Nickel-based electrodeposits for corrosion protection of smart card contacts

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2016

Vinod Kumar Murugan. (2016). Nickel-based electrodeposits for corrosion protection of smart card contacts. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69534>

<https://doi.org/10.32657/10356/69534>

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**NICKEL-BASED ELECTRODEPOSITS FOR CORROSION
PROTECTION OF SMART CARD CONTACTS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

07th July 2016

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Abstract

Reliability of smart cards depends extensively on the corrosion resistance of the electrical contacts they contain as these contacts are primarily exposed to the environment. Although corrosion as an entirety is a century old problem, the corrosion of thin electrical contacts has been rarely studied in a systematic manner. Cu is typically used as substrate material for electrical contacts and nickel based barrier layer coating have been essential to suppress copper diffusion through the gold topcoat. This thesis aims to bridge knowledge gaps in literature with regards to the corrosion behaviour of Ni and Ni-P barrier coated electrical contacts.

Much work has been dedicated to the corrosion resistance of electroless Ni-P deposits but research on electrolytic deposits is limited. The impact of electrodeposition parameters on corrosion resistance has not been well documented. This thesis aids the understanding of the electrodeposition parameters and their implications on corrosion resistance. Moreover, corrosion behaviour due to different arrangement of thin Ni and Ni-P stacks ($< 3 \mu\text{m}$) is unknown. This thesis also explores different thin Ni and Ni-P stacks and its corrosion resistance to salt spray (SS) and mixed flowing gas (MFG) environments. The corrosion behaviour of these stacks, corrosion mechanism and causes of corrosion disparity have been also discussed in this report. The thesis is bounded by three main considerations viz., method and type of deposition, and corrosion testing methods. Electrodeposition was the choice of deposition technique, Ni and Ni-P electrodeposits were chosen barrier layers and lastly, accelerated tests which simulate atmospheric corrosion were employed.

The research starts with a systematic study on the electrodeposition parameters and their influence on the corrosion resistance of electrical contacts. Corrosion products due to the neutral salt spray (NSS) and mixed flowing gas (MFG) tests were characterised through spectroscopic and diffractions studies. Electrical contacts exposed to NSS tests produced green corrosion residues which consist of CuCl (nantokite) and $\text{CuCl}_2(\text{OH})_3$

(clinoatacamite) and brown residues which consist of Cu_2O (cuprite). Electrical contacts exposed to MFG test produces copper sulfides (major) and nickel sulfides (minor). Also increasing the thickness of Ni consistently improved the corrosion resistance in both neutral NSS and MFG corrosion tests. However, the influence of Ni thickness on corrosion was overshadowed by the Ni-P thickness. Increasing the thickness of Ni-P deposits resulted in higher corrosion in the NSS environment and decreased corrosion under the MFG environment. Although initial results pointed towards a disparity that Ni-P may not be suitable for corrosion protection in environments with heavy chlorine concentration but appropriate for sulfur-containing corrosion media, subsequent in-depth studies revealed that this disparity was due to the high *edge porosity* caused by fast plating.

Subsequently, the arrangement of Ni and Ni-P on Cu was hypothesised to affect the eventual corrosion resistance of an electrical contact. The thickness of the overall barrier layer was kept constant and different stacks such as Ni/Au (*NA*), Ni-P/Ni/Au (*PNA*), Ni-P/Au (*PA*), Ni/Ni-P/Au (*NPA*) and Ni-P/Ni/Ni-P/Au (*PNPA*) stacks were examined. The discrete and coalesced pits formed due to MFG were explained with a proposed *dominant pit* concept. Results showed that multi-layer stacks, such as *PNA*, *NPA*, *PNPA*, displayed worse corrosion resistance than single-layered stacks (*NA*, *PA*). Removing Ni and Ni-P interfaces was effective in inhibiting corrosion in NSS and MFG environments as Ni/Ni-P interfaces accelerate corrosion due to galvanic coupling. Corrosion pits propagated horizontally and vertically through Ni and Ni-P films, depending on the way Ni and Ni-P were arranged within a stack. Tunnelling corrosion through Ni-P turned distinct with a reduction in Ni-P thickness. This was attributed to possibly higher percentages of discontinuities (i.e. porosity) with decreasing thickness. The reducing thickness coupled with the galvanic coupling between Ni and Ni-P layers further worsened the corrosion in stacks such as Ni-P/Ni/Ni-P/Au.

Based on the two aforementioned studies, disparity in corrosion resistance of Ni and Ni-P barrier layers under NSS and MFG corrosion tests was a recurring observation. When corrosion resistance of Ni/Au and Ni-P/Au stacks was assessed using NSS and MFG

corrosion tests, each stack emerged superior in only one test. To explain this disparity, factors that could influence corrosion resistance were examined first, namely: internal stress, surface wettability and sulfur co-deposition. None of these factors could explain for the disparity in corrosion performance. Corrosion product analysis was then performed to understand the corrosion product formation due to NSS and MFG. Detailed pits analysis revealed that the disparity was caused by the porosity and corrosion product migration. These concepts were supported experimentally.

Based on the understandings generated from the three main studies, some guidelines are proposed to improve the corrosion resistance of electronic contacts under the MFG and NSS corrosion tests. Optimisation of various parameters to generate the current stacking arrangement (i.e. Ni/Ni-P/Au) offer important but limited solution to enhance corrosion protection as individuals layers behave differently when coupled. Different stacking arrangements studied in this thesis show that single-layered stacks such as Ni/Au or Ni-P/Au offer better corrosion protection. The failure of bi-layered and tri-layered stacks does not necessarily stem from the design of such stacks but stem from the industrial practice to layer very thin coatings (such as Ni-P at 500 nm) on Ni under-plates. The increased defects in such thin Ni-P coatings accelerate galvanic corrosion due to difference in corrosion potentials and the small-anode-large-cathode phenomenon. The study on single layered stacks points to the most important aspect of this thesis. Ni-P as a single barrier layer deposited at lower current densities (≤ 1 ASD) and at higher thicknesses (≥ 2 μm) can improve overall good corrosion protection in both NSS and MFG corrosion tests.

Acknowledgements

The research reported in this thesis was conducted at the School of Materials Science and Engineering of Nanyang Technological University in Singapore under the supervision of Professor Chen Zhong and Associate Professor Huang Yizhong.

I would like thank to my supervisor Professor Chen Zhong for his guidance throughout the years. Drawing from his vast experience, he acted as a beacon and provided useful resources to enhance my capabilities. I would like to extend my appreciation to Associate Professor Huang Yizhong and Dr. Sudesh L. Wijesinghe (SIMTECH, Singapore) for the discussions on corrosion at critical junctures of this research. I sincerely thank Govindo Syaranamual, who is more than a friend and colleague.

I gratefully acknowledge the financial support from Economic development board (EDB), Singapore, and Nanyang technological university (NTU), Singapore. Most importantly, I wish to express my heart-felt gratitude to my guide Dr. Jason Jia Zhigang who saw me through my successes and failures.

I would like to dedicate this work to Mr. Murugan, Mrs. Malliga, and Mrs. Jayanthi for love is divine.

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Abbreviations

ACA	Advancing Contact Angle
ASD	Ampere per Square Decimetre
At. %	Atomic percentage
A.U.	Arbitrary Unit
BEI	Backscatter Electron Image
BSE	Backscattered Electron
CA	Contact Angle
CPS	Counts per second
DoE	Design of Experiment
EDS/EDX	Energy Dispersive X-ray Spectroscopy
EGT	Epoxy Glass Tape
EIS	Electrochemical impedance spectroscopy
EPMA	Electron probe Microanalysis
FIB	Focused Ion Beam
HRTEM	High Resolution Transmission Electron Microscopy
LM	Light microscopy
MFG	Mixed flowing gas
NSS	Neutral Salt Spray
PDP	Potentiodynamic polarization
RCA	Receding Contact Angle
RH	Relative humidity
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
SS	Salt Spray
Wt. %	Weight percentage
XRD	X-ray Diffraction
XPS	X-ray Photoelectron spectroscopy
XRD	X-ray Diffraction

XRF	X-ray Fluorescence
Z	Atomic Number

Chapter 1

Introduction

The lifespan of an electronic device shortens with the corrosion of its electronic contacts. However, a detailed understanding on corrosion behaviour of the stacking metallurgy has not been achieved and hence performance cannot be improved. The engineering challenge is to derive more corrosion resistant contacts, within the constraints of productivity and cost. A detailed understanding of the science behind the corrosion behaviour of these electrical contacts would be essential for this. This chapter offers the rationale for the research, and outlines the objectives and scope. The structure of the thesis is provided by an overview to the thesis in this chapter.

1.1 Hypothesis/Problem Statement

An electrical contact is an integral part of an electronic device and the corrosion of these contacts therefore reduces the lifespan of the entire device. Hence, the corrosion resistance of electrical contacts is considered an important quality standard in the electronic industry. Presently Ni/Ni-P/Au stacks are being employed to improve the corrosion resistance of copper electrical contacts but how these stacks function as a protection has not been studied in detail. The engineering challenge is to derive more corrosion resistant contacts, within the constraints of productivity and cost. A detailed understanding of the science behind the corrosion behaviour of these electrical contacts would be essential for this.

1.2 Objectives and Scope

There are four main objectives targeted in the corrosion study of electronic connectors. They are as follows:

- a) Study the influence of thickness and plating current density on the corrosion resistance of Ni/Ni-P/Au electrical contacts;
- b) Explore different Ni-based multi-layer stacking configuration on its corrosion protection on Cu substrate;
- c) Explain the corrosion behaviour of Ni and Ni-P based stacks under MFG and NSS corrosion tests; and
- d) Generate guidelines for improving the corrosion resistance of nickel-based protective coatings.

The scope of this entire research was bounded by three main constraints, namely: the method of deposition, the type of deposition and corrosion test method.

Material deposition can be through a variety of methods such as chemical vapour deposition (CVD), physical vapour deposition (PVD), hot metal processing, painting, plasma spraying, flame spraying, electroless plating and electrolytic plating [13]. Electrolytic plating or electrodeposition is more suitable for rapid large scale production of parts as it has high deposition rates, is site selective i.e. only conductive regions undergo deposition, and cost effective. In addition, qualities of the electrodeposits can be much easily controlled by controlling the electrodeposition parameters. Electroplating is widely used for metal deposition in the electronic connector industry as it boasts high deposition rates, high resolution, and high shape fidelity. Most importantly, electroplating has great compatibility with processes such as continuous reel-to-reel operation for selective deposition that is required in the flexible smartcard connector industry. Due to these reasons, electrodeposition has been widely employed for material deposition for the electrical connectors.

Cu/Au contacts have been shown to succumb to heavy corrosion due to copper migration through gold layers [14]. Thicker Au layers can reduce the copper migration but it drives up the cost of parts produced. Therefore inter-layers classified as diffusion barriers were introduced to reduced copper diffusion. Many diffusion barriers have been used within the connector industry such as Sn [15-17], Ni [4, 18], Ni-P [4] and NiPd [4], to improve the corrosion resistance. In addition other alloys and composites of Ni have been claimed to display superior corrosion resistance. However, these novel coatings are difficult to be adopted by industries as they pose new challenges such as poor solderability, loss of lustre and large scale processing incapability. Therefore to provide better understanding of materials which exist within the industry, Ni and Ni-P barrier layers were employed in the current work.

Accelerated tests work under the assumption that failures have a finite likelihood to occur during service, if they are observed at all during the testing. Therefore, it is widely accepted that improved laboratory test result correlates with longer service life [19]. Laboratory tests typically track improvements of experimental samples comparative to reference samples. Improvements include relatively lower corrosion product coverage, preservation of contact resistance and/or lower pitting density. Popular laboratory corrosion tests are limited to neutral salt spray (NSS) and mixed flow gas (MFG) test. These tests are conducted by small specimen volumes and small corrosion chambers, where the actual corrosion environment is simulated. NSS and MFG are well-known corrosion tests that have been used in the connector sector as a necessary product quality assurance tests.

1.3 Dissertation Overview

The thesis addresses the corrosion behaviour of electrical contacts with nickel based barrier layers. This thesis has been divided into seven chapters. The first chapter provides a rationale, and highlights of the goals and scope of the research. Chapter 2 covers the review on Ni and Ni-P electrodeposits, and corrosion types and tests pertinent to electrical contacts; this chapter also highlights knowledge gaps in literature. Chapter 3 explains the synthesis and characterization techniques used to study the properties and corrosion behaviour of electrical contacts. Chapter 4 covers the results and discussion on the effects of thicknesses of Ni and Ni-P, and current density on corrosion resistance. Chapter 5 makes a comparison on different stacking structures for enhanced corrosion resistance. Chapter 6 explains the disparity in corrosion resistance of Ni and Ni-P coatings after exposure to NSS and MFG tests. Chapter 7 sums up the thesis, and covers limitations and implications of the research. The extent to which the engineering target was met is discussed in this chapter together with opportunities and strategies for future work.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Relating plating parameters to corrosion resistance;
2. Understanding the corrosion resistance of different arrangements of Ni and Ni-P stacks;
3. Revealing the corrosion behaviour of Ni and Ni-P electrodeposits in MFG and NSS corrosion tests; and
4. Generating working solutions to improve the corrosion resistance of electronic contacts in both NSS and MFG corrosion tests.

Chapter 2

Literature Review

This chapter reviews available literature on topics which are most relevant to the focus of this thesis: the corrosion resistance of Ni and Ni-P electrodeposits in SS and MFG corrosion tests. It covers the electrodeposition of Ni and Ni-P, the corrosion resistance of Ni/Ni-P multilayers, and types of corrosion and corrosion test methods. This review has identified solutions, or the lack of them, to many key questions. Porosity of deposits (among many other factors) can affect the overall corrosion resistance of stacks. Ni-P has been repeatedly claimed to be more corrosion resistant than pure Ni which has been credited to the difference in the degree of crystallinity between Ni and Ni-P. Reports on the mechanisms of co-deposition of P reveals two unconfirmed divergent ideas which have been discussed in detail in this chapter. Typically a better corrosion protection has been attributed to an increase of P content in the electrodeposit. Ni-P films transforms from crystalline to amorphous as the P content in the film increases. The enhanced corrosion resistance is attributed to decreased defects in amorphous structures of Ni-P. However reasons for the enhanced corrosion resistance between two high P-content (amorphous) films is unclear. This review has revealed that works on Ni/Ni-P multilayers are scarce and the available studies has many important shortcomings.

