UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

THE EFFECTS OF SURFACE TREATMENTS ON PROPERTIES AND CORROSION PROTECTION OF AZ91D MAGNESIUM ALLOY

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A thesis submitted in fulfillment of the requirements for the degree of Master of Science in Manufacturing Engineering

Faculty of Manufacturing Engineering

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2018

DECLARATION

I declare that this thesis entitled "The Effects of Surface Treatments on Properties and Corrosion Protection of AZ91D Magnesium Alloy" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ………………………….

Name : ………………………….

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APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering.

Signature : ………………………………………………………

Supervisor Name : ………………………………………………………

Date : ………………………………………………………

DEDICATION

To my beloved family

ABSTRACT

Magnesium alloy, especially AZ91D is extensively applied in the electronic industries due to its low densities, excellent strength to the weight ratio, and good electromagnetic shielding. However, its poor performance in a corrosive environment has restricted its applications. In this work, the corrosion resistance of the AZ91D surface was investigated by comparing three surface treatment techniques known as the oxidation, PA-PVD, and the duplex treatment. The treated AZ91D were analysed using varied methods, encompassing, microstructure analysis via SEM and optical microscope, phases analysis using XRD characterization, and surface roughness analysis using surface profilometer, to name a few. The results captured the occurrence of grain recrystallization, the elimination of twin boundaries on the grain structure of untreated AZ91D and the elimination $Mg_{17}Al_{12}$ phase precipitation after the oxidation process in which the $Mg_{17}Al_{12}$ precipitate is believed to accelerate the corrosion rate by acting as cathode near the Mg matrix. The presence of MgO phase after oxidation process and duplex treatment also has increased the corrosion resistance of AZ91D by the development of oxide passive film on the AZ91D surface. Cross-sectional SEM images show that the Cr_2O_3 coating has successfully been deposited on the AZ91D surface with 2µm thickness. Throughout the thorough analysis, the study has concluded that, the oxidized AZ91D has the best corrosion resistance, followed by the duplex treatment and PA-PVD process. Further recommendations are also proposed in this thesis.

ABSTRAK

Magnesium aloi, terutamanya AZ91D digunakan secara meluas dalam industri elektronik kerana ketumpatannya yang rendah, kekuatan yang sangat baik kepada nisbah berat bahan, dan pelindung elektromagnetik yang baik. Walau bagaimanapun, prestasi yang buruk dalam persekitaran yang menghakis telah menyekat kepelbagaian aplikasinya. Dalam penyelidikan ini, rintangan kakisan permukaan AZ91D diselidiki dengan membandingkan tiga teknik rawatan permukaan yang dikenali sebagai pengoksidaan, PA-PVD, dan rawatan dupleks. AZ91D yang dirawat telah dianalisis dengan menggunakan pelbagai kaedah, merangkumi, analisis mikrostruktur melalui SEM dan mikroskop optik, analisis fasa menggunakan pencirian XRD, dan analisis kekasaran permukaan menggunakan profilometer permukaan,. Hasilnya adalah berlakunya penyusunan semula struktur butiran, penghapusan sempadan kembar pada struktur butiran AZ91D yang tidak dirawat dan penghapusan fasa $Mg_{17}Al_{12}$ selepas proses pengoksidaan di mana mendakan $Mg_{17}Al_{12}$ dipercaya mempercepatkan kadar kakisan dengan bertindak sebagai katod berhampiran dengan Mg matriks. Kehadiran fasa MgO selepas proses pengoksidaan dan rawatan dupleks juga telah meningkatkan rintangan kakisan AZ91D dengan perkembangan filem pasif oksida pada permukaan AZ91D. Imej keratan rentas SEM menunjukkan bahawa salutan Cr_2O_3 telah berjaya diaplikasikan pada permukaan AZ91D dengan ketebalan 2µm. Sepanjang analisis menyeluruh, kajian telah menyimpulkan bahawa AZ91D teroksidasi mempunyai rintangan kakisan terbaik, diikuti dengan rawatan dupleks dan proses PA-PVD. Cadangan lanjut juga dicadangkan dalam tesis ini.

