

# **UNIVERSITY OF SOUTHAMPTON**

FACULTY OF ENGINEERING AND THE ENVIRONMENT

Engineering Materials

## **Electrodeposition of Nickel Coatings on Aluminium Alloy 7075 through a Modified Single Zincating Process**

by

**Intan Sharhida Othman**

Thesis for the degree of Doctor of Philosophy

June 2016

UNIVERSITY OF SOUTHAMPTON

## **ABSTRACT**

FACULTY OF ENGINEERING AND THE ENVIRONMENT

Engineering Materials

Thesis for the degree of Doctor of Philosophy

### **ELECTRODEPOSITION OF NICKEL COATINGS ON ALUMINIUM ALLOY 7075 THROUGH A MODIFIED SINGLE ZINCATING PROCESS**

Intan Sharhida Othman

Electrodeposition on aluminium alloy substrates often is often difficult in producing a coating with good adhesion when compared to other metals. This is due to the rapid formation of oxide layers on the substrate's surface when exposed to air and water, preventing metallic bonds from forming between the nickel coating and the aluminium alloy substrate which in turn resulting in poor adhesion. Adhesion of the coating on the substrate influences the quality of the coating. To overcome this problem, a series of critical surface pre-treatment procedures are required for a successful electrodeposition process with a strong coating adhesion. The pre-treatment process consists of mechanical grinding and polishing, alkaline and acidic cleaning, zincating and activation process. This study focuses on the zincating process to obtain a strong adherence coating on the substrate.

An aim of this study was to replace the complex double zincating process. To this end, modification has been made to a conventional single zincating process, as the process results in a non-homogenous deposition of zinc particles on the substrate which leads to a poor adhesion of the coating. The modified process, for which the duration of the single zincating process was extended from 1 to 20 minutes, was based on the electrochemistry measurements of aluminium alloy 7075 substrate in the zincating

solution. For comparison, nickel coatings prepared using a double zincating process at 60/10, 60/20, 60/30, 60/40 and 60/50 seconds were also produced in this study.. By replacing the double zincating with a modified single zincating process, two pre-treatment steps of double zincating process will be eliminated. Thus, the waste disposal problem in terms of the chemical used in the zincating solution is reduced. In addition, copper activation was applied before the single zincating process in order to overcome the high dissolution of the substrate in the zincating solution.

The surface pre-treated samples were characterized after alkaline cleaning, acid cleaning, zincating process and copper activation at various immersion durations by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and atomic force microscopy (AFM). The modified single zincated samples were found to contain larger zinc particles, as compared to the conventional single and double zincated samples. The modified single zincating process also showed an increasing trend in the nucleation density and size of zinc particles with time. A gradual decrease in the surface roughness values with the extension of the modified single zincating duration was also observed.

Then, the influence of multiple zincating processes (conventional and modified single zincating with and without copper activation, and double zincating) at various durations on the coating adhesion was investigated using scratch adhesion test. Scratch failure modes were analysed using acoustic emission signals, frictional force, and microscopy observation. The conventional single zincating and double zincating processes resulted in poor adhesion of the nickel coatings to the substrate, as both the cohesive and adhesion failures occurred during the scratch test. The adhesion of the coating to the substrate was improved by extending the single zincating duration from 1 to 5, 10, 15 and 20 minutes, with only cohesive failure found for the samples. This result was supported by the number of acoustic emission activity ( $N_{AE}$ ) events recorded during the test, which showed the highest  $N_{AE}$  at about 130 for the sample produced from the conventional single zincating process. An increase in the zincating duration to 5 minutes resulted in a drastic reduction of the  $N_{AE}$  to 30. The similar adhesion behaviour was also observed on modified single zincated samples with copper activation.

The corrosion tests were carried out by immersing the coatings in a 3.5 wt. % NaCl solution at room temperature. It was found that a modified single zincating process at a longer duration provided a significant enhancement of corrosion resistance as compared to the conventional single zincating process, due to the increase in corrosion potential and decrease in corrosion current density of the conventional single zincated sample.

These much improved performance of coating adhesion and corrosion resistance may be explained by homogenous distribution of zinc particles and good coverage of the zinc particles on the aluminium alloy substrate.

