.39	0.015	0.001	0.0005	Balance

Specimens of dimensions of 30 mm by 30 mm by 3 mm were extracted from the ingot and plate, ground with progressively finer SiC paper (180, 400, 800,

1200, 2400 and 4000 grit), polished using 1.0 μm and 0.5 μm liquid diamond suspensions, cleaned with alcohol, and then irradiated with laser.

3.3 Lasers

Four types of lasers with pulse duration varying from millisecond, nanosecond, to femtosecond were used. Their specifications are shown in Table 3.2.

Table 3.2 Specification of four types of laser used in this study

Type of Laser	System	Beam profile	Wavelength (nm)	Pulse duration (s)	Repetition rate (Hz)
Nd:YAG	Lumonics JK702	TEM ₀₀	1064	$(0.3-2) \times 10^{-3}$	10-200
Nd:YAG	Rofin DQ $\times 50$ S	flat top-hat	1064	3.8×10^{-8}	6000
Excimer	krypton-fluorine (KrF)	flat top-hat	248	2.5×10^{-8}	10-100
Femtosecond	Ti:Sapphire Clark-MXR, CPA-2010	TEM ₀₀	775	1.5×10^{-13}	1000

In order to design different experimental work based on the scope of project, varied laser parameters were used in each study, and the detailed information is given in Chapters 4-6.

3.4 Corrosion Tests

The electrochemical corrosion behaviour of as-received and laser-irradiated AZ91D specimens was studied using a potentiostat/galvanostat corrosion measurement system (EG&G model 263A). The specimens were ground prior to the experiment, followed by washing with distilled water and ultrasonically cleaned in acetone. A potentiodynamic polarisation test was carried out in a Model K0235 Flat Cell Kit using an AgCl/Ag reference electrode as a reference electrode. The specimen was the working electrode, and they were immersed in the 150 ml of 3.5% NaCl solution with a pH of 7.25. The exposed area was about 1 cm². A polarization scan was carried out towards more noble values at a rate of 0.8 mV s⁻¹, after allowing a steady state potential to develop.

Moreover, corrosion rates of as-received and laser-irradiated specimens were also measured in the modified-simulated body fluid (m-SBF) using constant immersion test for five different intervals of time (2 h, 1 day, 3 days, 7 days, and 14 days). Before each test, the specimen was ground on progressively finer grades of emery papers (up to 4000) and then weighed. Cleaning of the specimen was done at the end of the immersion test by dipping it in a solution of 15% CrO₃ + 1% AgCrO₄ in 100 ml of water at boiling condition. An acetone washing followed this. The weight loss was measured after each experiment and the corrosion rate was calculated in mg/cm²/week.

In this study, the in vitro corrosion studies were carried out in the m-SBF maintained at a temperature of 36.5 ± 0.5 °C. The composition of m-SBF is given in Table 3.3. The solution was buffered with 2-(4-(2-hydroxyethyl)-1-piperazinyl) ethanesulfonic acid (HEPES) at a physiological pH of 7.4, and it had optimum ion concentrations for in vitro bioactivity assessment of artificial materials and biomimetic production of bone-like apatite (Oyane *et al.* 2003).

Table 3.3 Chemical composition of m-SBF (Source: Oyane *et al.* 2003)

Reagents	Amount
NaCl (g)	5.403
NaHCO ₃ (g)	0.504
Na ₂ CO ₃ (g)	0.426
KCl (g)	0.225
K ₂ HPO ₄ 3H ₂ O (g)	0.230
MgCl ₂ 6H ₂ O (g)	0.311
0.2 M NaOH (mL)	100
HEPES (g)	17.892
CaCl ₂ (g)	0.293
Na ₂ SO ₄ (g)	0.072
1 M NaOH (mL)	15

HEPES: 2-(4-(2-hydroxyethyl)-1-piperazinyl)ethanesulfonic acid

The electrochemical corrosion behaviour of as-received and laser-irradiated AZ91D specimens was also studied in modified seawater of 3.5 % NaCl solution using the potentiostat/galvanostat corrosion measurement system. The specimen preparation and measurement parameter setup are the same as in m-SBF.

3.5 Characterization of Materials

3.5.1 X-Ray Diffraction (XRD)

XRD is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Based on the principle of X-ray diffraction, a wealth of

structural, physical and chemical information about the material investigated can be obtained.

In the present work, structural identification of phases in the as-received materials and in laser-irradiated layers was performed by an X-ray diffractometry (Philips PW1830 series) using a continuous scan of Cu K α 1 radiation with 1.54056 nm wavelength was used to acquire the patterns using a step size of 0.02 degree.

3.5.2 Optical Microscopy and Scanning Electron Microscopy (SEM)

Optical microscopy was conducted using a Zeiss Axioskop2 MAT optical microscope. The resolution of a microscope is limited by the wavelength of the source of illumination; therefore, to reveal finer microstructural features, JEOL 5600 LV scanning electron microscope was used. The raw image digitally captured or produced by an electron microscope examination contains several artifacts and noise rooted in electrons, lens, alignment, vibration and other factors. Primarily noise can be divided into random noise and systematic noise. An important feature, if to be revealed above background, should have a reasonable signal-to-noise ratio (SNR). It has been reported that for distinction from the background, the SNR value should be at least 10. Random noise can easily be suppressed by means of digitally “averaging” several images of same microstructure. This is implemented by software while capture high quality images. Other principles such as wavelet improvement by FFT and logarithmic intensity were used in certain cases. These and other image enhancing capability have been used in current work.

For SEM imaging heavy etching was employed to provide better topographical contrast in secondary electron (SE) mode. Therefore, in order to investigate

solidification microstructure in the molten pool, laser-irradiated specimens were cross-sectioned, mounted and then polished to mirror polish and, wherever desired, etched with 4% Nital solution.

3.5.3 Energy Dispersive X-ray Spectroscopy (EDS)

High-energy electron and matter interaction often produce x-ray. Depending on the excitation voltage (kinetic energy of electrons) and the elements present in the matter, beam electrons knock off bound electrons from the ground (unexcited) state. As the electrons fall back from high-energy state to ground state, the extra energy associated is emitted in the form of electromagnetic radiation, possibly in the x-ray regime. Since the difference between ground state and excited state is well defined for chemical elements, the intensity and wavelength of x-ray radiation (above background) can be utilized to find the spatially resolved chemical composition of the specimens. The Energy dispersive X-ray spectroscopy (EDS or EDX) microanalysis has proven to be a very useful tool and now is popular attachment with most electron microscopes (SEM, TEM, STEM). The detector in this unit is 1024-channel Li-doped Si crystal which records the x-ray photo counts (intensity) as a function of energy over a period of time.

EDS signal comes from the volume of matter excited by an electron beam. The higher the voltage, the larger is the volume from which signal is registered by the detector and thus lower is the spatial resolution. The problem with higher voltage is the lateral resolution of such analysis spot is compromised. It is, therefore, required to reduce excitation volume to improve resolution. However, the low voltage represents lower energy of electrons that generates x-ray. The x-ray thus produced is often from low-energy (outer shell) of atoms due to the low energy difference between outer shells. It is less sensitive and often overlapping peaks of different elements are hard to distinguish. Hence, voltage

and resolution need to be optimized. By choosing an appropriate low voltage (LV), it is possible to analyze microstructural features with high resolution.

In the present work, EDS system attached to be the JEOL 5600 LV SEM was used to analyze the chemical composition of laser refined microstructural features.

3.5.4 Transmission Electron Microscopy (TEM)

TEM uses a high energy electron beam transmitted through a very thin sample to image and analyze the microstructure of materials with atomic scale resolution. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen, or recorded on film or digital camera such as CCD. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light, for example, 200kV electrons have a wavelength of $0.025\text{\AA}$. However, the resolution of electron microscope is limited by aberrations inherent in electromagnetic lenses, to about 1-2 $\text{\AA}$.

Rather the high resolution imaging mode of the microscope images, the crystal lattice of a material as an interference pattern between the transmitted and diffracted beams. This allows one to observe planar and line defects, grain boundaries, interfaces, etc. with atomic scale resolution. The bright-field/dark-field imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction, are also invaluable for giving information about the morphology, crystal phases, and defects in a material. Finally the microscope is equipped with a special imaging lens allowing for the observation of micromagnetic domain structures in a field-free environment. Moreover, TEM is capable of forming a focused electron probe, as small as 20 $\text{\AA}$, which can be positioned on very fine features in the sample for microdiffraction information or analysis of x-rays for compositional

information. The latter is the same signal as that used for EDS analysis, where the resolution is on the order of one micron due to beam spreading in the bulk sample. The spatial resolution for this compositional analysis in TEM is much higher, on the order of the probe size, because the sample is so thin. Conversely the signal is much smaller and therefore less quantitative. The high brightness field-emission gun improves the sensitivity and resolution of x-ray compositional analysis over that available with more traditional thermionic sources.

In the present work, microstructure of top surface layer in the laser-irradiated AZ91D Mg alloy was studied using a JEOL 2010 TEM equipped with EDS, operated with an accelerating voltage of 200 kV. A selected area electron diffraction technique (SAD) in TEM was used to extract crystallographic information. The TEM thin foils of laser-irradiated specimen in this study were obtained first by polishing mechanically on the side of substrate until the specimens were less than 30 μm thick. Disks of 3 mm diameter were punched from the foils for subsequent jet electro-polishing in a solution composed of an electrolyte of 750 ml methanol, 150 ml butoxyethanol, 16.74 g magnesium perchlorate, and 7.95 g lithium chloride at $-20\text{ }^{\circ}\text{C}$ and an applied voltage of 40 V. Finally, ion beam was used on a Gatan precision ion polishing system under conditions of 5.0 kV and an incident angle of $4\text{--}5^{\circ}$.

3.5.5 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a sensitive technique for investigating the elemental composition and the associated chemical bonding states of the near-surface region of a specimen. The technique relies on the emission of secondary electrons from the surface after the near surface atoms have been excited with x-rays. XPS provides the energy resolution needed to detect elemental peak position energy shifts due to chemical bond formation.

Information is typically obtained for the region within ~ 50 Å of the outer surface. Angle resolved XPS can allow analysis of regions even closer to the sample surface. Relative atomic concentration percentages can be determined with a sensitivity of 0.1 to 1 atomic % for Li and heavier elements. Analysis is carried out in an ultrahigh vacuum system ($\sim 10^{-9}$ Torr or better).

In the present work, surface chemistry of irradiated AZ31B Mg alloy following nanosecond pulse laser was studied using XPS (Kratos-Axis spectrometer) with monochromatic AlK α (1486.71 eV). High resolution scans were collected with pass energy of 40 eV and step of 0.1 eV. The analyzing chamber pressure fluctuated between 10^{-8} and 10^{-9} Torr. The spectra were calibrated using C 1 s peak position at 284.6 eV.

3.5.6 Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

TOF-SIMS is a surface-sensitive analytical method that uses a pulsed ion beam (Cs or microfocused Ga) to remove molecules from the very outermost surface of the sample. The particles are removed from atomic monolayers on the surface (secondary ions). These particles are then accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight). The resulting secondary ions are accelerated into the mass spectrometer where they are mass separated by measuring the time-of-flight from the sample to the detector and a mass spectrum is recorded. An Image may be generated by rastering a finely focused ion beam across the sample surface. A depth profile may be constructed by using an Ion beam to remove sequential layers of material from the surface while acquiring mass spectra at each depth. Therefore, three operational modes are available using TOF-SIMS: surface spectroscopy, surface imaging and depth profiling.

In the present work, TOF-SIMS (ION-TOF GmbH) was used to analyze vaporized Mg and Al species in the deposited plume induced by laser irradiation on AZ91D Mg alloy. The SIMS primary Ar⁺ ion beam was set at an energy of 10 keV and an average beam current of 2 pA. When the primary beam scanned along the middle line in the deposited plume, the masses of positive secondary ions were detected in the time-of-flight (TOF) mass analyzer. Moreover, mass-resolved images (MRIs) for typical element distribution near the irradiated surface were reconstructed from the mass spectrum data. Furthermore, TOF-SIMS depth profile was employed within the MRIs scan area to analyze the vaporized elements inside the deposited plume. In addition, each alloying element concentration in the deposited plume was calculated by multiplying the ion intensity with a coefficient. The coefficient was calculated by normalizing the ion intensity to the sum of the major elements in the as-received AZ91D Mg alloy such that the composition closed to the expected composition at the base material.

3.5.7 Differential scanning calorimetry (DSC)

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. The ability to determine transition temperatures and enthalpies makes DSC an invaluable tool in producing phase diagrams for various chemical systems.

In the present work, the specimens of AZ91D Mg alloy were cut into dimensions of 3mm × 3mm × 2mm and each specimen weighed approximately 30 mg. The specimens were then ground with progressively finer SiC papers (180, 400, 800 and 1200 grit) and cleaned using alcohol before DSC tests. The transformation temperatures of the specimens were measured using a PERKIN ELMER DSC7 in argon gas. The temperature range was from 300 to 500 °C, including holding 3 minutes at 500 °C. Various scanning rates (5, 10, 15, 20, 25, 30 and 40 K/min) were employed and both heating and cooling process were tested. Each specimen was placed in a graphite crucible (6.5 mm inner diameter and 2 mm height) in Ar for testing in order to avoid oxidation. Each scanning rate test was repeated three times.

3.6 Characterization of Surfaces

3.6.1 Atomic Force Microscopy (AFM)

AFM is used to measure surface topography of specimen on a scale from angstroms to 100 microns. This technique involves imaging a specimen through the use of a probe, or tip, with a radius of 20 nm. The tip is held several nanometers above the surface using a feedback mechanism that measures surface-tip interactions on the scale of nanoNewtons. Variations in tip height are recorded while the tip is scanned repeatedly across the sample, producing a topographic image of the surface. AFM in the microscopy suite is capable of producing images in a number of other modes, including tapping, magnetic force, electrical force, and pulsed force.

In the present study, surface topography of laser-irradiated specimens under low laser pulses was measured by Veeco Dimension 3000AFM in tapping mode. In tapping mode, the tip is oscillated above the sample surface, and data can be collected from interactions with surface topography, stiffness, and adhesion.

This results in an expanded number of image contrast methods compared to basic AFM. When surfaces produced with large number of laser pulses were too rough to be characterized with AFM, their topography was characterized using a Taylor Hobson Precision Talysurf profiler.

3.6.2 Measurement of Surface Energy

To investigate the effect of laser treatment on the surface energy, wetting experiments were conducted to observe the differences of wetting characteristics between the original and laser-treated surfaces. To eliminate the influence of surface roughness on the wetting behavior, both as-received and laser-irradiated surfaces were gently polished to the same roughness value of approximately 0.2 μm (Ra). The measurement of the contact angle was carried out in atmospheric conditions at room temperature using a FAT32 contact angle analyzer and a syringe pump with VCA Optima device (AST Products, Inc.).

The test liquids were double-distilled water, ethylglycol and formamide based on the acid-base approach, which was suggested by Oss et al.(1988). A droplet with the volume of 0.5 μl was released onto the surface of the specimen from a syringe needle. The contour of the liquid droplet on the solid surface was captured by a CCD camera after 5 s, which is to guarantee the liquid drops have reached the equilibrium. For each specimen and liquid, ten to twenty droplets were measured. The accuracy of the contact angle is within 1 degree.

3.6.3 Measurement of Optical Reflection

Laser-induced coloration of material surfaces is an interesting phenomenon, and it provides an alternative approach to many promising applications, such as decorations, product identification, biocompatible implants and photocatalysts.

Previous researchers suggested that such technique could be an effective method for controlling the optical properties of metals.

In the present work, optical reflection of mechanical-polished and laser-irradiated Mg and Mg alloy surface were measured using Ocean optics DT-Mini-2 system and Spectrometer Operating Software. The optical configuration is shown in Figure 3.1. All specimens were exposed to white light source via adapter. Reflected light from the surface was guided to HR4000 High-Resolution spectrometer to be analyzed by SpectraSuite software. Each reflection measuring test was repeated three times. Before each test, the environment factor, such as fluorescent light and natural light, was excluded as reference.

Figure 3.1 Optical configuration for the optical reflection measurement

Chapter 4

Kinetics of phase transformation and microstructural evolution of Mg alloy under non-equilibrium conditions

4.1 Introduction

In this chapter, kinetics of phase transformation and microstructural evolution of AZ91D Mg alloy under non-equilibrium conditions is discussed into three parts. First, calorimetric analysis of as-received material is investigated to study the activation energies and microstructural evolution of β -Mg₁₇Al₁₂ and eutectic structure in the microstructure. Second, solidification microstructure and phase transformation in the molten pool are studied following millisecond pulse Nd:YAG laser irradiation. Lastly, microstructure in-homogeneities in the molten pool due to multiple laser pulses effect are discussed, and heat transport is also estimated based on classic thermal models.

4.1.1 Calorimetric Analysis

AZ91D Mg alloy has been widely used in the automobile, communication and aerospace industries due to its good combination of mechanical and corrosion properties compared to other Mg-based alloys. It is well known that microstructure plays a critical role in determining properties of materials; therefore, a lot of work has been carried out to study the microstructure and the properties of AZ91D alloy. Ambat *et al.* (2000) and Jonsson *et al.* (2007) studied the effect of microstructure on the corrosion behavior of AZ91D alloy and pointed out that the size and morphology of β -Mg₁₇Al₁₂ phase have significant influence on corrosion behavior of the alloy. Similar results have also been reported by other investigators (Aung and Zhou 2002; Ambat *et al.* 2000; Song *et al.* 2004; Chang *et al.* 2008). Heat treatments may be performed to modify the microstructures and obtain more homogeneous composition of

AZ91D alloy. In order to predict adequately the thermal effect on the alloy properties, a better understanding of the kinetics of phase transformation is needed.

In order to predict microstructure effect on the alloy properties, a better understanding of the kinetics of phase transformation is needed. Calorimetric analysis is a suitable quantified method for the study of phase transformation under non-equilibrium condition, and several researchers have used the calorimetric techniques to study phase transformation in different materials (Bassani *et al.* 2005). However, it should be noted that researchers studying the activation energies of β -Mg₁₇Al₁₂ dissolution in Mg alloys reported considerably different values. Bassani *et al.* (2005) estimated the activation energy of β -Mg₁₇Al₁₂ dissolution in AM60 Mg alloy to be 185 kJ/mol. For AZ91D Mg alloy, Balasubramani *et al.* (2007) found the activation energy required for β -Mg₁₇Al₁₂ precipitation to be 5.21 kJ/mol and Wang *et al.* (2005) reported a much higher value of 1995 kJ/mol as the activation energy of eutectic structure transformation. This study was carried out to address the issue of discrepancy in activation energy values reported in the literature. Effort was also made to understand the kinetics of lamellar and bulk β -Mg₁₇Al₁₂ dissolution in AZ91D Mg alloy.

4.1.2 Solidification Microstructure

The effect of laser surface melting (LSM) on Mg alloys has attracted considerable attention in recent years because surface-related properties of the laser-treated layer can be enhanced significantly (Majumdar *et al.* 2003; Abbas *et al.* 2005; Liu *et al.* 2006; Mondal *et al.* 2008; Majumdar *et al.* 2010). Abbas *et al.* (2005) and Liu *et al.* (2006) found that the improved corrosion resistance of AZ31, AZ61 and WE43 Mg alloys following LSM was associated with the

increased concentration of Al and microstructure refinement in the laser-melted zone due to surface melting and rapid solidification during the laser process.

In the past study, most of researchers focused on the improved wear and corrosion resistances of Mg alloys after laser treatment, but no good understanding has been obtained on the microstructural evolution induced by laser irradiation (Majumdar *et al.* 2003; Abbas *et al.* 2005; Liu *et al.* 2006; Mondal *et al.* 2008). Therefore, an understanding of the as-received microstructure and its response to laser treatment is required for magnesium alloys in order to study the rapid solidification microstructure under non-equilibrium condition.

In this study, the microstructural evolution of an as-cast AZ91D Mg alloy following LSM was studied in three different regions of the laser-melted zone. Particularly, dissolution/precipitation of β -Mg₁₇Al₁₂ phase in the molten pool was examined carefully. Moreover, cooling rates of these regions were calculated from a numerical simulation based on the heat flow model in the literature (Brandes 1998; Harimkar *et al.* 2006; Basu *et al.* 2008). The aim was to study the kinetics of phase transformation and the effect of cooling rates on the solidification microstructure under rapid solidification condition induced by laser processing.

4.1.3 Microstructure In-homogeneities

In order to apply laser technique for large surface components in real engineering applications, overlapping adjacent traces as a result of multiple passes using scanning laser beam is usually necessary for production of area coverage. It has long been realized that laser beam overlapping may play a significant role in influencing the surface properties (Chong *et al.* 2003; Watkins *et al.* 1998; Reitz and Rawers 1992; Virtanen *et al.* 1994; Gao *et al.*

2007). Watkins *et al.* (1998) and Chong *et al.* (2003) claimed that overlapping was of particular importance in the case of corrosion resistance due to microstructure in-homogeneities in the molten pool.

Microstructure development in the molten pool is very complicated because of physical processes that occur due to the interaction of the heat source with the metal, including re-melting, heat and fluid flow, vaporization, dissolution of gasses, solidification, subsequent solid-state transformation, stresses, and distortion (David *et al.* 2003). These processes and their interactions profoundly affect solidification and microstructure evolution. In recent years, phenomenological modeling has provided unprecedented insight into understanding both the laser process and the materials. A variety of sophisticated models that employ analytical and numerical approaches are capable of describing many physical processes that occur during laser irradiation (Yang and DebRoy 1999; Mishra and DebRoy 2004; He *et al.* 2005; Wei *et al.* 2009; Nayak *et al.* 2004; Harimkar *et al.* 2006; Basu *et al.* 2008).

In this study, the effect of pulse laser beam overlap, including pulse duration and overlap rate, on microstructure in-homogeneities in the molten pool was analyzed. The heat transport mechanism was analyzed from a well-tested, transient, numerical heat transfer and fluid flow model (Yang and DebRoy 1999; Mishra and DebRoy 2004; He *et al.* 2005; Wei *et al.* 2009; Nayak *et al.* 2004).

4.2 Experimental Procedures

The material studied was as-cast AZ91D Mg alloy, and the laser used was millisecond pulse Nd:YAG laser. Detailed information of the material and laser is given in Sections 3.2 and 3.3. The laser processing parameters for different

experimental study are given below. All the laser experimental work was performed under high purity Ar gas protection.

4.2.1 Calorimetric Analysis

Kinetics of dissolution/precipitation of β -Mg₁₇Al₁₂ phase in as-received AZ91D Mg alloy was examined following calorimetric analysis using DSC tests. The detailed information of DSC tests is given in Section 3.5.7.

4.2.2 Solidification Microstructure

Microstructure evolution and phase transformation as well as phase precipitation in the molten pool of AZ91D Mg alloy after laser treatment was examined. The laser processing parameters for this work were: power density 3.82×10^4 W/cm², scanning speed 10 mm/s, frequency 100 Hz, and pulse duration 1.0 ms. The beam was defocused to 1 mm in diameter (the distance between two subsequent tracks was around 500 μ m). The laser-irradiated area was 10×10 mm² in square using scanning mode with 50% spot overlapping in the program.