2.1 Introduction

The demand to store, read and write information has increased tremendously in the past decade. Electrical contacts serve as a medium for such activities and are expected to survive potentially hostile environments during application. An electrical contact is defined as the interface between the current-carrying members of electronic device that assures the continuity of electric circuit, and the unit containing the interface [20]. This research deals with electrical contacts that serve as the interface between a terminal and the microcontroller in smart cards, as shown in Figure 2.1. Therefore such electrical contacts can also be termed as smart card contacts or electronic contacts.

Figure 2.1 Image of an electrical contact.

Copper, due to its low cost and high electrical conductivity, is prolifically used in electric cables and electronic contacts [21]. The limitation of copper lies with its low resistance to corrosion, thus, noble metals such as palladium and gold are applied as a top coat. However, copper is notorious for its fast diffusion through gold [22]. The rate of diffusion has been reported to depend on the physical and chemical properties of the metals, and on the temperature [22]. Microelectronics undergo high temperature processes such as glop-top and wire-bonding, and may suffer serious repercussions like loss in bondability / solderability and loss of conductivity [23]. The diffusion process consists of (a) inter-diffusion at the interface between the two films, (b) diffusion along the grain boundaries [24] and (c) diffusion into the interiors of the grains [23]. As a solution to this problem, Ni was employed as an intermediate diffusion barrier to reduce the copper diffusion through gold.

2.2 Electrodeposition of Nickel

Nickel deposition is widely performed through electroplating and electroless plating methods. Industrial electroplating consists of a cell with electrodes, an aqueous solution of metallic ions and rectifiers providing external current. Laboratory plating may include a third electrode, the reference electrode, for accurate measurement of potential at the interface between working electrode and electrolyte [25]. Electrodeposition of nickel is typically carried out in a conductive aqueous solution of nickel salt(s). The nickel in the solution present as Ni^{2+} gain electron from the external electrical source and are converted to metallic nickel (Ni^0) at the cathode. The opposite reaction occurs at the anode whereby the metallic nickel is dissolved to form divalent Ni cations. This way the concentration of nickel ions in the electrolyte are balanced by the soluble metal anode. In contrast, electroless plating involves oxidation (of the reducing agent) and reduction (of the metal ions) with both reactions occur at the same electrode. Due to the spontaneous chemical oxidation of the reducing agent, electroless plating does not require the supply of external power [26]. Electroless deposition results in coating that are more uniform in thickness than electrodeposited nickel coating; this is because the former is not affected by current density generated by an external current. In electrolytic plating current tends to concentrate at edges and points and tends to drop in recesses and cavities. Therefore, the thickness of deposits is thicker at the edges than other regions. The absence of such current distribution in electroless plating allows uniform thickness of deposits.

However, electrodeposition has been widely adopted by industries for critical advantages over electroless plating. Controlling parameters of an electroless plating bath has remained a challenge, especially when electrodeposits are very sensitive to bath condition [27]. Besides, an electroless bath produces relatively high amount of waste (oxidised reducing agents). This shortens the life of electroless baths. Furthermore, due to the complex composition and inclusion of additives, the disposal and recovery of the solution remains expensive. Most importantly, the deposition rate of electroless plating tends to be much

slower than electroplating, due to lower efficiency [28]. This also results in higher operating costs [27].

Electrolytic Ni based barrier layers have been of used in electronic contacts for decades. Lately, new binary and ternary nickel based alloys and composites have been reported. Examples of binary systems include Ni-W [29, 30], Ni-Al₂O₃ [31], Ni-Fe [32], Ni-Cr [33, 34], Ni-Co [35], Ni-Cu [36] Ni-SiO₂ [37], Ni-TiN [38, 39], Ni-SiC [40-42] and Ni-P [43]. Examples of ternary systems include Ni-Fe-Al₂O₃ [32], Ni-B-Zn [44], Ni-W-SiO₂ [45], Ni-Co-SiO₂ [46], Ni-Co-CeO₂ [47], Ni-Co-C [48], Ni-W-Fe [49], Ni-W-PCTFE [50], Ni-SiC Ni-Co-SiC [51], Ni-GNS-TiO₂ [52] and Ni-SiC [53].

Most of the abovementioned systems result in a heterogeneous bath where the solid micro or nano particles are suspended in the electrolytic bath. Heterogeneous electrolytic baths impose many practical problems. For example, low concentrations of added particles result in non-uniform coatings with regions of uneven particle co-deposition. This complication can be improved by increasing the concentration of particles in the electrolyte but introduces the danger of sedimentation. Sedimentation refers to the settling of particles at regions of the plating cell with low or no agitation. Usually sedimentation is observed at the bottom of the plating cell due to gravity. Cells with crevices or cavities on the walls may directly sediment towards these regions. Therefore, systems that result in homogenous electrolytic bath are preferred and accordingly this research employed homogeneous Ni and Ni-P baths.

2.2.1 Pure Nickel

Nickel is typically electrodeposited from nickel sulfamate or nickel sulfate (Watts) baths. Nickel sulfamate (Figure 2.2a) is the nickel salt of sulfamic acid while nickel sulfate (Figure 2.2b) is the nickel salt of sulfuric acid. The nickel sulfamate bath, developed as an alternative to the Watts bath, consists of nickel sulfamate (Ni (SO₃NH₂)₂) and boric acid (H₃BO₃); nickel chloride hexahydrate (NiCl₂·6H₂O) [54], anti-pitting agents and surfactants are optional components. The Watts bath typically consists of nickel sulfate

hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), nickel chloride hexahydrate and boric acid [55]; anti-pitting agents and surfactants are optional components. Boric acid acts at the pH buffer. Chloride aids in the dissolution of nickel anode and helps prevent anode polarisation. Anti-pitting agents and surfactants are used to prevent pitting of the deposits and to increase the wettability of the substrate surface.

Figure 2.2 Chemical structure of the nickel salts of (a) sulfamic and; (b) sulfuric acid.

The corrosion resistance of pure Ni plating have been increased by the technology of decorative multi-layer nickel electrodeposits. Brightness of such nickel electrodeposits can be varied through the use of organic and/or organometallic additives such as carriers, brighteners and auxiliary brighteners. Adsorption, hydrogenation and desorption processes govern the mechanism by which these additives add brightness to the nickel electrodeposit. Brightness results due to the production of fine-grained deposits and also due to the creation of flat crystals (and smoother surface). Most of the additives contain sulfur, which inevitably co-deposit with the nickel electrodeposits. Sulfur affects the electrochemical reactivity, mechanical properties (intrinsic stress, hardness and elongation percentage), and increases the brightness of the electrodeposits. Combining layers of bright, semi bright and matt nickel has been reported as a method to improve corrosion resistance of Ni coatings [56-60]. One such stacking arrangement was a double layer coating whereby a sulfur-free coating was covered by a semi-bright nickel coating. As the underlayer was sulfur-free, it was electrochemically nobler than the bright nickel layer. Therefore the corrosion preferentially occurred at the bright layer and pitting would not *tunnel* through the underlayer. The bright nickel layer essentially serves as a sacrificial anode. A similar reasoning is employed in triple-layer coating where the bright nickel (sacrificial layer) is *sandwiched* between a semi-bright top layer and a sulfur-free bottom layer. Once the top-

layer pits, the corrosion reaches the bright layer and the bright layer preferentially corrodes, instead of the top and bottom layers.

Much research has been dedicated to discovering compatible additives (mostly S containing) for the nickel electrolyte. Such additives have been used as brighteners, grain refiners, and /or stress relievers. Additives include saccharin [58, 61, 62], formaldehyde [58], coumarin [58, 63], thiourea [58, 64-67], sodium gluconate [68], quaternary ammonium chlorides [62], and sulfonic acid [54, 58], to name a few. Corrosion resistance of electrodeposits due to the additives have not been well studied, while the limited few credit the enhancement in corrosion resistance to grain size reduction, as shown in Figure 2.3 [5]. Figure 2.3a shows XRD patterns of electrodeposits prepared in different processing parameters. The grain sizes of 8 nm, 28 nm and 61 μm were acquired [5]. The corresponding corrosion rates calculated Tafel plot (Figure 2.3b) show that a decreasing corrosion rate with grain size reduction [5]. The explanation the enhanced corrosion resistance for nano-grained nickel layers (as compared to micro-grained nickel layers) have been scarce. A hypothesis reasoning provided by Mishra et al.[5] concurs that the passive films generated on nano-crystalline Ni may corrode faster than bulk Ni. The authors claim that the improvement in corrosion resistance arises from the higher activation barrier for the dissolution of passive film from nano-crystalline Ni relative to bulk Ni.

Figure 2.3 (a) XRD patterns and (b) Tafel plots for nano-crystalline Ni (8, 28 and 61 μm) [5]
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A study by Chou et al. [1] focused on using a Sn seal for gold/nickel finishes, as shown in Table 2.1. From the results, the authors implied that Ni layers are relatively more porous than Sn layer and hence the later behaves as a better barrier layer.

Table 2.1 Stack arrangement and plating thickness of samples [1]© IEEE.

Sample	Arrangement	Tin (μm)	Nickel (μm)	Gold (μm)
1	Ni/Au	-	1.27	0.38
2	Sn/Ni/Au	1	1.27	0.38
3	Ag/Ni/Au	1	1.27	0.38

Figure 2.4 a shows the cross section SEM micrograph and the optical image (inset) of sample 1 after MFG corrosion test. Likewise, Figure 2.4 b shows the corresponding images of sample 2. The seal layer was considered to be a pore-free and thus inhibits diffusion and creeping corrosion of the Cu substrate in stack arrangements such as Cu/Sn/Ni/Au, as evidenced in Figure 2.4 a and Figure 2.4 b. The effectiveness of silver (Ag) and Sn as a seal layer are out of the scope of this discussion; but the major flaw in this study, which removes validity of the experiments performed, is the thickness of layers as seen in Table 2.1. An additional 1 μm of barrier layer (be it Ag or Sn) was applied on samples 2 and 3 but not on sample 1. The lack of this extra layer could have adversely affected the corrosion performance of sample 1. An additional 1 μm of Ni to sample 1 may have reduced the wide gap in corrosion performance between the samples, or even remove any advantage of applying a different layer to the stack.

In addition, the thickness of gold topcoat used in all three samples (0.38 μm) was approximately six times thicker than that applied on a typical smart card contact.

Figure 2.4 SEM micrographs showing the cross-section of sample 1 and sample 2 after MFG corrosion test and inset show the optical image of connector after the corrosion test [1] © IEEE.

Working upon this limitation, Chou et al. [2] have recently reported an enhanced version of Sn seal for 0.13 μm thick gold topcoats based on the matrix given in Table 2.2. Similar to the aforementioned work [1], the authors attempted to highlight the importance of the Sn seal and in this instance studied the effects of heat treatment on the intermetallics and corrosion resistance of stacks with the Sn seal. However, in this work the thickness of the Sn seal was entirely undefined. In summary, assuming the shortfall in thickness is ignored and assuming the Sn seal admittedly improves the corrosion resistance, both works by Chou et al. [1, 2] show that porosity of the thin films affect the corrosion performance of contacts.

Table 2.2 Stack arrangement and plating thickness of samples [2] © IEEE.

Sample	Stacking arrangement	Tin (μm)	Nickel (μm)	Gold (μm)
1	Ni/Au	-	1.27	0.13
2	Sn-AP/Ni/Au	Yes	1.27	0.13
3	Sn-HT/Ni/Au	Yes	1.27	0.13

2.2.2 Nickel-phosphorus (Ni-P)

Ni-P alloys have been reported to exhibit enhanced diffusion barrier performance and corrosion resistance compared to pure Ni. Ni-P can be deposited via a myriad of ways such as vacuum deposition, rapid quenching, melt spinning, vapour deposition, electroless and electrolytic deposition. Among which electroless deposition remains popular due to its superior throwing power which allows uniform plating even in recesses. However, lower deposition rates, higher bath maintenance requirement, higher environmental impact, and higher production cost lessen the appeal for electroless Ni-P deposition.

Ni-P electrodeposition was pioneered by Brenner et al. [69, 70]. The indirect and direct mechanisms have been proposed to explain the co-deposition process of P with Ni.

The ‘indirect’ mechanism of the co-deposition of phosphorus (P) was proposed by Fedot’ev et al. [71] and Ratzka et al. [72]. The authors claimed that the presence of phosphine was necessary for the co-deposition of P, as shown by Eq. 2.1 - 2.3. Three main studies aligned with this mechanism. First, Zeller et al. [73] bubbled gaseous phosphine through a Ni-P bath and observed higher concentrations of P in the bath. Secondly, Harris et al. [74] detected phosphine from the Ni-P bath. Lastly, Zeng et al. [75] detected a nickel phosphine complex, $\text{Ni}(\text{PH}_3)_n$ during electrodeposition. These observations lead some credibility to the indirect mechanism.

However the indirect mechanism raises key concerns in three areas. Firstly, the reaction requires the presence of six atoms of H (reduced from six hydrogen ions) in the vicinity of H_3PO_3 . Secondly, in Eq. 2.2 the oxidation state of P first swings from (+3) to (-3). In the next (Eq. 2.3) reaction the oxidation state of P swings from (-3) to (0). In all, based on Eq.

2.2 and 2.3, the oxidation state of P rapidly transitions from (+3) to (-3) to (0). These swings in oxidation state seem unlikely. The direct mechanism, on the contrary, as shown by Eq. 2.4 to 2.6, offers better stoichiometric probability. In all, based on Eq. 2.4 to 2.6, the oxidation state of P transitions from (+3) to (+1) to (0). The third concern with the direct mechanism is associated with the pH of the bath. It is known that decreasing the pH of the Ni-P results in the increase of P content [74] but the indirect mechanism is inconsistent with the predicted trend. According to Eq. 2.3, decreasing the pH decreases the P content as the reactions shifts to the left. The direct mechanism instead follows the trend. Decreasing the pH increases the P content as the reaction shifts to the right in Eq. 2.5 and this in turn shifts Eq. 2.6 to the right.