## Table of Contents

<b>ABSTRACT .....</b>	<b>ii</b>
<b>List of tables .....</b>	<b>xvii</b>
<b>DECLARATION OF AUTHORSHIP .....</b>	<b>xxiii</b>
<b>Acknowledgements .....</b>	<b>xxv</b>
<b>Dedication .....</b>	<b>xxvii</b>
<b>Nomenclature .....</b>	<b>xxviii</b>
<b>1 INTRODUCTION .....</b>	<b>1</b>
<b>1.1 Background of Project .....</b>	<b>1</b>
<b>1.2 Problem Statement.....</b>	<b>4</b>
<b>1.3 Objectives .....</b>	<b>8</b>
<b>1.4 Thesis Outline.....</b>	<b>9</b>
<b>2 LITERATURE REVIEW.....</b>	<b>10</b>
<b>2.1 Electrodeposition Process for Surface Protection.....</b>	<b>10</b>
2.1.1 Introduction.....	10
2.1.2 Surface Pre- treatment Process for the Electrodeposition .....	13
2.1.3 Principles of Electrodeposition Process .....	14
2.1.4 Properties of Electrodeposited Materials .....	18
2.1.5 Factors Influencing the Properties of Electrodeposited Materials .....	22
<b>2.2 Electrodeposition of Nickel Coating .....</b>	<b>25</b>
2.2.1 Introduction.....	25
2.2.2 Fundamentals of Electrodeposition of Nickel .....	25
2.2.3 Faraday's Law for Nickel Coating.....	26
2.2.4 Functions of Constituents in the Watts Bath and Deposit Properties .....	27
<b>2.3 Electrodeposition on the Substrate of Aluminium and its Alloys.....</b>	<b>28</b>
2.3.1 Introduction.....	28
2.3.2 Properties of Aluminium and Its Alloys.....	29
2.3.3 Problems Associated with Electrodeposition on Aluminium and Its Alloys Substrates.....	30

2.3.4	Classification of Methods for Electrodeposition on Aluminium and Its Alloys .....	32
2.3.5	Preparation of Aluminium and Its Alloys Surfaces before Electrodeposition Process .....	34
<b>2.4</b>	<b>Zincating Process.....</b>	<b>41</b>
2.4.1	Introduction.....	41
2.4.2	Fundamentals .....	42
2.4.3	Nucleation and Growth of Zinc Particles .....	43
2.4.4	Factors That Influence the Properties of Zincated Samples .....	44
2.4.5	Environmental Issue of the Zincating Solution .....	59
<b>2.5</b>	<b>Adhesion of Coatings.....</b>	<b>60</b>
2.5.1	Introduction.....	60
2.5.2	Method of Adhesion Testing .....	63
2.5.3	Variables Affecting Scratch Test Results .....	64
2.5.4	Scratch Test Failure Modes .....	67
2.5.5	Evaluation of Coating Failure from Scratch Test .....	70
<b>2.6</b>	<b>Summary of the Literature Review .....</b>	<b>74</b>
<b>3</b>	<b>METHODOLOGY .....</b>	<b>75</b>
<b>3.1</b>	<b>Introduction.....</b>	<b>75</b>
<b>3.2</b>	<b>Surface Pre-treatment Procedures .....</b>	<b>76</b>
3.2.1	Substrate Material .....	76
3.2.2	Mechanical Surface Pre-treatment .....	76
3.2.3	Chemical Surface Pre-treatment .....	78
3.2.4	Multiple Zincating Processes .....	79
<b>3.3</b>	<b>Electrodeposition Process.....</b>	<b>81</b>
<b>3.4</b>	<b>Characterization Techniques and Testing.....</b>	<b>82</b>
3.4.1	Open-Circuit Potential Measurement.....	85
3.4.2	Scanning Electron Microscopy and Energy Dispersive X-ray .....	85
3.4.3	Atomic Force Microscopy .....	86
3.4.4	Scratch Adhesion Test.....	87
3.4.5	Corrosion Test.....	92

<b>4</b>	<b>RESULTS.....</b>	<b>93</b>
<b>4.1</b>	<b>Introduction.....</b>	<b>93</b>
<b>4.2</b>	<b>Electrochemical Behaviour of AA7075 Substrate during Various Surface Pre-treatment Processes .....</b>	<b>93</b>
4.2.1	Electrochemical Behaviour of AA7075 during Alkaline Cleaning and Acid Pickling Processes.....	93
4.2.2	Electrochemical Behaviour of AA7075 during Single Zincating Process .....	95
4.2.3	Electrochemical Behaviour of AA7075 during Various Double Zincating Durations .....	96
4.2.4	Electrochemical Behaviour of AA7075 during the Single Zincating Process with Copper Activation.....	104
<b>4.3</b>	<b>Surface Morphology and Element Composition of AA7075 Substrate after Various Surface Pre- treatment Processes .....</b>	<b>106</b>
4.3.1	Surface Morphology and Element Composition of AA7075 Substrate surface after Alkaline Cleaning and Acid Cleaning Processes .....	106
4.3.2	Surface Morphology and Element Composition of AA7075 Substrate after Copper Activation Process.....	108
4.3.3	Surface Morphology and Element Composition of AA7075 Substrate after Conventional and Modified Single Zincating Process at Various Durations .....	113
4.3.4	Surface Morphology and Element Composition of AA7075 Substrate after Double Zincating Process at Various Durations .....	118
4.3.5	Surface Morphology and Element Composition of AA7075 Substrate after Conventional and Modified Single Zincating Process at Various Durations with Copper Activation .....	124
<b>4.4</b>	<b>Surface Topography and Roughness of AA7075 Substrate after Various Surface Pre-treatment Processes .....</b>	<b>128</b>
4.4.1	Surface Topography and Roughness of AA7075 Substrate after Polishing, Alkaline Cleaning and Acid Cleaning .....	128
4.4.2	Surface Topography and Roughness of AA7075 Substrate after Copper Activation Process.....	131
4.4.3	Surface Topography and Roughness of AA7075 Substrate after Conventional and Modified Single Zincating Process at Various Durations .....	134
4.4.4	Surface Topography and Roughness of AA7075 Substrate after Double Zincating Process at Various Durations .....	137
4.4.5	Surface Topography and Roughness of AA7075 Substrate after Conventional and Modified Single Zincating Process at Various Durations with Copper Activation .....	140
<b>4.5</b>	<b>Surface Morphology and Composition of Interface of Nickel Coating Electrodeposited on AA7075 Substrate through a Conventional and Modified Single Zincating Process at Various Durations.....</b>	<b>143</b>

