



**EFFECT OF  $\text{NaVO}_3$  CONCENTRATION AND HCl  
PRE-TREATMENT ON CORROSION BEHAVIOR  
OF ANODIZED COATED AZ91D MAGNESIUM  
ALLOYS**

**By**

**KHALID AZADI BIN MAT AKHIR**

**(1130510717)**

A thesis submitted in fulfilment of the requirements for the degree of  
Master of Science

**School of Manufacturing Engineering  
UNIVERSITI MALAYSIA PERLIS**

**2014**

## ACKNOWLEDGEMENT

Alhamdulillah, thanks to God Almighty for His bless and strength that He has given to me to finish my research. Even though I faced many challenges during my research that make my research progression become low as well as my motivation. However, thanks to Allah S.W.T and Prophet Muhammad S.A.W, finally I got the strength to move on and capable to finish my research with the support from others.

First of all, most gratitude goes to my supervisor and co-supervisor, En Mohd Zamzuri Mohammad Zain, Dr Mohd Nazree Derman and Siti Norbahiyah binti Mohamad Badari, who providing valuable guidance and suggestions on this work. Their supervisions and support truly help me to keep this research going smoothly and thanks to Cik Siti Norbahiyah Mohamad Badari for her concerned and showing interest in my research and also offering valuable suggestion during various stages of my studies. My special thanks also go to the Dean of School Manufacturing Engineering, Dr Khairul Azwan Ismail for his valuable support.

My grateful thanks also go to the Technical Staff of Universiti Malaysia Perlis at Ulu Pauh Laboratory, En Mazlan, En Jasmin, En Suhelmi and also Technical Staff of Material Laboratory at Taman Muhibbah, En Wan Mohd Arif, who became the backbone of my experimental work. Without their tremendous technical support, I can't manage to complete this project at the time.

I would like to give my sincere appreciations to my research team, Khairiah and Shaza, who has offered their help during my laboratory session. I also acknowledge En Murizam and En Hafiz from School of Material for helping me in using X-Ray Diffraction software (XRD). I would also like to thank a long list of people for many enjoyable scientific discussions and personal conversations – Nurul Farah Wahida Nur Liyana, Ahmad Faizal, Fadzilah, Farah Alina, Puan Kartini, Pn

Marina and every else former and current of Manufacturing group members. Their time, expertise and warm friendship were very much appreciated.

I wish to thank Fundamental Research Grant and My Brain15 by the Ministry of High Education for financially supported during my research work starting from April 2012 until June 2014.

Finally, I want to express my appreciations to my beloved family- Ayah, Mak and not forgetting my wife Siti Nuriyah binti Hamid for their love and encouragement. Thank you very much for supporting me every step of the way.

KHALID AZADI BIN MAT AKHIR  
June 2014

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## LIST OF ABBREVIATIONS

EDX	Energy Dispersive X-Ray
Hr	Hour
La	Lanthanum
MAO	Micro-arc oxidation
Mg	Magnesium
MgO	Magnesium Oxide
Mg(OH) <sub>2</sub>	Magnesium Hydroxide
NaCl	Sodium Chloride
NaVO <sub>3</sub>	Sodium Metavanadate
PEO	Plasma Electrolytic Oxidation
SEM	Scanning Electron Microscope
V	Vanadium
V <sub>2</sub> O <sub>5</sub>	Vanadium Oxide
XRD	X-ray Diffraction

## LIST OF SYMBOLS

$\alpha$	Alpha Phase
$\beta$	Beta Phase
A/cm <sup>2</sup>	Current Density
R <sub>p</sub>	Resistance polarization
Cr	Corrosion Rate
mm/y	Millimetre per year
V	Voltage

**KESAN KEPEKATAN  $\text{NaVO}_3$  DAN  $\text{HCl}$  PRA-RAWATAN KE ATAS SIFAT  
PENGARATAN BAGI SALUTAN ANODIZING KE ATAS AZ91D  
MAGNESIUM ALOI.**