4.2.3 Microstructure In-homogeneities

In order to study effect of laser processing on microstructure in-homogeneities in the molten pool, two series of experimental work were performed. The main laser processing parameters were the same as in the previous study as Section 4.2.2, including power density 3.82×10^4 W/cm², scanning speed 10 mm/s, frequency 100 Hz, and beam diameter 1 mm. However, pulse duration was varied from 0.3 ms to 1.5 ms during laser irradiation in order to study the surface ripples and subsurface microstructure evolution, while overlap rate was

varied from 25% to 90% during laser irradiation in order to study the effect of overlapping on the microstructure evolution, as shown in Figure 4.1.

Figure 4.1 Schematic diagram of overlapping during laser processing

4.3 Calorimetric Analysis

Figure 4.2 shows typical XRD patterns of as-received AZ91D Mg alloy. Both α -Mg phase and β -Mg₁₇Al₁₂ intermetallics are shown in the as-received microstructures, as reported by previous studied (Ambat *et al.* 2000; Song *et al.* 2000; Zhou *et al.* 2007). Moreover, microstructure of the as-received AZ91D Mg alloy contained bulk and lamellar β -Mg₁₇Al₁₂ intermetallics distributed non-homogeneously in a matrix of α -Mg grains, as shown in Figure 4.3. The size of bulk β -Mg₁₇Al₁₂ intermetallics varies from 10 μ m to 100 μ m, while the space between lamellar β -Mg₁₇Al₁₂ intermetallics and α -Mg solid solution was in the range of 0.5-2 μ m.

The DSC curves at different scanning rates are shown in Figure 4.4. The dissolution of β -Mg₁₇Al₁₂ phase and the transformation of the eutectic structure could be determined using the binary Mg-Al phase diagram (Massalski and Okamotoet 1990). Moreover, the peak temperatures during the cooling process

including $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitation and eutectic transformation were also investigated, but they are not discussed in this work.

Figure 4.2 XRD patterns of as-received AZ91D Mg alloy, showing the presence of $\alpha\text{-Mg}$ phase and $\beta\text{-Mg}_{17}\text{Al}_{12}$ intermetallics.

Figure 4.3 SEM image of a typical microstructure in the as-received AZ91D Mg alloy, showing bulk and lamellar $\beta\text{-Mg}_{17}\text{Al}_{12}$ intermetallics distributed in $\alpha\text{-Mg}$ matrix.

Figure 4.4 DSC curves of the AZ91D under different scanning rates. (a) Heating process; (b) Cooling process.

Two peaks were observed for all scanning rates during the heating/cooling processes, including a wide peak ranging from 340°C to 430°C (peak 1) and a large and sharp peak at about 440°C (peak 2). It is believed that peak 1 is related to dissolution/precipitation of lamellar β -Mg₁₇Al₁₂ phase and peak 2 corresponds to the transformation of bulk β -Mg₁₇Al₁₂. Bassani *et al.* (2005) found a wide peak ranging from about 300 to 450°C and a small and sharp peak at about 440°C in AM60 alloy. It is further observed that peak 1 became less obvious at higher heating rates due to less time available for β -Mg₁₇Al₁₂ dissolution but the peak became more obvious at faster cooling rates due to more energy required for β -Mg₁₇Al₁₂ precipitation from the substrate. The temperature difference among the peaks was due to the occurrence of superheating/supercooling (Raynor 1970).

To study the kinetics of β -Mg₁₇Al₁₂ phase dissolution and eutectic transformation, the activation energy E can be obtained by means of Kissinger's equation (Tong and Liu 2008):

$$\frac{d(\ln(\alpha/T_p^2))}{d(1/T_p)} = -\frac{E}{R} \quad (4.1)$$

where R is the gas constant ($R = 8.314 \text{ J/mol}$), E is the activation energy, α is the heating rate (K/min), and T_p is the peak temperature in the DSC curve. Value of activation energy E can be obtained from the slope of the straight line obtained by plotting $\ln(\alpha/T_p^2)$ versus $1/T_p$, as shown in Figure 4.5. The activation energy for $\beta\text{-Mg}_{17}\text{Al}_{12}$ dissolution during heating, E_1 , is estimated from the slope of the fitted linear regression line 1 to be 178 kJ/mol , and the calculated value is in agreement with data of Bassani *et al.* (2005). Moreover, the reason for the slight difference between 178 kJ/mol and 185 kJ/mol for $\beta\text{-Mg}_{17}\text{Al}_{12}$ dissolution may lie in the difference in chemical composition between the alloys (AM60 versus AZ91D) (Pekguleryuz and Kaya 2003).

Figure 4.5 Kissinger's plot for the DSC data, 1- peak 1 and 2-peak 2

However, the activation energy for $\beta\text{-Mg}_{17}\text{Al}_{12}$ dissolution, E_1 , is far greater than 5.21 kJ/mol reported by Balasubramani *et al.* (2007). The main reason for the different values was due to the peak temperature difference of $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase dissolution measured in the different experiments. In the current study, the peak temperature based on seven heating rates was in the range of 340°C - 430°C , while the peak temperature based on three heating rates was from 319°C

to 400°C in work by Balasubramani *et al.* (2009). Furthermore, the activation energy E2 is calculated to be 788 kJ/mol, which is much smaller than 1995 kJ/mol reported by Wang *et al.* (2005). Our result is likely to be more accurate as a result of seven collected data from DSC tests compared to three plot data in the previous paper.

The typical microstructure evolution studied under SEM after the DSC measurements is shown in Figure 4.6. The supersaturated Mg with high-concentration Al regions occurred along the grain boundaries of the substrate, and β -Mg₁₇Al₁₂ particles grew as lamellar and bulk precipitation from the supersaturated Mg regions due to coring effect during the non-equilibrium process and consisted of eutectic structure with the Mg-solid solution. Ohno *et al.* (2006) also reported that the solidification and crystal growth of Mg solid solution proceeded under non-equilibrium condition using DSC tests, even though the cooling rate was very slow (1 K/min).

The grain size of α -Mg was found to decrease with scanning rates as a result of supercooling effect during solidification process (Raynor 1970), and the amount and size of eutectic structure also decreased with scanning rates due to less precipitation of β -Mg₁₇Al₁₂ in the supersaturated Mg regions. Based on the results of Bi *et al.* (2003), the extent of eutectic formation was dependent upon the amount of intimate contact between two eutectic-forming phases. In this study, the intimate contact between β -Mg₁₇Al₁₂ and α -Mg at low scanning rate was better than that at high scanning rate due to sufficient time for β -Mg₁₇Al₁₂ dissolution/precipitation.

Figure 4.6 Microstructure evolution of AZ91D specimens after the DSC measurement (a) 5 K/min (b) 15 K/min (c) 20 K/min (d) 40 K/min.

Celotto and Bastow (2001) have noted that the precipitation is sensitive to the amount of initial supersaturation of aluminum, forming the precipitates directly from the supersaturated matrix. EDS results in Figure 4.7 show the redistribution of Al in the α -Mg regions, which confirmed with the results of SEM observation. The concentration of Al in α -Mg solid solution was found to increase from 7.13 wt% to 8.78 wt% as the scanning rate increased from 5 K/min to 40 K/min.

Figure 4.7 Average Al content at the coarse α -Mg region center (more than 50 μm diameter) and in the supersaturated Mg regions near to the grain boundary as a function of scanning rate.

4.4 Solidification Microstructure

4.4.1 Microstructural Evolution

Figure 4.8 shows typical XRD patterns of AZ91D alloy before and after laser treatment. Both α -Mg phase and β - $\text{Mg}_{17}\text{Al}_{12}$ intermetallics are shown in the as-received and laser-treated microstructures. Figure 4.9 shows typical solidification microstructure of AZ91D Mg alloy induced by millisecond pulse Nd:YAG laser irradiation. As shown in Figure 4.9 (a), the periodic and successive structure was obtained in the irradiated surface after rapid solidification. After removed the oxides layer at the surface, the typical cellular/dendrite structure in the laser-melt zone was observed in Figure 4.9 (b)-(d). It can be found that the penetration depth of the laser-melted zone was more than 100 μm . Moreover, the refined microstructure was not uniform in the melt zone and coarse network of β - $\text{Mg}_{17}\text{Al}_{12}$ along the overlapped regions might be formed due to the inadequate energy distribution near the tail of Gaussian

distribution in the laser beam together with the re-melt process during laser irradiation (Liu *et al.* 2006; Guan *et al.* 2009).

Figure 4.8 XRD patterns of AZ91D Mg alloy, showing the presence of α -Mg phase and β -Mg₁₇Al₁₂ intermetallics, (a) as-received (b) laser-treated layer.

Figure 4.9 SEM images of typical solidification microstructure in the AZ91D Mg alloy following millisecond pulse Nd:YAG laser irradiation, (a) plane view of the irradiated surface, showing the periodic and successive structure (b) plane view of the top surface in the melted zone, showing the coupled eutectic structure (c) cross-section view of the melted zone, showing the thick melt depth (d) magnified view of the boundary between laser-melted region and substrate.

At the bottom of the melt zone, coarse dendrite structure was found derived from the partial melted bulk β -Mg₁₇Al₁₂ phase due to insufficient heat and relatively low cooling rate. Moreover, the re-solidified microstructure had grown epitaxially from the substrate due to the high temperature gradient, as shown in Figure 4.9 (d).

In the middle and the upper regions of the laser-melted zone, the refined microstructure did not change the morphology due to the ratio of temperature gradient (G) and solidification rate (V) G/V was nearly constant according to the simulation results of solidification conditions in the literature (Molian 1985; Liu *et al.* 2005; Nayak *et al.* 2004; Basu *et al.* 2008). Therefore, the microstructure was dependent on the cooling rates varying with the irradiation depth (Stefanescu and Ruxanda 2004), as shown in Figure 4.9 (b) and Figure 4.9 (c). At the top layer of the laser-melted zone (Figure 4.9 (b)), the coupled eutectic combined with equiaxed dendrite structure and fine cellular structure were formed due to the cooperative growth of α -Mg and β -Mg₁₇Al₁₂ happened under very high cooling rate (Stefanescu and Ruxanda 2004). Based on the kinetic undercooling theory in rapid solidification process (Greenwald et al 1978; Stefanescu and Ruxanda 2004), although due to the formation of β -Mg₁₇Al₁₂ dendrites was thermodynamically favored in the melted zone, the α -Mg cells propagated into the liquid from the original interface into the melted zone, while β -Mg₁₇Al₁₂ dendrites must nucleate first. Due to the much lower

entropy of fusion for pure Mg (Stefanescu and Ruxanda 2004), the α -Mg cells had a much higher growth rate than did the β -Mg₁₇Al₁₂ dendrites. In a situation governed by kinetics rather than thermodynamics, the faster growing phase predominated the microstructure. Therefore, Al in the melted zone was rejected by the α -Mg cells and β -Mg₁₇Al₁₂ precipitation was formed the eutectic structure at the cell boundaries together with the α -Mg cells.

Figure 4.10 indicates the whole morphology of the solidification microstructure within the laser-melted zone. Al-Mn intermetallics were also found in both laser-melted zone (they did not melt during laser processing due to high melting point) and substrate microstructure. Moreover, the heat affected zone (HAZ) in our experiment was very small due to the rapid laser heating and subsequent rapid cooling. The depth of HAZ is typically less than 50 μ m.

Figure 4.10 Three dimensional image of typical solidification microstructure of AZ91D Mg alloy in the laser-melted zone

The distribution of main elementary compositions based on EDS analysis is shown in Figure 4.11. It can be seen that average Al content increased in the

melted zone, which is likely due to relatively more Mg evaporation during laser process and the fine $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitation during the laser-induced solidification (Pierron *et al.* 2007; Mondal *et al.* 2008). Quantitative analyses of the micrographs confirmed that the Al content in the $\alpha\text{-Mg}$ matrix (79.2-82.4 wt% Mg) was in the range of 10.7-12.1 wt% and was enriched at the dendrite /cellular boundaries (61.3-65.8 wt% Mg) in the range of 30.8-33.3 wt %, which were higher than the value of 9.0 wt % in the untreated substrate (89.9 wt% Mg). This indicated that Al micro-segregation in the dendrite /cellular structure took place when the solute was ejected at the liquid/solid interface, and a boundary layer enriched Al developed in the liquid immediately ahead of the solidification front, resulting in the formation of $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitated in the inter-dendritic spaces (Molian 1985; Liu *et al.* 2005; Nayak *et al.* 2004; Basu *et al.* 2008; Mondal *et al.* 2008). The considerable amount of $\alpha\text{-Mg}$ supersaturated with Al is may be one of the reasons for the appearance of primarily $\alpha\text{-Mg}$ dendrites, even though the alloy has a nominally eutectic composition (Greenwald *et al.* 1978).

Figure 4.11 Distribution of main elements Al and Mg in the laser-melt zoned and substrate of AZ91D Mg alloy.

To obtain the thermal aspects of the solidification process that in turn has a bearing on the resulting microstructure, the cooling rates in the melted zone were calculated from a one dimensional heat flow model by the product of temperature gradient (G) within the solid at the solid/liquid interface and the solidification rate (V) of the solid/liquid interface. The governing equation is as follows (Molian 1985; Chong *et al.* 2003; Liu *et al.* 2005; Pierron *et al.* 2007; Mondal *et al.* 2008):

$$\rho(T)c_p(T)\frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(K(T)\frac{\partial T(x,t)}{\partial x}\right) + [1-R(T)]I_0(t)\alpha(T)e^{-\alpha(T)x} \quad (4.2)$$

where K is the thermal diffusivity of the material and is equal to $k/\rho C_p$; k is the thermal conductivity of the materials; R is the reflectivity and α is absorption coefficient of the material; ρ is the density of the material and C_p is the specific heat; I_0 is laser fluence. The initial condition of $T=T_0=298.15$ K was applied at time $t=0$. For AZ91D Mg alloy, $K= 55$ W/m K, $\rho= 1.81$ g/cm³, $C_p = 1050$ J/kg K (Nayak 2004).

To correlate the microstructure with the laser parameters employed, an attempt has been made to predict the thermal profile and related thermal history (heating/cooling rate, thermal gradient, etc.) resulting from the present laser treatment through numerical solution of the concerned transient heat balance equation (Eq. (4.2)) (Chong *et al.* 2003; Liu *et al.* 2005):

$0 < t < \tau$ (τ is pulse duration of laser),

$$T(x,t) = \frac{I_0\eta}{k} \left[\sqrt{\frac{4Kt}{\pi}} \exp\left(-\frac{z^2}{4Kt}\right) - z \operatorname{erfc}\left(\frac{z}{\sqrt{4Kt}}\right) \right] + T_0 \quad (4.3)$$

$t > \tau$,

$$T(x,t) = \frac{I_0\eta}{k} \sqrt{4K} \left[\sqrt{t} \times ierfc \frac{z}{\sqrt{4Kt}} - \sqrt{t-\tau} \times ierfc \frac{z}{\sqrt{4K(t-\tau)}} \right] + T_0 \quad (4.4)$$

where $ierfc(z) = \frac{1}{\sqrt{\pi}} e^{-z^2} - z erfc(z)$, $erfc(z) = 1 - erf(z)$.

Through differentiation of the above Equations (4.3) and (4.4) with respect to time, the cooling rates and solidification rate can be calculated to be:

$$\frac{\delta T(z,t)}{\delta t} = \frac{I_0\eta}{k} \left[\sqrt{\frac{K}{\pi t}} \exp\left(-\frac{z^2}{4Kt}\right) - \sqrt{\frac{K}{\pi(t-\tau)}} \exp\left(-\frac{z^2}{4K(t-\tau)}\right) \right] \quad (4.5)$$

and

$$\frac{\partial^2 T}{\partial z \partial t} = \sqrt{4K} \frac{\left[\frac{1}{2\sqrt{\pi t}} \exp\left(-\frac{z^2}{4Kt}\right) - \frac{1}{2\sqrt{\pi(t-\tau)}} \exp\left(-\frac{z^2}{4K(t-\tau)}\right) \right]}{\left[erf\left(\frac{z}{\sqrt{4Kt}}\right) - erf\left(\frac{z}{\sqrt{4K(t-\tau)}}\right) \right]} \quad (4.6)$$

The dendrite cell size or dendrite arm spacing in the laser-melted zone was measured to evaluate the rapid solidification microstructure induced by laser irradiation in the literature (Basu *et al.* 2008; Stefanescu and Ruxanda 2004; Chong *et al.* 2003; Nayak *et al.* 2004; Roósz *et al.* 1993). In this study, the measurements of dendrite cell size values were the results of the average of 300 calculations carried out in 15 different fields in the specimen. The effect of cooling rates on the dendrite cell morphology of the laser-melted zone can be understood from Figure 4.12, and Table 4.1 summarizes the calculated values for the cooling rates based on Eq. (4.5) and the experimental values for dendrite cell size measurement.

Figure 4.12 Measurement of dendrite cell size of three different regions in the melted zone from high magnification SEM images. (a) top surface layer (b) middle region in the melted zone (c) the boundary between the melted zone and the substrate.

Table 4.1 Summary of calculated cooling rates and average values of measured dendrite cell sizes in three different regions of the melted zone

Location	Cooling rate (K/s)	Dendrite cell size (μm)
Top surface layer	1.68×10^6	0.7 ± 0.1
Middle region	4.77×10^5	1.3 ± 0.1
Boundary	8.05×10^4	2.1 ± 0.1

It can be seen that as the cooling rate decreases with the melt depth from 10^6 K/s in the top surface to 10^4 K/s in the boundary of the laser-melted zone, the dendrite cell size increases from 0.7 ± 0.1 μm to 2.1 ± 0.1 μm. This agrees with the solidification theory that relates dendrite cell size and the cooling rate according to the literature (Greenwald *et al.* 1978; Chong *et al.* 2003; Nayak *et al.* 2004; Roósz *et al.* 1993; Ambat *et al.* 2000), described by the function $\lambda = B \gamma^{-n}$, where λ is average dendrite cell size in μm, γ is the cooling rate in K/s, B is a proportionality constant and n is an exponent ranging from 0.3 to 0.4. This relationship cannot be explained physically, but it can be useful in practice. In this case the relationship between the dendrite cell size and the cooling rate can be given by dendrite cell size $\lambda = 85 \gamma^{-0.33}$, where the constant B is 85 and n = 0.33.

4.4.2 Phase Transformation

The phase transformation of refined α -Mg and β -Mg₁₇Al₁₂ phase in the laser-melted zone was further investigated by TEM, as shown in Figure 4.13-4.15. Figure 4.13 (a) and (b) show the typical cellular/dendrite structure in the overlapped region. Moreover, Figure 4.13 (b) reveals that many individual particles were observed to be distributed randomly in the matrix, and the sizes of these particles were in the range of 50-200 nm. SAD patterns show that these particles exhibit the BCC crystal structure. Furthermore, quantitative analyses of elementary compositions in the particles were analyzed by EDS, including 63.11 wt% Mg, 32.83 wt% Al, 3.48 wt% Zn and 0.68 wt% Mn. Therefore, these nanoparticles were identified as β -Mg₁₇Al₁₂ phase. It should be noted that various types of Mg-Al, Mg-Mn, and Mg-Ca precipitates are generated in sizes ranging from nanometers to microns in Mg alloys processed via different methods (Luo *et al.* 2002; Coelho *et al.* 2008). However, rapid solidification induced by laser treatment result in a more homogeneous distribution as well as a relatively more refined scale.

Figure 4.13 (a) Bright-field TEM image of non-overlapped region in laser-melted AZ91D Mg alloy, showing lath-shaped β -Mg₁₇Al₁₂ formed along the

cellular/dendrite structure. (b) Bright-field TEM image of laser-melted AZ91D Mg alloy, showing β -Mg₁₇Al₁₂ formed along the cellular/dendrite structure and sub-micron and nanometer scale particles distributed within the matrix, SAD pattern from one of these particles exhibiting BCC structure.

Figure 4.14 shows that the typical orientation relationship (OR) between the individual nano particle and the matrix. The OR between the α -Mg matrix and plate-shape β -Mg₁₇Al₁₂ phase was found to be Burgers OR $((0001)_\alpha \parallel (110)_\beta)$, as shown in Figure 4.14 (a). It has been known that Burgers OR was the predominant Burgers OR of β -Mg₁₇Al₁₂ precipitation in AZ91D Mg alloy (Luo *et al.* 2002; Wang *et al.* 2006; Zhou *et al.* 2007). Moire fringes were observed in the particles due to overlapping effect between the nano-crystal and α -Mg matrix (Zhang and Weatherly 2005). Additionally, the OR between the α -Mg matrix and the spherical-shaped β -Mg₁₇Al₁₂ phase was found to be $(10\bar{1}2)_\alpha \parallel (113)_\beta$, as shown in Figure 4.14 (b).

Figure 4.14 (a) Bright-field TEM image of one individual plate-shape nano particle, SAD pattern showing Burgers OR $((0001)_\alpha \parallel (110)_\beta)$ between the particle and α -Mg matrix. (b) Bright-field TEM image of one individual

spherical-shape nano particle, SAD pattern showing OR $(10\bar{1}2)_\alpha // (113)_\beta$ between the particle and α -Mg matrix.

Furthermore, a large amount of cluster-shaped particles were observed in the overlapped region of laser-melted AZ91D Mg alloy, as shown in Figure 4.15. Figure 4.15 (a) shows cluster-shaped particles together with individual tiny particles in the matrix. The size of cluster-shaped particles was in the range of 200-400 nm, while the size of individual particles was in the range of 50-100 nm. Figure 4.15 (b) shows the morphology of one of these cluster-shaped particles, and it can be found that the nucleation and development of small particles above the existing particles. SAD pattern and EDS result confirmed that such cluster-shaped particles were β -Mg₁₇Al₁₂ precipitation. However, it should be noted that further effort need to study the specific OR among each crystal and the OR between single nano-crystal and the matrix.

Figure 4.15 (a) Bright-field TEM image of nanoparticles in the overlapped region of laser-melted AZ91D Mg alloy, showing cluster-shaped particles together with individual particles in the matrix (b) Magnified view of one of these cluster-shaped particles.

According to binary Mg-Al phase diagram in Figure 4.16, during solidification reaction sequence in as-cast AZ91D Mg alloy, the first solid to form would be α -Mg matrix due to the combination effect of thermodynamics and kinetics (Ding *et al.* 2006). On further cooling, depending on the prevalent solidification condition, the liquid composition in enriched Al region, such as grain boundary where supersaturated α -Mg region with high Al concentration (Luo *et al.* 2002; Wang *et al.* 2006; Zhou *et al.* 2007), could intersect the line of twofold saturation between α -Mg phase and β -Mg₁₇Al₁₂ phase. At this stage, the solubility limit of the primary solidification phase, α -Mg matrix, would be exceeded, and secondary solidification constituents $\alpha + \beta$ would form simultaneously from the liquid by a eutectic-type reaction $L \rightarrow \alpha + \beta$ in the structures, indicating as the lamellar structure in Figure 4.3. Moreover, due to heterogeneous chemical composition in the liquid during casting process, primary β -Mg₁₇Al₁₂ phase would form in certain high enriched Al region, and it would be elongated in the direction of the easiest heat loss, indicating as the bulk shape in Figure 4.3.

