CORROSION PERFORMANCE OF Zn-Al-Mg COATED STEEL WIRE ROD FOR OFFSHORE APPLICATION

MOHD NAIF HANIS BIN MOHD SOKRI

A project report submitted in partial fulfilment of the requirements for the award of the degree of Master of Engineering (Material Engineering)

> Faculty of Mechanical Engineering Universiti Teknologi Malaysia

> > SEPTEMBER 2017

Specially dedicated to my beloved family

ACKNOWLEDGEMENT

Firstly, I would like to express my deepest appreciation to my project supervisor, Prof Dr. Esah bte Hamzah for her guide in completing this project. It is an honor to be given a chance to be her student and also a chance to spend time with her which had given me a lot of valuable advice and knowledge. Congratulations too for her promotion recently!

Also huge thanks to my co-supervisor, Dr. Wan Fahmin Faiz bin Wan Ali for his continuous support, his knowledge sharing and his motivation during facing hard situations. His friendliness make him easy to approach and I'm very comfortable in working on this project with him.

Not forget to Dr. Myung Hyun Cho from Kiswire Sdn. Bhd for his support towards the project. I was given an access to Kiswire lab apparatus and equipment to complete the project..

Sincere appreciation to Kiswire staff who helped me during the experimental work and use of their research facilities especially to Mr. Afnan Aiman who has spent his precious time, sacrifice his weekend and lending his superb skill to help me on conducting the experiment and analysis.

Finally, thanks to my family especially my parents and also my friends for their morale support and encouragement which help me to complete this project. I will always be indebted to all of you.

ABSTRACT

The increase demand on improvement corrosion protection in steel structure for offshore industry lead to development on the hot-dip galvanizing process and the coating material alloy. It is crucial to provide long service life for all this structure to minimize cost of operation, time saving, and workload. This research project focusing on evaluating the Zn-Al-Mg alloy coated on steel wire rod. Prior to Zn-Al-Mg alloy coating, the steel wire rod was coated with pure Zn followed by Zn-Al coating for comparison purposes. This is to determine effect of the intermediate layer of coating on the performance of Zn-Al-Mg coating. Electrochemical test and salt spray test were done to evaluate corrosion performance of the steel wire after Zn-Al-Mg coating. The samples before and after corrosion test were analyzed with optical microscopy, scanning electron microscopy to obtain microstructure image and Energy Dispersive Spectrometry (EDS) for elemental analysis. It was found that iron diffusion increases with multiple galvanizing process. It was also found that Zn-Al-Mg corrosion performance is good due to the presence of Magnesium (Mg) which forms protective oxide. The result shows that the Zn-5Al wire coated with Zn-5.3Al-2Mg gives better corrosion performance compared to pure Zn coated wire which were coated with Zn-2.3Al-2Mg coating.

ABSTRAK

Penambahan permintaan terhadap peningkatan perlindungan kakisan dalam struktur keluli bagi industri pesisir pantai membawa kepada pembangunan proses penggalvanian dan bahan salutan aloi. Jangka hayat perkhidmatan yang panjang untuk semua struktur ini adalah penting untuk meminimumkan kos operasi, penjimatan masa, dan mengurangkan beban kerja. Projek penyelidikan ini memberi tumpuan kepada menilai salutan aloi Zn-Al-Mg pada rod dawai keluli. Sebelum proses salutan aloi Zn-Al-Mg, rod dawai keluli disalutkankan dengan Zn tulen diikuti oleh lapisan Zn-Al untuk tujuan perbandingan. Ini adalah untuk menentukan kesan salutan lapisan pertengahan pada prestasi lapisan Zn-Al-Mg. Ujian elektrokimia dan ujian penyemburan garam dilakukan untuk menilai prestasi kakisan dawai keluli selepas salutan Zn-Al-Mg. Sampel sebelum dan selepas ujian kakisan dianalisis menggunakan mikroskop optic dan mikroskop imbasan electron (SEM) untuk mendapatkan imej mikrostruktur. Spektrometri tenaga serakan (EDS) digunakan bagi analisis unsur. Kajian mendapati bahawa penyerapan besi meningkat dengan proses penggalvanian berganda. Ia juga mendapati bahawa prestasi kakisan Zn-Al-Mg lebih baik atas kehadiran Magnesium (Mg) yang membentuk lapisan oksida. Hasilnya menunjukkan bahawa rod keluli bersalut Zn-5Al yang kemudiannya dilapisi dengan Zn-5.3Al-2Mg memberikan prestasi kakisan yang lebih baik berbanding dengan rod keluli bersalut Zn tulen yang kemudiannya disalut Zn-2.3Al-2Mg.