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LIST OF SYMBOLS

GPa	-	Giga Pascal
ºC	-	Degree Celcius
Wt%	-	Weight percent
MPa	-	Mega Pascal
pH	-	Potential Hydrogen
V	-	Volts
μ	-	Micron
Ra	-	Surface Roughness
scfh	-	Standard Cubic Feet per Hour
Sccm	-	Standard Cubic Centimeter Per Minute
cm	-	Centimeter
HV	-	Vickers Hardness
HK	-	Knoop Hardness
kgf	-	Kilogram Force
mm	-	Milimeters
d	-	Displacement
mmpy	-	Milimeters per Year
mpy	-	Meter per Year
Cr	-	Corrosion Rate
K	-	Constant
EW	-	Equivalent Weight

LIST OF ABBREVIATIONS

Mg	-	Magnesium
MgO	-	Magnesium Oxide
MAO	-	Microarc Oxidation
PVD	-	Physical Vapor Deposition
CrN	-	Chromium Nitride
Cr_2O_3	-	Chromium Oxide
XRD	-	X-Ray Diffraction
EDX	-	Energy Dispersive X-Ray
RF	-	Radio Frequency
HCP	-	Hexagonal Closed Pack
NaCl	-	Sodium Chloride
N	-	Nitrogen
H	-	Hydrogen
TiN	-	Titanium Nitride
ZrN	-	Zircornia Nitride
AlN	-	Aluminium Nitride
OCP	-	Open Circuit Potential
TiAlN	-	Titanium Aluminium Nitride
VIS	-	Virtual Images Stitcher
SEM	-	Scanning Electron Microscope
OM	-	Optical Microscope
SE	-	Secondary Electrons
BSE	-	Back-scattered Secondary Electron
CRT	-	Cathode Ray Tube
kgf	-	Kilogram Force
d	-	Displacement

LIST OF PUBLICATIONS

W. A. S. W. Zulkifli, Zulkifli M. R., Juoi, J. M., and Y. Yusuf., 2017. Effect of Nitriding Temperature and Nitriding Time on MgAZ91D Alloy. *Journal of Mechanical Engineering*, 3(2), pp.177–184.

CHAPTER 1

INTRODUCTION

1.1 Background

Magnesium (Mg) and its alloys such as AZ91D are highly preferable material, especially in telecommunication industries and automotive industry (Fujisawa et al., 2014). Their high dimensional stability and excellent machinability allow the Mg and its alloys to be transformed into a complex shape (Zhang et al., 2015). The telecommunication industries need materials with lower densities, excellent strength to the weight ratio, and easier to cast. There are many materials that fit the application requirement, such aluminum alloy, magnesium alloy, and titanium alloy. However, only magnesium alloy offers the best shielding of electromagnetic emissions that does not disturb the wave from electronic parts. Thus, the surface modification could become a solution for Mg and its alloys, especially the AZ91D if it needs to be exposed to wear and corrosion environment (Zulkifli et. al., 2013).

Among the many techniques available for surface modification, the oxidation process is one of the conventional but simple methods that should be considered. The oxidation process can modify the surface of the metal to increase its surface hardness and corrosion resistance. In this process, the choice of suitable parameters such as time and temperature in the oxidation process is worth considering (Tan et al., 2016). For example, the use of temperature must take into consideration the AZ91D properties because it will affect the microstructure of the materials. The oxidation technique is one of the techniques that enhance the corrosion properties of Mg alloy with the growth of MgO phase. It is also a low-cost method for the corrosion improvement.