In summary, the work by Zeller et al. [73], Harris et al. [74] and Zeng et al. [75], although seemingly supportive of the indirect mechanism, fails upon deeper scrutiny. First the work by Zeller et al. where gaseous phosphine was bubbled into the Ni-P bath and a subsequently increase in P content was seen by the authors, proves Eq. 2.3, but not Eq. 2.1 – 2.2. The increase in concentration of P can be explained by Eq. 2.6 which is then supplemented by the reaction in Eq. 2.3. Secondly, the detection of phosphine during electrodeposition works by Harris et al. can be explained by either Eq. 2.7 or Eq. 2.8, where a quantity of elemental P generated at the surface (through Eq. 2.6) reacts with water or surface hydrides to be reduced to PH_3 . Lastly it is conceivable that any phosphine generated (via Eq. 2.5 – 2.6) can complex with Ni, justifying the claims of the third work (that supports the indirect mechanism) by Zeng et al. [75]. Therefore, the research thus far on the mechanism of P co-deposition remains inconclusive although logical reasoning points towards the pioneering direct mechanism.

The electrodeposition of Ni-P does not form a single homogeneous layer of Ni-P; instead, a single layer of Ni-P containing two discrete layers with two different P contents. NMR studies by Lashmore et al. [76] show that the shifts in Knight values indicated two phases of Ni-P. This phenomenon was confirmed by Crousier et al. [77] through cyclic voltammetry where one phase of Ni-P consisted of nickel (FCC) crystals supersaturated with phosphorus and other was an amorphous Ni-P matrix.

The absence of defects in amorphous structures of Ni-P results in its enhanced corrosion resistance [78-80]. Ni-P films transform from crystalline to amorphous as the P content in the film increases. An intermediate nano-crystalline stage has also been reported [81]. Moreover, literature provides a range of ratios of Ni : P, which determines the structural state of the Ni-P deposit; amorphous Ni-P deposits have been reported at 6 wt.% P by Rofagha [78], at > 8 wt.% by Lo [82], Lewis [83] and Parente [84], at > 9 at.% by McMahon [81], and at >10 wt.% by Krolkowski [85]. The morphology of Ni-P films changes with their P content [6] and the P content influences the corrosion resistance of these films. Crystalline nickel is plagued with defects such as grain boundaries, voids and dislocations and thereby prone to corrosion attack as these defects serve as preferential corrosion pathways. However, high P-content films are amorphous alloys that present no defects such as grain boundaries. It has been reported that higher P-content films display better corrosion resistance, as it moves from a crystalline to amorphous phase [80]. Works by Hannigan [18] also show that high-P deposits result in thinner corrosion film (2-3 μm) than medium-P deposits (7-8 μm); although thickness of corrosion product might not be the most accurate way of corrosion quantification.

Increasing P content forms *colony* like morphology whereby each colony consists of many grains with smaller grain size, as shown in Figure 2.5. This makes the coating smoother, hence brighter. It is reported that the addition of P into the nickel lattices refines the coarse nickel grain from the micrometre range to the nanometre range.

Figure 2.5 SEM micrographs of Ni-P electrodeposits with different P contents. (a) 0 wt.%, (b) 4.6 wt.%, (c) 9.1 wt.%, (d) 15.2 wt.% [6] © Springer.

In 2005, Malfatti et al. [86] has proposed a more detailed mechanism by which the co-deposited P improves corrosion resistance. The surface of Ni-P turns P rich as a result of selective dissolution of Ni during polarisation. Subsequent formation of $\text{Ni}_3(\text{PO}_4)_2$ prevents water adsorption and serves a protective barrier against further dissolution of nickel. The authors concluded that the transformation of amorphous Ni-P into a continuous layer of Ni_3P renders Ni-P extremely resistance to pitting corrosion. The formation of $\text{Ni}_3(\text{PO}_4)_2$, together with NiO, had already been suggested by Gajerski et al. [87] in 1995 but were formed at around 700 °C in air. Similarly works by Wierzbicka et al. [88] reported formation of $\text{Ni}_3(\text{PO}_4)_2$ in air at 1050 °C. Therefore the proposed mechanism by Malfatti et al. [86] seem unlikely.

Works by Bonino et al. [89] show the hydrogen gas evolution at the Ni-P electrodeposits increase as the P content in the film increases. Thus with high P content Ni-P films, hydrogen evolution is expected to be high, evidenced by the decrease in current efficiency [81, 89]. The most compelling work on this topic was performed by Zeller et al. [90]. The

authors identified a significant amount of hydrogen in the molecular form within the electrodeposits. The entrapped hydrogen caused voids which in turn made the electrodeposits brittle. The removal of the hydrogen did not significantly increase ductility. The authors concluded that the Ni-P electrodeposits did not display classical hydrogen embrittlement; but instead voids within the electrodeposits provide sites for fracture nucleation. Electrodeposited amorphous Ni-P alloys are extremely active in promoting hydrogen evolution reaction (HER), in which hydrogen gas is produced at the cathode through the reduction of hydrogen ions or water. The high activity of these materials is linked to its ability to absorb large amounts of hydrogen [91] and as a consequence high internal stress is induced during deposition.

Heat treatment of Ni-P has been reported to improve corrosion resistance and tribological properties of such films [92]. After the heat treatment the Ni-P film crystallises into Ni and Ni₃P phases. The reason for the enhanced corrosion, even after losing its amorphicity, has been suggested to stem from stable intermediate nickel compounds that form on the surface which act as a passive barrier film. However, heat treatment is not suitable for all substrates. An example would be electronic contacts which typically consist of a polymer carrier with low glass transition temperature (T_g) that warp under high temperatures.

Research on Ni-P coatings has been mostly confined to the electroless method [93-105]. A huge research gap exists in the electrolytic deposition of Ni-P. Pillai et al. [6] have attempted to bridge this by studying the effects of various processing parameters on the material properties of the electrodeposited Ni-P film. However, corrosion resistance properties were unstudied.

Moreover, apart from the handful of electrochemical studies conducted, which consistently show that Ni-P has better corrosion resistance than pure Ni, corrosion behaviour of electrodeposited Ni-P films have been not well understood.

2.3 Ni and Ni-P Multilayers

Ni and Ni-P barrier layers have mostly been studied individually. Limited research has been dedicated to multilayers consisting both Ni and Ni-P. As such, Ni/Ni-P multilayer coatings have been studied by Yen et al. [7] with association to tin (Sn) whisker formation. Although non-Ni based coating systems lie out of the scope of this thesis, the drawbacks and conclusions from these studies give some insight to experimental design and corrosion concepts. The coating structures viz., Cu/Ni/Sn (CNS) and Cu/Ni/Ni-P/Sn (CNPS) were studied under high temperatures (Figure 2.6a and Figure 2.6b). Sn whiskering was not observed in the CNPS structure (Figure 2.6c) but was observed in the CNS stack (Figure 2.6d). The compressive stress induced by the flux of Ni atoms through Sn was claimed to be the cause of the Sn whisker growth. As such, it was reported that the CNPS structure formed a stable Ni-P-Sn ternary phase (Figure 2.6e c.f. Figure 2.6f) which acted as an enhanced diffusion barrier. This supposedly decreased the diffusion rate and diffusion flux of the Ni atoms.

Figure 2.6 Schematic diagrams of (a) Sn/Ni-P/Ni/C (SNPC) and (b) Sn/Ni/Cu (SNC) multilayers and the respective surface morphologies (c and d), and respective cross-section images (e and f) [7] © IEEE.

Table 2.3 The six samples experimented in [3] © Elsevier.

Sample	Coating thickness from surface to substrate (μm)	Time to first red rust (h)	Time to first grey rust (h)
1	20 (low P)	120	
2	20 (medium P)	268	
3	20 (high P)	264	
4	6.5/13.5 (low P/high P)	384	288
5	9.5/1/9.5 (medium P/electroplated Ni/high P)	840	408
6	9.5/1/9.5 (low P/electroplated Ni/high P)	936	576

Based on the first to red rust method and sample 1-3, medium and high P content films show better corrosion resistance than low P content films. It is reasonable that both medium (8.9 wt.% P) and high P (11.5 wt.% P) content films has similar corrosion performance as Ni-P films with above 8 wt.% P content are amorphous. However, the discrepancy is noticed when comparing samples 5 and 6, which both work under the same concept of laterally diverting the corrosion to the sandwiched pure Ni layer. Sample 5 should exhibit better corrosion resistance than sample 6, as medium P-content Ni-P should decelerate the corrosion process better than low P-content film; but the opposite trend was observed in their study where both the time to first red rust and grey rust indicated sample 6 to be better.

In another study, multilayers such as Ni/Au, Ni-P/Au, Ni/Ni-P/Au and Ni/NiPd/Au (as shown in Table 2.4), were studied by Collins et al.[4]. The corrosion product coverage and cross-section images (as shown in Figure 2.7) indicate that the Ni/Au stack has the worst performance followed by the Ni-P/Au and Ni/Ni-P/Au stacks. The Ni/NiPd/Au stacks displayed the least surface corrosion.

However, upon closer scrutiny the testing matrix (Table 2.4) shows that the comparison of these stacks is biased. Firstly, it was reported that sample 2 had better corrosion resistance than sample 1 but the thickness of Ni and Ni-P were inconsistent. This discrepancy in the thickness could have accounted for the 18 % difference in corrosion coverage.

Table 2.4 Stack arrangement, plating thickness and quantification of corrosion product coverage over the surface area of samples in [4]© Wiley-Vch.

Sample	Stacking arrangement	Ni (μm)	Ni-P (μm)	NiPd (μm)	Au (μm)	Average S.A covered by corrosion product (%)
1	Ni/Au	Undefined	-	-	0.1	99
2	Ni-P/Au	-	1.2	-	0.1	81
3	Ni/Ni-P/Au	1.2	1.0	-	0.1	84
4	Ni/NiPd/Au	1.2	-	4	0.1	16

The second discrepancy stems from comparing samples 2 and 3. Sample 3 had an additional ~1 μm of Ni underlayer. This thicker barrier layer should have improved the corrosion resistance of sample 3 but conversely the corrosion performance was slightly worsened. This observation was left unaddressed in their report.

The last discrepancy arises from comparing sample 3 and 4. Sample 4 had an additional ~3 μm of electrodeposited barrier layer (NiPd). For such thin films, and additional 3 μm (236% increase in thickness) can adversely affect any comparison made. As such the studies involving multilayers of Ni and Ni-P and their corrosion behaviour lack in credibility and would require a more systematic experimental design.

2.4 Corrosion

Corrosion is defined as the destruction or degradation of a material because of reaction with its environment [106]. Corrosion is an electrochemical process that can be described as a collection of oxidative and reductive processes. For example, the half-cell reactions of copper are as given in Eq. 2.9 – 2.10:

An oxidative (anodic) reaction is indicated by the increase in valency or generation of electrons and a reductive (cathodic) reaction vice versa [106]. These reactions occur simultaneously, leading to the basic principle of corrosion: the rate of oxidation equals to the rate of reduction. While the anodic process results in the dissolution of metal, the cathodic process varies depending on the environment at the corrosion cell, as given from Eq. 2.11 – 2.13. Hydrogen evolution is most common, as acidic environments are frequently encountered due to pollutants present in the atmosphere. Oxygen reduction is abundant due to the presence of oxygen in the air.

Figure 2.7 Cross section images of (a) Ni/Au, (b) Ni-P/Au, (c) Ni/Ni-P/Au, and (d) Ni/NiPd/Au stacks and insets show the corresponding optical image of the surfaces of contact after MFG corrosion test [4] © Wiley-Vch.

Hydrogen evolution:

Oxygen reduction (acidic environment):

Oxygen reduction (neutral or alkaline environment):

Corrosion can be classified into eight main forms [106], namely: galvanic, crevice, intergranular, stress, pitting, erosion, selective leeching and hydrogen damage corrosion. Galvanic, crevice and pitting corrosion will be discussed here, as they are most relevant to this thesis.

2.4.1 Galvanic Corrosion

Galvanic corrosion is driven by the potential difference between dissimilar metals connected by a corrosive or conductive electrolyte. This potential difference generates electron flow between the metals. The metal with a higher affinity to reduce becomes cathodic and the metal with a lower affinity to reduce becomes anodic. The galvanic series form the basis for predicting the corrosion affinities of the metals coupled. The reduction potentials in the galvanic series are typically reported based on conditions such as room temperature and standard electrolyte conditions. Theoretically these reduction potentials vary with environmental conditions. Hence documenting the galvanic series for all environments at various temperatures would require infinite number of tests. Therefore, the galvanic series is typically used as a guide of possible galvanic effects. Galvanic corrosion has been cited as the cause of corrosion in many reports in literature. For an example in a study by Kim et al. [107], the phosphorus content between nodules of Ni-P electrodeposits were found to generate potential differences large enough to drive galvanic corrosion when exposed to an electrolyte containing gold cyanide.

Galvanic corrosion is affected by the environment [106], distance between the coupled metals [108], ratio of area between the anode and cathode [108]. A large cathode area accelerates the galvanic corrosion as it provides many empty surface sites for the adsorption, reduction and desorption of reactants. A large cathode exacerbates the corrosion of a small anode. Therefore the cathode/anode area ratio is a critical factor in determining the severity of corrosion. For example this phenomenon was reported by Prawoto [109] who worked galvanic corrosion between stainless steel and carbon steel; it was observed that the increase in total weight loss due to corrosion increased with the cathode/anode area ratio. Galvanic corrosion is also affected by the distance between the dissimilar metals. Especially with electrolytes with poor conductivity, the galvanic corrosion occurs nearer to the connection point where the two metals meet. Hence placing the cathode and anode far apart will theoretically increase the electrical resistance between the electrodes. Although this presents as a way to combat galvanic corrosion, this method cannot be used for applications such as multi layered stacks, welding, soldering and wire bonding, among many others. Lastly, galvanic corrosion can also be affected by the environment. For example Haney et al. [110] reported that zinc becomes less active and reduction potentials may be reversed in the presence of inhibitors such as nitrates, bicarbonates and/or carbonators that are present in the electrolyte.