Figure 4.16 Phase diagram of Mg-Al system (Raghavan 2007)

Unlike in casting, during laser surface melting, where the molten pool is moved through the material, the growth rate and temperature gradient vary

considerably across the molten pool. Based on our previous work (Guan *et al.* 2009; Guan *et al.* 2010), solidification occurs spontaneously by epitaxial growth on the partially melted primary β -Mg₁₇Al₁₂ grains, and conditions for the growth of cellular/dendrite structure as well as line-shape structure are optimum when one of the easy growth directions coincides with the heat-flow direction. During growth of the solid in the molten pool, cellular/dendrite structure form in the overlapped region and line-shape structure occur in the non-overlapped region. This is due to heat-flow controlled rather than interface controlled, as shown in Figure 4.9 (b)-(c).

It is well known that chemical composition plays a key role in determining the final microstructure during rapid solidification. In the laser-melted zone of AZ91D Mg alloy, the content of Al element increases significantly due to rapid solidification and selective vaporization. On one hand, in laser irradiation situation where rapid solidification occurs, and the solute is ejected by the α -Mg matrix at the liquid/solid interface when α -Mg phase propagates into the liquid from the original interface into the molten pool, resulting in a supersaturation of Al in the α -Mg matrix due to very high cooling rates (Guan *et al.* 2009; Bag and Zhou 2010; Cao *et al.* 2003). On the other hand, selective vaporization of Mg and Al elements takes place, and it causes Al content increasing in the melted zone due to the relatively more evaporation of Mg element (Cao *et al.* 2003; Zhou *et al.* 2007; Guan *et al.* 2010). Therefore, eutectic reaction takes place in the non-overlapped region due to the combination effect of thermodynamics and kinetics, leading to dots-like structure, as shown in Figure 4.9.

The high degree of supersaturated α -Mg matrix and the fine and uniform structure in the melted zone results in accelerated aging kinetics for β -Mg₁₇Al₁₂ precipitation (Cerri *et al.* 2002; Wang *et al.* 2006). When laser beam was fired, the temperature was high and nuclei formed because random atomic vibrations

were continually making tiny crystals of $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase. When temperature was lower, these tiny crystals were thermodynamically stable and grew as individual nano particles, as shown in Figure 4.13. The presence of specific orientation relationship between $\beta\text{-Mg}_{17}\text{Al}_{12}$ nano particles and $\alpha\text{-Mg}$ matrix substantiated the argument that these precipitates resulted from a solid-state transformation, as shown in Figure 4.14. According to the typical ORs $(0001)_{\alpha} \parallel (110)_{\beta}$ and $(10\bar{1}2)_{\alpha} // (113)_{\beta}$, we propose that the interface between plate-shape particles and matrix is coherent, while the interface between spherical-shape particles and matrix is incoherent. Such discrepancy is maybe related to precipitation sequence during rapid solidification in the melt zone. In addition, due to laser re-heating cycles during scanning process, a driving force tended to make dispersions of those tiny crystals coarsening in the overlapped region as a result of “quench-hold-quench” process (Ashby and Jones 2006; Banerjee *et al.* 2005; Lin and Yue 2005). During coarsening, such small precipitates shrunk and eventually vanished together, whilst large precipitates grew at their expense by solid-state diffusion. This would result in cluster-shaped particles in the microstructure, as shown in Figure 4.15.

4.5 Microstructure In-homogeneities

4.5.1 Heat Transfer and Liquid Flow

The basic laser-material interaction during LSM process is shown in Figure 4.17 (David and DebRoy 1992). Due to temperature gradient of surface tension in AZ91D Mg alloy is negative (Xiao and Zhang 2007), the surface tension at the cooler edge of the molten pool is higher than that in the center. Whenever a non-uniform temperature or concentration distribution exists along the interface between two fluids, Marangoni flows arise. The radially outward Marangoni flow creates a depression of the liquid surface beneath the laser beam and ridging of the liquid surface elsewhere (Valencia and Quested 2008). As the

beam passes to other areas of the surface, this distortion of the liquid surface is frozen in, creating a roughened ripples surface, as shown in Figure 4.17 (a). Furthermore, the vigorous re-circulatory liquid flow in the molten pool is shown in Figure 4.17 (b). It is believed that convection is the predominant heat transport mechanism, and the liquid flow is driven by buoyancy and surface tension forces (Yang and DebRoy 1999; He *et al.* 2005; Wei *et al.* 2009). Buoyancy effects originate from spatial variation of the liquid material density due to temperature variation and composition differences.

Figure 4.17 Schematic diagram showing the interaction between laser beam and the substrate material. (a) plane view (b) cross-section view.

The comprehensive numerical heat transfer and fluid flow model used in the calculations has been extensively validated for various materials (Yang and DebRoy 1999; He *et al.* 2003; Mishra and DebRoy 2004; Wei *et al.* 2009). In this model, the liquid metal in the molten pool is assumed to be incompressible and Newtonian. The effects of temperature on the thermophysical properties and absorption coefficient of the laser are ignored for simplicity. The detailed information about governing equations, boundary conditions, and convergence criteria is available elsewhere and is not repeated here.

In the molten pool, heat is transported by a combination of convection and conduction. The relative importance of convection and conduction in the overall

transport of heat can be evaluated from the value of Peclet number, Pe , which is defined by

$$P_e = U\sigma / \alpha_l \quad (4.7)$$

where U is scanning speed of the incident flux, σ is the energy distribution parameter of the incident flux, α_l is thermal diffusivity $\alpha_l = k/\rho C_p$ (k is thermal conductivity and C_p is specific heat). With the increasing laser beam overlapping, energy distribution of the incident flux increases significantly, and P_e increases largely correspondingly. Therefore, convection becomes more important heat transport mechanism in the molten pool.

Driving forces for liquid flow in the molten pool considered in the heat transfer and fluid flow model include the surface-tension (Marangoni flows) and the buoyancy forces (He *et al.* 2005). Surface tension Reynolds number, M_a , is used to describe the ratio of surface tension gradient force to viscous force, and is calculated as:

$$M_a = \frac{\rho L_R \Delta T |\partial\gamma / \partial T|}{\mu^2} \quad (4.8)$$

where ρ is the density of the materials, L_R is the characteristic length taken as the pool radius at the top surface of molten pool, ΔT is the temperature difference between the peak pool temperature and solidus temperature, μ is the typical liquid velocity and $\partial\gamma/\partial T$ is the temperature coefficient of surface tension. Moreover, the ratio of buoyancy force to viscous force is determined by Grashof number, G_r :

$$G_r = \frac{g\beta L_b^3 \Delta T \rho^2}{\mu^2} \quad (4.9)$$

where g is the gravitational acceleration, β is the thermal expansion coefficient, and L_b is a characteristic length for the buoyancy force in the liquid pool which is approximated by one eighth of the pool radius.

Therefore, the relative importance of buoyancy and surface-tension forces can be determined from the ratio of surface-tension Reynolds number (M_a) to Grashof number (G_r)

$$R_{s/b} = \frac{M_a}{G_r} = \left(\frac{\rho L_R \Delta T |\partial\gamma / \partial T|}{\mu^2} \right) / \left(\frac{g \beta L_b^3 \Delta T \rho^2}{\mu^2} \right) = \frac{L_R |\partial\gamma / \partial T|}{g \beta L_b^3 \rho} \quad (4.10)$$

Moreover, the order of the maximal liquid velocity can be approximated by

$$u_m^{3/2} \approx \frac{\partial\gamma}{\partial T} \frac{\partial\gamma}{\partial y} \frac{W^{1/2}}{0.664 \rho^{1/2} \mu^{1/2}} \quad (4.11)$$

where $\partial\gamma/\partial T$ is the temperature coefficient of surface tension, $\partial\gamma/\partial y$ is the average temperature gradient (G) in the molten pool, W is the molten pool radius and the other variables have been defined before.

4.5.2 Effect of Laser Processing on Microstructure Inhomogeneities

(1) Surface Ripples and Subsurface Microstructure

The surface ripples evolution of laser-melted AZ91D Mg alloy varied with pulse duration is shown in Figure 4.18. Both the height of ripples and the roughness of surface decreased significantly with the laser pulse duration. Moreover, extensive ablation and widespread melt formation took place at short pulse duration due to high peak energy during laser irradiation, as shown in Figure 4.18 (a).

Figure 4.18 Three-dimensional surface topography of laser-melted AZ91D Mg alloy with increasing laser pulse duration: (a) 0.3 ms; (b) 0.6 ms; (c) 1.0 ms; (d) 1.5 ms.

Cross-section views of laser-melt surfaces are shown in Figure 4.19. According to the physical properties of AZ91D Mg alloy in the literature (Molian 1985; Busk 2002) and the measured molten pool radius as $432 \mu\text{m}$ in this work, the ratio of surface-tension force to buoyancy force was calculated as 4.07×10^5 based on Eq. (4. 10). Therefore, the liquid flow is driven mainly by Marangoni flows and to a much less extent, by the buoyancy force. Moreover, due to the similar L_R and L_b values in the current four molten pools, the surface-tension Reynolds number (Ma) for Marangoni flows was found to be proportional to the temperature difference ΔT between the liquid below the laser beam and the melting temperature of the material.

Figure 4.19 Cross-section views of the irradiated AZ91D Mg alloy with increasing laser pulse duration: (a) 0.3 ms; (b) 0.6 ms; (c) 1.0 ms; (d) 1.5 ms.

Temperature distribution curve on the surface during laser irradiation was calculated from transient heat balance equation based on the heat flow model in Section 4.4.1, and the results are shown in Figure 4.20. At the top surface of the molten pool, peak temperature was found to be decreased from 3500 °C to 2000 °C with the increasing pulse duration. In other words, the temperature difference ΔT decreased. Based on Anthony and Cline (1977), the ripple height is proportional to the temperature difference ΔT . Therefore, the height of ripples of laser-melted surface decreased with pulse duration significantly, as shown in Figure 4.18. Moreover, according to Reynolds number (Ma) in Eq. (4.8), Marangoni flows enhanced sufficiently when ΔT was large at short pulse duration. Correspondingly, the free surface near the solidification front

oscillated much more strongly compared to long laser pulse due to large temperature gradients and rapid solidification rates (Liu *et al.* 2005; Pierron *et al.* 2007; Mondal *et al.* 2008). Therefore, the roughness of the solidified surface increased significantly.

Figure 4.20 Temperature distribution of laser-melted layer in AZ91D Mg alloy for different melt depths varies with progressively pulse duration: (a) 0.3 ms; (b) 0.6 ms; (c) 1.0 ms; (d) 1.5 ms.

Additionally, solidification discrete bands can be clearly in the subsurface microstructure, and the number of the bands increased significantly with pulse duration, as shown in Figure 4.19. Subsurface microstructure evolution together with these discrete bands was further investigated in Figure 4.21. The solidification morphology was mainly cellular/dendrite structures, which was related to liquid-solid interface stability factor, G (temperature gradient)/ R

(solidification rate) (Molian 1985; Liu *et al.* 2005; Guan *et al.* 2009; David and Vitek 1989).

Based on Mohanty and Mazumder's (1998) work, the formation of discrete bands was mainly because Marangoni flows could arrest the growth of the dendrites leading to a remelting, fresh epitaxial growth from previous partially molten grain. Therefore, when laser pulse duration was short, the unsteady motion of the solid/liquid front increased, and the frequent growth arrest and remelting caused by the fluctuating flow field was high. Correspondingly, the start-up situation got further repeated in the entire course, leading to more discrete bands in the microstructure. In other words, surface ripples had close relationship to the solidification discrete bands in the subsurface due to the Marangoni flows. At short laser pulse duration, Marangoni flows increased significantly due to enhanced temperature difference ΔT , leading to strong oscillation of free surface near the solidification front. Therefore, rougher ripples took place at the solidified surface and more solidification discrete bands formed in the subsurface microstructure.

Moreover, it can be found that equiaxed structure grew epitaxially along the discrete bands, and the size of equiaxed cells became coarse with the increasing pulse duration due to the re-melt process during laser irradiation (Molian 1985; Liu and DuPont 2004). Such coarse equiaxed structure can provide preferential site for pitting corrosion, resulting in accelerated corrosion behavior of laser-treated surface (Liu and DuPont 2004; Guan *et al.* 2009). The detail information will be given in Chapter 5.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 4.21 Solidification discrete bands in the molten pool of AZ91D Mg alloy with increasing laser pulse duration (a) 0.3 ms (b) high magnification of (a); (c) 0.6 ms (d) high magnification of (c); (e) 1.0 ms (f) high magnification of (e); (g) 1.5 ms (h) high magnification of (g).

(2) Effect of Overlapping on Microstructure Evolution

Figure 4.22 indicates the microstructure evolution of laser-melted AZ91D top surface with the increasing overlap rates. The solidification microstructure consisted of cellular/dendrite structure, which was derived from the refined α -Mg and β -Mg₁₇Al₁₂ phases based on our previous study (Guan *et al.* 2009; Guan *et al.* 2010). Moreover, coarse structure was formed in the overlapped area along laser traces, and the amount and size of such structure increased significantly with the laser overlap rates, as shown in Figure 4.22 (a)-(b).

Further investigation of these coarse structures was shown in Figure 4.23. At low overlap rate, fine cellular structure with the size around 2-3 μm were observed in the overlapped area, and small solidification cracks were also found in the microstructure, as shown in Figure 4.23 (a). When the overlap rate increased from 25% to 75%, cellular structure to dendrite structure transition took place near solidification front at the periphery of each molten pool, and more dendrite was found in the overlapped area, as shown in Figure 4.23 (b)-

(c). At high overlap rate as 90%, coarse equiaxed dendrite structure was formed, as shown in Figure 4.23 (d).

Figure 4.22 Scanning electron micrographs showing microstructure evolution of AZ91D Mg alloy surface before and after laser treatment (a) 25 % overlap rate; (b) 50 % overlap rate; (c) 75 % overlap rate; (d) 90 % overlap rate.

Figure 4.23 High magnification scanning electron micrographs showing solidification microstructure of laser-melted AZ91D alloy in the overlapped area with increasing overlap rates in Figure 4.24: (a) 25 % (b) 50 % (c) 75 % (d) 90 %.

Cross-section views of the molten pool in the laser-melt specimens were also investigated, as shown in Figure 4.24-4.26. With the increasing overlap rates, the bottom of molten pool became flat. However, the melt depths were nearly 150 μm for all molten pools. Moreover, the small solidification cracks were also found at low overlap rate, as shown in Figure 4.24 (a). Further investigation of the microstructure evolution was observed using SEM in Figure 4.25 and Figure 4.26. At low overlap rate, fine cellular structure was found in the end of previous laser trace and needle-shape dendrite structure was formed along the laser trace, as shown in Figure 4.25 (a)-(b) and Figure 4.26 (a)-(b). It

also can be found that few cellular/dendrite structures were found in the non-overlapped area of the molten pool. When overlap rate was high, coarse equiaxed dendritic structures replaced fine cellular and cellular-dendrite structure in the overlapped area, and the solidification microstructure became much more homogenous, as shown in Figure 4.25 (c)-(d) and Figure 4.26 (c)-(d).

Figure 4.24 Cross-section views of laser-irradiated AZ91D Mg alloy with increasing overlap rates (a) 25 % (b) 50 % (c) 75 % (d) 90 %.

It is known that the liquid-solid interface stability factor, G (temperature gradient)/ R (solidification rate) determine the morphology of solidification microstructure (Molian 1985; David and Vitek 1989; Wang and Matthys 1996; Kou 2002; Liu and DuPont 2004; Guan *et al.* 2009). According to He *et al.*

(2005) and Wei *et al.* (2009), when laser energy density increases, the value of G/R decreases. In the present work, the fine cellular structure was found at low overlap rate, the equiaxed-dendritic microstructure was formed at high overlap rate and a cellular-dendritic microstructure in between after rapid the solidification, as shown in Figure 4.23 and Figure 4.25. This is in agreement with their findings (He *et al.* 2005; Wei *et al.* 2009). However, it should be noted that the explanation presented here is given on the qualitative basis for the rapid solidification. Quantitative determination of the microstructure evolution requires not only the parameter G/R , but also the thermodynamics and kinetics of solidification (Nayak *et al.* 2004; DebRoy and David 1995).

Figure 4.25 Scanning electron micrographs showing cross-section views of solidification microstructure in laser-melted AZ91D Mg alloy with increasing overlap rates: (a) 25 % (b) 50 % (c) 75 % (d) 90 %.

Figure 4.26 High magnification scanning electron micrographs showing cross-section view of solidification microstructure in laser-melted AZ91D Mg alloy with increasing overlap rates: (a) 25 % (b) 50 % (c) 75 % (d) 90 %.

In addition, at low overlap rate, the temperature gradient (G) increased significantly, resulting in larger tensile stresses when the specimens solidified and contracted unevenly (Zheng *et al.* 2004). It is worthwhile to note that Mg alloys have high thermal expansion coefficient ($16.1 \times 10^{-6}/\text{K}$ between 20 °C and 400 °C), so the thermal stress of low overlap rate are expected to be higher than that of high overlap rate (Zhou *et al.* 2007; Qian *et al.* 2008; Guan *et al.* 2009). Therefore, small cracks formed in the solidification microstructure, as shown in Figure 4.22 (a) and Figure 4.24 (a). With the increasing overlap rates, the laser energy density delivered to the surface increased significantly due to the

increasing incident flux, resulting in the temperature gradient (G) decreased in the molten pool (He *et al.* 2003; He *et al.* 2005). According to Eq. (4.8) and (4.11), the maximal liquid velocity would decrease, lead to the surface tension force (Marangoni flows) increase. Therefore, homogenous but coarse microstructure formed at high overlap rate due to the enhanced Marangoni flows. These solidification cracks and coarse microstructure would accelerate the corrosion behavior of the laser-melt layer, and the detail information will be given in Chapter 5.

Quantitative analyses of chemical compositions based on EDS measurement found that with the increasing overlap rates, average Al concentration in the overlapped area increased from 11.5 wt% to 16.7 wt%, whereas average Mg concentration decreased from 87.1 wt% to 82.2 wt% simultaneously. The reason for the chemical compositions change was due to the enhanced vaporization effect with the increasing overlap rates during laser irradiation (Chen *et al.* 2009; Guan *et al.* 2009; Guan *et al.* 2010).

4.6 Summary

Under non-equilibrium condition, kinetics of phase transformation in the as-received AZ91D Mg alloy was firstly studied; After millisecond pulse Nd:YAG laser irradiation, solidification microstructure and phase transformation as well as microstructure in-homogeneities in the molten pool was further analyzed. The main conclusions are listed as following:

(1) Activation energies for $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase dissolution/precipitation and eutectic structure transformation were calculated as 178 kJ/mol and 788 kJ/mol by calorimetric analysis. Microstructure evolution after DSC tests revealed that the size and morphology of eutectic structure decreased with scanning rates due to less discontinuous precipitation of $\beta\text{-Mg}_{17}\text{Al}_{12}$ in the supersaturated Mg

regions. The concentration of Al in α -Mg solid solution increased from 7.13 wt% to 8.78 wt% as the scanning rate increased from 5 K/min to 40 K/min.

(2) Solidification microstructures of laser-melted AZ91D occurred through the refinement of original α -Mg phase and β -Mg₁₇Al₁₂ intermetallics in the molten pool. Typical cellular/dendrite structures and a large number of β -Mg₁₇Al₁₂ nano-particles as well as enhanced Al concentration were observed due to the combined effect of rapid solidification, selective vaporization and laser re-heating cycles. The dendrite cell size increased with the decreasing cooling rates from the top surface to the bottom. The relationship between dendrite cell size and cooling rates was derived from heat flow model and solidification theory as $\lambda=85 \gamma^{-0.33}$.

(3) Microstructure in-homogeneities took place in the molten pool mainly attributed to non-uniformity distribution of laser beam, fluctuating liquid-solid interface stability, Marangoni convection and laser re-melted process. Moreover, tiny solidification cracks could be formed in the microstructure due to high thermal stress. Furthermore, numerical analysis revealed that Marangoni convection played a predominate role in determining the solidification microstructure, and Marangoni convection was depended on laser multiple pulses processing, including pulse duration and overlap rate, due to the energy density effect.

Chapter 5

Effect of Laser Surface Melting on Corrosion Behaviour of AZ91D Mg Alloy

5.1 Introduction

In this chapter, corrosion resistance of AZ91D Mg alloy before and after millisecond pulse Nd:YAG laser irradiation is examined into two parts. First, degradation behaviour of as-received and laser-treated surfaces is analyzed in modified body simulated fluid (m-SBF) at 37 °C. Secondly, electrochemical behaviour of laser-treated surface is further studied in 3.5 wt. % NaCl solution to investigate the effect of microstructure in-homogeneities on corrosion resistance.

5.1.1 Degradation Behaviour in Modified Body Simulated Fluid

In recent years, research and development work on Mg and Mg-based alloys for bio-implant applications has increased significantly (Staiger *et al.* 2006). Unfortunately, the Mg alloy implants corrode very quickly in the pH level of 7.4-7.6 and high chloride environment of the physiological systems. Consequently, the implant will lose its mechanical integrity before the tissues sufficiently heal (Staiger *et al.* 2006; Liu *et al.* 2007; Kannan and Raman 2008). Therefore, improving corrosion resistance is an important issue for the application of magnesium alloys as biodegradable load-bearing implants.

As one of the most widely used Mg alloy AZ91D, β -Mg₁₇Al₁₂ intermetallic phase in the microstructure normally helps to improve the corrosion resistance (Ambat *et al.* 2000; Jonsson *et al.* 2007), but the effectiveness of this phase in improving the corrosion resistance depends on its amount and distribution in the α -Mg matrix (Aung and Zhou 2002; Song *et al.* 2004; Zhang *et al.* 2006;

Chang *et al.* 2008). A fine and homogeneous β -Mg₁₇Al₁₂ phase provides an effective anti-corrosion barrier; however, the presence of coarse and non-homogeneously distributed β -Mg₁₇Al₁₂ phase could deteriorate the corrosion performance as it can act as a galvanic cathode (Aung and Zhou 2002). The beneficial effect of β -Mg₁₇Al₁₂ phase on the corrosion resistance may be enhanced significantly using laser surface melting due to the refinement microstructure and the increased concentration of Al element (Majumdar *et al.* 2003; Liu *et al.* 2006). The objective of this research was to study how laser surface melting could be explored to improve corrosion resistance of AZ91D alloy in m-SBF.

5.1.2 Microstructure In-homogeneities and Corrosion Resistance

As mentioned in Section 4.1.3, microstructure in-homogeneities play an important role in corrosion resistance of laser-treated surface. Reitz and Rawers (1992) observed that accelerated corrosion occurred near laser beam overlap region, and iron element segregated near the periphery of each molten pool was responsible for accelerated corrosion in zirconium alloys. Watkins *et al.* (1998) demonstrated that overlapping resulted in microstructural non-uniformity within the re-heated and re-melted area, which would lead to preferred sites for corrosion development. Similarly, Gao *et al.* (2007) confirmed that overlapping pool of laser-melted layer in AZ91HP Mg alloy was liable to be corroded due to non-uniform microstructure. Moreover, Guan *et al.* (2009) reported that coarse structure in the overlapped area of laser-treated AZ91D Mg alloy provided preferential site for pitting corrosion.