TABLE OF CONTENT

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	V
	ACKNOWLEDGEMENTS	vi
	ABSTRACT	vii
	ABSTRAK	viii
	TABLES OF CONTENTS	ix
	LIST OF FIGURES	xiii
	LIST OF TABLES	xiv
	LIST OF SYMBOLS AND ABBREVIATIONS	xvii

1	INTRODUCTION	1
	1.1 Introduction	1
	1.2 Objective of the study	5
	1.3 Scope of the study	5

2 LITERATURE REVIEW 6

2.1 Introduction	6
2.2 Electrochemical Corrosion of Metal	7
2.3 Corrosion Control by Coating	8
2.4 Method of coating	10
2.4.1 Hot-Dip Galvanizing	11
2.5 Coating Material	12
2.5.1 Zinc Coating	13
2.5.1.1 Phase of Fe-Zn	13
2.5.1.2 Zeta (ζ) phase	13
2.5.1.3 Delta (δ) phase	14
2.5.1.4 Gamma1 (Γ 1) and (Γ) phase	14
2.5.2 Zn-Al Coating	14
2.4.2.1 Phase of Fe-Zn-Al	15
2.5.3 Zn-Al-Mg	17
2.5.3.1 Phase of Al-Zn-Mg	17
2.6 Dross Formation on Galvanizing Bath	19
2.6.1 Alloy Mixing Procedure	20
2.6.2 Strip Entry Temperature	20
2.6.3 Alloy Composition	21
2.7 Corrosion Test	22
2.7.1 Salt Spray Test (SST)	22
2.7.2 Electrochemical Impedence Spectroscopy (EIS)	22

3 METHODOLOGY

3.1 Introduction	24
3.2 Material	26
3.3 Coating by galvanizing process	26
3.4 Sample Preparation for galvanizing process	26
3.4.1 Sample Preparation for Metallography Studies	28
3.5 Corrosion Test	29
3.5.1 Electrochemical test	29
3.5.2 Salt Spray Test	31
3.6 Metallurgical Analysis of Test Samples	32
3.6.1 Optical Microscopy	32
3.6.2 Scanning Electron Microscopy	32
3.6.3 Field Emission Scanning Electron Microscopy (FESEM)	33

4	RESULTS AND DISCUSSION	34
	4.1 Introduction	34
	4.2 Coating appearance	35
	4.3 Analysis on the coating layer	35
	4.4 Electrochemical Test Results	43
	4.5 Salt Spray Test Results	47
	4.5.1 Weight Loss Measurement After Salt Spray	54

24

CONCLUSIONS AND RECOMMENDATIONS	56
5.1 Conclusion	56
5.2 Recommendation	57

5

REFERF	ENCES	58

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE

1.1	Wire rope used for suspension bridge	2
1.2	Wire rope used for offshore application	2
1.3	Steel wire rod ready to be hot-dipped in galvanizing bath	3
1.4	Dross formation covering surface of Zn-alloy molten bath	4
1.5	Pimples developed on galvanized steel surface due to dross interaction	4
2.1	Wire rope construction	7
2.2	The electrochemical reactions associated with the corrosion of zinc in an acid solution	8
2.3	Isothermal section of the Fe-Al-Zn phase diagram 450°C	16
2.4	Phase diagram of Al-Mg-Zn system projection	18
3.1	Summary of the overall research methodology	25
3.2	Wire rod dimension	26
3.3	Galvanizing process flow for samples used in study	27
3.4	Schematic drawing of samples used in the research	28