2.4.2 Crevice Corrosion

Crevice corrosion refers to the localised corrosion which occurs within a crevice or any other shielded region on a metal surface exposed to aggressive solutions [106]. In crevice corrosion, the crevice allows the entry of aggressive solution but keeps the corrosion products inside the sufficiently narrow region [111]. The consequence of crevice corrosion can lead to pit formation, similar to that of pitting corrosion (Chapter 2.5.3). The mechanism of crevice corrosion occurs with consumption of electrons (generated by the formation of metal ion) by the oxygen reduction reaction. With time, the oxygen within the crevice depletes due to the restricted convection. However, the overall oxygen reduction rate does not change as it continues on an external area. An excess of metal ions are produced, which results in the migration of chloride ions into the crevice. The increased

rate of corrosion within the crevice results in an increased rate of oxygen reduction on adjacent surfaces, providing cathodic protection to the external surfaces. Therefore during crevice corrosion the dissolution of metal is localised within the shielded regions and the remaining external surfaces succumbs to little or no damage.

2.4.3 Pitting Corrosion

Pitting corrosion is used to describe localised corrosion spots that form cavities. Pits can be the consequence of crevice corrosion, galvanic corrosion and pore corrosion [112]. Pitting is typically insidious as the net loss of material is small but perforation is rapid. Pits are usually minuscule and tend to be covered by corrosion products; they occur in varying number and depth even under similar conditions and tend to undercut the surface resulting in higher subsurface than surface damage. As a result, pits are difficult to detect or to measure quantitatively. The pit initiates at a weak spot of the metal/passive film, such as a defect, impurity or scratch. Post initiation, the mechanism for pit propagation is similar to that of crevice corrosion, essentially because the pit serves as a crevice. Notably, metals which pit are susceptible to crevice corrosion but the reverse is not true.

2.5 Corrosion tests

Numerous corrosion tests such as electrochemical, cabinet (includes NSS), immersion, atmospheric (includes MFG), seawater, freshwater, soil and many others have been used to evaluate the corrosion performance and behaviour of samples [113]. These corrosion tests can be generally classified into two categories, namely: laboratory or field tests. Laboratory tests entail small specimen volumes and small corrosion chambers, where the actual corrosion environment is simulated. In comparison, field tests encompass atmospheric exposure of a vast number of samples at one or more geographical settings. Typically field tests require long exposure times as corrosion tends to be extremely slow. For example, crevice and pitting corrosion often requires a long incubation time; at times, six to twelve months may be needed before an attack commences [106]. Accelerated corrosion tests increases the corrosion rates of material and enable the relative assessment

of materials in much shorter period of time. Environmental exposure tests are most relevant in present times, as both pollution and competition between manufacturers are high. Shorter production lead times pressure industries to test the quality of produced parts through accelerated corrosion tests. These tests are usually discussed and pre-agreed upon by suppliers, manufacturers and clients [114], according to industry standards. For the electronic industry, accelerated laboratory tests such as salt spray (SS) and mixed flowing gas (MFG) are favoured. Literature on corrosion of electronic contacts will be discussed in the next section but technical details of SS and MFG corrosion tests will be mentioned in Chapter 3.

2.5.1 Mixed Flowing Gas

MFG test is a standardized laboratory test conducted in a test chamber. Temperature, relative humidity, concentration of corrosive gas and other critical variables are carefully defined, monitored and controlled. Researchers such as Reid, Collins, Dalton and Hannigan have reported many articles based on the MFG corrosion test [4, 8, 12, 18, 115-118]. Electronic components and devices most commonly fail by corrosion due to (relatively high) concentration of corrosive gases, typically sulfur and/or chlorine containing gases [117].

Works by Garfias-Mesias and Reid [117] has validated the MFG corrosion test by comparing data from laboratory tests to field tests. Literature shows that Cu coupons exposed to outdoor environments showed typically thicker Cu_2S film than the coupons placed indoors. In some cases the data displayed that corrosion outdoors was ten times more severe than indoors, indicating that results from MFG tests are conservative in nature.

Works by Krumbein [119] has shed light into the corrosion process under MFG. Decreasing the relative humidity (RH) within the chamber has been reported to decrease corrosion, indicating the participation of water in the corrosion process. Krumbein has also classified the corrosion products based on its morphology over the sample surface. The variations include *blooms*, *needles*, *droplets* and *haloes*. Important aspects of blooms and haloes

would be highlighted here as they are pertinent to this thesis. Blooms form typically in high-SO₂ and high relative humidity (RH) environments and often accompanied by haloed. Blooms are mounds of corrosion product and under prolonged high RH environments these mounds are not friable. In many cases, corrosion products tend to accumulate along the outer surface of the bloom. This accumulation is usually found as thin films or stains of corrosion product which are called haloed.

Corrosion products on copper substrates due to 1 day Class III MFG have been studied by Reid et al. [8]. The different classes of MFG are highlighted in Table 2.5. As shown in Figure 2.8, a duplex corrosion film consisting of Cu₂O (closer to the substrate) and Cu₂S developed on the substrate surface. In addition the authors reported that the Cu₂S film was highly porous which would allow for the penetration of water and gases. Prolonging the exposure time (to 10 days) did introduce new corrosion products such as CuO, CuS and 3CuO·SO₃·2H₂O but the major product was Cu₂S [12]. The corrosion occurs primarily via the porosity in the thin gold topcoat and is then accelerated by the galvanic coupling between the nobler gold layer and less noble undercoat (typically Ni) or substrate (typically Cu) [18]. This is further worsened by the small-anode and large-cathode phenomenon [4, 115].

Table 2.5 Nominal test parameters for MFG corrosion test.

Class	H ₂ S (ppb)	Cl ₂ (ppb)	NO ₂ (ppb)	SO ₂ (ppb)	% RH	T (°C)
II	10	10	200	200	70	30
III	100	20	200	200	70	30
IV	200	50	200	200	75	50

Figure 2.8 Cross-sectional TEM image of the corrosion film after 1 day MFG showing the corrosion products and pores (indicated by arrows) [8] © Wiley-Vch.

2.5.2 Salt Spray

Evidenced by recent works [32, 120-127], salt spray (SS) test thrives as one of the oldest widely used corrosion test. SS is still extensively used in the automotive, aerospace, painting and coating industries. However, studies have shown some shortcomings of SS. SS can be misapplied and misused thereby generating erroneous information [128]. Salt spray tests reportedly have restricted reproducibility and pose difficulties in corrosion quantification [3]. Nevertheless SS can be useful to determine relative corrosion performance within a batch of specimens. Typical corrosion quantification techniques that follow the salt spray tests are macroscopic and microscopic examinations [123, 124, 129, 130], contact resistance [131], pits counting, and mass loss measurements [132, 133]. As part of a larger study, a novel method to quantify cosmetic corrosion has been report by Zhu et al. [134]; it involves colour measurements determined by a spectrophotometer (also known as a colorimeter).

Visual examination is a quick and convenient method to quantify corrosion level and allows grading the entire surface area of sample. However, at times this method can be influenced by perceptions and hence leads to erroneous conclusions. Contact resistance

measurements allow for the determination of extent of corrosion on the surface. High levels of corrosion lead to accumulation of corrosion products on the surface hence an increase in contact resistance. As electrical contacts require low contact resistance to be able to read the information from an embedded chip, any increase in contact resistance is undesired. Contact resistance can be a convenient way to quantify corrosion however the location of measurements tends to influence the results. Discussion on mass loss and pits counting results are stated in Chapter 6 and Chapter 7, respectively.

Results from the SS may not predict the actual performance in the natural environment [128], similar to any other laboratory accelerated corrosion test. Nevertheless, SS is a process control tool whereby if the substrate passes a standard number of hours without failure it serves as a good indication that the process is within specification.

2.6 Thesis in Context to Knowledge Gaps

The literature review shows that research on corrosion resistance of electrical contacts, Ni-P deposits and Ni deposits have been approached from many angles. Also the corrosion resistance has been assessed by a myriad of corrosion tests. Points shall be discussed to place this thesis in context to the knowledge gaps in literature.

Much work has been done on electroless Ni-P deposition [79, 86, 98, 104, 135-137] but studies on electrodeposition is scarce. Electrodeposition has strong industrial importance for reasons mentioned in the earlier sections. Therefore studying the corrosion resistance properties of Ni-P electrodeposits is imperative. This thesis focused entirely on electrolytic Ni-P deposition.

Although Ni-P is touted for its enhanced corrosion resistance, it has been largely studied without much comparison to pure Ni. There is insufficient research, on the impact of Ni-P electrodeposition parameters and the combined effect of Ni and Ni-P electrodeposits on corrosion resistance. This thesis sheds light on this topic.

In addition, works on the corrosion resistance of multi-layers stacks are scarce and the available studies has many shortcomings. Multi-layers and hybrid techniques can reportedly improve corrosion performance of coatings [3, 138, 139] but literature has been limited to thick inter-layers (18-50 μm). Particularly, works by the Gu et al. [3] who reported highly corrosion-resistant Ni-P/Ni/Ni-P coatings for steel substrates, ensured highly-dense, pore-free and defect-free coatings by maintaining coating thickness at 20 μm and by employing electroless Ni-P deposition. In contrast, multi-layer coatings for copper electrical contacts – which are focused in this thesis - require thin electrodeposits (lesser than 3 μm).

The corrosion tests employed in most research with regards to Ni and Ni-P corrosion have been largely limited to electrochemical aspects such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) scans. None have explored other pertinent tests like SS and MFG which might more accurately simulate atmospheric corrosion. The corrosion resistance of Ni and Ni-P stacks under SS and MFG environments has been studied in this thesis.

Chapter 3

Experimental Methodology

This chapter describes the experimental methods for the electrodeposition and corrosion tests executed in Chapter 4 through 6. The techniques and theories used for material characterization and methods of data analysis are discussed. The experimental details of the corrosion tests used are also highlighted in this chapter. Accelerated corrosion tests (SS and MFG tests) were chosen to rapidly assess relative corrosion resistance of samples, which otherwise require months or years under normal field tests. SS and MFG tests also exist as standard corrosion tests used as important process control tools in the electronic industry.

3.1 Material Characterization

Material characterization refers to the process by which the structure and properties of a material are probed and measured. Characterization is essential in explaining the material's performance in the various applications or tests. Many techniques were utilized to characterize and quantify different properties of electrical contacts before and after corrosion. These techniques include light microscopy (LM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electron probe microanalysis spectroscopy (EPMA). A brief introduction into principles of various techniques and experimental details are given in the sections below.

3.1.1 Light Microscopy

Light microscopy (LM) or optical microscopy (OM) exists as the primary means for researchers to examine the microstructure of materials [140]. Metallurgists using light microscopy have created a special field called *metallography* [140]. LM was mainly used in corrosion studies for pits counting and to observe relatively any large features on the surface of the electronic contacts. Some principles regarding image formation, resolution, effective magnification, depth of field and the instrumentation will be discussed here.

Image formation can be illustrated by the path of light in a compound light microscope. A sample (object) is placed between one to two focal lengths from an objective lens. Light rays from the object converge at the objective lens and are then focused between two lens (objective and eyepiece) forming a magnified inverted image. These light rays are further converged by the second lens (eyepiece) to form a final magnified virtual image on the human eye retina. A modern microscope is commonly equipped with a device to swap from the eyepiece to the projector lens to record a real image.

Resolution is defined as the minimum distance between two points at which these two points can be visibly distinguished one from the other. Resolution of a microscope is determined by its parameters as shown in Eq. 3.1.

$$R = \frac{0.61\lambda}{\mu \sin \alpha} \quad 3.1$$

where μ is the refractive index of the medium between the object and the objective lens and α is the half-angle of the cone of light entering the objective lens. In short $\mu \sin \alpha$ is called numerical aperture (NA). The NA of the objective lens describes its magnification capability where a higher NA provides higher magnification.

Magnification of a microscope describes its ability of enlarging the image of a sample. Magnification is determined by Eq. 3.2.

$$M = M_1 M_2 = \frac{(v_1 - f_1)(v_2 - f_2)}{f_1 f_2} \quad 3.2$$

where M , v and f refer to the magnification, distance between the image and lens, and focal length of the lens, respectively; the subscript $_1$ and $_2$ refer to the objective lens and eyepiece/projector lens, respectively. Although, it appears that there is no limitation to increase magnification, effective magnification is restricted by the resolution of the human eye. Increasing the magnification beyond the resolution of the human eye (around 0.2 mm) solely makes the image bigger for viewing comfort but does not add more detail to an image.

Depth of field (D_f) refers to the range of position of an object in which the sharpness of the image does not vary. This affects when the image of a three-dimensional object is out of focus when the object lies too close or too far from the lens. D_f can be calculated through Eq. 3.3 which indicates that the depth of field and resolution are inversely related.

$$D_f = \frac{2R}{\tan \alpha} = \frac{1.22\lambda}{\mu \sin \alpha \tan \alpha} \quad 3.3$$

A light microscope includes an illumination system, objective lens, a pair of eyepiece, photomicrographic system and specimen stage. Analysis can be done under transmitted light or reflected light; the former is typically used for transparent or semi-transparent materials like polymers and the latter is typically used for opaque materials like metals [140]. The illumination system provides the visible light for the specimen to be observed. The objective lens determines the total magnification of the microscope as the eyepieces usually have a fixed magnification of 10 x. The objective lens generates the primary image of a specimen, and determines the final resolution of the image. The NA of a light microscope varies from 0.16 to 1.40. The NA for dry lens immersed in air is about 0.95 and higher a NA can be reached by using a lens immersed in an oil medium. While higher magnifications at higher resolutions are most sought after, depth of field is also crucial for achieving high-quality images of features; most often resolution and depth of field are achieved in the expense of the other as shown in Table 3.1

Table 3.1 Techniques to enhance resolution or depth of field.