However, as of now, there has been no concentrated effort to study the effect of microstructure in-homogeneities on the corrosion resistance of laser-treated surface. The aim of this work was to study how microstructure in-

homogeneities affect electrochemical behaviour of laser-treated AZ91D Mg alloy. Polarization study in 3.5% NaCl solution was examined because the susceptibility to corrosion in chloride containing environments has been a serious concern for Mg alloy (Ambat *et al.* 2000; Pardo *et al.* 2008).

5.2 Experimental Procedures

The material studied was as-cast AZ91D Mg alloy, and the detail information was mentioned in Section 3.2. The laser used was a millisecond pulse Nd:YAG laser, and the detailed information is given in Section 3.3. The laser processing parameters for different experimental study are given below.

5.2.1 Degradation Behaviour

For degradation behaviour in m-SBF study, laser processing parameters are given in Table 5.1. The laser beam was defocused to 1 mm in diameter, and laser-irradiated area was $15 \times 15 \text{ mm}^2$ in square. All the detailed information about immersion tests and electrochemical behaviour was described in Section 3.4.

Table 5.1 Main Processing parameters employed for m-SBF tests

Specimen ID	Power density (W/cm^2)	Scanning speed (mm/s^1)	Frequency (Hz)	Overlap (%)	Pulse duration (ms)
A	3.82×10^4	5	100	50	1.0
B	3.82×10^4	10	100	50	1.0
C	3.82×10^4	20	100	50	1.0
D	3.82×10^4	30	100	50	1.0

5.2.2 Electrochemical Behaviour

For electrochemical behaviour in 3.5 wt. % NaCl solution study, laser processing parameters are given in Table 5.2. The laser beam was defocused to 1 mm in diameter, and laser-irradiated area was $15 \times 15 \text{ mm}^2$ in square. All the detailed information about electrochemical behaviour was described in Section 3.4.

Table 5.2 Main Processing parameters employed for modified seawater tests

Specimen ID	Power density (W/cm^2)	Scanning speed (mm/s^1)	Frequency (Hz)	Overlap (%)	Pulse duration (ms)
E	3.82×10^4	10	100	5	1.0
F	3.82×10^4	10	100	25	1.0
G	3.82×10^4	10	100	50	1.0
H	3.82×10^4	10	100	75	1.0

5.3 Degradation Behaviour in Modified Body Simulated Fluid

Microstructure of as-received AZ91D alloy mainly consisted of α -Mg phase as the alloy matrix, bulk β - $\text{Mg}_{17}\text{Al}_{12}$ intermetallic phase, and lamellar β - $\text{Mg}_{17}\text{Al}_{12}$ phase, as shown in Figure 5.1(a). The β - $\text{Mg}_{17}\text{Al}_{12}$ phase in the as-received alloy was found to be distributed non-uniformly in the α -Mg matrix.

Microstructure of the AZ91D alloy was changed significantly during the laser surface melting process. In laser-irradiated specimens, almost all of the β - $\text{Mg}_{17}\text{Al}_{12}$ intermetallics were refined in the laser-melted zone resulting in a more uniform microstructure, and the solidification microstructure was mainly cellular/dendrite structure with the continuous network of β - $\text{Mg}_{17}\text{Al}_{12}$ phase precipitated accumulated in the inter-dendritic spaces (Figure 5.1 (b)-(e) and Figure 5.2 (a)-(b)). Moreover, coarse equiaxed dendrite structure were found to

be precipitated along the overlapped regions due to high solidification rate caused by re-melt process (Dubé *et al.* 2001; Liu *et al.* 2006), therefore, compared to other laser-irradiated specimens, more coarse equiaxed dendrite structure were found in A due to more re-melt regions under slow laser scanning rate, as shown in Figure 5.1 (b) and Figure 5.2 (a). Furthermore, with the scanning rates increasing, less re-melt regions and small cracks were found in the laser-melted zone of the specimens C and D due to more internal stress during the very fast cooling process (Figure 5.1 ((d)-(e) and Figure 5.2 (c)-(d)).

Quantitative analysis of the chemical compositions in the laser-irradiated specimens were measured using EDS, and the measurements of the composition values were the results of the average of around 30 calculations carried out in 10 different fields in the specimen. It can be found that the average Al content in the α -Mg matrix was increased as 10.4-11.3 wt% and was enriched at the dendrite /cellular boundaries in the range of 12.6-14.5 wt%, which were higher than the value of 8.97 wt% in the as-received substrate. The increased average Al content in the melted zone is likely due to more Mg evaporation during the laser process and the fine network β -Mg₁₇Al₁₂ precipitation during the laser-induced solidification.

As laser scanning rate decreased from A to D, the laser irradiation time decreased more than three times, and the temperature gradients in the melt zone increased significantly. This process resulted in larger tensile stresses when the specimens solidified and contracted unevenly. It is worthwhile to note that magnesium alloys have high thermal expansion coefficient ($16.1 \times 10^{-6}/K$ between 20 °C and 400 °C), so the thermal stress in the melted zone of high scanning rate specimens C and D are expected to be higher than of A and B. However, the further quantitative measurement on the effect of laser parameters on the cracking formation is still needed.

Figure 5.1 Scanning electron micrographs showing original surfaces of AZ91D alloy before corrosion tests (a) as-received alloy (b) specimen A (c) specimen B (d) specimen C (e) specimen D.

Figure 5.2 Scanning electron micrographs showing microstructure evolution of AZ91D alloy before after laser surface melting (a) specimen A (b) specimen B (c) specimen C (d) specimen D.

Variation of corrosion rate with immersion time for the as-received and laser-treated specimens is presented in Figure 5.3. Specimens A and B for varying time all gave lower corrosion rates than the as-received microstructure due to the refined β -Mg₁₇Al₁₂ phase. Moreover, the specimen B showed the lowest corrosion rate, compared to other laser-irradiated specimens. The corrosion rate of A was higher than B due to the coarser dendrite structures in the overlapped regions, which was more likely to be corroded and decreased the overall corrosion resistance (Liu *et al.* 2006). Moreover, the corrosion rates of specimens C and D were found to increase largely with increasing exposure time due to small cracks in the melted zones (Figure 5.3 (b)).

Figure 5.3 Corrosion rate for as-received and laser-treated surface in m-SBF (a) after 2 h (b) after 2 weeks.

The typical surface features for corrosion initiation and growth stages of specimens A and B after different times of exposure were shown in Figure 5.4-5.5. Corrosion started initially at localized sites of the overlapped regions in specimen A and the localized attack invaded the entire surface with continued exposure. After 2 weeks immersion in m-SBF, the overlapped regions in specimen A were highly damaged, as shown in Figure 5.4. For specimen B, corrosion in the form of pitting initiated preferentially along the grain boundaries, but pits were clearly observed to be present within α -Mg grains after an exposure of 3 days. Corrosion was propagated with increasing exposure time but the degree of corrosion was lower in specimen B (Figure 5.5) compared with specimen A (Figure 5.4). The results are consistent with the assessment that B gives the best corrosion resistance.

Figure 5.4 Corrosion rate for specimen A in m-SBF as a function of exposure time.

Figure 5.5 Corrosion rate for specimen B in m-SBF as a function of exposure time.

In order to understand the effect of microstructural features on corrosion mechanism in greater detail, the corroded surfaces of 2 h and 2 weeks exposures were carefully analyzed under SEM. Selected SEM micrographs for corroded surfaces of as-received specimen and laser-irradiated A-C specimens conditions are shown in Figure 5.6-5.7.

In the initial 2 h exposure time, corrosion of the as-received microstructure occurred preferentially in α -Mg matrix and the eutectic area, and intergranular and pitting corrosion was found along the original β -Mg₁₇Al₁₂ phase (Figure 5.6 (a)). For laser-irradiated A to C microstructures, deep corrosion was observed along the overlapped regions while some localized corrosion was found within the matrix (Figure 5.6 (b) and Figure 5.6 (d)). Coarse dendrite structure in A specimen and small crack in C were the reasons for the increased corrosion rate.

After immersion for 2 weeks the microgalvanic corrosion at α -Mg matrix and eutectic phase accelerated in the as-cast microstructure (Figure 5.7 (a)). In the A microstructure localized pits were found to spread laterally along the laser passages and cover the whole surface resulting in uniform corrosion (Figure 5.7 (b)). Although localized pitting corrosion in B microstructures was propagated, the degree of corrosion was lower than that of A (Figure 5.7 (c)). Moreover, cracks in C accelerated the corrosion rate to a large extent in Figure 5.7 (d).

Figure 5.6 Scanning electron micrographs showing corroded surfaces of (a) as-received specimen (b) A specimen (c) B specimen (d) C specimen in m-SBF after 2 h exposure

Figure 5.7 Scanning electron micrographs showing corroded surfaces of (a) as-received specimen (b) A specimen (c) B specimen (d) C specimen in m-SBF after 2 weeks exposure

The results suggest that laser treatment has significant influence on corrosion behaviour of the magnesium alloy due to the refined β -Mg₁₇Al₁₂ phase. In the as-received microstructure, the bulk and lamellar β -Mg₁₇Al₁₂ phase is highly cathodic to the α -Mg phase and can thus act as an effective cathode to cause microgalvanic corrosion (Ambat *et al.* 2000; Aung and Zhou 2000; Song *et al.* 2004; Jonsson *et al.* 2007; Chang *et al.* 2008). In the laser-irradiated specimens, the original microstructure were refined to the cellular/dendrite structure with the continuous network of β -Mg₁₇Al₁₂ phase precipitated accumulated in the inter-dendritic spaces due to rapid solidification, which resulted in more than 10% average aluminum in the melt zones compared with the as-received specimen. However, in terms of the non-uniform microstructure irradiated by laser, the corrosion resistance of laser-irradiated specimen was largely depended on the laser parameter. Coarse dendrite structure in the overlapped regions and small crack in the melt zone will accelerate corrosion rate due to improper scanning rate.

The electrochemical corrosion behaviour of laser-irradiated microstructures was investigated by comparing with that of the as-received microstructure. The potentiodynamic polarization curves of all the microstructures in m-SBF are shown in Figure 5.8. The values of corrosion potential (E_{corr}), Tafel slope (β_c) and the corrosion current density (i_{corr}) for each polarization curve are summarized in Table 5.3.

Figure 5.8 Potentiodynamic polarization curves for as-received and laser-treated AZ91D alloy in m-SBF

Table 5.3 E_{corr} , β_c and I_{corr} values for AZ91D alloy before and after laser irradiation in m-SBF solution

Specimens	E_{corr} (V)	β_c (V)	I_{corr} (mA/cm ²)
As-received	-1.725	0.731	0.0722
A	-1.449	0.149	0.0085
B	-1.412	0.128	0.0075
C	-1.570	0.214	0.0317
D	-1.605	0.303	0.0541

As shown in Figure 5.3, corrosion potential E_{corr} for laser-treated microstructures was shifted to less negative values (-1.605 to -1.412 V) than that of as-received alloy (-1.725 V), indicating less corrosion susceptibility for the laser-treated microstructures. It is further noted that cathodic current i_{corr} was much lower for all laser-treated microstructures at all potentials, indicating that the laser-treated samples had lower corrosion rates. This observation is found to be in only partial agreement with the results of immersion tests (Figure 5.3): after the laser treatment, the immersion corrosion rate is indeed lower for microstructures A and B but in fact higher for microstructures C and D. However, the discrepancy can be explained because the cracks in

microstructures C and D are shown to accelerate corrosion during immersion tests (Figures 5.6 (d) and 5.7 (d)). The β_c values are similar for microstructures A and B (0.149 V and 0.128 V) or C and D (0.214 V and 0.303 V), indicating the same electrochemical reactions for A and B or for C and D. The difference in β_c value between A and B on the one hand and C and D on the other may be attributed to the cracks in specimens C and D.

5.4 Effect of Microstructure In-homogeneities on Electrochemical Behaviour

In order to study the effect of microstructure in-homogeneities on corrosion behaviour of laser-treated AZ91D Mg alloy, polarization study of as-received material and laser-treated surfaces with different overlap rates was further analyzed in 3.5% NaCl solution, as shown in Figure 5.9. The values of E_{corr} , β_c and i_{corr} for each polarization curve are summarized in Table 5.4.

Figure 5.9 Potentiodynamic polarisation curves for AZ91D Mg alloy before and after laser irradiation in 3.5% NaCl solution.

Table 5.4 E_{corr} , β_c and I_{corr} values for AZ91D alloy before and after laser irradiation in 3.5% NaCl solution

Specimens	E_{corr} (V)	β_c (V)	I_{corr} (mA/cm ²)
As-received	-1.504	0.184	0.016
E	-1.488	0.154	0.012
F	-1.459	0.113	0.010
G	-1.382	0.064	0.005
H	-1.425	0.078	0.008

Figure 5.9 shows that the E_{corr} values of laser-treated microstructures were shifted to less negative values showing more cathodic behaviour compared with as-received microstructure. It is noted that E_{corr} value of as-received AZ91D Mg alloy is in agreement with other researchers' finding (Ambat *et al.* 2000; Pardo *et al.* 2008). The cathodic part of the curve reveals that the cathodic currents were much lower for all laser irradiation specimens at potentials. In other words, the laser-treated microstructure was less active anodically with lower I_{corr} value compared with as-received material, resulting in improved corrosion resistance of AZ91D Mg alloy.

Table 5.4 shows that the β_c values are similar for microstructures E and F (0.154 V and 0.113 V) or G and H (0.064 V and 0.078 V), indicating the same electrochemical reactions for E and F or for G and H. The difference in β_c value between E and F may be attributed to the cracks formed in the microstructure due to high thermal stress, as shown in Figure 4.21 (b). The difference in β_c value between G and H may be attributed to the coarse structure formed in the overlapped area, as shown in Figure 4.21 (c) and (d). This is supported by the results in m-SBF, as shown in Figure 5.4 and Figure 5.5.

5.5 Summary

After millisecond pulse Nd:YAG laser irradiation, corrosion behaviour of AZ91D Mg alloy in modified body simulated fluid and 3.5 % NaCl solution was analyzed. The main conclusions are:

- (1) Refined homogeneous microstructure led to improved corrosion resistance of laser-treated surface. The general and pitting corrosion resistances were significantly enhanced due to the refined continuous network of β -Mg₁₇Al₁₂ phases and the increased average Al concentration.
- (2) Coarse structure in the overlapped regions caused by microstructure inhomogeneities provided preferential site for pitting corrosion, resulted in poorer corrosion resistance. Additionally, solidification cracks in the microstructure attributed to high thermal stress also accelerated the corrosion rate significantly.

Chapter 6

Surface Energy of Laser-treated Mg Alloy and Material Loss

6.1 Introduction

In this chapter, surface energy and wettability of AZ91D Mg alloy before and after millisecond pulse Nd:YAG laser irradiation is examined based upon the acid-base theory. Moreover, material loss including selective vaporization of Mg and Al alloying elements during laser irradiation is analyzed to understand the improved surface properties of laser-treated AZ91D Mg alloy regarding to Al enrichment.

6.1.1 Surface Energy

The understanding of surface energy and wettability characteristics of engineering materials is of great interest in both engineering and scientific fields. In many technological applications, plasma-assisted processing is used to modify the surface of materials and change the wettability characteristics of the material (Kinbara *et al.* 2003; Anders 1997; Zhang *et al.* 2004; Kooten *et al.* 2004). Nowadays, laser surface engineering is widely considered as a promising process to improve the surface performance without altering the global properties of the bulk materials, and it is also reported to alter surface energy and wettability characteristics of engineering materials (Lawrence and Li 1999; Man *et al.* 1997; Zhao *et al.* 2006).

Lawrence and Li (1999) found that the wettability of alumina/silica-based oxide could be improved by laser irradiation when surface melting occurred and the improved changes of the wetting and adhesion, especially for the increased polar component of the surface energy, were attributed to surface re-solidification microstructure. Man *et al.* (1997) demonstrated that the conical

structures in Si_3N_4 and LT_{35} ($\text{TiC} + \text{Al}_2\text{O}_3$) generated by excimer laser could provide extra adhesion and mechanical locking sites which were important for adhesion bonding. Zhao *et al.* (2006) observed that the surface energy of a copper plate increased when the power of the pulsed Nd:YAG laser was 1500 or 2000 W, and the wettability of Sn-Ag and Sn-Ag-Cu eutectic solders on copper surface was improved after laser irradiation.

However, little literature is available in the public domain on the relationship between the laser rapid solidified microstructure and surface energy of Mg alloys. The current work attempts to study the effect of laser irradiation on surface energy and wettability of AZ91D Mg alloy, and the changes in surface energy were investigated by the contact angle measurement based on the acid-base theory (three-liquid method) (Oss *et al.* 1988; Gindl *et al.* 2001).

6.1.2 Material Loss

Material loss is a common occurrence in several important laser processing operations. Moreover, material loss is a serious problem in the fabrication of many important engineering alloys, especially for laser welding. It has been showed that material loss causes significant changes in the microstructure and properties of laser-treated region (Cieslak and Fuerschbach 1988; Zimmerman *et al.* 1991; Cao *et al.* 2003; He *et al.* 2006; Jandaghi *et al.* 2009).

Based on previous research, vaporization of alloying elements and liquid metal ejection were reported to be the two main mechanisms of material loss during laser process (Moon and Metzbower 1983; Khan and DebRoy 1984; Willmott and Huber 2000; David *et al.* 2003). Vaporization of alloying elements is driven by high temperature and excess pressure above the irradiated surface. Due to vaporization rates of different elements, selective vaporization usually occurs during laser irradiation process. For example, vaporization of Mg and Al

elements during laser welding of Al-Mg alloys has been found to affect mechanical properties, corrosion resistance, and hot crack susceptibility of the weldment significantly (Cieslak and Fuerschbach 1988; Cao *et al.* 2003; Jandaghi *et al.* 2009).

Additionally, the selective vaporization of Mg and Al also played a significant role in the surface properties of laser-treated Mg alloys in terms of expanding solid solution range of alloying elements in the molten pool (Wang *et al.* 2007; Guan *et al.* 2009; Coy *et al.* 2010). In order to study the mechanism of selective vaporization of Mg and Al elements during laser process, a lot of work has been carried out. Jandaghi *et al.* (2009) reported that the ratio of Al to Mg concentrations increased linearly in terms of pulse duration during laser welding using laser induced breakdown spectroscopy. DebRoy and co-workers (David and DebRoy 1992; Zhao and DebRoy 2001; He *et al.* 2004) developed a theoretical model to evaluate the composition change during laser welding of aluminum alloy, and the calculations showed that the vaporization rate of Mg was about two orders of magnitude greater than that of Al.

However, it should be noted that a good understanding about the kinetics and dynamics of selective vaporization of Mg and Al elements as well as material loss during laser processing is still missing. In this work, we investigated the effect of laser irradiation on material loss of laser-treated AZ91D Mg alloy through crater and plume evolution. The craters were observed at the irradiated surface, and the plumes were deposited onto a silicon sheet for further analysis. The chemical composition of vaporized Mg and Al species in the deposited plume was examined using SEM and TOF-SIMS. The liquid material ejection on the irradiated surface and inside the plume was discussed using SEM and EDS.

6.2 Experimental Procedures

The material studied was as-cast AZ91D Mg alloy, and the detailed information is given in Section 3.2. The laser used was the millisecond pulse Nd:YAG laser described in Section 3.3. The laser processing parameters are described below.

6.2.1 Surface Energy Measurement

In this study, laser processing parameters are given in the following: power density $2.55 \times 10^4 \text{ W/cm}^2$, scanning speed 10 mm/s, frequency 100 Hz, pulse duration 1.0 ms, and spot overlap 50%. The beam was defocused to 1 mm in diameter, and the laser-irradiated area was $10 \times 10 \text{ mm}^2$ in square.

XRD was used to identify phases in the as-received alloy and in the laser-treated layer. Microstructural features of all specimens were studied using JEOL 5600 LV SEM equipped with EDS. The EDS measurements provided information on the chemical composition.

Contact angle measurement was carried out in atmospheric condition at room temperature using contact angle analyzer and syringe pump with VCA Optima device. The contact angle is defined as the angle between the solid surface and a tangent, drawn on the surface of liquid droplet, passing through the solid-liquid-vapor triple-point, as shown in Figure 6.1. Three test liquids (formamide, deionized water and ethylglycol) were used in the measurement to allow the surface energy to be calculated quantitatively based on the acid-base theory (three-liquid method) (Oss *et al.* 1988; Gindl *et al.* 2001). The detailed information about the tests was described in Section 3.6.2.

Figure 6.1 Illustration of contact angle measurement

6.2.2 Material Loss Analysis

The interaction between laser and AZ91D Mg alloy was examined using laser-induced crater on the irradiated surface and laser-generated plume above the surface to investigate material loss and selective evaporation of alloying elements during laser processing.

The fixed laser parameters were repetition rate 50 Hz and pulse duration 1.0 ms. The average power varied from 8 W to 38 W (power density varied from $4.79 \times 10^4 \text{ W/cm}^2$ to $2.27 \times 10^5 \text{ W/cm}^2$), and the laser beam was defocused to nearly 250 μm in diameter.

The experimental setup for vaporization study is shown in Figure 6.2. A hydrogen-terminated silicon sheet was placed on the AZ91D Mg alloy base material. The Si sheet was H-terminated by first cleaning in organic solvents and aqueous solutions usual for Si technology and subsequent immersion in a 2.5% HF aqueous solution for 15 s (Ishizaka and Shiraki 1986). During laser irradiation, non-volatile debris from the plume was deposited onto the Si sheet.

The deposited Si surface was analyzed using TOF-SIMS. Each scan area at the surface was about $200 \mu\text{m} \times 200 \mu\text{m}$, and the scan area for MRI was $500 \mu\text{m} \times$

500 μm . In addition, the depth profile area was 150 $\mu\text{m} \times 150 \mu\text{m}$. The detailed information about TOP-SIMS analysis is described in Section 3.5.6.

Figure 6.2 Schematic diagram showing the experimental set-up for deposited plume

6.3 Surface Energy

Contact angle measurement was carried out for the as-received alloy and laser treated specimens to study effect of the laser irradiation on the surface property. Contact angles were found to be considerably smaller for the laser treated specimens than for the as-received alloy for all the three types of liquids used (47.34° vs 70.21° for formamide, 51.55° vs 72.88° for deionized water, and 32.97° vs 63.75° for ethylglycol), as shown in Figure 6.3. This indicates that irradiation by Nd:YAG laser increased the surface wettability of AZ91D Mg alloy significantly.

Zhao *et al.* (2006) used Nd:YAG laser to treat surface of copper sheets and found that the surface wettability was improved. They attributed the increase in wettability to the laser-induced microstructural change. The change in surface

morphology did not play a role in their case, because they polished the surface after the laser irradiation.

In the current study, the specimens of the as-received alloy and those treated with laser were polished to the same roughness value of approximately $0.2\ \mu\text{m}$ (Ra). Therefore, the change in wettability is not due to the laser-induced change of surface morphology and thus must be related to the change in microstructure.

Figure 6.3 Contact angles for formamide (F), deionized water (W) and ethylglycol (E) on (a) to (c) as-received AZ91D alloy; (d)-(f) laser-treated AZ91D Mg alloy.