3.5	Preparation for FESEM characterization	29
3.6	Electrochemical experimental setup	30
3.7	Polarization curves for a corrosion system under activation control (Tafel behaviour)	31
3.8	Arrangement of samples inside chamber for salt spray test	31
4.1	The research sample as recieved	35
4.2	Optical micrograph of input steel sample with (cross-section)	36
4.3	Cross-sectional analysis of pure Zn coated sample	37
4.4	Cross-sectional analysis of Zn-5Al coated sample	38
4.5	Cross-sectional analysis of Zn-5.3Al-2Mg coated sample	40
4.6	Thickness of coating layer for Zn-5.3Al-2Mg coated sample	41
4.7	Cross-sectional analysis of Zn-2.3Al-2Mg coated sample	42
4.8	Thickness of coating layer for sample Zn-2.3Al-2Mg coated sample	43
4.9	Tafel curves of Zn galvanized on low carbon steel in 3.5% NaCl solution	44
4.10	Electrochemical test results showing the corrosion potential for coated samples	46
4.11	Electrochemical test results showing the current density for coated samples	46
4.12	Electrochemical test results showing the corrosion rate (mmpy) for coated samples	47
4.13	Visual Inspection of coated steel before and after salt spray	48

4.14	Scanning Electron Micrograph (SEM) pitting corrosion that occur on pure Zn coated sample	50
4.15	Scanning Electron Micrograph (SEM) pitting corrosion that occur on Zn-5Al coated sample	51
4.16	Scanning Electron Micrograph (SEM) pitting corrosion that occur on sample Zn-5.3Al-2Mg coated sample	52
4.17	Scanning Electron Micrograph (SEM) pitting corrosion that occur on sample Zn-2.3Al-2Mg coated sample	53
4.18	Corrosion rate (mmpy) determined from salt spray test for coated samples	55
4.19	Corrosion rate (mmpy) determined from salt spray test compared to corrosion rate from Tafel polarization	55

LIST OF TABLES

TABLE NO.	TITLE	PAGE
3.1	Galvanizing Parameter of Wire Rod	28
4.1	Weight loss (g) for coated samples after exposed to salt	54
	spray test	

LIST OF SYMBOLS

°C	Degree Celsius
Κ	Kelvin
μm	Micron
1	liter
Μ	Mega
Pa	Pascal
Å	Angstrom
Н	Hydrogen
0	Oxygen
SO	Sulphur dioxide
Zn	Zinc
Fe	Ferrous
Al	Aluminum
Mg	Magnesium
NaCl	Sodium Chloride
CO2	Carbon dioxide
t	Time (min)
H2O	Water

CHAPTER 1

INTRODUCTION

1.1 Introduction

Wire rope have been used widely in many applications worldwide as support system for heavy structures such as crane rope, mining rope, elevator, bridge, and offshore platform. The wire rope consist of several strands of metal wire laid (twisted) into a helix. This component are prone to corrosion in corrosive environment such as sea and polluted environment which will contribute to degradation of component material and lead to early failure. However, such problem can be mitigated by metal coating process on components which act as isolator between the substrate with the surrounding environment. Figure 1.1 and 1.2 shows examples on the application of wire ropes.



Figure 1.1: Wire rope used for suspension bridge



Figure 1.2: Wire rope used for offshore application

Coating process have been used in industry for so many years to change the surface property of material in order to serve many purpose such as increasing wettability, corrosion resistance, or wear resistance. Basically it is used to enhance the ability of materials to withstand interaction with multiple specific environments that might induce from the weather, environment exposure and application of the material itself.

One of the most used coating on steel is Zinc known as galvanized steel. This is done by applying Zn on substrate which normally use hot-dip galvanizing process. This method has been applied years ago for the purpose of inhibiting corrosion against the substrate metal. Galvanized coat will act as a galvanic protector to the substrate as zinc element is more anodic to most of metal and alloy especially steel. The coating will promote protective layer on the substrate and corrosion process will take place on zinc first before it affecting the substrate thus it will slow down the corrosion process on the metal. Figure 1.3 shows a typical hot-dipping galvanizing process.