Setting	To enhance resolution	To enhance depth of field
NA	Use an objective lens with higher NA	Use an objective lens with lower NA and reduce NA by closing the aperture diaphragm
Magnification	Use higher magnification	Use lower magnification
Eyepiece	Use one compatible with objective lens	Use high-power eyepiece
Wavelength	Use shortest possible wavelength	Use longest possible wavelength

In all the experiments in this thesis, a light microscope (Nikon Eclipse LV150N) was used in the experiments to perform pits counting. The objective lens was set at a maximum of 40 x and the eyepiece at 10 x.

3.1.2 Scanning Electron Microscopy

Scanning electron microscope (SEM) works by rastering a focused electron beam over the surface area of a sample. SEM offers a large depth of field in the order of 10^4 micrometres. The instrumentation, contrast formation and operation variables will be briefly discussed.

SEM consists of an electron gun and a series of electromagnetic lenses and apertures. A thermionic or field emission (FE) electron gun condenses a fine electron probe for surface scanning. FE electron guns are preferred as they provide high beam brightness which in turn provides higher resolution. The electron beam goes through several electromagnetic lenses, including condenser lenses and one objective lens. The condenser lenses reduce the crossover diameter of the electron beam and then the objective lens demagnifies the electron beam and focuses it on the sample surface. The electron beam is rastered over the sample surface, i.e. the probe moves over the sample surface line by line. The electron signals from each pixel of the raster are received by a detector. The detector then processes the signal and casts an image on the screen. Two types of electron signals can be gathered from SEM, namely: secondary and backscattered electrons. When electron beams with high energy strike the atoms of the sample, they produce inelastic and elastic collisions; and the former creates secondary electrons and the latter creates backscattered electrons. Topographic contrast, i.e. the variation of geometric features on the sample surface, can be obtained from secondary electrons. Compositional contrast, i.e. the variation in grey levels in an SEM micrograph due to the variation in elemental composition in the sample, can be obtained from the backscattered electrons.

The key part of a detector (typically an Everhart-Thornley detector) is the scintillator, which converts electrons to photons. The photons are directed through a light tube which eventually get amplified in a photomultiplier tube. The output from the photomultiplier is further amplified for display on the screen.

In SEM, resolution and depth of field remain as important aspects of imaging. The resolution of an SEM image depends on the cross-sectional diameter of the scanning probe.

An estimation of the probe diameter (d_p) is given in Eq. 3.4.

$$d_p = \left(\frac{4i_p}{\beta \pi^2 \alpha_f^2} \right)^2 \quad 3.4$$

where i_p is the probe current, β is the beam brightness and α_f is the convergence angle of the probe which is determined by the working distance and final aperture diameter. As beam brightness is proportional to accelerating voltage of the electron beam, the former is typically increased by increasing the latter. However, a higher voltage increases the interaction volume hence reducing topographical contrast. Beam brightness can also be increased by using a field emission which is 100-1000x brighter than thermionic emission. Resolution can also be improved by using smaller a probe current and working distance. Working distance is defined to be the distance between the final aperture and sample surface. However a smaller probe current will reduce the amount of collected signal hence can result in a high signal-to-noise ratio. Similarly, reducing the working distance reduces topographical contrast. Therefore, the aforementioned parameters must be optimized for the best resolution and contrast.

In all the experiments in this thesis, surface morphology of plated surface and pitting resulting from corrosion was assessed using a field emission scanning electron microscope (FESEM, JOEL 7600F). The accelerating voltage and probe size were 10 kV and 7 a.u. for morphological analysis. Samples were tilted to a maximum of 20° for pits counting at the edges.

3.1.3 Energy Dispersive X-ray Spectroscopy

The EDS discussed here would be the instrument which is commonly included as a part of a SEM. EDS used the same electron beam that was for image formation to excite the electrons in the atoms. EDS serves as a suitable microanalysis tool as the electron probe can be focused onto small regions. When a high energy particle, such as an X-ray photon, neutron or in this case an electron, strikes an electron in an inner shell of an atom the former

knocks an electron into the outer shell. X-ray photons are resulted during electron relaxation. The energy of the X-ray is dependent of the atomic number of the atom and energy difference between the outer and inner shell. The X-ray generated is detected by a Si(Li) detector that is placed at a certain angle from the vertical. This angle that is between the plane of the specimen surface and the detector is called the *take-off angle*. The take-off angle influences signal detection, as for a rough surface may interfere with the X-ray photon that is emitted from reaching the detector, as seen in Figure 3.1. This problem can be circumvented by employing higher take-off angles and ensuring a microscopically flat sample surface.

Figure 3.1 Illustration of interference of X-ray detection due to low take-off angle.

In all the experiments in this thesis, elemental composition of corrosion products, and pits were determined using EDS (Oxford Inca) which was attached to FESEM (JOEL 7600F). An accelerating voltage of 15 kV and probe size current of 10 a. u. were used for compositional assessment.

3.1.4 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is the most effective method to determine the crystal structure of a material. Unlike EDS, XRD can identify crystalline chemical compounds which allow different phases with the same composition to be differentiated. A beam of X-ray is used as a probe to determine the crystal structure of a material. X-rays are produced at an X-ray tube by accelerating electrons through a high-voltage field which then collide onto a metal

target. The collision causes the kinetic energy of electrons to be converted to mostly heat energy and some to X-ray radiation (less than 1 %). The X-ray generated spans a few angstroms in wavelength called continuous X-ray or white X-rays. As XRD requires a monochromatic radiation source, X-rays are filters to block out most radiation but allow characteristic X-rays. Characteristic X-rays form according to the nature of the target used for electron retardation. When the highly accelerated electron hits the target (typically copper or molybdenum), it excites an inner shell electron to a higher-energy state. The vacancy created by the promoted electron will be filled by an electron in an outer shell. For example, a vacancy in the K-shell can be filled by an electron from the L or M shell, which causes a characteristic K_α or K_β X-rays (Figure 3.2). As the probability of an L shell electron filling a K shell vacancy is higher than that by an M shell electron, the intensity of K_α is higher than K_β X-ray. K_α contains two characteristic lines ($K_{\alpha 1}$ and $K_{\alpha 2}$), which are called K_α doublet. This doublet is the widely used monochromatic X-ray source for XRD, as the wavelength difference between the doublets is too small to be decoupled.

Figure 3.2 Schematic illustration of characteristic X-ray radiation (redrawn from [9]).

XRD is based on the phenomenon of wave interferences, described by Bragg's Law (Eq. 3.5). Two parallel light waves with the same wavelength travelling in the same direction, can either be in phase or out of phase. Constructive interference occurs when the phase difference is $n\lambda$ (where n is an integer), and destructive interference occurs when the phase difference is $n\lambda/2$. λ denotes the wavelength of the characteristic X-ray used for diffraction.

Typical CuK_α and MoK_α wavelengths are 1.5418 Å and 0.7107 Å. The path difference is dependent on the incident angle (θ) and the distance between the parallel crystal planes (d).

$$n\lambda = 2d \sin \theta \quad 3.5$$

Based on Bragg's Law and wavelength of the incident beam used, the spacing between atomic planes of a crystal during constructive interference at a given incident angle can be obtained. With the calculated d and lattice parameters (a), the crystal structure of the material can be deduced based on Eq. 3.6. The Miller indices (hkl) stands for a series of parallel planes in a crystal with spacing of d_{hkl} . Manual calculation for the possible (hkl) at a certain Bragg 2θ are often unnecessary as they have been determined and published by the International centre for diffraction data (ICDD).

$$\frac{a}{d_{hkl}} = \sqrt{h^2 + k^2 + l^2} \quad 3.6$$

Instrumentation of an XRD system consists of a X-ray tube, Soller and divergence slits, sample stage, antiscatter, receiving and Soller slit, monochromator and a detector. The X-rays generated from the tube passes through special slits that collimate the X-ray beam. These slits are made from a set of closely spaced thin metal plates to prevent beam divergence. X-rays are then diffracted by the samples and converge at the receiving slit and then a monochromator. The monochromator is placed in the path of the diffracted beam rather than the incident beam as to better suppress any undesired wavelengths and background radiation before entering the detector.

In the experiments reported in this thesis, crystalline corrosion products were identified with X-Ray diffraction (XRD, D8 Bruker Advance), at a scan rate of 1.5 deg/min using Cu K_α radiation. Individual crystalline phases in the corrosion products were identified using the ICDD-PDF-2 database.

3.1.5 X-Ray Fluorescence Spectrometry

Coating thickness measurements were carried out using X-Ray fluorescence technique. X-ray fluorescence spectrometry analyses the elements in a sample by detecting characteristic X-rays emitted from the sample as a response to radiation by primary X-rays. XRF has also been adapted to measure and calculate the coating thickness of multi-layered stacks. The main parts of such an adapted XRF consist of an X-ray source, sample stage, detector, data collection and processing system. Similar to an XRD system X-rays are generated in an X-ray tube. These X-rays strike the sample and are absorbed by the atoms of the elements in the sample. Due to the absorption of energy by the electrons of the atom, the inner shell electrons are promoted to an outer shell. To return to a stable state, the atom (now an unstable ion) requires electrons from the outer shell to fall back to its inner shell. This releases characteristic X-rays which correspond to the energy levels between the shells, and make the measured spectrum unique to each element [141]. A detector then measures the secondary radiation (fluorescence) due to the relaxation of electron. The fluorescence count rates are known to be influenced by other elements in the sample. This is called the matrix effect [141]. Two general models have been developed to make correction for this matrix-effect, namely: empirical coefficient (EC) and fundamental parameter (FP) methods [141]. The FP method is based on the work by Sherman who in the 1950s derived a mathematical equation that describes that intensity of each characteristic radiation is related to the composition of a sample [141]. Presently, the complex equations that are associated with matrix-effect corrections through the FP method are solved by computers. Based on proprietary fundamental methods, and accurate calibration of the system, the adapted XRF instrument computes the thickness and composition of the multi-layered coating.

In the experiments reported in this thesis, the thickness and P-content of electrodeposited Ni, Ni-P and Au thickness were determined with XRF (Fisherscope XDLVM). The instrument was calibrated with known standards of Ni, Ni-P and Au.

3.1.6 X-Ray Photoelectron Spectroscopy (XPS)

Similar to XRD and XRF, the primary source of radiation in XPS are X-rays [142]. The X-rays are usually Mg K_{α} radiation which are radiated onto the surface of a sample [143]. This causes the ejection of a core level electron, resulting in the phenomenon called *photoemission*. The kinetic energy (E_k) of the ejected photoelectron is then measured by the electron spectrometer, and the binding energy of the electron (E_B) is calculated with Eq. 3.7 [142].

$$E_B = h\nu - E_K - W \quad 3.7$$

where $h\nu$ is the photon energy of the primary X-rays and W is the work function of the spectrometer. The probability of an electron to suffer an energy loss and the probability for it to be received by the electron energy analyser determine and limit the interaction volume to be in the scale of nanometres [143]. This makes XPS analysis, unlike EDS, surface sensitive.

The X-ray photoelectron spectroscopy (XPS) analysis of the specimens of Ni-based contacts after exposure to the NSS and MFG environments was performed on a PHI Quantera II photoelectron spectrometer equipped with an Al-anode (K_{α} 1486.6 eV). The spot diameter was 400 μm and the step lengths were 1 eV and 0.1 eV for wide and narrow scanning, respectively. The data was recorded as binding energy versus intensity count plots via a data logger system. The data reduction was performed by deconvoluting the high resolution composite XPS peaks of the individual species according to their different oxidation states using the non-linear least square method. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. Vacuum pressure of the XPS system was at 9×10^{-7} Pa and the voltage used was 1486.6 eV (Al K_{α}) at 50 W. The take-off angle was 45° and charge neutralization was used during XPS measurements. Sputtering was employed to analyse the material beneath the top few nanometres of corrosion product. An area of 1.5 by 1.5 mm was sputtered with Argon gas for 0.3 minutes. The voltage employed was 2 kV. Calibration of the sputtering process was carried out

using SiO₂, around 5- 10 nm of SiO₂ was removed under the same sputtering conditions. The aim of sputtering was not to determine the exact thickness of the corrosion products, but to identify the compounds that were responsible for different coloured corrosion residues. FIB cross sections (not shown in this report) indicated that the corrosion products were sufficiently thick (few microns) such that the Cu substrate did not contribute any peaks to the spectra.

3.1.7 Electron Probe Microanalysis Spectroscopy (EPMA)

Electron microprobe analysis (EMPA) uses a beam of electrons as the primary source to excite the electrons in the atoms of the sample [144]. The X-rays emitted are analysed for their energies and intensities where the energies are characteristic to the atoms undergoing emission [144]. This provides an atomic identification. EPMA can be performed in two modes, namely: the energy dispersive (ED) or the wavelength dispersive modes. The detection limit for the former and latter are 1000 ppm and 100 ppm, respectively [144]. However the WD mode, also known as wavelength dispersive spectroscopy (WDS), is usually preferred as it is more accurate and have lower detection limits [144]. Spatial resolution and probing depths can range from 0.1 μm to 5 μm , depending on the primary beam energy used [144]. EPMA serves as a non-destructive quantitative elemental analysis of constituents in the top few micrometres of inorganic materials [144].

3.1.8 Spectrophotometry

Discoloration due to corrosion test was used to quantify extent of corrosion. A colorimeter measures and assigns quantitative data on the colour of the surface. This prevents subjective perception of colour across individuals, thus increasing reproducibility of colour values.