On the other hand, the coating technique can improve the corrosion resistance of AZ91D, especially using the Plasma Assist – Physical Vapor Deposition (PA-PVD) coating technique with anti-corrosion compound (Altun & Sen., 2006). However, the surface treatment of the coating technique has its weakness; the interface between the substrate surfaces and coating will minimize the protection of the corrosion resistance with the beginning of the coating cracks and porosity, thus allowing the surface of the substrate exposed to the corrosion. Therefore, the combination of both techniques known as duplex treatment (combining oxidation and PA-PVD coating in a controlled environment) attempts to enhance the corrosion resistance of Mg and its alloys. Before the duplex technique implementation, oxidation must be ensured to enhance the mechanical properties of the AZ91D surface such as surface hardness in order to improve the rigidity of the material's surface. This is to improve the tightening between substrate surface and coating. In this study, the work focused solely on oxidation in which the conventional tube furnace technique is carried out to oxidize AZ91D as well as PA-PVD and the duplex treatment investigates their relation with the morphology, characterization, mechanical properties, and corrosion performance of the desired AZ91D.

1.2 Problem Statement

Magnesium alloy, especially AZ91D is widely applied in the electronic and telecommunication industries due to its low densities, excellent strength to the weight ratio, easier to cast with a thin wall, and good electromagnetic shielding. Among the available materials, such as aluminum alloy, magnesium alloy, and titanium alloy, AZ91D is the best candidate as it can shield electromagnetic emissions because the magnesium alloys that have been utilized in the development of electronic products can absorb electromagnetic waves. Therefore, the material is suitable to be used as chassis in many electronics and telecommunication product such as the walkie-talkie. However, much literature argue that the applications of AZ91D can be restricted due to its poor performance in a corrosive environment (Taheri et al., 2012; Cao et al., 2016; Shanmugam et al., 2014). For instance, a telecommunication company reported that, its application in the offshore environment could lead to damage or malfunction of devices due to corrosion. Previous studies have documented various available techniques to choose from to improve the corrosion resistance of Mg alloys, such as the micro arc oxidation (MAO) (Guo et al., 2012), ion implantation (Xie et al., 2015), nitriding (Tacikowski et al., 2011), and other surface treatment process. Notably, the best technique is usually simple process which is saving time and energy, low in cost yet effective. Yet, studies that considered these aspects while enhancing the corrosion resistance of AZ91D surface, is scarce. Thus, in this study, the enhancement of the corrosion resistance of the AZ91D surface will be investigated by comparing the three surface treatment techniques, namely, the oxidation, the Plasma-Assist Physical Vapor Deposition (PA-PVD), and the duplex treatment.

1.3 Objectives

This study is conducted to embark on the following objectives:

i. To investigate the influence of surface treatments on the microstructure, grain size, phases and case depth of AZ91D Magnesium Alloy.

ii. To investigate the influence of surface treatments on the surface roughness and surface hardness and its relationship with coating-substrate adhesion Of AZ91D Magnesium Alloy.

iii. To analyze and compare the corrosion performance of the untreated against the treated AZ91D and its correlation with the surface treatment of AZ91D Magnesium Alloy.

1.4 Scope of Work

This research aims to investigate the effect of surface treatment process on the AZ91D properties to enhance its corrosion performance. The scope of research includes works such as analyzing the surface morphology, surface roughness, and microstructure using the optical microscope and scanning the electron analysis. The analysis on phases is obtained by way of x-ray diffraction. The analysis of surface hardness and case depth is done with microhardness test. Corrosion performance of the surface treated AZ91D against the untreated AZ91D is performed using the linear polarization technique.

1.5 Organization of Thesis

This report focuses on the influence of surface treatment on the AZ91D properties for corrosion protection enhancement. The organization of this report is as follows;

Chapter 1 presents a short introduction which include of background of the study, problem statement, research objectives, scope of work and thesis organization. Chapter 2 revolves on literature review and past studies from other researchers that related to the study. In this chapter, literature about suface treatment, corrosion properties and effects of the surface treatment will be more highlighted. Chapter 3 explains the method on experimental setup, experimental procedures, and characterization that were involved in the testing. Chapter 4 discussed the result and analysis from this study. The result is reflected according to the research objectives. Chapter 5 presents the brief summary and conclusion of this research work. The recommendation for future work from the study is also included in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discusses the literature review from the scholarly paper, which includes the current knowledge including fundamental findings, and also theoretical and procedural contributions to a specific topic. The chapter's aim has been to understand the current state of the research being carried out in the relevant field before restructuring the new work in this research to minimize any problems when the experiment is carried out.