<b>4.6</b>	<b>Adhesion of Nickel Coatings on AA7075 Substrate Produced from Multiple Zincating Processes .....</b>	<b>146</b>
4.6.1	Effect of Conventional and Modified Single Zincating Process at various Durations on the Adhesion of the Nickel Coatings Electrodeposited on AA7075 Substrate .....	146
4.6.2	Effect of Various Double Zincating Durations on Adhesion of the Nickel Coatings Electrodeposited on AA7075 Substrate .....	156
4.6.3	Effect of Conventional and Modified Single Zincating Process at various Durations with Copper Activation on the Adhesion of the Nickel Coatings Electrodeposited on AA7075 Substrate.....	166
<b>4.7</b>	<b>Electrochemical Corrosion Behaviour of Nickel Coatings on AA7075 Substrate Produced from Multiple Zincating Processes.....</b>	<b>176</b>
4.7.1	Introduction.....	176
	Electrochemical Corrosion Behaviour of Nickel Coatings on AA7075 Substrate Produced from Conventional and Modified Single Zincating Process at Various Durations.....	176
4.7.2	.....	176
	Electrochemical Corrosion Behaviour of Nickel Coatings on AA7075 Substrate Produced from Double Zincating Process at Various Durations .....	177
4.7.3	.....	177
4.7.4	Corrosion Behaviour of Nickel Coatings on AA7075 Substrate Produced from Conventional and Modified Single Zincating Process at Various Durations with Copper Activation.....	179
<b>5</b>	<b>DISCUSSIONS.....</b>	<b>181</b>
<b>5.1</b>	<b>Introduction.....</b>	<b>181</b>
<b>5.2</b>	<b>Electrochemical Behaviour of AA7075 Substrate during Various Surface Pre- treatment Processes .....</b>	<b>181</b>
<b>5.3</b>	<b>Surface Morphology and Elemental Composition of AA7075 Substrate after Various Surface Pre-treatment Processes.....</b>	<b>187</b>
<b>5.4</b>	<b>Surface Topography and Roughness of AA7075 after Various Surface Pre- treatment Processes .....</b>	<b>190</b>
	<b>Surface Morphology and Elemental Composition of Coating's Interface between Nickel Coatings and AA7075 Substrate through a Conventional and Modified Single Zincating Process at Various Durations .....</b>	<b>192</b>
<b>5.5</b>	<b>Adhesion of the Nickel Coatings Electrodeposited on AA7075 Substrate Produced from Multiple Zincating Processes.....</b>	<b>194</b>



5.6	Electrochemical Corrosion Behaviour of the Nickel Coatings Electrodeposited on AA7075 Substrate Produced from Multiple Zincating Processes .....	201
5.7	Overall Discussion of the Results.....	203
6	CONCLUSION .....	206
7	FUTURE WORKS.....	214
REFERENCES		