A spectrophotometer was used to measure the colour of samples before and after the corrosion test, in the L*a* b* (CIELAB) colour space. A positive L* value suggests a bright surface while a negative value represents darkness. A positive a* value indicates a

red hue on the surface while negative value represents a green hue. A positive value b^* indicates a yellow hue on the surface while a negative value represents a blue hue. The change in colour of the samples in all three aspects L^* , a^* and b^* , given by ΔE^*_{Lab} , reflects the discoloration due to the corrosion test. The most discoloured areas were selected for colour measurements in the current work. ΔE^*_{Lab} was calculated through Eq. 3.8.

$$\Delta E^*_{\text{Lab}} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad 3.8$$

3.1.9 Residual Stress

In the experiments within this thesis, residual internal stress was measured using a deposit stress analyser (Model 683EC, Specialty Testing & Development Co.). The flexible bent strip exists as one of the pioneering, simplest and widely used stress determination device [145]. The test strips were made up of nickel and can measure a range of 0.7 – 206.8 MPa. These strips have two *legs* which are long and narrow with a surface area of 7.74 cm². Electrodeposition only occurs on one side of each leg as the other side is insulated. Tensile and compressive properties of the electrodeposits are measured using the direction and extent of spread between the legs. If the legs spread with the deposit on the outer side, stress is tensile in nature. In contrast, if the legs spread with the deposit in the inner side, the deposit stress is compressive in nature. The extent of spread from the centre is measured using a measuring block scale. The stress within the deposit is related to the spread and thickness of deposit through the Eq. 3.9 [146].

$$S = \frac{KUM}{3T} \quad 3.9$$

where S stands for the residual stress in MPa, M denotes the correction modulus of elasticity differences between the deposit and substrate (dimensionless quantity), U denotes the number of increments spread (dimensionless quantity), T denotes the deposit thickness in micrometres and K is the strip calibration constant (MPa· μm).

3.1.10 Focused Ion Beam (FIB)

The basic FIB system comprises of vacuum systems, a liquid metal ion source (LMIS), an ion column, a stage, computer system, detectors and a computer system [10]. In addition, gas injector systems are used for either chemical vapour deposition (CVD) or enhanced etching. Vacuum systems are used to avoid contamination and to prevent electrical discharges in the high voltage ion column.

LMIS extends the ability for a FIB system to provide a small probe size of approximately 5 nm in diameter. Figure 3.3 is a pictorial representation of a typical LMIS; it consists of a tungsten needle attached to a reservoir of metal source. Gallium (Ga) is currently the most commonly used LMIS as it has a low melting point of 29.8 °C hence any reaction or interdiffusion between Ga and tungsten can be suppressed. Its low volatility at the melting point and low vapour pressure conserves the supply of metal as the liquid would not evaporate and yield a long service life. In addition, its low surface energy promotes viscous behaviour and Ga has excellent mechanical, electrical and vacuum properties. Notably, emission characteristics of Ga enable high angular intensity with a small spread in energy. The extractor electrodes pull Ga from the tungsten (W) tip and effectively ionize it by field evaporation.

Figure 3.3 A pictorial representation of a liquid metal ion source (redrawn from [10]).

The ion column then accelerates the Ga^+ ions towards the stage. Milling occurs on the sample surface due to the physical sputtering of the target. This causes a series of elastic

collision where the momentum from the Ga^+ ions is transferred to the target atoms within a collision cascade region. The surface lying atom may be ejected if it receives sufficient kinetic energy to overcome the surface binding energy (SBE) of the target material. In contrast, inelastic scattering generates phonons, plasmons (in metals), and the emission of secondary electrons.

The ion beam also allows for the ion beam assisted CVD of precursor organometallic gas. Gas sources such as W or platinum (Pt) are usually used within the FIB system. The gas is usually introduced around $100\text{ }\mu\text{m}$, in controlled amounts, above the sample source via a capillary and adsorbs on the surface but decomposes solely when the ion beam strikes. Consecutive adsorption and decomposition steps result in the accumulation of W or Pt in the ion scanned area. The primary ion beam current density must be reduced for deposition as otherwise milling would occur.

Cross-sections were carried out using a FIB workstation (FEI 600i). The method of cross-section and imaging have been described in detail elsewhere [147] hence it is briefly mentioned here. Firstly, a gallium ion beam of high current (around 7000 pA) was employed to mill through the area of interest to create a trench. This cross-section was then polished at medium currents (between 1000 and 3000 pA) to remove re-deposited particles and artefacts, and to smoothen the surface. Finally, the cross section was imaged with secondary electrons at a lower beam current of around 70 pA and at a lower voltage of 5 kV .

3.1.11 Telescope-Goniometry

Studying wettability typically involves the measurement of contact angles as the primary data. This translates to the degree of wettability of a surface. Small contact angle (lesser than 90°) indicate high wettability while larger contact angles (above 90°) indicate low wettability, shown in Figure 3.4. The angle bound by the tangent between the solid-liquid surfaces (γ_{sl}) and the tangent between the liquid-vapour (γ_{lv}) is termed as contact angle. γ_{sv} represents the tangent between the solid-liquid surfaces.

Contact angle is most widely measured with a telescope-goniometer. This instrument consists of a horizontal stage to place the sample, a micrometre pipette to inject a liquid drop, and illumination source, a telescope with a protractor eyepiece and camera.

Figure 3.4 Pictorial representation of contact angles formed by sessile liquid drop on a smooth solid surface (redrawn from [11]).

There are some limitations with this technique of contact angle measurement. The liquid drop that forms on the surface might be unsymmetrical. This limitation is overcome by averaging the CAs measured on both sides. Also, there exists the uncertainty of assigning a tangent line to the droplet profile, especially for small contact angle below 20° . Despite its limitations, the goniometer method is a convenient way to measure CA if high accuracy is not needed. Accuracy has been reported to be around $\pm 2^\circ$.

The *tilted plate* method, or *inclined plate* method, was devised by McDougall and Ockrent [148] which was used to find the CA when the sessile drop begins to roll off. This method measures both the advancing and receding contact angles by tilting the solid surface. The advancing angle, θ_a , denotes by the CA at the lower point of the stage and the receding angle, θ_r , denotes the CA at the higher point of the stage, as shown in Figure 3.5.

Figure 3.5 Pictorial representation of the *tilted plate* method (redrawn from [11]).

Contact angle (CA) and sliding angle (SA) were measured using Dataphysics OCA 20 contact angle instrument. Water droplets of 1 μL and 5 μL were used for static and dynamic contact angle measurements, respectively [149]. Static CA measurements were performed on droplets placed at random locations on the metal contacts. Dynamic CA was measured on droplets placed at the middle of the contacts while tilting the base from 0 to 90 $^\circ$.

3.2 Accelerated Corrosion Tests

The most prevailing reason of failure in electronic components is the high corrosion rate of metals due to relatively high concentrations of corrosive gases such as sulfur and/or chloride containing gases. As corrosion in the natural environment tends to be slow, accelerated test like salt spray and mixed flowing gas tests serve as rapid methods to assess the relative corrosion resistance of samples.

3.2.1 Salt Spray

Salt spray test been used in many industries like automotive, aerospace, paints and coatings and electronics. NSS tests are widely accepted by the industries world-wide since its inception decades ago. In this study, the NSS test was carried out in accordance to ASTM standard B117 for 96 hours.

Samples were placed in a test cabinet on jigs and a salt spray/fog produced by atomization of a sodium chloride solution (NaCl) solution acts as the corrosive electrolyte. The

operating conditions, as defined by ASTM standard B117, are summarized in Table 3.2.

The precision and accuracy of corrosion evaluation through salt spray is known to be influenced by many factors such as sample preparation, conditioning, removal of corrosion products, cleaning, drying, location of sample in the chamber and number of samples in the chamber, etc. Statistical validation of the salt spray test report that data uncertainty might be high, even after rejecting outliers [132]. Although it has been known that the results do not reflect field data sometimes [150, 151], it has been widely used in some industries, e.g. automotive, because it is a low cost standardized corrosion test. This is due to the procedure of performance and design parameters of the test cabinet [132]. Beyond its limitations, the salt spray test has endured [132]. There are two main reasons that keep salt spray relevant and popular. Firstly, the test seems very straightforward, compared to electrochemical techniques such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) scans or cyclic voltammetry (CV). Secondly, there has been a strong history of salt spray usage among industries such that many customers and suppliers are reluctant to change. The salt spray test has existed as an useful process control tool [128]. For instance, for any given part produced, passing a stipulated number of hours after salt spray exposure indicates that the process is within specification. This gives both the customers and suppliers a quick measure of the quality of products.

Table 3.2 Operating conditions for NSS.

S/n	Parameter	Value
1	Concentration of NaCl solution (wt. %)	5
2	pH of solution at 35°C	6.5 – 7.2
3	Temperature in chamber (°C)	35
4	Period of testing (h)	96

3.2.2 Mixed Flowing Gas

The proliferation of printed circuit board (PCB) and component failure mode due to corrosion, motivated many laboratories to develop accelerated corrosion test methods. IBM, AT&T and Battelle laboratories were pioneers in the development of the MFG test [152]. The resulting work developed MFG into a test consisting parameters such as temperature, relative humidity (RH) and concentration of gaseous pollutant. These variables are carefully defined, monitored and controlled [153]. Two to four gases can be used in the MFG tests while the typical exposure period could be 4, 10 or 21 days. Lengthening the duration often reduces ambiguity in assessing corrosion performance. In this thesis, MFG tests were in accordance with ASTM B845 – 97 Method E, which comprises of two gases: H_2S and SO_2 . The concentration of the gases and relative humidity are summarized in Table 3.3. The length of corrosion test was 10 days.

Table 3.3 Operating condition for MFG (ASTM B845 – 97: Method E).

Parameters	Quantity
Hydrogen sulphide, H_2S (ppb)	100 ± 20
Sulphur dioxide, SO_2 (ppb)	500 ± 100
Temperature ($^{\circ}\text{C}$)	25 ± 1
Relative Humidity (%)	75 ± 3
Air changes (m/h)	3 - 5
Air velocity (m/h)	60
Duration	10

Figure 3.6 shows a typical schematic of MFG testing equipment. Purified air is conditioned to targeted relative humidity and temperature and then mixed with specific concentrations of gaseous pollutants such as H_2S , NO_2 , SO_2 , Cl_2 in the mixing tee. The damp gaseous mixture is then injected into the chamber. Homogeneity of gaseous pollutants inside the chamber is ensured with fan(s). The gases in the chamber are slowly replaced with fresh pollutants at a fixed rate. Expelled gases are purified through filters for environmental concerns. The relative humidity and temperature of the air are monitored by an embedded

probe and display.

Figure 3.6 Schematic diagram of MFG testing equipment (adapted from [12]).

Concentrations of gaseous pollutants are measured manually, by chemical sensor tubes. These tubes work under atmospheric pressure and discolour when gas from the chamber is drawn through the chemical sensor. Figure 3.7 shows an example H₂S chemical sensor discoloured due to H₂S exposure; the reading indicates a concentration of 120 ppm.

Figure 3.7 A H₂S chemical sensor discoloured due to H₂S exposure.

Calibration of the MFG chamber and the test procedure is executed by exposing a set of copper coupons inside the chamber. Prior to exposure, the copper coupons are thoroughly cleaned with dilute acid and electro-degreasing steps. The weight gain of coupons due to the corrosion products formed is normalized over the area of copper coupons and duration of exposure, yielding an mdd value as shown in Eq. 3.10. The mdd values serves as an indication of the corrosivity of the chamber and repeatability of tests. However, exact corrosivity of samples varies slightly between batches as IEC standards recommend mdd limits between 1.2 – 2.4 a.u.. However relative corrosion between samples tested in a single batch highly match the trend seen in another batch of samples.

$$\text{Mdd} \left[\frac{\text{mg}}{\text{dm}^2} \cdot \text{day} \right] = \frac{\text{Weight gain [mg]} \times \text{duration [day]}}{\text{Area of copper coupon [dm}^2\text{]}} \quad 3.10$$

3.3 Substrate Preparation

The substrate was copper foil of 35 μm in thickness. The foil was laminated onto adhesive coated epoxy glass tape (EGT) using a thermal rolling process. The adhesive was cured at an elevated temperature and the desired pattern was prepared by photolithography. The resulting electronic contacts were used as the working electrode in the plating bath.

3.4 Electrodeposition

Electrodeposition was carried out in a 4 L beaker. The anode was a platinum-coated titanium basket containing nickel balls. The current was regulated with an Agilent galvanostat (model: E3633A). Copper substrates were acid-washed, electrolytically degreased and micro-etched prior to Ni plating. Pure nickel plating was performed at 60 $^{\circ}\text{C}$, Ni-P plating at 65 $^{\circ}\text{C}$, and gold electrodeposition at 65 $^{\circ}\text{C}$. The inter-electrode distance was kept at 2 cm in all plating conditions

Basic constituents in the electrolytic bath for nickel electrodeposition were 100 g/L nickel sulfamate and 50 g/L of boric acid. Nickel sulfamate serves as the primary source of nickel while boric acid serves as the pH buffer [6].

Ni-P electrodeposition was performed with a typical Ni-P electrolytic bath [73] composed of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (150 g/L), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (45 g/L), H_3PO_3 (40 g/L), H_3PO_4 (85%, 0.7 cm^3/L), H_3BO_3 (50 g/L) and patented additives as complexing agents. The pH of the bath was adjusted to 1.4 with sulfamic acid or sodium hydroxide. Nickel sulfamate serves as the primary source of nickel while nickel chloride improves anode dissolution, solution conductivity and uniformity of thickness distribution of electrodeposits. Phosphorous acid serves as the phosphorus source, phosphoric acid serves as a levelling and brightening agent and boric acid acts as the buffering agent [6]. Gold electrodeposition was carried out using a proprietary alkaline cyanide bath.

Chapter 4*

Corrosion resistance of electroplated Ni/Ni-P/Au electronic contacts

The reliability of electronic connectors is hugely affected by atmospheric corrosion. This work studies the corrosion resistance of Ni/Ni-P plating metallurgy as a function of current density and electrodeposit thickness. Neutral salt spray (NSS) and mixed flowing gas (MFG) tests displayed discrepancies. Increasing the thickness of Ni-P electrodeposits worsened corrosion in NSS tests, while increasing the thickness of Ni-P deposits improved corrosion resistance in MFG test. This disparity was likely due to the intrinsic corrosion susceptibility of Ni-P in a chlorine or sulfur based environment. The corrosion products due to NSS and MFG were analysed to better understand the corrosion of the electrical contacts. Electrical contacts exposed to NSS tests produced green corrosion residues which consist of CuCl (nantokite) and $\text{CuCl}_2(\text{OH})_3$ (clinoatacamite) and brown residues which consist of Cu_2O (cuprite). Electrical contacts exposed to MFG test produces copper sulfides (major) and nickel sulfides (minor)

* This section published substantially as [43].