The microstructure in the as-received condition contained bulk and lamellar β - $\text{Mg}_{17}\text{Al}_{12}$ intermetallics distributed in a matrix of large α -Mg grains, as shown in Figure 6.4. The microstructure was observed to be free of gas porosity, which usually exists in large numbers in die castings (Huang *et al.* 2000). After laser irradiation, XRD analysis indicated no difference in phases present in the as-received alloy and laser-treated specimens and the phases were identified to be α -Mg solid solution and β - $\text{Mg}_{17}\text{Al}_{12}$ intermetallic (Guan *et al.* 2009). The laser-

treated surface consisted of a continuous network of $\beta\text{-Mg}_{17}\text{Al}_{12}$ phase precipitated at the dendrite/cellular boundaries of $\alpha\text{-Mg}$ and the primary $\alpha\text{-Mg}$ solid phase, as can be seen from Figure 6.5 (a) and (b). Moreover, the sizes of cellular structure and dendrite spacing were less than $1\text{ }\mu\text{m}$ due to high solidification rate in the top surface layer of the laser-melt zone (Stefanescu and Ruxanda 2004).

Figure 6.4 SEM micrographs showing as-received microstructure of AZ91D Mg alloy

Figure 6.5 SEM micrographs showing laser-treated microstructure of AZ91D Mg alloy, (a) low magnification view, (b) high magnification view.

The change of chemical composition in the laser melt zone is also noteworthy. EDS analyses showed that the average content of Al in the laser treated surface increased to 10-13 wt% from 8.97 wt% for the original microstructure. Furthermore, Al micro-segregation was also found in the inter-dendritic spaces. Based on the kinetic undercooling theory in rapid solidification process during the laser treatment, when the solute was ejected at the liquid/solid interface, and a boundary layer enriched Al developed in the liquid immediately ahead of the solidification front, resulting in the formation of $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitated in the inter-dendritic spaces (Greenwald *et al.*1978; Stefanescu and Ruxanda 2004). The increased Al content in the melt zone might be due to relatively more evaporation of Mg at high temperatures during the laser process and the fine $\beta\text{-Mg}_{17}\text{Al}_{12}$ precipitation during the laser-induced solidification (Guan *et al.*2009; Pierron *et al.*2007).

An interesting part of the research is the quantitative measurement of surface energy of the AZ91D alloy before and after laser irradiation. The correlation between contact angle and free energies of solid surface and liquid was well developed 200 years ago in terms of Young's equation (Young 1805):

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

where γ_{sv} , γ_{lv} , and γ_{sl} are the solid-vapor, liquid-vapor, and solid-liquid interfacial energy respectively, and θ is the contact angle, as illustrated in Figure 6.1. It is clearly impossible to use Young's equation to find free energy of a solid surface (γ_{sv}) using only one type of liquid because the interfacial energy between the new surface under study and the liquid (γ_{sl}) is unknown, though the value of γ_{lv} for commonly used liquids can be found from the literature (see Table 6.1) and the contact angle can be measured experimentally.

Table 6.1 Data of surface tension and components of the test liquids, mJ/m²
(Oss *et al.* 1988; Gindl *et al.* 2001)

Term	Formamide (F)	Deionization water (W)	Ethylglycol (E)
γ_{lv}	58.00	72.80	47.99
$\gamma_{lv}^d (= \gamma_{lv}^{LW})$	39.00	21.80	29.00
$\gamma_{lv}^p (= \gamma_{lv}^{AB})$	19.00	51.00	18.99
γ_{lv}^+	2.28	25.50	1.92
γ_{lv}^-	39.60	25.50	47.00

The acid-base theory or three-liquid method was used in the study. The theory has been developed in the recent decades (Oss *et al.* 1988; Gindl *et al.* 2001). According to the theory, the solid/liquid interfacial tension can be described by the following equations:

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2 \left(\sqrt{\gamma_{sv}^{LW} \gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^+ \gamma_{lv}^-} + \sqrt{\gamma_{sv}^- \gamma_{lv}^+} \right) \quad (6.2)$$

$$\gamma_{sv} = \gamma_{sv}^{LW} + \gamma_{sv}^{AB} \quad \text{Or} \quad \gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \quad (6.3)$$

$$\gamma_{lv} = \gamma_{lv}^{LW} + \gamma_{lv}^{AB} \quad \text{Or} \quad \gamma_{lv} = \gamma_{lv}^d + \gamma_{lv}^p \quad (6.4)$$

$$\gamma_{sv}^{AB} = 2 \sqrt{\gamma_{sv}^+ \gamma_{sv}^-} \quad (6.5)$$

$$\gamma_{lv}^{AB} = 2 \sqrt{\gamma_{lv}^+ \gamma_{lv}^-} \quad (6.6)$$

where γ_{sv}^{LW} and γ_{lv}^{LW} are Lifshitz-van der Waals components (the dispersive component γ_{sv}^d and γ_{lv}^d), γ_{sv}^{AB} and γ_{lv}^{AB} are Lewis acid-base components (the polar component γ_{sv}^p and γ_{lv}^p), γ_{sv}^+ and γ_{lv}^+ are the electron-acceptor parameters of the acid-base surface free energy component, and γ_{sv}^- and γ_{lv}^- are the electron-donor parameters of the acid-base surface free energy component. The following equation can be derived from Equations (6.2) to (6.6):

$$2\left(\sqrt{\gamma_{sv}^{LW}\gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^{+}\gamma_{lv}^{-}} + \sqrt{\gamma_{sv}^{-}\gamma_{lv}^{+}}\right) = \left(\gamma_{lv}^{LW} + 2\sqrt{\gamma_{lv}^{+}\gamma_{lv}^{-}}\right)(1 + \cos \theta) \quad (6.7)$$

The van Oss model presupposes that the total surface energy is the summation of non-polar component and acid-base component. From mathematical point of view, three liquids are needed to solve the three equations made in this model. In the equation derived, the tension components for liquid γ_{lv}^{LW} , γ_{lv}^{+} and γ_{lv}^{-} are all known for the three liquids used, as shown in Table 6.1, and the contact angle θ was measured experimentally. Therefore, the equation contains only three unknown tension components for solid (γ_{sv}^{LW} , γ_{sv}^{+} , and γ_{sv}^{-}) and their values can be found by solving the three equations (one for each liquid).

When the values of the three tension components are obtained, value of γ_{sv}^{AB} can be calculated using Equation 6.3 and free energy for the solid surface γ_{sv} can be calculated as the sum of γ_{sv}^{AB} and γ_{sv}^{LW} , as described in Equation 6.3. The calculated results are summarized in Table 6.2. The table shows clearly that the laser surface melting leads to a significant increase (by 58%) in the total surface energy γ_{sv} from 25.80 to 40.76 mJ/m², while also increasing the polar component of the surface energy γ_{sv}^p , from 4.83 to 13.53 mJ/m².

Table 6.2 Surface energy components and total surface energy (γ_{sv}) obtained, mJ/m²

Specimen	$\gamma_{sv}^{LW}(=\gamma_{sv}^d)$	$\gamma_{sv}^{AB}(=\gamma_{sv}^p)$	$\gamma_{sv}(=\gamma_{sv}^{AB} + \gamma_{sv}^{LW})$
As-received	20.97	4.83	25.80
Laser-treated	27.23	13.53	40.76

Moreover, in order to obtain all possible intermolecular reactions including polar-polar, polar-non polar and non polar-non polar forces of the surface energies for further research, the combination of a non-polar liquid (such as

heptane or diiodomethane) with two polar liquids (such as water and formamide or water and ethyl glycol) should be used during the contact angle measurement. In addition, the advancing or receding angles should also be discussed further because the difference between these two is attributed to the roughness and homogeneity according to Cassie and Wenzel (Wenzel 1949; Swain and Lipowsky 1998).

For the adhesion energy of a liquid to a solid surface (the work of adhesion), W_{ad} , is given by the Young-Dupre equation (Lawrence and Li 1999):

$$W_{ad} = \gamma_{lv}(1 + \cos \theta) \quad (6.8)$$

In this study, the adhesion energies of three test liquids to the laser-treated surface are calculated and summarized in Table 6.3. It can be found that the increased surface energy of laser-treated alloy has a positive effect upon the action of wetting and adhesion.

Table 6.3 Adhesion energies of three test liquids to the laser-treated surface, mJ/m^2

Specimen	W_{ad} for Formamide (F)	W_{ad} for Deionization water (W)	W_{ad} for Ethylglycol (E)
As-received	77.64	94.23	69.22
Laser-treated	97.30	118.07	88.25

The increase in surface energy and wettability of the laser-treated AZ91D Mg alloy is thought to be related to the laser-induced change in re-solidification microstructure and chemical composition. The dendrite and cellular structure in the molten zone is known to affect an increase in γ_{sv} , and thus an improvement in the wettability characteristics and an increase in the adhesion at the interface

in contact with the control liquids. This conclusion is in strong agreement with the findings of Lawrence and Li (1999), who studied the increased polar component of surface energy resulting from the melting and resolidification of the mild steel surface, thus creating a different microstructure that quite possibly improved the action of wetting and adhesion. Moreover, further researches are required to understand the mechanism better. For example, the test surface should be polished further to lower than 0.2 micron in order to study the effect of dendritic morphology on the contact angle measurement. Besides, laser melting induces thermal stresses (Haranzhevskiy *et al.* 2004; Qian *et al.* 2008) and it would be interesting to study how the residual stresses affect the surface energy.

Magnesium alloys have been increasingly used as structural materials for the aerospace, automotive and electronic industries, but the alloys' poor corrosion resistance limits their wider application (Ambat *et al.* 2000; Zhang *et al.* 2004; Olk and Haddad 2007). The current study indicates that laser irradiation may be used to improve wetting and adhesion of the magnesium alloy substrates for better coating quality.

6.4 Material Loss and Selective Vaporization

During laser irradiation process, intense radiation flux from the laser is transformed to the target material and raises the temperature of the target surface rapidly. When surface temperature is high enough, melting and superheating of the subsurface layer takes place, and the superheated liquid undergoes an explosion that turns the liquid into a mixture of liquid and vapor. Moreover, the escaping vapor exerts a large recoil force on the subsurface and, as a consequence, liquid metal droplets may be expelled from the molten pool. Therefore, vaporization of alloying elements and liquid metal ejection are the

two main mechanisms of material loss during the laser process (Khan and DebRoy 1984; Willmott and Huber 2000; Mundra 1994).

The material loss process is illustrated in Figure 6.6. When laser-pulse interacts with the material, superheating of subsurface layer happens, leading to the rate of homogeneous nucleation increases dramatically in the molten pool. Moreover, the nucleation frequency in the depth of the substrate is normally higher than that closer to the surface (Yoo *et al.* 2000), as shown in Figure 6.6 (a). Under some value of superheating, the nucleation can coalesce into a bubble and the pressure gradient across the thin liquid film separates the bubble from the outside space (Figure 6.6 (b)).

Furthermore, the bubble inflates into a large vapor volume due to continuing vaporization from its surface (Figure 6.6 (c)). With laser-pulse termination, fast plume expansion results in a dramatic decrease of vapor pressure above the substrate surface that, in its turn, causes the vapor bubble to grow further and to burst eventually (Figure 6.6 (d)). Finally, the liquid material ejection either falls down onto the splashed surface or remains inside the plume, and the crater formed in the molten pool.

Figure 6.6 Schematic representation showing material loss via alloying elements vaporization and explosive melt ejection during laser irradiation process: (a) superheating of the subsurface layers; (b) nucleation coalescence

into a bubble; (c) bubble inflation due to vaporization; (d) bubble bursting after laser-pulse termination.

6.4.1 Plume Analysis

Figure 6.7 shows surface morphology of one typical deposited plume on Si sheet after laser irradiation. It can be found that the deposited plume has an ellipse shape and the dimension is nearly $500\text{ }\mu\text{m} \times 1500\text{ }\mu\text{m}$, and the average thickness of the deposited plume was estimated as 322 nm. Moreover, MRIs scanning area and depth profile area at the bottom of the deposited plume are also illustrated in Figure 6.7. Furthermore, a few liquid ejection of molten material was also observed at the surface, indicating phase explosion phenomenon with a mixture of liquid and vapor during laser processing (Yoo *et al.* 2000).

Figure 6.7 SEM image of the deposited plume on the Si sheet

The MRIs results are shown in Figure 6.8. Each MRI shows a chemical mapping of an element component in the deposited plume. According to the color contrast of Si element in Figure 6.8 (a), the boundary between the deposited plume and the Si substrate was indicated as the white line. It can be found that the concentration of Mg is quite uniform in the whole area, while the

concentration of Al increases with the distance far from the boundary. Moreover, Zn element was very few in the deposited plume. Furthermore, the signal of Mg, Al and Zn elements below the boundary line was due to edge effect during deposition process of the plume to the Si sheet.

Figure 6.8 Mass-resolved images (MRIs) of the bottom region in the deposited plume: (a)-(d) showing chemical mapping of different elements analyzed by SIMS.

The normalized Mg and Al contents in the depth profile area are shown in Figure 6.9. It can be found that Mg dropped rapidly from the surface (position a) to the subsurface (position b, position c, and position d) of the deposited plume, while Al increased first from position a to position b and then decreased from position c to position d. Moreover, Al content was higher than Mg in the deep subsurface of the deposited plume, as indicated from position c to position d in Figure 6.9. Furthermore, the corresponding subsurface locations of b, c and d were estimated to be 181 nm, 265 nm and 1.228 μm , respectively. In other words, at the initial stage of vaporization process, the number of Mg species deposited on Si sheet was less than that of Al species. With the increasing time of vaporization, the deposited Mg species increased rapidly compared to that of Al. At the final vaporization stage in this work, the deposited Mg species remained increasing, while the deposited Al species dropped to nearly zero.

The ratio of Mg:Al contents both at the surface and in the subsurface of the deposited plume was further discussed. At the surface, the ratio was calculated

as 61.3:1, which was much higher than the base metal composition 10:1. With the increasing sputtering time, Mg concentration decreased rapidly, while Al concentration increased. When the sputtering time increased to the subsurface at position b, Al was enriched and the ratio of Mg:Al reduced to 9.66:1. When the sputtering time further increased to position c, the ratio of Mg:Al reduced to 1.21:1, and the final ratio of Mg:Al was 3:1 at position d due to very low Mg and Al contents. Such results also show that positions a, b and c were within the deposited plume as well as position d was close to Si substrate, and this is in agreement with the average thickness of the deposited plume on Si sheet as 322 nm.

Figure 6.9 Chemical contents of the vaporized Mg and Al at the bottom region of the deposited plume using TOF-SIMS depth profile, while a, b, c and d showing four positions of Al content change.

The chemical contents of vaporized Mg and Al species at the surface of whole deposited plume were also calculated and listed in Table 6.4. It can be found that from the bottom region (200 μm) to the top region (1400 μm), Mg concentration dropped rapidly from 96.6 wt% to 0.3 wt%, and the ratio of Mg:Al contents decreased significantly from 64.9:1 to 0.9:1. Moreover, from 200 μm to 500 μm , the content of Mg did not decrease too much and the average ratio of Mg:Al was more than 50:1. This is in agreement with the

results in Figure 6.3 and Figure 6.4, and it indicates that the vaporization of Mg element is far exceeded than that of Al element during laser irradiation. Furthermore, Al concentration increased from the bottom region to the middle region (800 μm) and then decreased until the top region. Such trend is similar to the result in Figure 6.8.

Table 6.4 Chemical composition of the vaporized Mg and Al elements at the surface in the deposited plume

Distance (μm)	Mg content (wt%)	Al content (wt%)	Mg/Al
200	96.6	1.5	64.9
500	93.8	1.8	51.9
800	76.3	3.3	23.0
1100	5.2	0.5	10.3
1400	0.3	0.3	0.9

The possible kinetics of selective vaporization of Mg and Al alloying elements during laser irradiation on AZ91D Mg alloy will be discussed briefly in the following.

Firstly, according to previous studies, the vaporization rate of Mg was about two orders of magnitude greater than that of Al (David and DebRoy 1992; He *et al.* 2004). Moreover, the ratio of Mg:Al content was high as 10:1 in the base metal composition. Therefore, the combined effect of different vaporization rate and original chemical composition would result in the great ratio of Mg:Al contents in the plume, especially at the surface of the bottom region, as shown in Figure 6.8 and Table 6.4.

Secondly, the distribution of vaporized Mg and Al elements in the plume can be explained using a simple model, as shown in Figure 6.10. At the bottom of the plume, which was indicated as core region, the density of vaporized Mg and Al species was very high and the local vapor pressure exceeded the ambient pressure when the plume generated from the molten pool surface. According to

Table 6.4, the core region was estimated from the molten pool surface to 800 μm in the current deposited plume. Moreover, when the plume expanded into the surrounding environment, the vapor pressure decreased significantly. Simultaneously, the pressure difference between the core region and the atmosphere would lead to a shell region at the top of the plume. Correspondingly, the density of vaporized Mg and Al species decreased significantly in such shell region, and this was shown as the low contents of Mg and Al from 1100 μm to 1400 μm in the deposited plume in Table 6.4. This conclusion is in strong agreement with the findings of Li *et al.* (2007), who observed three different regions of the deposited plume in polyimide film and polycarbonate substrates. Furthermore, our result also supports DebRoy's calculation that the vaporization was concentrated in a small active region where local vapor pressure exceeded the ambient pressure under the laser beam based on the theoretical models (Zhao and DebRoy 2001).

Figure 6.10 Schematic showing core region and shell region in the plume generated from the molten pool

Thirdly, the discrepancy distribution of Mg and Al elements both at the surface and in the subsurface of the deposited plume was possibly attributed to the rate of transport of vaporized species from the molten pool surface to the plume. It has been reported that the rate of transport of the vaporized alloying elements

depends on the nature of the boundary layer and the diffusivities of the vaporized species (Collur *et al.* 1987). Based on Chapman-Enskog theory (Collur *et al.* 1987; Mundra 1994), the diffusivities of Mg and Al vapors in Ar gas at various temperatures are calculated and presented in Table 6.5. It is clear from the table that the diffusivity of Al is nearly two to three times than that of Mg at high temperature range from 2500 K to 3500 K. Therefore, we propose that the transport rate of vaporized Al species is higher than that of Mg species during vaporization process, especially at the initial stage. This is maybe the reason for the enrichment of Al content both in the middle region at the surface and as in the subsurface of the deposited plume, as shown in Figure 6.8, Figure 6.9 and Table 6.5.

Table 6.5 Diffusivities of magnesium and aluminum vapors in argon gas $\times 10^4$, m^2/s

T (K)	Magnesium	Aluminum
1000	1.02	1.31
1500	1.31	1.78
2000	1.71	3.52
2500	2.45	6.57
3000	3.86	9.18
3500	5.48	14.57

6.4.2 Plume Evolution

Figure 6.11 shows the surface morphology evolution of deposited plumes on Si sheet with the decreasing laser power. When laser power decreased from 38 W to 8 W, the length of the deposited plumes decreased from $\sim 2000 \mu\text{m}$ to $\sim 500 \mu\text{m}$. Moreover, the amount of liquid ejection at the surface was also decreased significantly, especially from 26 W to 8 W, as shown in Figure 6.11 (b)-(d). It should be noted that the size of deposited plume and the amount of liquid ejection increased linearly with the laser power, therefore, the shape of deposited plume and the amount of the ejection were highly depended on the

distance between the Si sheet and the irradiated spot during the deposition process. This is attributed to the discrepancy of the deposited plume at high laser power, as shown in Figure 6.11 (a).

The mass spectrum peak data of main elements were extracted from chemical maps for selected areas in the plume using TOP-SIMS, and the normalized chemical contents of Mg and Al at the surface of all deposited plumes were shown in Figure 6.12. Figure 6.12 (a) shows that Mg content decreases linearly with laser power, and Mg content at the bottom region of the deposited plume decreased from 96.2 wt% to 1.8 wt% when laser power decreased from 38 W to 8 W. Moreover, Mg content dropped significantly from the bottom region to the top region of the deposited plume, especially for high laser power at 38 W, 26 W and 15 W. In other words, vaporization of Mg element increases with laser power significantly, and the vaporization of Mg element is dominant mechanism at high laser power.

Figure 6.11 Morphology evolution of deposited plume on the Si sheet with different laser power: (a) 38 W (b) 26W (c) 15 W (d) 8 W.

For Al content, the situation is more complicated. As shown in Figure 6.12 (b), for all deposited plumes, Al content increased from the bottom region first, and then dropped to the top region. When laser power decreased from 38 W to 15 W, Al content in the deposited plume increased significantly, especially at the bottom region. The reason for such phenomenon is attributed to relatively high diffusivity of Al vapors during vaporization process (Collur *et al.* 1987; Mundra 1994), and it is in agreement with the results in Figure 8 and Table 6.4. For low laser power as 8 W, very little Al content was found at the Si sheet, and this is similar to Mg content in Figure 6.12 (a).

Figure 6.12 Chemical compositions of the vaporized Mg (a) and Al (b) elements at the surface in the deposited plumes at various laser powers.

6.4.3 Crater Evolution

Figure 6.13 shows the surface morphology evolution of laser-induced craters on AZ91D surface correspondent to the plumes in Figure 6.11. When laser power was very high, large volume of melt was found above the crater, and the crater feature became coarse and poorly defined in the irradiated area. Moreover, micron-sized liquid ejection was present in the regions beyond the rim of the crater (Figure 6.13 (a)). With laser power decreased, the volume of the melt as well as the size of liquid ejection decreased dramatically. However, the amount of liquid ejection was found to be increased significantly at the widespread splashed surface (Figure 6.13 (b)). When laser power further decreased, less melt was observed above the crater. Both the amount and the size of the liquid ejection decreased correspondingly (Figure 6.13 (c)). According to the analysis in Figure 6.6, it can be found that the formation of craters with splashed surface were possible due to the vapor ejection from the substrate depth, while the outer colder layer might be re-solidified at the edge of irradiated spot, as shown in Figure 6.13 (b) and (c). When the laser power was sufficient low, only partial melt of the substrate was found at the surface, and the rim of the crater became unclear. Little liquid ejection was observed at the irradiated surface (Figure 6.13 (d)).

Figure 6.13 Morphology evolution of laser-induced craters on AZ91D Mg alloy with different laser power: (a) 38 W (b) 26 W (c) 15 W (d) 8 W.

Surface topography of the craters and the melt was further studied using stylus profilometer, and the results are shown in Figure 6.14. Figure 6.14 (a) displays the volume of the melt above the crater was quite large at high laser power. When laser power decreased, the craters exhibited a deep-hole shape with rim above the surface, as shown in Figure 6.14 (b)-(d). Moreover, the melt above the surface was found to be on the rim of the crater, and the volume of such melt decreased linearly with the laser power. Furthermore, with the laser power decreasing, both diameter and depth of the crater decreased significantly while maintaining the deep-hole shape.

Figure 6.14 Cross-sectional view of the craters at various laser powers: (a) 38 W (b) 26 W (c) 15 W (d) 8 W.

Quantitative analyses of main elementary composition for the liquid ejection and the center of the craters were analyzed using EDS, and the results are shown in Figure 6.15. For liquid ejection, with the laser power decreasing, Mg content increased while Al content decreased linearly. Moreover, Mg content was found to be lower than that as-received composition, especially at high laser power, while Al content was higher than that as-received composition.