## List of Figures

Figure 1-1 Comparison between conventional single and double zincating with modified single zincating process .....	7
Figure 2-1 Types of deposits produced from electrodeposition process (a) homogenous, (b) dispersed phase, (c) multilayer, (d) patterned and (e) gradient (from Ref. [67]) .....	13
Figure 2-2 An electrolytic cell for electrodeposition of metal from an aqueous solution.....	16
Figure 2-3 Illustration of several stages in electrodeposition process, (1) migration of hydrated metal ions to a cathode, (2) surrender of the hydration sheath, (3) formation of adsorbed atoms and (4) formation of crystal nuclei at the cathode surface [66] .....	17
Figure 2-4 Scanning electron micrographs of electroless Ni-P layers on aluminium alloys at respective electroless duration (a) 1, (b) 2, (c) 3 and (d) 4 minutes (from Ref. [19]) .....	20
Figure 2-5 Cross-section of nickel coating electrodeposited on an Al 2014 alloy (from Ref.[18])	21
Figure 2-6 Potentiodynamic polarization curves obtained from the corrosion test of the aluminium coatings deposited on AZ91D magnesium alloy produced using BCP and GP methods with and without zincating process in 3.5 wt.% NaCl solution (from the ref. [95]) .....	22
Figure 2-7 SEM micrographs showing the topography of 100 $\mu\text{m}$ thick nickel layers deposited at 323 K and at various current densities, (a) 0.5 $\text{A}/\text{dm}^2$ and (b) 20 $\text{A}/\text{dm}^2$ (from Ref.[72]) .....	23
Figure 2-8 Methods of producing coatings on aluminium alloys .....	34
Figure 2-9 Surface pre- treatment procedures for wrought aluminium alloys that contain high amount of silicon or do not contain interfering microconstituents (1100 and 3003) and for aluminium casting alloys 413,319,356 and 380 (from the Ref. [108]) .....	36
Figure 2-10 Surface pre-treatment procedures for all wrought aluminium alloys, for .....	37
Figure 2-11 Surface pre-treatment procedures for most aluminium casting alloys, for wrought aluminium alloys that contain less than approximately 3% Mg (1100, 3003, 3004, 2011, 2017, 2024, 5052, 6061) and for aluminium alloys whose identities are not known (from Ref. [108])	37
Figure 2-12 Zincating pre- treatment process (a) as-received ion beam sputter-deposited aluminium film, (b) first zincating process, (c) acid immersion process and (d) second zincating process (from Ref. [43]) .....	43
Figure 2-13 Proposed model of the nucleation and growth of zinc particles (from Ref. [42] ) ..	44
Figure 2-14 Effect of concentration of the zincating solution on the weight of the zinc immersion coating formed on 2S alloy sheet at a temperature of 21° C (from Ref. [46]) .....	46
Figure 2-15 (a) Effect of the concentration of the zincating solution on the weight of the zinc immersion coating formed during a given time, (b) details of the components concentration in the different zincating solution (from Ref. [107]) .....	47
Figure 2-16 Mixed potentials as a function of time at various zincate concentrations. (a) 0.5, (b) 0.1, (c) 0.05, (d) 0.01 and (e) 0 M. Sodium hydroxide concentration is at 3.0 M, temperature at 25° C and rotation speed at 230 rpm (from Ref. [50]) .....	48

Figure 2-17 The potential difference between commercial purity aluminium after various pre-treatment conditions in a concentrated simple zincating solution (100 g/l ZnO + 500 g/l NaOH) (from the Ref. [5]) .....	49
Figure 2-18 Effect of different conditioning treatments on the weight of zinc immersion coating on 2S alloy. Treatment A, carbonate-phosphate cleaner; treatment B, same cleaner + 25% sulphuric acid etch + zinc dip; treatment C, same cleaner + double zinc dip; treatment D, Alcoa R5 Bright Dip + zinc dip (from Ref. [46]) .....	50
Figure 2-19 Effect of different wrought aluminium alloys on the weight of zinc immersion coating using same conditioning treatment, concentrated simple zincating solution of 100 g/l ZnO + 525 g/l NaOH (from Ref. [46]) .....	51
Figure 2-20 Effect of temperature of the zincating pre-treatment on the weight of the zinc immersion coating deposited on 2S aluminium alloys sheet (from Ref. [46]) .....	52
Figure 2-21 FE-SEM images of zincated specimen for 10 s (a) zincating temperature of 20 C, (c) zincating temperature at 50 C, while (b) and (d) are the further grown deposit of (a) and (c), respectively (from Ref. [42]) .....	53
Figure 2-22 Effect of solution concentration on adhesion of zinc deposit obtained after 30 seconds immersion in zincating solution (from Ref. [5]) .....	55
Figure 2-23 Effect of solution concentration on adhesion of zinc deposit obtained after 3 minutes immersion in zincating solution (from Ref. [5]) .....	55
Figure 2-24 Effect of solution concentration on adhesion of zinc deposit obtained after 5 minutes immersion in zincating solution (from Ref. [5]) .....	55
Figure 2-25 Adhesion strength of Ni-P electrodeposition on various type of zincating treatment (from Ref. [1]) .....	58
Figure 2-26 Secondary electron of the surface after zincating pre- treatment (a) without zincating, (b) single, (c) double, (d) triple (from Ref. [1]) .....	59
Figure 2-27 Illustration of the local stress state during scratching procedure [from ref. [146]] ..	64
Figure 2-28 Schematic diagram showing the map of the main scratch test failure modes in terms of substrate and coating hardness (from ref.[139]) .....	67
Figure 2-29 Failure modes classification of scratch test results .....	68
Figure 2-30 Illustration of the main stages in buckling failure modes in the scratch test. (i) pile-up ahead of the moving indenter, (ii) interfacial failure leading to buckling. Through- thickness cracking results in removal of coating material, (iii) SEM micrograph of buckle failure in TiN coated stainless steel (from ref. [139]) .....	69
Figure 2-31 Illustration of the main stages in wedge spallation failure modes in the scratch test. (i) wedge crack forms some way ahead of the moving indenter, (ii) further motion drives the coating up the wedge opening up an interfacial crack, (iii) through- thickness cracking close to the indenter leads to spallation, (iv) SEM micrograph of a wedge spallation failure in an alumina scale (from ref. [139]) .....	70
Figure 2-32 Illustration of critical load damage features in progressive load test (from ref. [167])	72