Figure 1.3: Steel wire rod ready to be hot-dipped in galvanizing bath

The hot dip galvanizing method has been continuously being researched all over the world by means to create a better galvanizing process in term of cost whether it is direct and indirect, simplification, and time saving process. Also at the same time creating Zn alloy coating that have the best corrosion protection in the specific environment where the material are used. The Zn coated materials are being widely used in many applications such as street furniture, building frameworks, balconies and also in oil and gas industries where the structures are exposed in very extreme corrosive environment. Researchers actively studying on producing Zn coated alloy to increase service life of these structures and components.

About 30 years ago, researchers have develop a combination of aluminum and magnesium in zinc-based alloy coating with various composition which has been proven to give better corrosion protection to the steel substrate. These alloys have been continuously investigated to obtain the best alloy composition for the coating and to optimize the coating process.

Recently, a wire rope producing company (Kiswire Sdn. Bhd) has successfully produced Zn-Al-Mg coating on their products, however the faced difficulty in stabilizing dross formation on top of the molten bath. The dross basically is a scum that formed whether due to dissolution of iron where it will react with molten bath material, or the oxidation of bath alloy itself. The dross will float on top of the alloy molten bath due to its low density and adheres to the coated substrate and compromise coating quality and integrity by inducing crack initiation and also reduce corrosion protection performance of the coating. Figure 1.4 shows the dross formation which covering surface of Zn-alloy molten bath while Figure 1.5 shows pimples developed on galvanized steel surface due to dross interaction during galvanizing process.



Figure 1.4: Dross formation covering surface of Zn-alloy molten bath



Figure 1.5: Pimples developed on galvanized steel surface due to dross interaction

1.2 Objective of the study

The main objectives of this research project are as follows;

- 1. To investigate the microstructural features of the various coating layer.
- 2. To determine the effect of elements on the composition of the coating alloy.
- 3. To investigate the corrosion performance of the newly developed Zn-Al-Mg coating.

1.3 Scope of the study

- 1. Obtaining samples of Zn-Al-Mg alloys from Kiswire Sdn. Bhd.
- 2. Microstructural study on the Zn-Al-Mg samples using optical, SEM, and EDS.
- 3. Identification of metallic element that can improve on the stabilization of the molten Zn-Al-Mg alloy.
- 4. Corrosion test on coated samples using salt spray and electrochemical method.

REFERENCES

- [1] Childs, P.R., 2013. Mechanical design engineering handbook. Butterworth-Heinemann.
- [2] Callister, W., & Rethwisch, D. (2007). Materials science and engineering: an introduction. Materials Science and Engineering (Vol. 94). https://doi.org/10.1016/0025-5416(87)90343-0
- [3] Fontana, M.G., 2005. Corrosion engineering. Tata McGraw-Hill Education.
- [4] Gabe, D. R., Wilcox, G. D., & Carter, V. E. (2010). General principles of protection by coatings. Shreir's Corrosion, 2519–2531. https://doi.org/10.1016/B978-044452787-5.00135-9
- [5] Peißker, P. (n.d.). Corrosion Handbook Corrosive Agents and Their Interaction with Materials Corrosion Prevention and Protection Verbundwerkstoffe Plasma Spray Coating Automotive Paints and Coatings.
- [6] Chivers, A. R. L., & Porter, F. C. (2013). Zinc Coatings. Corrosion: Third Edition, 2, 13:41-13:53. https://doi.org/10.1016/B978-0-08-052351-4.50102-3
- [7] Nimmo, B., & Hinds, G. (2003). Beginners Guide to Corrosion. NPL, February, (February), 1–10.
- [8] Tracton, A. A. (2007). Coatings Materials.
- [9] X. G. Zhang, Corrosion and electrochemistry of zinc, Plenum Press, New York, (2006).
- [10] Y.Q. Liu, A. Das, and Z. Fan, Thermodynamic Predictions of Mg-Al-M (M = Zn, Mn, Si) Alloy Compositions Amenable to Semisolid Metal Processing, Mater. Sci. Technol., 2004, 20, p 35-41
- [11] KoÈ ster W, GoÈ decke T. Das Dreisto€ system Eisen-Aluminum-Zink. Z Metallkde 1970;61:642