**ABSTRAK**

Magnesium dan magnesium aloi mempunyai beberapa ciri yang sangat baik seperti ketumpatan paling rendah dalam logam industri, nisbah kekuatan kepada berat yang tinggi, penyerapan gegaran dan elektromagnet ciri-ciri perisai gelombang. Oleh kerana sifat-sifat ini, magnesium dan magnesium aloi boleh digunakan dalam pembuatan komponen untuk kenderaan bermotor, barangan elektronik dan dalam pembuatan barangan sukan. Di samping itu, magnesium dan magnesium aloi lebih mudah dikitar semula daripada resin sintetik, sekaligus menjadikan ia sebagai bahan mesra alam. Rintangan yang rendah terhadap kakisan ataupun pengaratan telah menghadkan penggunaan magnesium dan magnesium aloi di dalam perindustrian. Salutan anodizing adalah salah satu teknik yang kos rendah, efektif dan mudah untuk digunakan bagi menghasilkan lapisan logam ke atas substrat. Kajian ini berkaitan dengan penyediaan filem oksida ke atas permukaan AZ91D magnesium aloi oleh salutan anodizing dan  $\text{HCl}$  pra-rawatan sebelum anodizing dalam larutan yang mengandungi  $\text{La}(\text{NO}_3)_3$  dan / atau  $\text{Mg}(\text{NO}_3)_2$ , dengan penambahan kepekatan  $\text{NaVO}_3$  dalam larutan. Lapisan anodizing telah dihasilkan pada permukaan AZ91D magnesium aloi dan kesan kepekatan  $\text{NaVO}_3$  dan  $\text{HCl}$  pra rawatan telah dikaji. Satu sebatian kimia  $\text{AlO}$ ,  $\text{MgO}$  dan  $\text{VO}$  dikesan dari puncak corak XRD bagi mengesahkan pembentukan lapisan oksida pada permukaan AZ91D magnesium aloi. Rintangan kakisan AZ91D magnesium aloi telah meningkat dengan mendadak dengan kadar kakisan 0.2 mm/y telah diperolehi. Morfologi penyembuhan diri boleh

diperhatikan daripada SEM imej menunjukkan pemulihan bagi  $\text{NaVO}_3$  yang kaya dengan oksida dari penyelesaian  $\text{NaCl}$  yang teruk. Keputusan yang baik bagi setiap larutan ini dikekalkan untuk penambahbaikan oleh  $\text{HCl}$  pra-rawatan. Satu permukaan kasar telah diperolehi selepas merendam dalam larutan  $\text{HCl}$  selama 20s dan diikuti dengan proses anodizing, telah menghasilkan kadar kakisan sehingga 0.19 mm/y. Dua puncak yang dikesan telah mengandungi sebatian kimia  $\text{VO}$  dan  $\text{MgO}$  dikesan dari corak XRD. Perlindungan kakisan AZ91D magnesium aloi telah meningkat dengan cara-cara berikut; pembentukan morfologi penyembuhan diri untuk pulih daripada alam sekitar yang teruk dengan penambahan  $\text{NaVO}_3$  dan pembentukan lapisan oksida yang pasif pada permukaan AZ91D aloi magnesium oleh rendaman dalam larutan  $\text{HCl}$ . Berdasarkan eksperimen elektrokimia potentiodynamics polarisasi dan keputusan ujian rendaman, larutan yang mengandungi  $\text{NaVO}_3$  dan  $\text{HCl}$  pra-rawatan berjaya meningkatkan rintangan kakisan pada AZ91D aloi magnesium. Hasil kukuh yang ditunjukkan di sini akan menyumbang kepada permintaan yang luas kepada magnesium aloi dalam bidang industri automotif.

**EFFECT OF  $\text{NaVO}_3$  CONCENTRATION AND HCL PRE-TREATMENT ON  
CORROSION BEHAVIOR OF ANODIZED COATED AZ91D MAGNESIUM  
ALLOYS**