Figure 2-33 Optical micrographs of critical load failure events for the CrN coating with scratch direction from left to right. (a) $L_{C1}$ , (b) $L_{C2}$ and (c) $L_{C3}$ .	72
Figure 2-34 Correlation between the amplitude of frictional force and failure mode for DLC coating.	74
Figure 3-1 Dimension of the substrate.	76
Figure 3-2 Entire process of electrodeposition nickel on AA7075 substrate	77
Figure 3-3 Electrodeposition process arrangement of nickel coating on AA7075 substrate.	83
Figure 3-4 Electrochemical experiment arrangement used for zincating process and corrosion test.	86
Figure 3-5 Schematic diagram of Atomic Force Microscope [148, 180]	87
Figure 3-6 Schematic diagram of scratch adhesion test system [167]	88
Figure 3-7 Typical results of scratch test which shows the AE signal and friction force versus scratch distance (f), optical micrograph of the scratch track (e) and SEM images of the failure events ((c) and (d)). An EDX analysis using the 'point and ID' mode was used and drawn on the fracture surfaces, in order to check whether the substrate is revealed or not ((a) and (b)).	91
Figure 3-8 Through-thickness cracking (cohesive) failure modes in the scratch test (a) brittle tensile cracking, (b) ductile tensile cracking, (c) hertz cracking and (d) conformal cracking [123]	91
Figure 3-9 Interfacial (adhesive) failure modes in the scratch test (a) buckling, (b) buckle spallation, (c) wedging/ spallation and (d) recovery spallation [123].	92
Figure 4-1 Changes in immersion potential of AA7075 substrate in alkaline solution (10 wt. % NaOH) at room temperature. The labels 1, 2 and 3 indicate the first, second and third stage, respectively.	94
Figure 4-2 Changes in immersion potential of AA7075 substrates in acid solution (50 vol. % $\text{HNO}_3$ ) at room temperature. The labels 1, 2 and 3 indicate the first, second and third stage, respectively.	95
Figure 4-3 Changes in immersion open circuit potential ( $E_{OC}$ ) of the AA7075 substrate during the single zincating process. The labels 1, 2 and 3 indicate the first, second and third stage, respectively.	96
Figure 4-4 Changes in immersion open circuit potential ( $E_{OC}$ ) of the AA7075 substrate during the double zincating process. (a) The changes of $E_{OC}$ during the zincating process up to 3600 seconds. (b) A time- expansion plot for the initial stage of the zincating process (a). (c) A time-expansion plot for the second stage of the zincating process (a). (d) A time- expansion plot for the third stage of the zincating process (a).	99
Figure 4-5 Changes in immersion open circuit potential ( $E_{OC}$ ) of the AA7075 substrate during the single and double zincating process. (a) The changes of $E_{OC}$ during the zincating process up to 3600 s. (b) A time-expansion plot for the initial stage of the zincating process (a).	102
Figure 4-6 Comparison in immersion open circuit potential (EOC) of various substrates during the single and double zincating process	103

Figure 4-7 Changes in immersion open circuit potential ( $E_{OC}$ ) of the AA7075 substrate with copper activation during single zincating process for 1000 seconds .....	105
Figure 4-8 Changes in immersion open circuit potential ( $E_{OC}$ ) of the AA7075 substrate with and without copper activation during the single zincating process and double zincating process for 1000 seconds.....	106
Figure 4-9 SEM morphology of AA7075 substrate after various surface pre- treatment processes (a) as- received substrate, (b) alkaline cleaning (10 wt. % NaOH, 10 s, room temperature (RT)) and (c) acid cleaning (50 vol. % HNO <sub>3</sub> , 20 s, RT).....	108
Figure 4-10 SEM micrographs (SEI and BEI modes) of AA7075 substrates after copper activation process in 0.5 M H <sub>2</sub> SO <sub>4</sub> + 3.13 x 10 <sup>-4</sup> M CuSO <sub>4</sub> at RT for (a) 5, (b) 10 and (c) 15 minutes.....	110
Figure 4-11 EDX analysis of particles after copper activation, confirming they are copper particles.....	110
Figure 4-12 EDX analyses of AA7075 substrates after copper activation process at various durations (a) 5, (b) 10 and (c) 15 minutes .....	111
Figure 4-13 EDX analysis of average copper composition (wt. %) present on AA7075 substrates after various copper activation duration. ....	112
Figure 4-14 EDX analysis of other elements composition (wt. %) present on AA7075 substrates after various copper activation duration .....	113
Figure 4-15 SEM micrographs of AA7075 substrates after (a) conventional single zincating process at 1 minute and modified single zincating process at various durations: (b) 5, (c) 10, (d) 15 and (e) 20 minutes. ....	115
Figure 4-16 Analysis of zinc particles size deposited on AA7075 substrate at 1, 10 and 20 minutes of zincating process.....	116
Figure 4-17 EDX analysis of particles after modified single zincating process for 10 minutes, confirming they are zinc particles. ....	117
Figure 4-18 EDX analysis of sample surfaces for the conventional and modified single zincating processes at various durations.....	118
Figure 4-19 SEM micrographs of AA7075 substrate after double zincating process at various durations (a) 60/10, (b) 60/20, (c) 60/30, (d) 60/40, (e) 60/50 seconds and (f) zinc stripping process.....	121
Figure 4-20 Analysis of zinc particles size deposited on AA7075 substrate at 60/10, 60/40 and 60/50 seconds of zincating process .....	122
Figure 4-21 EDX analysis of zinc composition (wt. %) present on AA7075 substrates after various double zincating durations. FZ: first zincating process, ZS: zinc stripping process .....	123
Figure 4-22 EDX analysis of sample surfaces after various double zincating durations .....	123
Figure 4-23 SEM micrographs of AA7075 substrates after (a) conventional single zincating process at 1 minute and modified single zincating process at various durations, such as (b) 5, (c) 10, (d) 15 and (e) 20 minutes with copper activation.....	126