- [12] Urednicek M, Kirkaldy JS. Mechanism of iron attack inhibition arising from additions of aluminum to liquid Zn(Fe) during galvanizing. Z Metallkde 2007;64:649.
- [13] Osinski K. The influence of aluminum and silicon on the reaction between iron and zinc. Doctoral Thesis. Technical University, Eindhoven, 1983.
- [14] Tang N.Y. Thermodynamics and kinetics of alloy formation in galvanized coatings. In: GoodwinFE, editor. Zinc-based steel coating systems: production and performance. Warrendale, PA:TMS, 2008. p. 3
- [15] Schuerz, S., Fleischanderl, M., Luckeneder, G. H., Preis, K., Haunschmied, T., Mori, G., & Kneissl, A. C. (2009). Corrosion behaviour of Zn-Al-Mg coated steel sheet in sodium chloride-containing environment. Corrosion Science, 51(10), 2355–2363. https://doi.org/10.1016/j.corsci.2009.06.0194
- [16] Schuerz, S., Luckeneder, G.H., Fleischanderl, M., Raab, A.E. and Mori, G., 2011. Corrosion protection of zn-al-mg coated steel with and without plastic deformation in chloride containing environment. Corrosion Management, (99), pp.9-15.
- [17] Mondolfo, L.F., "Structure of Aluminum: Magnesium: Zinc Alloys", Met. Rev., 16, 95-124 (1971) (Equi. Diagram, Experimental, Review, 621)
- [18] Su, X., Zhou, J., Wang, J., Wu, C., Liu, Y., Tu, H., & Peng, H. (2017). Thermodynamic analysis and experimental study on the oxidation of the Zn-Al-Mg coating baths. Applied Surface Science, 396, 154–160.
- [19] L'Heureux, S., Goutière, V., Langlais, J., Waite, P. and Tremblay, D.A., 2012.
 A New Approach to Identify Aluminum Dross Reduction Opportunities Using an Integrated Weighing System. In Light Metals 2012 (pp. 1045-1050).
 Springer International Publishing. Vancouver
- [20] Kurobe, J., & Iguchi, M. (2004). Size effect on dynamic behavior of dross in model hot dip plating bath. Nippon Kinzoku Gakkaishi/Journal of the Japan Institute of Metals, 68(9), 792–799. https://doi.org/10.2320/matertrans.44.885
- [21] Sawaitul, P., Chowriwar, S. A., & Lade, I. P. (2250). Minimization of Dross Formation During the Continuous Galvanizing Process in the Steel Industry. International Journal of Emerging Technology and Advanced Engineering Website:Www.ijetae.com,2(1).Retrievedfrom http://www.ijetae.com/files/Volume2Issue1/IJETAE_0112_08.pdf

- [22] Dutta, M., Halder, A. K., & Singh, S. B. (2010). Morphology and properties of hot dip Zn-Mg and Zn-Mg-Al alloy coatings on steel sheet. Surface and Coatings Technology, 205 (7), 2578-2584. https://doi.org/10.1016/j.surfcoat.2010.10.006
- [23] Yao, C., Lv, H., Zhu, T., Zheng, W., Yuan, X., & Gao, W. (2016). Effect of Mg content on microstructure and corrosion behavior of hot dipped Zn–Al– Mg coatings. Journal of Alloys and Compounds, 670, 239–248. https://doi.org/10.1016/j.jallcom.2016.02.026
- [24] Turgoose, S. and Cottis, R.A., 2000. Corrosion Testing Made Easy: Electrochemical Impedance and Noise. National Association of Corrosion Engineers, Houston.
- [25] Verink, E.D., 1994. Corrosion testing made easy.[ed.] BC Syrett. The basics.