Figure 6.15 Chemical compositions of main elements at the irradiated surface at various laser powers (a) inside the liquid ejection (b) in the center of the craters.

Furthermore, element composition for the rim region of the craters was also analyzed, and it can be found that the distribution of Mg and Al contents were the same as that of liquid ejection. The reason for the chemical composition change is due to selective vaporization of Mg and Al elements during laser irradiation, as discussed in Section 6.4.1 and Section 6.4.2. In addition, the element composition of Mg and Al in the center of craters was found to be similar to the base metal composition.

6.5 Summary

Surface energies of AZ91D Mg alloy before and after millisecond pulse Nd:YAG laser irradiation were studied. Additionally, material loss during laser processing was also analyzed. The main conclusions are:

- (1) Results obtained from contact angle measurements revealed that laser treatment enhanced wettability significantly and led to drastic increase in total surface energy from 25.80 to 40.76 mJ/m² and in polar component of the surface energy from 4.83 to 13.53 mJ/m², thus improving the action of

wetting and adhesion. The change in surface energy is attributed to the refined microstructure and the increased Al concentration in the irradiated area due to laser induced surface melting and rapid solidification.

- (2) Material loss, including selective vaporization of Mg and Al alloying elements and liquid metal ejection, increased significantly with laser fluence during irradiation. Al concentration was enriched in both molten pool and ejected liquid. Ratio of Mg:Al contents in the core region of laser-generated plume was more than 50:1, which is attributed to the combined effect of different vaporization rate of Mg and Al species and original chemical composition in the substrate. Moreover, transport rate of vaporized Al species was nearly three times higher than that of Mg species due to high diffusivity of Al vapors in Ar gas during laser processing. The enrichment of Al at the irradiated surface played a very important role in improving the surface properties of laser-treated AZ91D alloy.

Chapter 7

Interaction between Short Pulse Laser and Mg

7.1 Introduction

In this chapter, effect of short pulse laser irradiation, including nanosecond and femtosecond, on pure Mg and AZ91D as well as AZ31B Mg alloys is discussed in three parts. First, microstructural evolution of AZ91D Mg alloy following nanosecond pulse Nd:YAG laser irradiation is examined and compared with that of millisecond pulse Nd:YAG laser irradiation. Local boiling and superheating phenomenon is also analyzed. Additionally, surface coloration of AZ31B Mg alloy following nanosecond pulse Nd:YAG laser and Excimer laser irradiation is studied. Second, periodical surface structure on pure Mg as well as structure color on AZ31B Mg alloy following femtosecond laser irradiation is examined. Mechanism of ripples formation and their potential application is also studied.

7.1.1 Nanosecond Pulse Laser

(1) Boiling and Subsurface Superheating

In order to study the effect of laser surface treatment on Mg alloy further, nanosecond pulse Nd:YAG laser was used. However, instead of improving surface properties of Mg alloy following nanosecond pulse laser irradiation, local boiling phenomenon and various craters were achieved at the surface.

During short-pulse (several nanoseconds or shorter) laser irradiation, surface boiling usually takes place due to high temperature at the surface induced by high laser influence, and it can directly influence surface feature and microstructure of the irradiated area (Jacobs and Rikken 1987; Bhattacharya *et*

al. 1991; Rubahn 1999; Craciun *et al.* 2002). Jacob and Rikke (1987) studied the local boiling effects and bubble formation at the solid-liquid interface, and they found that the morphology of laser-irradiated surface was severely affected by local boiling effects and/or gas evolution occurring during laser irradiation.

Moreover, subsurface superheating phenomenon has been investigated to be an important procedure during nanosecond laser irradiation (Steen 2003; Bhattacharya *et al.* 1991; Rubahn 1999; Craciun *et al.* 2002; Tillack *et al.* 2004). Surface of the target is being cooled by the latent heat of evaporation, while a finite amount of laser energy is deposited within a certain depth from the surface of the target. In contrast to the surface latent heat cooling mechanism, the cooling mechanism inside the target is the conduction of heat into the bulk. This will result in internal temperatures being higher than the evaporating surface temperatures, so called subsurface superheating. The high subsurface superheating temperatures may lead to nucleation of the gaseous phase at the near surface, thereby leading to “microexplosions” of the material of the target at some stage of the incoming laser pulse. According to Craciun *et al.* (2004), these “microexplosions” inside the target would cause volume expulsion of the material.

However, little effort was made to gain a good understanding of the interaction between nanosecond pulse laser and Mg alloy, and the effect of nanosecond pulse laser irradiation on the solidification microstructure of Mg alloy is also missing. The current research was carried out to study effect of nanosecond pulse Nd:YAG laser irradiation on AZ91D Mg alloy. Special attention was made to understand the kinetics of rapid solidification and phase transformation as well as the mechanism of boiling effect and crater formation during laser irradiation.

(2) Surface Coloration

Laser-induced coloration of material surfaces is an interesting phenomenon, and it provides an alternative approach to the understanding of coloration theory and also to many promising applications, such as decorations, product identification, biocompatible implants and photocatalysts (Malhotra *et al.* 1991; Zhao *et al.* 1997; Bichevin *et al.* 1998; Anpo and Takeuchi 2003; Takemoto *et al.* 2004; Bartlett 2006; He *et al.* 2008; Zheng *et al.* 2002; Li *et al.* 2009; Qian *et al.* 2008).

Different mechanism of coloration was proposed according to various laser-material interactions. Malhotra *et al.* (1991) reported laser-induced darkening in semiconductor-doped glasses with picosecond pulses, and they suggested that darkening was due to removal of the electrons from the microcrystallites to states in the amorphous glass host. Zhao *et al.* (1997) and He *et al.* (2008) ascribed laser-induced coloration of WO_3 to photoinduced thermochromism, and this was different from ordinary photochromism induced by UV light.

Besides these works on semiconductor materials, studies have also been carried out on non-semiconductor materials. Zheng *et al.* (2008 and 2009) studied color change of different material surfaces following laser irradiation, and they found that the color generation was the result of controlled surface oxidation during laser beam interaction with the metal surfaces. According to this correlation, Qian *et al.* (2008) demonstrated formation of different oxides layer on the irradiated Ti surface, and proposed that morphological change of irradiated area played an important role in determining the laser-induced coloration. Moreover, Qian *et al.* (2008) analyzed surface coloration on TiO_2 film irradiated with excimer laser, and explained that the darkening effect was due to trapping of light in the surface defects formed rather than anatase to rutile phase transformation as reported by others.

Recent studies have showed that the application of Mg alloys can be explored to more fields due to advanced surface engineering technology (Zheng *et al.* 2008; Bull 2005; Ma *et al.* 2008; Gray and Luan 2002; Abbas *et al.* 2005; Guan *et al.* 2009 and 2010). In this work, surface coloration was achieved on AZ31B Mg alloy following both KrF Excimer laser and nanosecond pulse Nd:YAG laser irradiation. The current study attempts to characterize surface morphology and chemistry of irradiated areas, with the aim of furthering understanding of laser processing that lead to laser-induced darkening effect.

7.1.2 Femtosecond Pulse Laser

(1) Periodical Surface Structure

The generation of laser-induced periodic surface structures (LIPSS), also termed as ripples, is a universal phenomenon during laser irradiation (Emmony *et al.* 1973; Driel *et al.* 1982; Sipe *et al.* 1983). In current years, the formation of ripples induced by femtosecond lasers has been widely reported on different materials (Wu *et al.* 2003; Bonse *et al.* 2005; Miyaji and Miyazaki 2006; Tomita *et al.* 2007; Hsu *et al.* 2008; Huang *et al.* 2009; Dufft *et al.* 2009).

According to previous studies, most of the ripples can be classified into two groups (Dufft *et al.* 2009; Borowiec and Haugen 2003; Qian and Zhou 2005; Bonse *et al.* 2000; Costache *et al.* 2002; Miller and Haglund 1998). One is called low-spatial-frequency LIPSS (LSFL), with a spatial period close to the wavelength of the incident light. The other is called high-spatial-frequency LIPSS (HSFL), with a spatial period significantly smaller than the wavelength of the incident light. Moreover, micrometer-spaced grooves, which were perpendicular to the ripples, have also been observed by Bonse *et al.* (2005) and Borowiec and Haugen (2003) at the irradiated surface of materials.

However, the nature of those structures is still quite controversially discussed in the literature. Moreover, few results have been published for the effect of femtosecond laser irradiation on Mg alloys. In this study, we firstly report periodical surface structure on the surface of pure Mg irradiated by femtosecond laser, and further analyze the mechanism of structure formation in terms of the interaction between incident light and surface plasmons of metal.

(2) Structure Color

It is well known that when surface structures are aligned in arrays, they can separate mixed “white” light into light of different wavelengths due to diffraction grating behaviour (Palmer 1999; Freund 2007). In nature, such structural color is responsible for blues and greens of the feathers of many birds, as well as certain butterfly wings and beetle shells. Moreover, variations in the periods of these structures result in an iridescent effect, as seen in peacock feathers, soap bubbles, films of oil, and mother of pearl, because the reflected color depends upon the viewing angle.

Nowadays, the applications of LIPPS on surface modification have attracted many attentions. Vorobyev and Guo (2008) produced ripples over an extended area by scanning laser beam across a metal surface, and they suggested that such technique was an effective method for controlling the optical properties of metals. Their studies as well as the calculations of Dusser *et al.* (2010) show that the possibility of achieving material modifications using femtosecond laser irradiation could generate specific color patterns. Moreover, Ramirez *et al.* (2010) fabricated nanogratings, known as self-organized nanostructures with subwavelength periodicity, in certain parameter ranges during femtosecond-laser processing of transparent materials, resulting in characteristic birefringent modifications.

However, few results have been published for the effect of femtosecond laser irradiation on structure color of Mg alloy. In this study, we firstly report structure color on the surface of AZ31B Mg alloy irradiated by femtosecond laser at near damage threshold fluence. Ripples with broad distribution of spatial periods smaller than laser wavelength were observed. Moreover, we demonstrate the iridescent effect on the surface of Mg alloy by writing large-area ripples with a single laser beam. This technique can be possibly applied to potential application of Mg alloy, such as diffractive devices, product identification and tracking as well as biomaterials.

7.2 Experimental Procedures

The material studied was ingot pure Mg, as-cast AZ91D Mg alloy and wrought AZ31B Mg alloy, and the detailed information is given in Section 3.2. The lasers used were the nanosecond pulse Nd:YAG laser, KrF excimer laser, and Ti:sapphire femtosecond laser described in Section 3.3. The laser processing parameters used are given below.

7.2.1 Nanosecond Pulse Laser

(1) Microstructural Evolution of AZ91D Mg Alloy Irradiated by Nd:YAG Laser

The nanosecond pulse Nd:YAG laser robot system was used for the following parameters: power density 1.37×10^8 W/cm² (peak power 9.65×10^5 W), scanning speed 10 mm/s, frequency 6000 Hz, and pulse duration 38 ns. The laser beam was delivered to the specimen surface through an optical fiber (0.6 mm in diameter) fixed on the robot arm, parallel to the normal of the plates. The focal length of the focal lens was 200 mm. Defocused beam was used with a square beam spot of 1.2 mm side length. The laser-irradiated area was 10×10

mm² in square using hatched scanning mode with 50% overlapping in the program. Moreover, when the laser beam was fired, the processing environment to the laser-irradiated area was under shrouding Ar gas at a pressure of 2.0 bar (2.0×10^5 Pa) using well sealed chamber.

(2) Local Boiling of AZ91D Mg Alloy Irradiated by Nd:YAG Laser

The nanosecond pulse Nd:YAG laser robot system was used for the following parameters: power density 1.37×10^8 W/cm², scanning speed 1000 mm/s, frequency 6000 Hz, and pulse duration 38 ns. The beam profile used was in flat top-hat mode, so the energy of laser was uniformly distributed to the surface of specimen. The laser-irradiated area was 10×10 mm² in square using hatched scanning mode with 50% overlapping in the program. Moreover, the laser was operated using a square beam spot of 1.2 mm side length, and the specimen was placed in a well-sealed chamber using 2.0 bar Ar gas flow.

(3) Surface Coloration of AZ31B Mg Alloy Irradiated by Nd:YAG Laser

The nanosecond pulse Nd:YAG laser robot system was used for the following parameters: scanning speed 10 mm/s and frequency 6000 Hz. The irradiated area was single track line in the surface with the length of 10 mm. Moreover, the values of laser average power were varied from 40 W to 110 W for line No. 1 to No. 5, as shown in Figure 7.1. The average irradiation time was nearly 1 s for each line.

Figure 7.1 Photo showing darkening effect of the irradiated areas with increasing laser power on AZ31B Mg alloy surface induced by nanosecond pulse Nd:YAG laser in air, where **1** represented 40 W, **2** represented 60 W, **3** represented 70 W, **4** represented 90 W, **5** represented 110 W.

(4) Surface Coloration of AZ31B Mg Alloy Irradiated by Excimer Laser

The KrF Excimer laser was used by the following parameters: laser fluence 655 mJ/cm^2 and repetition rate 10 Hz. Laser beam was operated with a square beam spot of 3 mm side length, and the number of laser pulses was varied from 100 to 800. Moreover, in order to demonstrate the effect of O_2 , the specimens were irradiated in air, under 0.5 bar Ar using nozzles and 2.0 bar Ar using well-sealed chamber, respectively.

7.2.2 Femtosecond Pulse Laser

Ti:Sapphire femtosecond laser was used. The polarization of the incident laser radiation is horizontal (p-polarized). The sample surface was irradiated under normal incidence by focused linearly polarized laser in air. The laser processing parameters for different experimental study are given in the following.

(1) Periodical Surface Structure on Pure Mg

The single pulse energy was nearly 20 μJ , and the number of laser pulses was varied from 1 to 1000 pulses. Pure Mg was used in this study to discuss fundamental physical phenomenon.

(2) Structural Color on AZ31B Mg Alloy

The single pulse energy was nearly 30 μJ , and the laser-irradiated area was $20 \times 20 \text{ mm}^2$ in square using hatched scanning mode in the program. The laser scan times were varied from 1 to 100. Wrought AZ31B Mg was used in this study to explore potential practical application.

XRD was used to identify phases in the as-received alloy and in the laser-treated layer. Microstructural features of all specimens were studied using JEOL 5600 LV SEM equipped with EDS. Surface topography with low laser pulses was measured using AFM in tapping mode. The surfaces produced with large number of laser pulses were too rough to be characterized with AFM, so their topography was characterized using a Taylor Hobson Precision Talysurf profiler. Moreover, optical reflection of irradiated area at the specimen surface was measured using Ocean optics DT-Mini-2 system and Spectrometer Operating Software. Furthermore, surface chemistry was studied using XPS with Kratos-Axis spectrometer. The spectra were calibrated using C 1 s peak position at 284.6 eV. The detailed information of material and surface characterization was mentioned in Section 3.5 and Section 3.6.

7.3 Effect of Nanosecond Pulse Laser on Mg Alloys

7.3.1 Microstructural Evolution of AZ91D Mg Alloy Irradiated by Nd:YAG Laser

Figure 7.2 shows typical XRD patterns of AZ91D Mg alloy before and after laser treatment. Both α -Mg phase and β -Mg₁₇Al₁₂ intermetallics are shown in the as-received and laser-treated microstructures.

Figure 7.2 XRD patterns of AZ91D Mg alloy, showing the presence of α -Mg phase and β -Mg₁₇Al₁₂ intermetallics, (a) as-received (b) millisecond laser-treated layer (c) nanosecond laser-treated layer.

Figure 7.3 shows typical solidification microstructure of AZ91D Mg alloy irradiated with nanosecond pulse Nd:YAG laser. As shown in Figure 7.3 (a), the molten materials spread out in the irradiated surface and many holes were also observed in the melt. Moreover, Figure 7.3 (b) indicates that the melted depth was nearly 50 μ m, which was much shallower than the millisecond laser-melt depth, as shown in Figure 4.9 (c). As shown in Figure 7.3 (b)-(c), very fine microstructure was obtained in the laser-melt zone due to high laser fluence and rapid solidification rate after nanosecond laser irradiation. Moreover, these fine structures in the top layer were directed at the surface. This could be related

to the manner of changing cooling rates in the laser melting process, which reached its maximum at the top surface (Molian 1985; Liu *et al.* 2005; Pierron *et al.* 2007; Mondal *et al.* 2008). Furthermore, the structures became coarse and epitaxial in the boundary region of the laser-melted zone due to low cooling rates and high temperature gradient, as shown in Figure 7.3 (b) and (d).

Figure 7.3 SEM images of typical solidification microstructure in the AZ91D Mg alloy following nanosecond pulse Nd:YAG laser irradiation, (a) plane view of the irradiated surface, showing the molten materials and holes (b) cross-section view of the melted zone, showing the shallow melt depth (c) magnified view of the middle region and top surface (d) magnified view of the boundary between laser-melted region and substrate.

In addition, according to the heat flow model (Eq. (4.2)), cooling rates in the nanosecond laser-melted zone were found to be much higher than that in millisecond laser-melted zone, and they were decreased with the melted depth from 1.25×10^7 K/s in the top surface to 3.73×10^5 K/s in the boundary. However, the solidification microstructure in the nanosecond laser-melt surface was too brittle and too shallow to be used for TEM sample preparation in this study. Moreover, the dendrite size is also difficult to be measured in this work.

The distribution of main elementary compositions based on EDS analysis is shown in Figure 7. 4. It can be seen that average Al content increased in the melted zone, which is similar to Fig. 4.11. However, local holes accompanied by partially melt $\beta\text{-Mg}_{17}\text{Al}_{12}$ phases were found in HAZ, and this is possible attributed to superheating phenomena due to low melting point during nanosecond pulse laser irradiation. Quantitative analyses of elementary compositions found that Al content was in the range of 11.81-14.59 wt% in the $\alpha\text{-Mg}$ matrix and was enriched in the fine structures in the range of 29.97-33.03 wt%. Moreover, the peak temperature on top surface after single nanosecond laser pulse was estimated to be 3700 K according to Eq. (4.3). The temperature is much higher than that for the millisecond laser. This is supported by previously reported result that the greater the incident power, the greater the peak temperature attained during laser irradiation (Guan *et al.* 2009). Such high surface temperature would result in much more Mg evaporation during high laser fluence irradiation process compared to that in millisecond laser process (Liu *et al.* 2005), and it was also in agreement with the XRD result in Figure 7.2.

Figure 7.4 Distribution of main elements Al and Mg in the laser-melted zone and substrate of AZ91D Mg alloy.

The current study aimed to understand effect of millisecond and nanosecond pulse Nd:YAG laser irradiation on the solidification microstructure of AZ91D Mg alloy. The differences observed between results for the two types of lasers are explained on the basis of different laser fluence. However, it should be noted that repetition rate is 100 Hz for the millisecond irradiation and 6000 Hz for the nanosecond irradiation. In general, at a given pulse duration, high repetition rate would lead to heat accumulation (Luby *et al.* 1995; Eaton *et al.* 2005). However, in our case, either 100 Hz for millisecond-pulse or 6000 Hz for nanosecond-pulse laser irradiation may not be high enough to lead to significant heat accumulation. Further effort is needed to elucidate the effect of pulse repetition rate on the solidification microstructure.

7.3.2 Local Boiling and Superheating of AZ91D Mg alloy Irradiated by Nd:YAG Laser

Figure 7.5 displays the effect of nanosecond pulse Nd:YAG laser irradiation on AZ91D Mg alloy in a well-sealed chamber using 2.0 bar Ar gas flow. It can be seen that various craters and their development occur at the irradiated surface,

and the diameter of the craters is in the range of 10 μm to 50 μm , as shown in Figure 7.5 (a). Figure 7.5 (b) shows that the typical shape of the crater is a combination of conical profile with ripples present at the wall of the hole. Moreover, molten materials surrounding the craters were also observed in the liquid layer at the surface.

Figure 7.5 Typical SEM images of AZ91D Mg alloy surface following nanosecond pulse Nd:YAG laser irradiation: (a) various craters (b) high magnification of the craters in (a).

The surface topography of craters was further studied using stylus profilometer, as shown in Figure 7.6. It can be found that the diameter of typical big craters is nearly 50 μm , which is in agreement with the SEM results in Figure 7.5. Meanwhile, the average depth of the craters was found to be 15 μm according to the profile of the craters.

Figure 7.6 Surface heights of typical craters (bottom) measured along the path shown as the dotted line (upper) at the AZ91D Mg alloy surface following nanosecond pulse Nd:YAG laser irradiation.

Cross-sectional views of the laser-irradiated AZ91D Mg alloy surface were further investigated using SEM, as shown in Figure 7.7. Figure 7.7 (a) presents that the melt depth is around 20 μm , which is much shallower than 150 μm induced by millisecond pulse Nd:YAG laser according to the previous study (Zhou *et al.* 2007; Guan *et al.* 2009; Guan *et al.* 2010). Figure 7.7 (b) shows that the molten materials can be seen clearly inside the crater. Moreover, the size of the crater is consistent with the results in Figure 7.6. However, no cellular/dendrite solidification microstructure was found in the melt layer. Furthermore, Quantitative analyses of elementary compositions based on EDS found that Al content in the melted layer was in the range of 10.2-11.1 wt%, which was slightly higher than the average value of 9.0 wt% in the untreated substrate. This was due to relatively more Mg vaporization during laser irradiation (Zhou *et al.* 2007; Guan *et al.* 2010). According to our experimental work, the combined effect of various craters and no solidification

microstructure as well as less Al concentration in the melt layer resulted in no improvement of surface properties of AZ91D Mg alloy following nanosecond pulse Nd:YAG laser irradiation.

Figure 7.7 SEM images showing cross-sectional views of AZ91D Mg alloy surface following nanosecond pulse Nd:YAG laser irradiation: (a) craters in the melted layer (b) high magnification of (a).

Thermal effect in laser processing of metals is thought to be an important factor responsible for the precision and quality of the produced structures. In short-pulse laser system, assume that the thermalization in the electron subsystem is very fast, therefore, the heat transport inside the metal can be described with the following one-dimensional two-temperature-components model (Peercy 1986):

$$C_e \frac{\partial T_e}{\partial t} = k_e \nabla^2 T_e - g(T_e - T_l) + S; \quad (7.1)$$

$$C_l \frac{\partial T_l}{\partial t} = g(T_e - T_l); \quad (7.2)$$

$$S = I(t)A\alpha \exp(-\alpha z); \quad (7.3)$$

where T_e and T_l are the electron and lattice temperatures, C_e and C_l are the heat capacities of the electron and lattice subsystems, $I(t)$ is the laser intensity, g is the constant of the electron-phonon coupling, S is the laser heating source, α is the absorption coefficient, A is the surface transmission, z is the coordinate axis

at the direction perpendicular to the surface, k_e is the electron thermal conductivity.