2.2 AZ91D

Magnesium is an element with an atomic number of 12. It is a solid gray shiny particle which is similar to the other elements in the second column in group 2 of the periodic table. All of the group 2 elements have the same electron configuration in the outer shell and has a similar crystal structure. Magnesium is the ninth richest element on earth (Housecroft & Sharpe., 2008). Magnesium is produced naturally in combination with other elements where it is has a 2^+ oxidation state. Magnesium has a lower density than aluminium, and the alloy is valued for its lightweight and strength.

2.2.1. Overview of AZ91D

Magnesium (Mg) and its alloys, specifically AZ91D are taken into consideration because of their light weight and superior specific strength. AZ91D is symbolized for 90% Magnesium, 9% Aluminium, and 1% Zinc. It also has a high strength-to-weight ratio with density values of only 2/3 of aluminium and 1/4 of iron (Gray and Luan., 2002). Mg also has high thermal conductivity, high dimensional stability, and excellent machinability; it is also easily recycled to make it suitable for the automotive industry. For example, vehicle interior parts, body, chassis and also other applications (Friedrich and Schumann., 2001).

Pure magnesium exists in a hexagonal closed packed (HCP) crystal structure, and is a light weight non-ferrous light alloy. Besides that, it also has a low elastic modulus with 45 GPa and is a soft metal. Magnesium or magnesium alloy is hard to deform at room temperature. Therefore, most fabrication of magnesium alloy is done by casting or hot work at 200 °C to 350 °C due to the low melting temperature. Magnesium alloy is chemically unstable and susceptible to corrosion in the marine environment (Callister, 2007).

The advantage of Mg alloy that makes people use them is their low density as the Mg alloy is well-known to be the lightest structural metal (Buha., 2008). Besides that, the low corrosion resistance behaviour in the Mg alloy in any of its part is because the Mg alloy is an active element chemically, and the surface of Mg is not particularly protected for corrosion. Mg also easily attracted to oxygen (Avedasian and Baker., 1999). Furthermore, Mg alloys have a low oxidation resistance characteristically in the air at high temperatures, which means that it is easier to oxidize at high temperatures. Other than that, Mg alloys may cause fires through engineering processes, such machining, casting and also heat treatment. Most of their surfaces can easily be degraded by the process. Poor oxidation resistance considerably limits their wider engineering applications. Hence, the improvement of Mg alloys by increased corrosion resistance would improve the variety of the applications of Mg alloys.

Magnesium is the lightest material with excellent castability and wealth deposition. However, it has limitations such as low creep resistance, lower tensile properties which include strength and ductility, low wear and corrosion resistance. In their application, surface treatment is an effective approach. In addition, magnesium's melting point is at 650 °C, and their boiling point is 1107 °C where it is more similar to the aluminium properties (Ali et al., 2015). The latent heat of fusion for Mg alloy is 0.37 MJ/Kg, and latent heat evaporation is 5.25 MJ/Kg. The electrical resistivity of Mg alloy at 20ºC is 4.45 μΩ cm which is the reason for its high demand in telecommunication sectors.

There are 25 metals with a suitable atomic size to structural composites of the magnesium. However, there are only few proper alloying components that are involved in the mg alloying elements. The suitability is frequently confined by the relative valence electron impact such as 'Mg' and O which prompts the development of the stable compound. There are just about ten components which have reflected as alloying components for Mg alloy. The right alloying elements for the magnesium alloys include aluminium, zinc, manganese, zirconium, silver, yttrium and also rare earth components such as copper, nickel, and iron which is observed as unkind contaminations that need to be controlled properly to maintain the nature of the magnesium behaviour. The aluminium content of the magnesium alloying elements is to provide the materials hardness and also the strength of the material at standard room temperature which helps the magnesium alloy cast easier for production suitability. Zinc elements are providing the material strength; however, the presence of this element will increase the microporosity that will reduce the corrosion resistance ability. The element of manganese helps offset traced elements during