Figure 4-24 Analysis of zinc particles size deposited on AA7075 substrate at 1, 10 and 20 minutes of zincating process with copper activation .....	127
Figure 4-25 EDX analysis of sample surfaces for the conventional and modified single zincating processes at various durations with copper activation .....	128
Figure 4-26 AFM images of AA7075 substrate after various surface pre-treatment processes. (a) after polishing using 1 $\mu$ m diamond paste, (b) after alkaline cleaning in 10 wt.% NaOH at room temperature for 10 seconds, (c) after acid pickling in 50 vol.% HNO <sub>3</sub> solution at room temperature for 20 seconds. ....	130
Figure 4-27 Surface roughness of after various surface pre- treatment processes prior to zincating process .....	131
Figure 4-28 AFM images of AA7075 substrates after (a) immersion in 0.5 M H <sub>2</sub> SO <sub>4</sub> solution without copper particles for 20 seconds at room temperature and copper activation process in 0.5 M H <sub>2</sub> SO <sub>4</sub> + 3.13 x 10 <sup>-4</sup> CuSO <sub>4</sub> solution at (b) 5, (c) 10 and (d) 15 minutes at room temperature.....	133
Figure 4-29 Surface roughness (Ra) of AA7075 substrate at various durations of copper activation process. ....	134
Figure 4-30 AFM images (three dimensional view) of AA7075 substrate after (a) conventional single zincating process at 1 minute and modified single zincating process at various durations, such as (b) 5, (c) 10 , (d) 15 and (e) 20 minutes .....	136
Figure 4-31 Surface roughness of substrates after conventional and modified single zincating process at various durations. CZ: conventional single zincating process, MZ: modified single zincating process.....	137
Figure 4-32 AFM images of AA7075 after double zincating process (a) first zincating at 60 seconds, (b) zinc stripping in 50 vol. % HNO <sub>3</sub> at room temperature for 30 minutes, (c)- (d) double zincating at 60/10, 60/30 and 60/50 seconds, respectively. ....	139
Figure 4-33 Surface roughness of double zincating process. FZ: first zincating at 60 seconds, SZ1: second zincating at 60/10 s and SZ5: second zincating at 60/50 s. ....	140
Figure 4-34 AFM images (three dimensional view) of AA7075 substrate after (a) conventional single zincating process at 1 minute and modified single zincating process at various durations, such as (b) 5, (c) 10, (d) 15 and (e) 20 minutes with copper activation.....	141
Figure 4-35 Surface roughness of modified single zincating processes with copper activation. CZ: conventional single zincating process, MZ: modified single zincating process. ....	142
Figure 4-36 SEM morphology and EDX analysis on the cross-section of the nickel coatings electrodeposited on AA7075 substrate through (a) conventional single zincating process at 1 minute and modified single zincating process at various durations, such as (b) 5, (c) 10, (d) 15 and (e) 20 minutes .....	145
Figure 4-37 Frictional force and acoustic emission signal intensity as a function of the scratch distance for nickel coatings produced at (a) conventional single zincating process at 1 minute and modified single zincating process at various durations, (b) 5, (c) 10, (d) 15 and (e) 20 minutes.....	147