4.1 Introduction

Copper is heavily used in electrical cable and electronic connectors due to its low cost and high electrical conductivity [21, 115], but exhibits low corrosion resistance. Therefore, gold (Au) or palladium (Pd) is typically applied as a topcoat but this only marginally improves corrosion resistance as copper diffuses rapidly through plated gold [22]. This diffusion is further exacerbated through processes like wire bonding and encapsulation which require high temperatures. Consequently, electrical contacts suffer from loss in wire bondability, weakened bond strength and loss of conductivity [23].

To inhibit or decelerate Cu diffusion, Ni has been used as diffusion barriers, forming for example the Cu/Ni/Au tri-layer stack as reported in [154]. However defects like grain boundaries, voids and dislocations are present in crystalline nickel. Since such defects are preferential corrosion pathways, crystalline nickel are more susceptible to corrosion [106]. Therefore, Ni-P alloys have been proposed to be strategically deposited between the pure Ni and Au topcoat, as it exhibits enhanced diffusion barrier performance than pure Ni [24]. Ni-P layers with high phosphorous content present no grain boundaries [155], display better corrosion resistance [156] and drastically reduce the required gold thickness as a topcoat [77, 157].

Limited research has been dedicated to the electrolytic deposition of Ni-P, as compared to the electroless method. Electrolytic Ni-P baths have advantages like lesser sludge formation and allows for the better control of deposition rate. The effect of various processing parameters of Ni-P electrodeposition have been well studied by Pillai et al. [6]. However, the effects of these parameters on corrosion resistance are unclear. This study aims to bridge the knowledge gaps in two areas: firstly to understand the impact of Ni-P electrodeposition parameters on corrosion resistance and secondly to understand the combined effects of Ni and Ni-P electrodeposits on corrosion resistance.

Also majority of the research has used electrochemical corrosion tests like electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP) to ascertain the

corrosion behaviour of Ni-P films [78, 93, 94, 158]. None have explored other pertinent tests such as salt spray (SS) and mixed flowing as (MFG) test, which might more representative of atmospheric corrosion. The typical cause of failure in electronic devices have been known to be due to high concentration of corrosive gases such as sulfur and/or chloride in the atmosphere [117].

This study follows the design of experiment (DoE) approach. The effect of thicknesses of Ni and Ni-P, and plating current density (Ni-P) on corrosion resistance were studied. Corrosion was simulated using the two atmospheric corrosion tests: neutral salt spray (NSS) and mixed flowing gas (MFG) tests. Microstructure and composition of electrodeposits were analysed to better understand the corrosion process in the two accelerated corrosion test.

4.2 Experimental Methods

The preparation of substrates and the description of the baths have been mentioned in Chapter 3. Ni was electrodeposited at thicknesses (0.8 or 1.6 μm) under current density of 420 A/m^2 and Ni-P was electrodeposited at thicknesses (0.1 or 0.5 μm) under two different current densities (210 or 850 A/m^2). The current densities and thickness measurements are summarised in Table 4.1.

Table 4.1 Current setting for required thickness for Ni and Au electrodeposition.

	Current (A)	Current density (A/m^2)	Thickness (μm)	
			Low	High
Ni-P	5.06	850	0.1	0.5
	1.25	210	0.1	0.5
Ni	2.5	420	0.8	1.6
Au	0.4	70	0.05	

The systematic study of the three factors: Ni-P and Ni thickness, and Ni-P current density, were systematically varied using a DoE approach as shown in Table 4.2. The factors had

two levels and the entire experiment was replicated once to enable standard deviation calculations. Corrosion resistance of samples was evaluated through MFG and NSS tests.

Table 4.2 DOE table with 3 factors, two levels and one replication set.

Block No.	Ni thickness (μm)	Ni-P thickness (μm)	Ni-P current density (Am^{-2})	Run No.
1	0.8	0.1	210	1
1	1.6	0.1	210	2
1	0.8	0.5	210	6
1	1.6	0.5	210	4
1	0.8	0.1	850	5
1	1.6	0.1	850	3
1	0.8	0.5	850	8
1	1.6	0.5	850	7
2	0.8	0.1	210	5
2	1.6	0.1	210	7
2	0.8	0.5	210	3
2	1.6	0.5	210	2
2	0.8	0.1	850	1
2	1.6	0.1	850	4
2	0.8	0.5	850	8
2	1.6	0.5	850	6

4.3 Results and discussion

4.3.1 MFG test results

Two blocks of the electronic contacts patterns were tested. The electrical contacts in block 1 were more corroded than contacts in block 2, possibly due to the variation between batches of the MFG tests (Table 4.3). Discoloration ranging from black corrosion products to yellowish stains was observed. Corrosion was randomly distributed.

The ΔE^*_{Lab} values shown in Table 4.3 express the colour change due to corrosion. A higher ΔE^*_{Lab} indicates more severe corrosion. The non-consecutive run order ensures that the

experiment was executed in a random sequence to eliminate bias. The ΔE^*_{Lab} values were statistically analysed with the STATGRAPHICS Centurion XVI (version 16.1.17).

Table 4.3 Selected optical images and ΔE^*_{Lab} values of Blocks 1 and 2 samples after 10 day MFG test.

Run no.	Block 1	ΔE^*_{Lab}	Run no.	Block 2	ΔE^*_{Lab}
1		52.7	5		14.5
2		37.5	7		5.5
6		12.6	3		4.7
4		8.2	2		2.2
5		51.1	1		3.8
3		36.6	4		3.3
8		29.5	8		6.0
7		33.0	6		8.6

Results from the main effects plot (Figure 4.1) show that positive factors translate to a proportional increase in discoloration. In contrary, the negative factors cause a proportional decrease in discoloration. Actions such as decreasing the thickness of Ni, decreasing the thickness of Ni-P and increasing the current density at which Ni-P is deposited increase ΔE^*_{Lab} . This is because increasing the thickness of Ni and Ni-P offers better corrosion protection. They protect the copper substrate as a result of their intrinsically better resistance to corrosion [159]. Thicker coatings better prevent the corrosive medium from contacting the substrate [160]. Increasing the Ni-P current density resulted in a 1-2 wt.% decreases in P content in the Ni-P film and lower P content has been attributed to higher exchange current and reactivity [80].

Figure 4.1 Main effects plot for ΔE^*_{Lab} (MFG test) where 1 ASD (ampere per square decimetre) = 100 Am^{-2} .

The main effects plot is useful to understand the relationship (either positive or negative) and the strength of relationship between the factors (plating parameters) and response (corrosion resistance). Further statistical analysis enables one to pinpoint the more influential factors and calculate the combined effects of two (or more) factors. The

standardized Pareto chart as shown in Figure 4.2 narrows into the individual factors and their combined effect on corrosion performance. The horizontal axis (standardised effect) is an estimate of the relative effect of the factors, quantified by a dimensionless value. The vertical line signifies level of significance (at 95 % confidence level); the factors closer to this line have considerable influence and those beyond the line have highly significant influence on corrosion performance. The results show that Ni-P thickness was the sole factor that has high influence on the corrosion resistance under an MFG environment. Thin films between 0.1 to 0.5 μm have been reported to be porous but this porosity is also known to decrease with increasing thickness [22, 115, 161]. As such, our results were aligned with previous work, where increasing the Ni-P film thickness reduces the sulfur assisted corrosion likely due to a reduction in the film's porosity.

Figure 4.2 Impact of factors on corrosion after 10-day MFG test.

4.3.2 MFG corrosion product analysis

The color of the electrical contacts changed from gold to brown to black as the corrosion products accumulated on the surface. Surface morphology of a sample after exposure to MFG (Block1, run 1) is shown in Fig. 4.3. EDX analysis of the indicated region in Figure 4.3 shows the presence of C (10.2 at.%), O (34.3 at.%), S (12.9 at.%), Ni (8.2 at.%), Cu (31.7 at.%) and Au (2.7 at.%). Samples with heavy corrosion were chosen for analysis to increase signal-to-noise ratio. A significant amount of copper was observed on the surface,

hence majority of the corrosion products were either sulfides or oxides of Cu, consistent with literature [12, 162]. The corrosion took the form of pitting and creeping corrosion; the pit is best described as a bloom and the creeping corrosion as a halo [115]. The presence of creep corrosion was confirmed via cross sections performed at the halo and bloom, and pitting was observed solely at the latter.

Figure 4.3 SEM micrographs of module surface after 10-day MFG test. (a) top view (b) magnified image. EDX scan performed at the boxed region.

The corrosion mechanism has been proposed by Reid et al. [115] for the Cu/Ni/Au stack. A porous gold layer exposes the Ni undelayer where oxygen is lower in concentration. The less thermodynamically stable Ni behaves as the anode and the noble gold layer behaves as the cathode. The large area of cathode (porous gold layer) exacerbates Ni corrosion through the large cathode-small anode phenomenon [163]. The electrolyte for this corrosion process is the water layer formed on the gold surface due to the high humidity. The aggressive, or corrosive, ions are HS^- ions that are formed as the hydrogen sulfide gas dissolves and then dissociates in the water layer. As the Ni layer corrodes, copper moves to the top surface by diffusion along the grain boundaries and other defects. The copper subsequently oxidises to sulfides and oxides.

4.3.3 Salt spray test results

Fresh samples were exposed to NSS test for 96 h. After the corrosion test, corrosion products were accumulated at the edges of the electrical contacts (i.e. the region where the metal contact interfaces with the epoxy glass tape carrier). The extent of discoloration was

Table 4. 4 Optical images and ΔE^*_{Lab} values of Blocks 1 and 2 samples after 96 h NSS test.

Run no.	Block 1	ΔE^*_{Lab}	Run no.	Block 2	ΔE^*_{Lab}
1		10.9	5		9.4
2		3.3	7		3.3
6		10.6	3		9.9
4		11.1	2		28.9
5		13.5	1		12.6
3		4.2	4		4.5
8		13.2	8		13.8
7		8.9	6		8.9

quantified using a spectrophotometer. The optical images of samples and measured ΔE^*_{Lab} values are shown in Figure 4.4. The ΔE^*_{Lab} values were statistically analysed.

This main effects plot (Figure 4.4) indicates that ΔE^*_{Lab} decreases with increasing Ni thickness, decreasing Ni-P thickness, and increasing Ni-P plating current density. However, the gradient of the line reveal that ΔE^*_{Lab} are much more influenced by the Ni and Ni-P thickness.

Figure 4.4 Main effects plot for ΔE^*_{Lab} (NSS test).

The standardized Pareto chart, as shown in Figure 4.5, shows the individual factors and their combined effect on the corrosion performance against NSS. All the factors were below the line of significance, likely due to two possibilities. None of the factors may have significantly impacted the corrosion resistance of the electrodeposits in a salt fog environment, implying the presence of other unknown factor(s) that might be more influential factors. Alternatively, colour measurement may not be the most ideal of corrosion quantification method due to the migratory nature of corrosion products due to

the NSS corrosion test. Nevertheless, Ni-P thickness and combined effect of thicknesses of Ni and Ni-P have considerable influence on corrosion (Figure 4.5). Although Ni-P is commonly perceived to exhibit better corrosion resistance than Ni, the NSS test displayed a reversed trend where a thicker Ni-P layer resulted in less corrosion resistance, probably due to different operating mechanisms. Upon careful consideration of the gases and solutions involved in the corrosion tests, NSS tests induce corrosion damage mainly through chlorine assisted process. While in the MFG test, corrosion may predominantly occur through sulfide assisted process when higher concentrations of sulfides are present [164]. Further analysis is provided next through the corrosion mechanism study.

Figure 4.5 Impact of factors on corrosion after 96 h NSS test.

In summary of the test results, Ni-P displayed better protection in the MFG environment than NSS probably due to its intrinsic good corrosion resistance to sulfur-assisted corrosion. However, it could not provide the same level of corrosion protection in neutral chloride solution. Discussion based on microstructural and compositional analyses will be given in the subsequent section.

4.3.4 Salt spray corrosion product analysis

The corrosion products on surface due to NSS were studied with SEM. Morphologies of the corrosion products after NSS tests are shown in Figure 4.6. Elemental analysis of this corrosion residues via EDX analysis presented: oxygen (51.1 at.%), chlorine (16.3 at.%), nickel (6.1 at.%) and copper (26.5 at.%).

Figure 4.6 SEM micrographs of corrosion products after to NSS corrosion test (a) top view (b) magnified image.

Elemental mapping of the corrosion residues at other regions revealed similar elements, as shown in Figure 4.7. The unaffected region consists of mainly Ni. The corroded region (right hand side of the SEM image) is largely composed of Cu, Cl and O.

Figure 4.7 EDX mapping of corrosion product on the surface of module after 96 h NSS test.

In order to study origin of the green and brown stains on the modules, the corrosion residues were removed with dilute HCl solution, distilled water and blown dried with nitrogen gas. Regions that were covered by green residues were examined using SEM. Highly noticeable pits were observed at regions which were previously covered by green residues, as shown in Figure 4.8. Pitting corrosion was the main type of corrosion. Similar to green residues, pitting corrosion could be also seen at the regions which were previously covered by brown residues. However, there were less pitting and the shapes of the pits were predominantly shallow. Although, EDX analysis of the brown and green corrosion products revealed similar elemental composition, the brown stains may be due to difference in Cu oxidation states.

Figure 4.8 (a) & (d) Optical images of the corrosion residues 96-hr SS corrosion tests prior to acid cleaning; (b) & (c) SEM micrographs of pits revealed after acid cleaning of brown stained-region; (e) & (f) SEM micrographs of pits revealed after acid cleaning of green stained-region.