**ABSTRACT**

Magnesium and its alloys have some excellent properties, such as the lowest density of industrial metals, a high strength-to-weight ratio, vibration absorbency and electromagnetic wave shield characteristics. Because of these properties, magnesium and its alloys can be applied in the manufacture of components for motor vehicles, in housing for electronics, and in the manufacture of sporting goods. In addition, magnesium and its alloys are more easily recycled than synthetic resins, which make these materials eco-friendly. The poor resistance of magnesium and its alloys to corrosion has limited the application of these materials in corrosive environments. Anodizing coating is one of the most cost effective and simple techniques for introducing a metallic coating to a substrate. This study deals with the preparation of oxide films on AZ91D magnesium alloy by anodizing coating in a solution containing  $\text{La}(\text{NO}_3)_3$  and/or  $\text{Mg}(\text{NO}_3)_2$ , with additive  $\text{NaVO}_3$  concentration in the solution. The anodizing coating on the AZ91D magnesium alloy has been carried out and the effect of  $\text{NaVO}_3$  concentrations and pre-treatment was investigated. A chemical compound of  $\text{AlO}$ ,  $\text{MgO}$  and  $\text{VO}$  was detected from the diffraction peaks of XRD pattern confirming the formation of an oxide layer on the surface of AZ91D magnesium alloy. The corrosion resistance of AZ91D magnesium alloy increases remarkably with corrosion rate of 0.2 mm/y was obtained. A self-healing morphology could be observed from SEM images indicated the recovery of the  $\text{NaVO}_3$  rich oxide film from the severe environment of  $\text{NaCl}$  solution. This result is

remained constant for further improvement by HCl pre-treatment. A rough surface was obtained after immersing in HCl solution for 20 s and followed by anodizing, has yielded the corrosion rate up to 0.19 mm/y. Two peaks assigned for VO and MgO was detected from XRD patterns. The corrosion protection of AZ91D magnesium alloy has been increased by the following ways; the formation of self-healing morphology to recover from the severe environment by the addition of NaVO<sub>3</sub>, and formation of a passive oxide layer on the surface of AZ91D magnesium alloy by immersion in HCl solution. Based on the electrochemical experiments of potentiodynamics polarization and immersion test result, coating with NaVO<sub>3</sub> and HCl pre-treatment successfully increased the corrosion resistance of AZ91D magnesium alloy. The result demonstrated here will strongly contribute to the broad application of magnesium alloy in the field of the automotive industry.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Economic pressure causes the nation to struggle in minimizing the fuel consumption. Due to that issue, utilizing the lightweight material in automotive industries becomes a prominence solution in reducing the fuel consumption, hence the emission of pollutants. Automotive industry has select aluminium which is a low density ( $2.7 \text{ g/cm}^3$ ) as compared to other metals as the main material in their vehicle parts production. However, the widespread use of aluminium has leads to the shortage of the source, thus indirectly cause the aluminium to become an expensive metal. A lot of researchers had study on other alternative materials that suits automotive applications. Magnesium is the best alternative solution to reduce the weight of each component in automotive. Magnesium alloy is a promising engineering material due to the properties of low density about  $1.74\text{g/cm}^3$  with high specific strength compared to other common material used in automotive such as iron, ferrous, etc. (Cheong, 2006). However, the low corrosion resistance of magnesium has limited its application. To overcome this problem, many researchers have studied to develop an advanced coating to reduce the corrosion and wear resistant of magnesium.

Magnesium, magnesium alloys, and magnesium composites are strong candidates for the existing and emerging engineering applications due to their low

density and high strength to weight ratio. In a dry atmospheric condition magnesium-based materials are quite stable from corrosion perspective due to the reasonably protective nature of their oxide. However, in aqueous environment, magnesium is anodic to most other metals due to its strongly negative electrode potential (Table 1.1). Owing to its poor corrosion properties, magnesium-based materials are prone to galvanic corrosion, which can result in severe pitting. Thus, this will reduce the mechanical performance and greatly limits the usage of magnesium-based materials (Gupta & Ling, 2010).

Table 1.1: Corrosion potential of commonly used metals and alloys in 3–6% NaCl solutions (ibchem.com, 2003)

Metal or Alloy	Corrosion Potential (V)
Mg	-1.73
Mg alloys	-1.67
Zn	-1.05
Al (99.99%)	-0.85
Mild steel	-0.78
Cast iron	-0.73

It is well known that magnesium (Mg) alloys are not corrosion resistant and require surface treatments or coatings in many applications. A variety of surface finishing processes are being used to protect magnesium alloys from corrosion, which include Electrochemical Coating (MAO, Nickel Composite Coating, Anodizing), Gas Phase Deposition (CVD & PVD), Thermal Spray Coating etc. These coating techniques should be considered to enhance a protective surface treatment becomes an essential part of the manufacturing process for magnesium components that are to be used in humid or corrosive environments.