Figure 4-38 Coefficient of friction and acoustic emission signal intensity as a function of the scratch distance for nickel coatings produced using (a) conventional single zincating process at 1 minute and modified single zincating process at various durations, (b) 5, (c) 10, (d) 15 and (e) 20 minutes.....	149
Figure 4-39 Average critical loads of nickel electrodeposited on AA7075 produced at various single zincating durations as measured by scratch testing.....	150
Figure 4-40 Correlation between number of acoustic emission activity ( $N_{AE}$ ) and various single zincating durations .....	151
Figure 4-41 Optical micrographs of the scratch tracks of nickel electrodeposited on AA7075 substrate produced with the conventional single zincating process for 1 minute and modified single zincating process for 5, 10, 15, and 20 minutes.....	154
Figure 4-42 SEM images and EDX analysis showing the middle and end of the scratch tracks of nickel electrodeposited on AA7075 produced at (a) conventional single zincating process for 1 and (b) modified single zincating process for 20 minutes .....	155
Figure 4-43 Frictional force and acoustic emission signal intensity versus scratch distance curves of nickel coatings produced at various double zincating durations (a) 60/10, (b) 60/20, (c) 60/30, (d) 60/40 and (e) 60/50 seconds. ....	157
Figure 4-44 Coefficient of friction and acoustic emission signal intensity versus scratch distance curves of nickel coatings produced using various double zincating durations (a) 60/10, (b) 60/20, (c) 60/30, (d) 60/40 and (e) 60/50 seconds. ....	159
Figure 4-45 Average critical loads of nickel electrodeposited on AA7075 produced at various double zincating durations measured by scratch testing .....	160
Figure 4-46 Correlation between number of acoustic emission activity ( $N_{AE}$ ) and double zincating durations .....	161
Figure 4-47 Optical micrographs of the scratch tracks of nickel electrodeposited on AA7075 produced at various double zincating durations.....	164
Figure 4-48 SEM images showing the middle and end of the scratch tracks of nickel electrodeposited on AA7075 produced at 60/10 and 60/50 seconds of double zincating durations.....	165
Figure 4-49 Variation of the frictional force and acoustic emission signal intensity curves as a function of the scratch distance for nickel coatings produced at (a) conventional single zincating process at 1 minute and modified single zincating process at various durations, such as (b) 5, (c) 10, (d) 15 and (e) 20 minutes with copper activation.....	167
Figure 4-50 Variation of the coefficient of friction and acoustic emission signal intensity curves as a function of the scratch distance for nickel coatings produced at (a) conventional single zincating process at 1 minute and modified single zincating process at various durations, such as (b) 5, (c) 10, (d) 15 and (e) 20 minutes with copper activation .....	169
Figure 4-51 Average critical loads of nickel electrodeposited on AA7075 substrate produced from conventional and modified single zincating process at various durations with copper activation.....	170



Figure 4-52 Correlation between number of acoustic emission activity ( $N_{AE}$ ) and conventional and modified single zincating process at various durations with copper activation .....	171
Figure 4-53 EDX analysis on a void which is formed from electrodeposition process. ....	172
Figure 4-54 Optical micrographs of the scratch tracks of nickel electrodeposited on AA7075 produced at conventional single zincating process for 1 minute and various modified single zincating durations for 5, 10, 15 and 20 minutes with copper activation.....	174
Figure 4-55 SEM images showing the middle and end of the scratch tracks of nickel electrodeposited on AA7075 produced at (a) conventional single zincating for 1 minute and (b) modified single zincating process for 20 minutes, with copper activation .....	175
Figure 4-56 Tafel polarization curves of the as received AA7075 substrate and electrodeposited nickel coatings on AA7075 substrate produced at conventional and modified single zincating process at various durations. ....	177
Figure 4-57 Tafel polarization curves of as- received AA7075 substrate and electrodeposited nickel coatings on AA7075 substrate produced at various double zincating durations. ....	178
Figure 4-58 Tafel polarization curves of the as- received AA7075 substrate and electrodeposited nickel coatings on AA7075 substrate produced at conventional and various modified single zincating durations with copper activation process. ....	180
Figure 5-1 Comparison of immersion open circuit potential ( $E_{OC}$ ) of AA7075 substrate during single and double zincating process with pure zinc plate during the single zincating process .	185
Figure 5-2 Schematic representations of the various zincating processes on AA7075. (a) conventional and modified single zincating process and (b) double zincating process. ....	188
Figure 5-3 EDX analysis on copper detection of copper activated AA7075 substrates at 10 minutes.....	190
Figure 5-4 Direction of the bubbles moving upwards of the sample .....	193
Figure 5-5 Average critical loads of nickel electrodeposited on AA7075 produced from conventional and modified single zincating process with and without copper activation .....	197
Figure 6-1 Correlation between the surface morphology and the EOC curve for single zincating process with and without copper activation .....	209