In Equations (7.1)-(7.3), a thermal conductivity for the lattice subsystem is neglected. Electrons can be heated to very high transient temperature because the electron heat capacity is much less than the lattice heat capacity (Dou *et al.* 2001). Three characteristic time constants τ_e , τ_l and τ_L can be introduced in (7.1)-(7.3). $\tau_e = C_e/g$ is the electron cooling time, $\tau_l = C_l/g$ is the lattice heating time, and τ_L is the laser pulse duration. It should be noted that this two temperature analyses are mostly used for ultra-short pulse laser irradiation on metal. However, to the best of our knowledge, the valid heat transfer model after nanosecond pulse laser processing is missing. Therefore, we assume $\tau_L \gg \tau_l$ is satisfied and the electron temperature is equal to the lattice temperature $T_e = T_l = T$. Equations (7.2)-(7.4) can be summarized as:

$$C_e \frac{\partial T_e}{\partial t} = k_e \nabla^2 T_e + IA\alpha \exp(-\alpha z); \quad (7.4)$$

Therefore, the main source of energy losses during nanosecond pulse duration is heat diffusion into the irradiated substrate, because there is enough time to thermalize the optical energy and to propagate the heat (Steen 2003). Further discussion about heat transfer model during nanosecond laser irradiation is needed for better understanding.

The crater formation is illustrated in Figure 7.8. During nanosecond pulse laser irradiation on Mg alloy, incident light under high fluence (power density $1.37 \times 10^8 \text{ W/cm}^2$) creates a large population of heat on the surface of target. Moreover, the conducted heat can be accumulated to melt the materials due to low melting point 595°C for AZ91D Mg alloy (Housh *et al.* 1990). Furthermore, when surface temperature exceeds the critical point, boiling effect takes place (Rubahn 1999; Steen 2003), as shown in Figure 7.8 (a).

Figure 7.8 Schematic representation showing the stages of laser-induced crater formation. (a) surface absorption and thermal conduction (b) surface melting and boiling (c) plasma expansion and shock waves (d) cavitation bubble generation (e) bubble oscillation and crater formation.

Motion of planar vaporization interface is sustained by local heat flow provided that (Bhattacharya *et al.* 1999):

$$L_v \frac{dS}{dt} = -K_s \left(\frac{\partial T_v}{\partial x} \right)_{x=S} \quad (7.5)$$

where K_s is thermal conductivity of solid at the surface, T_v is vaporization temperature, L_v is latent heat of vaporization, and dS/dt is the velocity of the vaporizing interface. According to Equation (7.5), it can be concluded that the target with large ratio of latent heat of vaporization to thermal conductivity increases the degree of subsurface superheating (Bhattacharya *et al.* 1999). For AZ91D Mg alloy, thermal conductivity was measured as 55 W/mK (Davis 2002), but to the best of our knowledge the latent heat of vaporization has not been experimentally determined.

However, Figures 7.5 and 7.7 display expulsion of molten material from near surface of AZ91D Mg alloy. Based on previous work (Bhattacharya *et al.* 1999; Craciun and Craciun 1999; Craciun *et al.* 2002), the melted matter observed at the surface is related to internal temperatures being higher than the evaporating surface temperatures, so called subsurface superheating. Therefore, we speculate that subsurface superheating occurs during laser irradiation.

The high subsurface superheating temperatures may lead to nucleation of the gaseous phase at the near surface, thereby leading to “microexplosions” of the material of the target at some stage of the incoming laser pulse. According to Craciun *et al.* (1999 and 2002), these “microexplosions” inside the target would cause volume expulsion of the material (see Figure 1 in Craciun and Craciun 1999 and Figure 4 in Craciun *et al.* 2002). Therefore, we propose that the various craters and the molten materials are caused by laser-induced explosive volume boiling, as shown in Figure 7.8 (b).

Moreover, when subsequent laser pulse is focused into the liquid material at the boiling surface, it induces optical breakdown through nonlinear absorption, which leads to plasma formation, as shown in Figure 7.8 (c).

It is generally accepted that plasma expansion is accompanied by the emission of shock waves and the generation of cavitation bubbles (Jacobs and Rikken 1987; Yoo *et al.* 2000; Chen *et al.* 2004). In general, plasma expands adiabatically at a supersonic velocity, creating high-pressure shock waves in front of it. As the laser plasma cools, the shock front rapidly detaches from the plasma because its velocity is much greater than the particle velocity behind it. The laser induced bubbles continue to expand outward until all its initial kinetic energy is converted into potential energy. Subsequently, under the external pressure of a liquid, the bubbles begin to implode adiabatically. Moreover, the melted matter caused by volume expulsion can act as “fresh” defects, lead to a next preferential laser irradiation for craters formation (Li *et al.* 2006), as show in Figure 7.8 (d).

Both the temperature and the pressure inside the cavity rise again, leading to the bubble’s rebound. Usually a bubble oscillates for several cycles until all the energy is dissipated and all gases dissolve into the surrounding liquid, especially for multiply laser pulses irradiation. The oscillation of bubble results

in the conical profile with ripples structures at the wall. As a consequent, a typical crater with average depth several microns is formed, as shown in Figure 7.5 (b) and Figure 7.6. Finally, in such a way, many gathered cluster of craters were formed after several consecutive laser pulses, which resulted in various sizes of the craters at the surface (Figure 7.5 (a)), as show in Figure 7.8 (e).

It should be noted that such craters were also obtained on the irradiated surface of ingot pure Mg and wrought AZ31B Mg alloy following the same laser processing, as shown in Figure 7.9. However, the amount and size of craters decreased significantly compared to that of AZ91D Mg alloy. Therefore, we propose that alloying elements in Mg alloys influences the mechanism of crater formation during subsurface superheating and explosive volume boiling. Further effort for deep understanding is still needed.

Figure 7.9 Typical SEM images of craters on the irradiated surface following nanosecond pulse Nd:YAG laser: (a) pure Mg; (b) closed-up of (a); (c) AZ31B Mg alloy; (d) closed-up of (c).

7.3.3 Surface Coloration on AZ31B Mg alloy

(1) Nd:YAG Laser

Figure 7.1 displays the darkening effect at AZ31B Mg alloy surface following nanosecond pulse Nd:YAG laser irradiation. It can be found that the irradiated areas at high laser power were very black from naked eyes, as indicated as No. **3**, No. **4** and No. **5** in the figure.

Figure 7.10 shows the optical reflection measurement of AZ31B Mg alloy surface before and after laser irradiation. When laser power was low, reflection pattern of irradiated areas No. **1** and No. **2** was similar to that of non-irradiated area, but reflection intensity decreased linearly with the increasing laser power. When laser power was high, the reflection pattern of irradiated areas No. **3**, No. **4** and No. **5** experienced flattened reflectance spectra, and the reflection intensity dropped significantly. Moreover, it can be found that the darkening areas were quite uniform over the spectral range from 200 nm to 1100 nm, and the average reflection intensity was nearly 0.13% of non-irradiated area in the visible light wavelength range from 390 nm to 750 nm.

Figure 7.10 Optical reflection measurement of non-irradiated area and irradiated areas at AZ31B Mg alloy surface in Figure 5.1.

Morphological evolution of AZ31B Mg alloy surface after laser irradiation was investigated using SEM, as shown in Figure 7.11 and Figure 7.12. At low laser power, the breakdown took place along fine scratch at the polished surface, and the irradiated areas increased with laser power. Moreover, micro-cracks were observed at the irradiated areas, as shown in Figure 7.11 (a)-(b), Figure 7.12 (a)-(b).

When laser power increased to 70 W and above, a large number of micron size cauliflower-like clusters together with some large protruding particles were observed at the irradiated areas, as shown in Figure 7.11 (c)-(e). High magnification in Figure 7.12 (c)-(e) shows that the size of cauliflower-like clusters increased with laser power, and the protruding particles with less compact were above the clusters. Furthermore, as shown in Figure 7.11 (c)-(e), it is interesting to note that the density of protruding particles located in the center region of irradiated areas decreased with laser power significantly, but the density of protruding particles located at the boundary region did not change too much.

(a)

(b)

(c)

(d)

(e)

Figure 7.11 SEM images showing morphological evolution of AZ31B Mg alloy surface after irradiation with progressive laser power: (a) 40 W (b) 60 W (c) 70 W (d) 90 W (e) 110 W.

(a)

(b)

(c)

(d)

(e)

Figure 7.12 High magnification SEM images for surface morphological evolution in Fig. 5.11: (a) 40 W (b) 60 W (c) 70 W (d) 90 W (e) 110 W.

Surface topography of the darkening areas was further investigated using Talysurf surface profiler. The typical cauliflower-like clusters and large particles were found to be protruding above the substrate nearly $1.03\text{ }\mu\text{m}$ and $4.67\text{ }\mu\text{m}$, respectively. Moreover, Figure 7.13 shows the surface roughness R_a of AZ31B Mg alloy before and after laser irradiation.

When laser power increased from 40 W to 70 W, R_a increased from $0.11\text{ }\mu\text{m}$ to $2.69\text{ }\mu\text{m}$ correspondingly. The reason for the maximum R_a value at 70 W was attributed to the cauliflower-like clusters and protruding particles at the irradiated area, as shown in Figure 7.11 (c).

When laser power further increased to 110 W, R_a dropped linearly to $0.96\text{ }\mu\text{m}$, and the reason was related to less protruding particles at the irradiated area, as shown in Figure 7.11 (c)-(e). Furthermore, the size distribution of clusters and particles located in the center region of irradiated areas was also studied, as shown in Figure 7.14. It can be found that the size of protrude particles decreased from $16\text{ }\mu\text{m}$ to $9\text{ }\mu\text{m}$ when laser power increased from 70 W to 110 W. This is in agreement with SEM results in Figure 7.12.

Figure 7.13 Surface roughness R_a of AZ31B Mg alloy before and after laser irradiation.

Figure 7.14 Size distribution of clusters and particles at the irradiated areas of the AZ31B Mg alloy surface: (a) 70 W (b) 90 W (c) 110 W.

Surface chemistry of the irradiated area was analyzed in the following using XPS and EDS. Figure 7.15 shows the O 1s spectra at AZ31B Mg alloy surface. It can be found that the binding energy peak at 531.5 eV was the peak of O 1s at non-irradiated surface, and the binding energy peak at 530.5 eV was the peak of O 1s at irradiated areas. The peak position change was likely due to the effect of $\text{Mg}(\text{OH})_2$ and MgCO_3 (Ardizzone *et al.* 1997; Fournieret *et al.* 2002). Before laser irradiation, $\text{Mg}(\text{OH})_2$ and MgCO_3 existed at the polished surface of AZ31B Mg alloy due to atmosphere reaction (Ardizzone *et al.* 1997). After laser irradiation, $\text{Mg}(\text{OH})_2$ and MgCO_3 disappeared gradually at the surface as a result of laser ablation, and the final peak position was attributed to MgO at the darkening area.

Figure 7.15 XPS spectra showing O 1s peak at non-irradiated area and irradiated areas at AZ31B Mg alloy surface by nanosecond pulse Nd:YAG laser in air, where **1** represented 40 W, **2** represented 60 W, **3** represented 70 W, **4** represented 90 W, and **5** represented 110 W.

Quantitative analysis of EDS shows that both cauliflower-like clusters and protruding particles at the darkening area were identified as MgO, as shown in Figure 7.16. Additionally, average oxygen content at the irradiated areas increased from 5 wt% to 37 wt% with laser power, and such value was much higher than the average value of 4 wt% at the non-irradiated area.

Figure 7.16 Morphology and chemical composition of typical cauliflower-like clusters and protruding particle at the irradiated area of AZ31B Mg alloy with 70 W: (a) SEM image (b)-(c) Chemical composition for the cluster (A) and particle (B).

Based on above analysis, it can be found that our results are in agreement with previous findings of the interaction of short laser pulse with target material. It has been reported that the interaction of short laser pulse with target material leads to the formation of clusters and particles at the surface, further, the major advantage of short laser pulses for cluster synthesis was the presence of laser-ejected small species during laser material processing (Itina *et al.* 2007; Geohegan *et al.* 1998; Marine *et al.* 2000; Pereira *et al.* 2004).

When laser pulse is focused into the irradiated surface of AZ31B Mg Alloy during nanosecond pulse laser process, it induces optical breakdown through nonlinear absorption, which leads to plasma formation. At the meantime, the metal surface would be strongly excited due to high laser influence, causing rapid ejection of laser-ejected small species based on the finding of Tillack *et al.* (2004) and Itina *et al.* (2007). In the presence of oxygen, oxidation reaction would happen inside the ablated material plume, resulted in formation of oxides (Qian *et al.* 2005). Subsequently, the oxides would deposit to the surface during rapid cooling condensation and plume collapse process (Matsubara *et al.* 2003; Zhent *et al.* 2008; Li *et al.* 2009).

However, it should be noted that the total laser irradiation time in this work was nearly 1 second as mentioned in the experimental procedure. According to Qian *et al.* (2008), the material redeposition would not be sufficient during the ultrafast laser process, and it was suggested that the effect of surface tension became another important contributor to the protrusion of irradiated surface. When laser power was high, hydrodynamic development at the irradiated areas occurred in addition to vaporization due to high thermal conductivity of Mg alloys (Avedesian and Baker 1999; Zhang *et al.* 1997). Hydrodynamic ablation resulted in the removal of material in the form of droplets, therefore isolated melt was formed, finally leading to the cauliflower-like clusters at the irradiated areas, as shown in Figure 7.11 and Figure 7.12.

In addition, Luk' yanchuk *et al.* (1998) reported that a decrease of laser fluence could induce a decrease of the aggregate size, thus leading to nucleation and development of particles above the clusters. Meanwhile, the shape of particles would become less compact due to greater volumetric heating upon successively repetitive pulse irradiation (Luk'yanchuk *et al.* 1998; Pereira *et al.* 2004). Thereby, more large protruding particles were found at the irradiated areas where laser energy was low, as shown in Figure 7.11 and Figure 7.14. Moreover, both clusters and particles can trap light at the rough surface due to their morphology and topography based on the previous study (Qian *et al.* 2005; Qian *et al.* 2008; Zheng *et al.* 2008), and such effect will reduce the reflectance and cause the darkening effect, as shown in Figure 5.1.

Therefore, the surface morphology of irradiated areas played the dominate role in determining the laser-induced darkening effect on AZ31B Mg alloy surface after nanosecond pulse laser irradiation. In addition, the chemistry variation of irradiated areas due to oxidation also contributed to the darkening surface (Zheng *et al.* 2008; Lu and Qiu 2000; Li *et al.* 2009).

(2) Excimer Laser

Observation of AZ31B Mg alloy surface after excimer laser irradiation by naked eyes is shown in Figure 7.17. It can be found that surface coloration was obtained at the irradiated areas after laser irradiation. Moreover, when laser irradiated in air and under Ar nozzles, the color became darker significantly with the increasing laser pulses. However, when laser irradiated in Ar chamber, the evolution of color change was not obvious.

In order to study morphological evolution of the irradiated areas at AZ31B Mg alloy surface, the specimens before and after laser treatment were investigated using SEM. Before laser irradiation, the polished surface of AZ31B Mg alloy

was very smooth due to fine ground. After laser irradiation, the surfaces were roughened significantly with the increasing number of laser pulses.

Figure 7.17 Photo showing colors of irradiated areas with progressive laser pulses on AZ31B Mg alloy in air, under Ar nozzles and in Ar chamber, respectively.

The results of irradiated areas under Ar nozzles are suitable to investigate the morphological evolution with progressive laser pulses due to the controlled environment, as shown in Figure 7.18. Figure 7.18 (a)-(b) displays network structures at the surface when laser pulses were as low as 100 and 200. When laser pulses increased to 300, granular structures together with small white particles were observed at the surface, as shown in Figure 7.18 (c). At large laser pulses from 400 to 800, the number of white particles increased significantly, and surface features became coarse and poorly defined, as shown in Figure 7.18 (d)-(f).

Moreover, the irradiated surfaces both in air and in Ar chamber were also observed, and the results of both after 800 laser pulses irradiation are shown in Figure 7.19. Figure 7.19 (a) presents a large number of white particles at the coarse surface after laser irradiation in air. Figure 7.19 (b) displays network structures and few granular structures as well as few white particles at the

smooth surface after laser irradiation in Ar chamber. It should be noted here that the surface morphology features of three irradiated areas were similar, and the subsequent study would be mainly focused on the results using Ar nozzles.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 7.18 SEM images showing morphological evolution of AZ31B Mg alloy surface after irradiation with progressive laser pulses under Ar nozzles: (a) 100 pulses (b) 200 pulses (c) 300 pulses (d) 400 pulses (e) 500 pulses (f) 800 pulses.

Figure 7.19 SEM images showing surface morphology of AZ31B Mg alloy after irradiation with 800 laser pulses in air (a) and in Ar chamber (b).

Since SEM images cannot reveal all specific information of morphological evolution in the irradiated area when laser pulses are low (Figure 7.18 (a)-(b)), those areas were further characterized using AFM. Figure 7.20 shows clearly that surface topography of the irradiated areas changed from network structures when laser pulses were 100 to granular structures together with small particles when laser pulses were 200. Figure 7.21 presents the distinct boundary between irradiated area and non-irradiated area in the periphery region, and the irradiated area was found to be above the non-irradiated area based on line profile drawn from AFM image, as shown in Figure 7.21 (b).

When laser pulses increased to 300, granular structures and small particles totally replaced previous network structures at the irradiated areas, as shown in Figure 7.18 (c)-(f). However, such area was too rough to be characterized with AFM, so the Talysurf surface profiler was used to study the surface topography. Figure 7.22 shows that the small particles were protruded above the surface of

irradiated area. This observation lends support to the assumption that these small white particles formed as a result of material redeposition during laser irradiation. Moreover, according to Talysurf profiler measurement, surface roughness Ra of the irradiated areas was found to be increased linearly from 382 nm to 641 nm with laser pulses from 100 to 800.

Further investigation of chemical composition of irradiated areas was carried out using EDS. Quantitative analyses of small white particles found that oxygen and magnesium contents were about 38 wt% and 59 wt%, respectively, which was believed to be magnesium oxide (MgO). Figure 7.23 shows the distribution of oxygen element in the periphery region of the irradiated area when laser pulses were 800, and oxygen concentration was found to be increased significantly from non-irradiated area to irradiated area. In addition, the distribution of average oxygen content at all irradiated areas as a function of laser pulses was also studied, as shown in Figure 7.24. Oxygen contents were found to be increased linearly with the laser pulses in three cases. However, oxygen contents at the area irradiated in Ar chamber were much less than that in air and under Ar nozzles. This indicates that the darkening effect of AZ31B Mg alloy surface was accompanied by laser-induced oxide formation.

Figure 7.20 AFM images showing surface topography of AZ31B Mg alloy after irradiation under Ar nozzles with (a) 100 pulses and (b) 200 pulses.

Figure 7.21 AFM images showing irradiated areas of AZ31B Mg alloy after irradiation with 200 laser pulses under Ar nozzles: (a) AFM image at the boundary between irradiated area and non-irradiated area. (b) Line profile of AFM image shown in (a).

Figure 7.22 3D surface profiler image showing irradiated area of AZ31B Mg alloy after irradiation with 300 laser pulses under Ar nozzles.

Figure 7.23 Distribution of oxygen element in the boundary between irradiated area and non-irradiated area of AZ31B Mg alloy after irradiation with 800 laser pulses under Ar nozzles.

Figure 7.24 Average oxygen content at the irradiated area of AZ31B Mg alloy as a function of laser pulses in air, under Ar nozzles, and in Ar chamber.

Based on the above analysis, the formation of laser-induced surface coloration of AZ31B Mg alloy upon with progressive laser pulses will be discussed briefly in the following.

After a few initial laser pulses, the surface of AZ31B Mg alloy was heat treated and molted under the current laser fluence. Subsequently, surface tension of the liquid led to surface curling, thereby resulting in the formation of network structures at the irradiated area, as shown in Figure 7.18 (a) and Figure 7.20 (a).

With the increasing laser pulses, the Mg alloy surface would be strongly excited, causing rapid ejection of species (Tillack *et al.* 2004; Itina *et al.* 2007). Correspondingly, oxidation and material re-deposition occurred in the presence of oxygen in nearby air, resulting in protruded oxides particles at the surface, as shown in Figure 7.22 and Figure 7.23. This is similar to the findings in our previous work after Nd:YAG laser irradiation. However, it should be noted that the average laser fluence difference between Nd:YAG laser ($2.61 \times 10^4 \text{ mJ/cm}^2$) and Excimer laser (655 mJ/cm^2) was large during experimental procedure. Therefore, the morphology of oxides and surface features after Nd:YAG laser irradiation was much more compact compared to that of Excimer laser irradiation, as shown in Figure 7.12 and Figure 7.18. Such results are in agreement with the conclusions of Luk'yanchuk *et al.* (1998) and Pereira *et al.* (2004).

When laser pulses were very large, the network structures and the oxide particles further interacted with each other (Zhao *et al.* 1997; Swaddle 1997), leading to coarse surface features with granular structures as well as more oxide particles at the irradiated area, as shown in Figure 7.18 (c)-(f) and Figure 7.19 (a).

However, when laser irradiated AZ31B Mg alloy in well-sealed chamber with 2.0 bar Ar gas flow, few oxide particles and granular structures were investigated at the surface due to less oxidation, as shown in Figure 7.19 (b). Moreover, the 2.0 bar Ar gas inside the chamber would minimize Mg evaporation, thus leading to less nucleating sites for the oxide formation. In

addition, the darkening effect of irradiated areas could be explained in terms of trapping of light in the surface morphology (granular structures and oxide particles) formed due to hydrodynamic ablation (Zhang *et al.* 1997; Zheng *et al.* 2002).

Therefore, the mechanism of surface coloration of AZ31B Mg alloy after excimer laser irradiation and nanosecond pulse Nd:YAG laser irradiation was mainly attributed to the combined effect of morphological difference and compositional variation at the irradiated area. The current study indicates that laser-induced darkening of Mg alloy surface might be has potential application in many fields, such as product identification and biocompatible implants.

7.4 Effect of Femtosecond Pulse Laser on Mg and Mg alloy

7.4.1 Ripples on Pure Mg

Morphological evolution of Mg surface after laser irradiation with progressively laser pulses was investigated using SEM, as shown in Figure 7.26 and Figure 7.26. When laser pulses were 50, random nanostructures were produced at the surface, as shown in Figure 7.25 (a). When laser pulses increased to 200, random nanostructures grew and coalesced into micro size wavelike structures (grooves) and fine ripples at the surface, as shown in Figure 7.25 (b). Moreover, orientation of grooves was found to be parallel to the laser polarization direction, while orientation of ripples was perpendicular to the laser polarization direction. Furthermore, Figure 7.26 (a) shows that the grooves were irregular, and the space was around 1-3 μm . However, the ripples had regular shape, and the period was estimated as 450-650 nm, which was appreciably less than the wavelength of incident light 775 nm.

When laser pulses were 300, the irradiated area expanded and the grooves as well as ripples increased correspondingly, as shown in Figure 7.25 (c) and Figure 7.26 (b). Figure 7.26 (b) shows that the morphology of ripples was more obvious than the previous structure in Figure 7.26 (a). When laser pulses further increased to 500, the irradiated area together with grooves and ripples expanded significantly, as shown in Figure 7.25 (d). Moreover, a large number of micron size cluster structures were observed in the peripheral area of the irradiated surface. Figure 7.26 (c) shows that the ripples were clear and straight above the grooves, while the grooves became smooth. Figure 7.26 (d) shows that the ripples were less obvious above the cluster structures, while the spacing of ripples decreased.