## List of tables

Table 2-1 Coating processes used to protect functional surface (from the Ref. [66]).....	11
Table 2-2 Comparison of electrochemical methods for metal deposition (from Ref. [67, 68])....	11
Table 2-3 Selection of processes which may be involved in electrodeposition process (from Ref. [67, 86]).....	14
Table 2-4 Types of nickel electroplating solution and some deposits properties (from the Ref. [99]).....	28
Table 2-5 Properties of selected aluminium and its alloys at room temperature (from ref. [101])	29
Table 2-6 The standard electromotive force (EMF) table (from the Ref. [5]).....	31
Table 2-7 Mean coefficient of linear expansion of the common metals (from the Ref. [5]).....	31
Table 2-8 Metals for possible direct deposition on aluminium (from the Ref. [5]) .....	32
Table 2-9 Various types of finishes (from the Ref. [100]) .....	33
Table 2-10 Control of alkaline cleaner (from Ref. [5]) .....	39
Table 2-11 Various type of modified zincating solutions for use with aluminium alloys (from Ref.[108]).....	45
Table 2-12 Effect of various pre-treatment conditions on the zinc deposits of commercial purity aluminium (from the Ref. [5]) .....	49
Table 2-13 Potentials of some metals and aluminium alloys in 53 g/l NaCl + 3 g/l H <sub>2</sub> O <sub>2</sub> with reference to the 0.1 KCl calomel electrode (from Ref. [5]).....	51
Table 2-14 A summary of previous research on zincating process of aluminium and its alloys .....	56
Table 2-15 Hazard identification of chemicals used in zincating solution.....	60
Table 2-16 Various methods of adhesion test (from Ref. [67]).....	63
Table 2-17 Intrinsic and extrinsic parameters influencing the scratch test results .....	64
Table 2-18 Summary of the list of references on each technique .....	71
Table 3-1 Composition of alkaline cleaning solution .....	78
Table 3-2 Composition of acid cleaning solution .....	78
Table 3-3 Composition of the zincating solutions used to produce nickel deposits on AA7075 substrate.....	80
Table 3-4 Matrix table of samples produced at various immersion durations of zincating processes.....	80
Table 3-5 Concentration of chemical reagents in modified Watt's bath solution.....	82

Table 3-6 Summary of characterisation techniques and testing .....	83
Table 4-1 Slope value for steady state potential of specimens produced from double zincating process using various first zincating durations.....	100
Table 4-2 Element composition (wt. %) of the substrate surface as determined by EDX after various surface pre- treatment processes.....	108
Table 4-3 Tafel polarization parameters for the electrodeposited nickel on AA7075 substrate produced at conventional and modified single zincating process at various durations.....	177
Table 4-4 Tafel polarization parameters for the electrodeposited nickel coatings on AA7075 substrate produced at various double zincating durations.....	179
Table 4-5 Tafel polarization parameters for the electrodeposited nickel coatings on AA7075 substrate produced at conventional and various modified single zincating durations with copper activation.....	180
Table 5-1 Comparison table of Tafel polarization parameters for the electrodeposited nickel coatings on AA7075 substrate produced at conventional and modified single zincating process without and with copper activation.....	203
Table 5-2 Summary of the zincating process used by other researchers.....	204
Table 6-1A summary of previous research on zincating process of aluminium and its alloys .	206
Table 6-2 Duration for multiple zincating process used in this research .....	210









# DECLARATION OF AUTHORSHIP

I, **Intan Sharhida Othman**

declare that the thesis entitled

**Electrodeposition of Nickel Coatings on Aluminium Alloy 7075 through a Modified  
Single Zincating Process**

and the work presented in the thesis are both my own, and have been generated by me as the result of my own original research. I confirm that:

- this work was done wholly or mainly while in candidature for a research degree at this University;
- where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
- where I have consulted the published work of others, this is always clearly attributed;
- where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
- I have acknowledged all main sources of help;
- where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
- none of this work has been published before submission, or [delete as appropriate] parts of this work have been published as: [please list references]

Signed: .....

Date: 29 April 2016

## Acknowledgements

First and foremost, all praises to Allah S.W.T. for his everlasting blessing and guidance to me in completing this study. I would like to take this opportunity to express my sincere gratitude to my supervisors, Professor Marco Starink and Dr. Shuncai Wang, for their helps and supports throughout my PhD. study. It was a great experience working under their supervision and I am deeply indebted to them for their continuous guidance and encouragement.

I am also thankful Dr. John Nunn at National Physics Laboratory, Teddington, United Kingdom for helping me with the scratch test and Dr. Jurgita Zekonyte at national Centre for Advanced Tribology at Southampton University (nCats) for the surface topography observation and surface roughness measurement using the atomic force microscopy (AFM). I also would like to acknowledge and appreciate Professor Steve Bull from the Newcastle University, who willing to share his knowledge on adhesion of the coating.

I am very much thank the assistance of all the staffs in the School of Engineering and Environment, in particular Mrs. Sue Berger for the administration support and Mr. David Beckett, Mr. Eric and all the technical staffs for the technical support throughout my PhD. study. My sincere appreciation also goes to Dr. Richard Wills for his helps and guidance during my working period in the electrochemistry laboratory. I also would like to thank all my research colleagues for sharing these wonderful moments of PhD. journey together; Dr. Chao Ma, Dr. Chuanting Wang, Dr. Danial Bull, Dr. Yang He, Feifei Zhang, Dr. Pawee Kuchita and many more.

Finally, words cannot truly express my deepest gratitude and appreciation to my beloved husband, parents, parents in law, sons and family members, who always gave me their love and emotional support throughout my PhD. journey, without their supports, this PhD. would not be easily went through.