For laser pulses were larger than 500, more cluster structure took place at the surface, and the grooves and fine ripples disappeared gradually. Moreover, surface melting began to develop due to the accumulation thermal effect. It is noted that such micron grooves and nano ripples were also observed on the irradiated surface of AZ31B and AZ91D Mg alloys following femtoscond laser irradiation. Here we focus on analyzing pure Mg to discuss fundamental physical phenomenon.

Figure 7.25 SEM images showing morphological evolution of Mg surface after irradiation with progressively laser pulses: (a) 50 pulses (b) 200 pulses (c) 300 pulses (d) 500 pulses.

Further investigation of surface topography at the irradiated area was carried out using AFM, and the results were shown in Figure 7.27 and Figure 7.28. Figure 7.27 (a) and Figure 7.28 (a) display that the surface has irregular rough topography due to dotlike nanoscale protrusions when the number of laser pulses was small. With the increasing laser pulses, these nano protrusions gathered together and grew as grooves and intermediate fine ripples at the surface, as shown in Figure 7.27 (b) and Figure 7.28 (b). At large laser pulses, the intermediate ripples developed into clear fine ripples among the grooves, as shown in Figure 7.27 (c)-(d) and Figure 7.28 (c)-(d). Moreover, the period of ripples is found in the range of 480-600 nm, and the average value decreased with the number of laser pulses. This is in agreement with SEM results. Furthermore, surface roughness R_a of measured area was measured as 27.9 nm, 89.6 nm, 107.6 nm, and 119.2 nm, respectively, which was much rougher than that of non-irradiated polished surface 7.6 nm.

Figure 7.26 SEM images showing evolution of two ripples on Mg surface after irradiation with progressively laser pulses: (a) 200 pulses (b) 300 pulses (c) 500 pulses, showing fine ripples above grooves (d) 500 pulses, showing fine ripples above cluster structures.

Figure 7.27 AFM images showing topographical evolution on Mg surface. The probed areas were about $10 \times 10 \mu\text{m}^2$ for all the measurements. The detail of surface roughness was described in the text: (a) 50 pulses (b) 200 pulses (c) 300 pulses (d) 500 pulses.

Figure 7.28 AFM images of surface profile measurement in Figure 5.28: (a) 50 pulses (b) 200 pulses (c) 300 pulses (d) 500 pulses.

The formation of grooves and ripples on Mg alloy surface following femtosecond laser scan irradiation at near-damage-threshold fluence will be discussed briefly in the following.

It is known that strong excitation of metal surface irradiated by femtosecond laser leads to rapid ejection of species, such as electrons, photons or atoms, and the excited electrons will transfer energy to the metal lattice by typical electron-phonon coupling (Liang *et al.* 2004; Leonardo *et al.* 2007). At the initial few laser pulses, nano protrusions were produced randomly at the irradiated surface due to non-thermal melting as well as material re-deposition effect within several picoseconds during rapid cooling condensation and plume collapse process (Matsubara *et al.* 2003; Zheng *et al.* 2008; Li *et al.* 2009). Such nano protrusions were mainly attributed to laser-ejected species and plasma confinement during irradiation process (Schmidt *et al.* 2000; Itina *et al.* 2007). When the number of laser pulses increased, the kinetic energy and the temperature of ejected species increased significantly.

Correspondingly, the expansion of high energy caused the scattering of the ejected species, thereby lead to the nano protrusions expanded and so did the irradiated area occupied by these structures, as shown in Figure 7.27 (a). Meanwhile, surface plasmons (SP), both localized and propagating along the surface, would be excited by coupling the incident light to such nano protrusions (Keilmann and Bai 1982; Clark and Emmony 1989; Huang *et al.* 2009). As the number of laser pulses increased further, the nano protrusions grew and the developed nanostructures further excited the SP. Subsequently, the SP would interfere with the incident laser light wave, and this interference resulted in the formation of ripples, as shown in Figure 7.27 (a)-(d) and Figure 7.28 (a)-(d).

Furthermore, due to orientation of ripples being perpendicular to direction of laser polarization, it has been suggested that such ripples can be explained as the interference between incident light field and the electric field of plasma wave (Bonse *et al.* 2000; Marine *et al.* 2000; Pereira *et al.* 2004). However, the period of ripples in this study 480-600 nm was found to be not followed the classical relationship $\Lambda = \lambda / (1 \pm \sin \theta)$ obtained for the sub-wavelength ripples (Miller and Haglund 1998).

Considering the effect of SP, the revised scattering model can be expressed as follows (Huang *et al.* 2009):

$$\Lambda = \frac{\lambda}{\frac{\lambda}{\lambda_s} \pm \sin \theta} \quad (7.6)$$

where λ_s is the wavelength of SP, and λ_s in the air/metal interface is given by:

$$\lambda_s = \lambda \sqrt{\frac{\epsilon_m + \epsilon_d}{\epsilon_m \epsilon_d}} \quad (7.7)$$

where $\varepsilon_m = \varepsilon'_m + i\varepsilon''_m$ is the dielectric constant of the metal, and $\varepsilon_d = \varepsilon'_d + i\varepsilon''_d$ is the dielectric constant of the dielectric medium (Raether 1988). According to Eq. (7.6), in normal incidence ($\theta=0^\circ$), it can be obtained that the simple relationship $\Lambda=\lambda s$. In other words, the interference fringes will induce permanent ripples on material surface with Λ equal to λs , which is always smaller than λ . This is in agreement with the experimental observations and is precisely the origin of the sub-wavelength characteristic of fine ripples (Figure 7.26 and Figure 7.28).

In addition, it should be noted that ripples here have a broad distribution of spatial periods, and it indicated that the effective dielectric constants for both air and Mg alloy surfaces may vary significantly by laser irradiation process, and this can affect the overall effective refractive index for the SP, thus lead to the various periods of ripples (Bonch-Bruевич *et al.* 1992; Vorobyev and Guo 2005).

Moreover, the average periods of ripples decreased with laser scan times slightly due to grating-assisted SP-laser coupling mechanism (Bonse *et al.* 2000; Huang *et al.* 2009; Yang *et al.* 2006). Our results are in agreement with Shimotsuma's work (Shimotsuma *et al.* 2003). They fabricated self-organized grating structures, which were aligned perpendicular to laser polarization direction, with the period of 140-320 nm inside silica glass after femtosecond laser irradiation. Moreover, they interpreted this phenomenon in terms of interference between the incident light field and the electric field of the bulk electron plasma wave, resulting in the periodic modulation of electron plasma concentration and the structural changes in glass.

On basis of previous studies, non-uniform free electron density due to surface roughness might play a significant role for periodic structure formation (Wu *et al.* 2003; Miyaji and Miyazaki 2006; Hsu *et al.* 2008; Dufft *et al.* 2009). Therefore, we propose that the formation of grooves is related to the combined

effect of initial surface roughness and the interference of laser and SP. As shown in Figure 7.27 and Figure 7.28, grooves deepened and widen at large laser pulses, and this is caused by the efficient transfer of laser fields to SP (Huang *et al.* 2009). Moreover, the surface of pure Mg was heat treated and molted due to its high thermal conductivity (418 W/mK at 20 °C, McDonald and Stull 1955; Avedesian and Baker 1999). Surface tension of the liquid led to surface curling, and highly localized heating as well as large thermal gradients caused the development of severe strain fields, finally resulted in the formation of isolated melt (cluster) on the surface, as shown in Figure 7.26 (d) and Figure 7.27 (d).

In summary, the interference between SP and incident laser light is possibly the dominant mechanism for the formation of nano ripples on pure Mg following femtosecond laser irradiation. We speculate that the ripples with broad distribution of spatial periods are due to the varying effective refractive index for SP during laser irradiation. Moreover, we propose that grooves are caused by the combined effect of initial surface roughness of Mg and the interference between laser and SP.

7.4.2 Iridescent Effect on AZ31B Mg Alloy

Figure 7.29 displays the iridescent effect on the surface of AZ31B Mg alloy after irradiation by femtosecond laser scan 10 times. Optical properties of laser-irradiated Mg alloy are found to be changed significantly, and the surface exhibits different colors at different viewing angles by naked eyes. It is noted here that such iridescent effect were also observed on the irradiated surface of pure Mg and AZ91D Mg alloys following similar femtoscond laser processing. Here we focus on analyzing AZ31B Mg alloy due to its practical background and predominantly homogeneous α -Mg microstructure.

Figure 7.29 Photographs of iridescent effect on the irradiated surface of AZ31B Mg alloy after femtosecond laser scan 10 times.

Figure 7.30 shows the reflectance of typical surfaces before and after laser irradiation using spectrophotometer. The noise signal of the wavelength below 475 nm was attributed to environment effect. Before laser irradiation, the reflectance of surface was nearly 100% in the visible spectral range from 475 to 750 nm due to fine polished. After laser irradiation, three dominate peaks appeared in the spectra, and the corresponding wavelength of colors were blue, green and orange, respectively. Moreover, small wide peaks were also observed between 570 nm and 600 nm, and this belonged to yellow color wavelength range. This is in agreement with the observation of Figure 7.29. Furthermore, it should be noted that the spectra pattern for all irradiated surfaces was the same, but the reflectance decreased to 10%-70% regarding to non-irradiated surface when laser scan times increased from 10 to 50. The reduction of reflectance at large laser scan times was due to light trapping at the darken surface when laser irradiation time was long (Kannan and Raman 2008; Zhang *et al.* 1997).

Figure 7.30 Reflectance of non-irradiated area at the polished surface and irradiated areas at the surface of AZ31B Mg alloy with progressive laser scan times

Morphological evolution of above irradiated surfaces was investigated using SEM, as shown in Figure 7.31. When laser scan times were 10, fine ripples were produced above micro size wavelike structures (grooves) on the surface, as shown in Figure 7.31 (a). Moreover, orientation of ripples was found to be perpendicular to laser polarization direction, while the period was estimated in the range of 400-650 nm, which was appreciably less than the wavelength of incident light 775 nm. Furthermore, orientation of grooves was parallel to laser polarization direction (perpendicular to the ripple structures), and the period range was around 1-3 μm .

When laser scan times increased to 30 and 50, grooves expanded and clusters structure was developed in the irradiated area due to surface melting under accumulation thermal effect. Moreover, the orientation of ripples was the same as pervious results, but the period decreased slightly, as shown in Figure 7.31 (c)-(f).

For laser scan times were larger than 100, more surface melting took place at the whole surface, and the grooves and ripples disappeared gradually. It can be

concluded here that the structures of grooves and ripples were highly depended on laser fluence. This is in accord with the finding of Bonse *et al.* (2005) (see Fig. 6 in Ref). Unfortunately, they did not give further explanation about the grooves formation.

Figure 7.31 SEM images showing morphological evolution of AZ31B Mg alloy surface after irradiation with progressively scan times: (a) 10 times (b)

magnified image for (a); (c) 30 times (d) magnified image for (c); (e) 50 times (f) magnified image for (e).

Further investigation of surface topography at the irradiated areas was carried out using AFM, and the results were shown in Figure 7.32 and Figure 7.33. According to surface profile, the period of ripples was found to be in the range of 450-620 nm. This is in agreement with SEM results. Moreover, Figure 7.32 (a) and Figure 7.33 (a) show that shallow grooves as well as randomly nano protrusions were produced when laser scan times were few. With the increasing laser scan times, nano-ripples replaced nano protrusions on the irradiated area, as shown in Figure 7.32 (b). Figure 7.33 (b) reveals that the average period of such ripples is 530 nm. When laser scan times were 50, the average period of ripples decreased to 450 nm, as shown in Figure 7.32 (d) and Figure 7.33 (d). Furthermore, grooves were identified as valleys in the Figure 7.32, and they were deepened and widen with the increasing laser scan times. In addition, surface roughness R_a of measured area was measured as 113.3 nm, 136.9nm, 164.5 nm, and 187.5 nm, respectively, which was much rougher than that of non-irradiated polished surface 7.6 nm.

Figure 7.32 AFM images showing topographical evolution on AZ31B Mg alloy surfaces. The probed areas were $10 \times 10 \mu\text{m}^2$ for all the measurements: (a) scan 5 times; (b) scan 10 times; (c) scan 30 times; (e) scan 50 times.

Figure 7.33 AFM images of surface profile measurement in Figure 7.32: (a) scan 10 times; (b) scan 10 times; (c) scan 30 times; (d) scan 50 times.

Based on the above results, it can be found that the iridescent effect on AZ31B Mg alloy surface induced by femtosecond laser irradiation is attributed to the structure color caused by nano ripples as diffraction gratings. Moreover,

according to the discussion of formation of grooves and ripples in Section 7.4.1, the interference between surface plasmons (SP) and incident laser light is the dominant mechanism for the formation of ripples. Finally, we conclude that the current technique can be applied to other type of Mg alloys by adjusting laser parameters according to their thermal properties.

7.5 Summary

During short pulse laser irradiation on Mg and Mg alloys, local boiling and superheating, surface coloration, and periodical surface structure were investigated at the surface. The main conclusions are listed below:

- (1) During nanosecond pulse Nd:YAG laser irradiation on AZ91D Mg alloy, molten materials and holes observed at the surface are caused by the combined effect of melting and boiling. Moreover, melt depth was found to be around 50 μm , and several micron scale microstructure was formed at high cooling rates of 10^5 - 10^7 K/s. Additionally, various micron craters occurred at the surface when irradiated in Ar gas chamber. These craters were formed as a result of subsurface superheating, explosive volume boiling and plasma expansion accompanied by generation of cavitation bubbles.
- (2) Laser-induced darkening surface was obtained on AZ31B Mg alloy following nanosecond pulse Nd:YAG laser and Excimer laser irradiation in the presence of air. The color of irradiated areas became dark rapidly, and oxygen content at the irradiated area as well as surface roughness increased significantly. It was proposed that the darkening effect was mainly attributed to light trapping in the rough surface caused by hydrodynamic ablation oxidation and material redeposition processes during laser

irradiation. Surface chemistry variation played a second role in determining the color change.

- (3) During femtosecond pulse laser irradiation on Mg and Mg alloys in air, micro-grooves and nano-ripples were formed at the surface. Most significantly, orientation of nano-ripples was perpendicular to laser polarization, and period of nano-ripples was in a broad distribution range. It was suggested that the interference between surface plasmons and incident laser light might play the most important role in the formation of ripples, and the initial surface roughness together with such interference lead to the formation of grooves. In addition, iridescent effect was observed at large irradiated area due to ripples acting as diffraction gratings.

Chapter 8

Conclusions and Recommendations

8.1 Introduction

In this chapter, the main conclusions of this thesis are summarized, and possible further researches are recommended.

8.2 Summary and Conclusions

8.2.1 Kinetics of Phase Transformation and Microstructural Evolution of Mg Alloy under Non-equilibrium Conditions

We have carried out the study of kinetics of phase transformation in as-received microstructure of AZ91D Mg alloy. Moreover, we also analyzed the solidification microstructure and microstructure in-homogeneities in the molten pool after millisecond pulse Nd:YAG laser irradiation. The following conclusions can be drawn from this part of study:

- (1) Activation energies for β -Mg₁₇Al₁₂ phase dissolution/precipitation and eutectic structure transformation were calculated as 178 kJ/mol and 788 kJ/mol using calorimetric analysis method. After DSC tests, the size and morphology of eutectic structure decreased with scanning rates due to less discontinuous precipitation of β -Mg₁₇Al₁₂ in the supersaturated Mg regions. Additionally, the concentration of Al in α -Mg solid solution increased from 7.13 wt% to 8.78 wt% as the scanning rate increased from 5 K/min to 40 K/min.
- (2) Solidification microstructures of laser-treated AZ91D Mg alloy occurred through the refinement of original α -Mg matrix and β -Mg₁₇Al₁₂ intermetallics in the molten pool. Typical cellular/dendrite structures and a large number of β -

Mg₁₇Al₁₂ nano-particles as well as enhanced average Al concentration were observed due to rapid solidification and selective vaporization as well as laser re-heating cycles. The dendrite cell size increased from several hundred nanometers to several microns with the decrease in cooling rates from 10⁶ K/s at the top surface to 10⁴ K/s at the bottom in the molten pool. The relationship between dendrite cell size and cooling rates was derived from heat flow model and solidification theory as $\lambda = 85 \gamma^{-0.33}$.

(3) Microstructure heterogeneities in the molten pool are mainly attributed to non-uniform distribution of laser beam, fluctuating liquid-solid interface stability, Marangoni convection and laser re-melted process. Moreover, tiny solidification cracks could be formed in the microstructure due to high thermal stress. Furthermore, numerical analysis based on heat flow model revealed that Marangoni convection played a predominant role in determining the solidification microstructure, and Marangoni convection depended on laser multiple pulses processing, including pulse duration and overlap rate, due to the energy density effect.

8.2.2 Surface-related Properties of Laser-treated Mg Alloy

We have examined corrosion behaviour and surface energy of AZ91D Mg alloy before and after millisecond pulse Nd:YAG laser irradiation. Material loss including selective vaporization of Mg and Al alloying elements during laser irradiation was also discussed. Following are main conclusions:

(1) Refined homogeneous microstructure led to improved corrosion resistance of laser-treated surface in modified body simulated fluid and 3.5 % NaCl solution. The general and pitting corrosion resistances were significantly enhanced due to the refined continuous network of β -Mg₁₇Al₁₂ phases and the enhanced Al concentration. However, coarse structure in the overlapped regions caused by microstructure in-homogeneities provided preferential site for pitting

corrosion, resulted in poorer corrosion resistance. Additionally, small cracks in the microstructure attributed to high thermal stress also accelerated the corrosion rate significantly.

(2) Results obtained from contact angle measurements revealed that laser treatment enhanced wettability significantly and led to drastic increase in total surface energy from 25.80 to 40.76 mJ/m² and in polar component of the surface energy from 4.83 to 13.53 mJ/m², thus improving the action of wetting and adhesion. The change in surface energy was attributed to the refined microstructure and the increased Al concentration in the irradiated area.

(3) The enrichment of Al at the irradiated surface played a very important role in improving the surface properties of laser-treated AZ91D alloy. Material loss, including selective vaporization of Mg and Al alloying elements and liquid metal ejection, increased significantly with laser fluence during irradiation. Al concentration was enriched in both molten pool and liquid ejection. Ratio of Mg:Al contents in the core region of laser-generated plume was more than 50:1, which was attributed to the combined effect of different vaporization rate of Mg and Al species and original chemical composition in the substrate. Moreover, transport rate of vaporized Al species was nearly three times higher than that of Mg species due to high diffusivity of Al vapors in Ar gas during laser processing.

8.2.3 Interaction between Short Pulse Laser and Mg

We have investigated the study of short pulse laser including nanosecond and femtosecond irradiation on Mg and Mg alloys. Following are main conclusions:

(1) During nanosecond pulse Nd:YAG laser irradiation on AZ91D Mg alloy, molten materials and holes observed at the surface were mainly caused by the

combined effect of melting and boiling. Moreover, melt depth was found to be around 50 μm only, and several micron scale microstructure was formed at high cooling rates of 105-107 K/s. Additionally, the occurrence of various micron craters took place at the surface when irradiated in Ar gas chamber. These craters were formed as a result of subsurface superheating, explosive volume boiling and plasma expansion accompanied by generation of cavitation bubbles.

(2) Laser-induced darkening surface was obtained on AZ31B Mg alloy following nanosecond pulse Nd:YAG laser and Excimer laser irradiation in the presence of air. The color of irradiated areas became dark rapidly, and oxygen content at the irradiated area as well as surface roughness increased significantly. It was proposed that the darkening effect was mainly attributed to light trapping in the rough surface caused by hydrodynamic ablation oxidation and material redeposition processes during laser irradiation. Surface chemistry variation played a second role in determining the color change.

(3) During femtosecond pulse laser irradiation on Mg and Mg alloy in air, micro-grooves and nano-ripples were formed at the surface. Most significantly, the orientation of nano-ripples was perpendicular to laser polarization, and period of nano-ripples was in a broad distribution range of 450-620 nm. It was suggested that the interference between surface plasmons and incident laser light might play the most important role in the formation of ripples, and the initial surface roughness together with such interference possibly lead to the formation of grooves. In addition, iridescent effect was observed at large irradiated area due to ripples with broad distribution of periods acted as diffraction gratings.

8.3 Recommendations for Future Work

Related areas for further researches can include the following:

- (1) Effect of pulse repetition rate on microstructure development of laser-treated Mg alloy may be studied to investigate heat accumulation and rapid melting as well as solidification process;
- (2) Effect of wavelength, absorption coefficient and thermalphysical properties of laser on surface processing of Mg alloys may be discussed to improve the investigation of laser-material interaction further;
- (3) In-situ temperature detection, including single pulse irradiation and large area scanning, may be needed to observe real thermal history of laser and Mg alloy during surface processing. This will be useful to study phase transformation and solidification development of materials in different phases;
- (4) Laser-ultrasonic hybrid processing may be developed for millisecond pulse Nd:YAG laser irradiation on Mg alloy in order to improve microstructure homogeneity in the molten pool (Gureev 1994; Venkannah and Mazumder 2009);
- (5) Thin-film molten pool may be developed in Mg alloy using optimum parameter following nanosecond pulse laser processing. Compared with thick-film molten pool formed following millisecond pulse laser irradiation, further increased cooling rate will allow complete elimination of intermetallic particles for the improvement of surface-related properties. Moreover, effects of overlapping involved in large area treatment may not be significant, in terms of re-heating and re-melting of previous melted track during nanosecond pulse laser irradiation;
- (6) Oxidation of Mg alloys is a serious problem for their further application in both industry and bio-implants. It is worthwhile to study the effect of laser

surface processing on the oxidation resistance of Mg alloys in terms of microstructure, topography and chemistry.

(7) In order to improve interaction between bio-implants and cells (such as bone and stent), surface texturing following short pulse laser irradiation is an advanced technique to change surface topography and surface chemistry of biodegradable Mg alloys. Further experimental work both in vivo and in vitro is needed. Additionally, laser-based fabrication of bio-micro-devices and tissue scaffolds for high-resolution micro/nano processing of Mg alloys is also an attractive field.

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List of Publications:

1. Guan Y.C., Zhou W., Zheng H.Y., Li Z.L., 2011. Crater Formation on Magnesium Alloy Surface Irradiated with Nanosecond Pulse Nd:YAG Laser, *Journal of Laser Micro/Nanoengineering*, In press.
2. Guan Y.C., Zhou W., Zheng H.Y., Li Z.L., 2010. Solidification Microstructure of AZ91D Mg Alloy after Laser Surface Melting, *Applied Physics A: Material Science Processing*, 101(2), p. 339-344.
3. Guan Y.C., Zhou W., Zheng H.Y., Li Z.L., 2010. Surface Modification of AZ91D Magnesium Alloy using Millisecond, Nanosecond and Femtosecond Lasers, *Key Engineering Materials*, 447-448, p. 695-699.
4. Guan Y.C., Zhou W., Zheng H.Y., 2009. Effect of Laser Surface Melting on Corrosion Behaviour of AZ91D in Simulated-modified Body Fluid, *Journal of Applied Electrochemistry*, 39(9), p. 1457-1464.
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