XRD analysis of the green and brown colours is shown in Figure 4.9. The green corrosion residues consist of mainly CuCl (nantokite) [165] and $\text{CuCl}_2(\text{OH})_3$ (clinoatacamite) while brown corrosion product is dominated by Cu_2O (cuprite) [166]. The rest of the diffraction peaks are from Cu, Ni in the substrate.

Figure 4.9 XRD pattern of corrosion products on the surface of contact (Block 2, run order 2).

Magnified images of pits post acid wash show that the pits are voids in the Ni layer. Figure 4.10 shows that the centre of the pit, area (a), was exposed Cu substrate and copper chlorides. Region (b) revealed delamination of Au topcoat and also the dissolution of P, making region (b) the exposed Ni layer. Region (c) remained intact where Au and P contents are higher.

Pits observed were not all hollow. Typically, shallow and deep were observed as shown in Figure 4.11. The bottom of shallow pits can be seen in SEM, while the deep pits exhibited dark pits. Focused ion beam (FIB) was employed to produce cross section of these pits. Deep pits were investigated by tilting the sample and shifting focus deeper into the pit.

Figure 4.10 EDX analysis of a pit due to NSS exposure.

Figure 4.11 SEM image of shallow and deep pits due to NSS exposure.

FIB-milled cross section images reveal, as shown in Figure 4.12, deep pits extended vertically down. The two adjacent deep pits are most probably interconnected by hollow tunnels. Similarly, cross section analysis was performed on a shallow pit for comparison with the deep ones. The shallow pits seem to be stand-alone, i.e. may not be subterraneanly connected to adjacent pits (Figure 4.13). Heavy corrosion leads to deep pits extended down below the surface (till the Cu substrate) and two adjacent deep pits are likely interconnected by hollow tunnels. Shallow pits may exhibit nickel undercutting, where copper is corroded, leaving a void in the Cu substrate. Copper is likely to move to the surface through the defects in the Ni layer.

Figure 4.12 SEM micrographs of (a) FIB-SEM cross section images at pits; inset with focus shifted to show the contents inside the pits, and (b) magnified image of the contents of the pit; and (c) pictorial representation of the pits.

Figure 4.13 (a) FIB-SEM cross section image of a shallow pit (inset shows the pit prior to cross section); and (b) pictorial representation of the pit.

4.4 Summary

MFG and NSS tests were employed to determine the corrosion resistance of the Cu/Ni/Ni-P/Au electronic contacts. Colorimeter was employed to provide a quantifiable parameter to assess the degree of corrosion. The quantification assisted with the statistical analysis in identifying key factors in the design of experiment (DoE) study.

Corrosion analysis reveals copper sulfide and copper oxide in the MFG test, and chloride, chlorohydroxides and oxides of copper deposits in the NSS test. NSS test results in pitting corrosion, where pits displayed heavy corrosion with interconnected hollow tunnels or

stand-alone pits as a result of Ni undercutting. MFG resulted in pitting and creeping corrosion which are associated with sulfur-assisted corrosion.

Ni thickness consistently improved the corrosion resistance of electrical contacts in both MFG and NSS tests. Generally, thicker Ni layers improved corrosion resistance but the degree to which Ni enhances the corrosion resistance was limited, due to the overwhelming effects of Ni-P.

Ni-P significantly affected corrosion resistance of the electrical contacts. Ni-P was observed to possess weak corrosion resistance to a salt fog environment but has increased corrosion resistance to MFG. The results suggest that Ni-P may not be a suitable corrosion protection coating against heavy Cl^- attack in an aqueous medium, but it has shown excellent resistance to sulfur-containing corrosion media.

However, subsequent in-depth studies reveal that these findings regarding the disparity in corrosion resistance of Ni-P in MFG and NSS was due to the high *edge porosity* caused by fast plating (refer to Chapter 6).

Chapter 5*

Investigation of Nickel-based Multi-layer Stacks for the Corrosion Protection of Copper Contacts

This chapter investigates the corrosion performance of Ni/Au (NA), Ni-P/Ni/Au (PNA), Ni-P/Au (PA), Ni/Ni-P/Au (NPA) and Ni-P/Ni/Ni-P/Au (PNPA) coating stacks for electrical contact application. The five stacks were exposed to sodium chloride neutral salt spray test (NSS) and acidic mixed flowing gas test (MFG). Post-corrosion analyses were carried by X-ray diffraction, focused ion beam microscopy, scanning electron microscopy, energy dispersive spectroscopy, spectrophotometry and pits counting to evaluate the performance the stacks. Pitting behaviour due to the MFG was explained through a proposed dominant pit concept. Results showed that multi-layer stacks, such as PNA, NPA, PNPA, displayed worse corrosion resistance than single-layered stacks (NA, PA). The pitting in multi-layer stacks is attributed to Ni/Ni-P interfaces that accelerate the corrosion due to galvanic coupling. Removing these interfaces was effective for corrosion prevention against salt fog and MFG environments. Corrosion that occurred in the nickel layer grew longitudinally while in the Ni-P penetrated vertically. This was attributed to the way Ni and Ni-P were arranged within a stack. The tunnelling corrosion through the Ni-P layer became more striking as the Ni-P thickness was reduced, possibly due to increase in the film porosity.

* This section published substantially as [167].

5.1 Introduction

Electrical contacts serve as the medium for information exchange between a reader and an embedded chip. The reliability of these contacts becomes pertinent as it determines the lifespan of the entire electronic device. Pure copper (Cu) or copper alloys have been widely used as conducting lines as they are cost-effective and are highly electrical conductive [168]. However, Cu remains susceptible to oxidation and corrosion, and even a thick topcoat of gold (Au) does not inhibit corrosion due to the rapid diffusion of copper through gold [22, 23]. Once the entire thickness of the Au film is penetrated, Cu accumulates on the surface and high concentrations of Cu exist immediately below the gold-air interface. To prevent the copper-gold inter-diffusion, nickel (Ni) and nickel alloys have been typically used as diffusion barriers. Among nickel based alloys, nickel phosphorus (Ni-P) has been suggested as effective coatings for enhanced corrosion resistance [80, 104, 105, 157, 158].

Extensive work has been done on electroless Ni-P deposition [79, 86, 98, 104, 135-137] but studies on electrodeposition of Ni-P is scarce. Electrodeposition has been of interest to industries as it boasts faster deposition rate and requires lower maintenance of the electrolytic bath. Studies based on electrochemical and weight loss tests have been performed to understand the change in corrosion behaviour due to bath temperature [169], applied potential [169], phosphorous (P) content [78, 82, 85] and grain size [78].

Although Ni-P is reported to be more corrosion resistant, most studies omit the comparison of Ni-P to pure Ni. Multi-layers have been reported to have improve the corrosion resistance of coatings [3, 138, 139] but current research has been limited to thick inter-layers (18-50 μm) on stainless steel substrates [3]. In contrast, multi-layer coatings for electronic copper contacts require thinner electrodeposits ($< 3 \mu\text{m}$ in total). Moreover, inconsistencies in literature regarding the corrosion resistance of multi-layers stacks compared to bi-layer stacks render these studies inconclusive [170, 171].

This chapter explores the corrosion resistance of copper electrical contacts electrodeposited with single and multi-layers of Ni and Ni-P. Neutral salt spray (NSS) and mixed flow gas (MFG) corrosion tests were used. MFG tests are able to simulate the environment of more developed regions in the world, such as countries with high industrialization or pollution [117, 172]. NSS is a widely used laboratory cabinet test involving atomized salt solution introduced onto samples [151].

5.2 Experimental Methods

Nickel based barrier layers with a gold topcoat were achieved by electrodeposition. Five different arrangements were investigated, viz.: Ni/Au (*NA*), Ni-P/Ni/Au (*PNA*), Ni-P/Au (*PA*), Ni/Ni-P/Au (*NPA*) and Ni-P/Ni/Ni-P/Au (*PNPA*). Figure 5.1 depicts the five arrangements used in this study.

Figure 5.1 Pictorial representation of the multi-layer barriers over Cu substrate (not shown).
[Current density in Am^{-2} , plating time in s, P content in wt.%]

The total thickness of Ni and/or Ni-P stacks was 2.2 μm and gold thickness was maintained at 50 nm. Table 5.1 provides the current density and temperature setting used. The methods of substrate preparation, description of the electrolytic baths, material characterization

methods and choice of corrosion tests have already been mentioned in great detail in Chapter 3.

Table 5.1 Current density and temperature setting for the various electrodeposits.

	Pure Ni	Ni-P	Au strike	Au
Current density (A/m ²)	1800	580	90	50
Temperature (°C)	60	65	60	65

5.3 Results and Discussion

5.3.1 Material characterization

The thickness and phosphorus (P) content of electrodeposits were measured with X-ray fluorescence technique and are shown in Figure 5.1. Notably, Ni-P films that ranged from 0.2 to 2.2 μm were of similar P content.

The microstructure of the Ni and Ni-P electrodeposits were studied using X-ray diffraction (XRD) and results are shown in Figure 5.3. Pure Ni stacks exhibited crystalline peaks of (111), (200) and (220) and peaks due to the Cu substrate. However, the Ni-P deposits did not display any Ni peaks indicating that the Ni-P layer was of high phosphorous content and amorphous in structure.

5.3.2 MFG corrosion test

The five stacks were exposed to the MFG environment for 10 days. Figure 5.2 shows the optical images of the five stack arrangements *NA*, *PNA*, *PA*, *NPA* and *PNPA* after the MFG test.

Every stack displayed corrosion on the surface in the form of brown specks, in varying degrees. Each brown speck could be described as a *halo* with a *bloom* at the centre – terms coined by Krumbein [119]. Figure 5.4a shows the sample surface prior to acid cleaning,

with evident blooms and halos. Figure 5.4b shows the surface of a sample (*NPA*) after acid cleaning, in which locations that were previously occupied by blooms were revealed as pits.

Figure 5.2 Optical images of samples: (a) Ni/Au (*NA*), (b) Ni-P/Ni/Au (*PNA*), (c) Ni-P/Au (*PA*), (d) Ni/Ni-P/Au (*NPA*), and (e) Ni-P/Ni/Ni-P/Au (*PNPA*) after a 10 day MFG corrosion test.

Figure 5.3 XRD patterns of Ni and Ni-P electrodeposits on a copper substrate.

Figure 5.4 Optical images of *NPA* sample after 10 day MFG test (a) prior to acid cleaning showing blooms and halos and (b) after acid cleaning showing pits at locations that were previously blooms.

Based on this observation, the corrosion centre was considered to be the major pit concealed under the bloom. Dummy samples were used to check the solubility of corrosion products. Notably, the corrosion residues at the bloom were insoluble in common inorganic and organic solvents such as water, acetone and ethanol, even upon sonication. Subsequently, it was found that dilute aqueous hydrochloric acid (HCl) coupled with sonication removed corrosion residues; test samples were then cleaned accordingly. The blooms were revealed as pits and smaller pits could only be seen under higher magnification under SEM.

In addition, focused ion beam (FIB) aided cross sections were executed to confirm that blooms concealed underlying pits. Figure 5.5a is an optical image of the brown speck on an electrical contact, and Figure 5.5b and Figure 5.5c (magnified) are SEM micrographs of the corresponding region. Figure 5.5d shows a cross section SEM micrograph at a bloom. Platinum (Pt) was deposited onto the sample surface prior to FIB milling, to prevent any artefacts.

Although the bloom was merely 6 μm in diameter, the corroded region underneath was 22 μm wide and 13 μm deep. Heavy Ni undercutting (attack of the copper under the nickel) directly under the bloom was observed. Cross sections performed away from the bloom, as shown in Figure 5.5e, did not display any undercutting. Thus the source of creeping corrosion product (halo) was established to be the major pit directly under the bloom. EDX

scans of the corroded region, as shown in Figure 5.6, revealed elements such as Ni and O at the bloom. The immediate region around the bloom revealed high concentrations of Ni. The halo contained Cu, O and S elements, consistent with literature [115].

Figure 5.5 Optical and SEM images of the bloom and halo showing: (a) optical image of an electrical contact after 10-day MFG test, and (b) and (c) SEM micrographs of the boxed region in (a), (d) and (e) cross section images of samples at the bloom and away from the bloom, respectively.

Every bloom concealed an underlying pit. However, pits that were not concealed by blooms were also observed. Herein, the proposed *dominant pit concept* serves as an explanation for this occurrence. Characteristic to localized corrosion, pits initiate randomly across a metal contact. Some pits get initiated faster (or earlier) than others and the autocatalytic nature of pitting corrosion coupled with the defects in the metal contact propagate the pitting process. These pits are termed as dominant pits. With time, the dominant pit forms a bloom, and subsequently forms creeping corrosion products (halo). It is conceivable that dominant pits in proximity can result in the overlap of halos. Incidentally, such halos were observed as shown in Figure 5.7a. Multiple halos had coalesced into a single asymmetric halo due to proximally located dominant pits.

Concurrently, some shallower (minor) pits co-exist with the dominant pits as seen in Figure 5.7b. Thus not every pit will result in a bloom and halo.

Figure 5.6 (a) SEM micrographs of mapped region (b) EDX elemental map – White: Cu, Blue: Ni, Green: O, Purple: S, Yellow: Pt, Red: C.

Figure 5.7 SEM micrographs of *NA* samples, sonicated in dilute HCl solution such that the stains of the halo (if any) are retained. Images show: (a) coalesced halos (outlined) due to proximally located dominated pits and (b) minor pits that did not form a bloom or halo.

Corrosion was assessed through visual, spectrophotometric (colour measurements) and pits counting methods. Visually, corrosion product coverage over the surface of the samples was highest for *NPA*, followed by *NA* samples. However, *PNA* and *PNPA* samples,

although relatively speckle-free, appeared dull when compared to the state before the corrosion test. These observations were captured and quantified by the colour measurements, as shown in Table 5.2. *PA* stacks displayed the best corrosion resistance in MFG, evidenced by the least corrosion product on the surface.

Table 5.2 Colour difference and pit counting data after a 10 day MFG.

	<i>NA</i>	<i>PNA</i>	<i>PA</i>	<i>NPA</i>	<i>PNPA</i>
ΔE	10	8	3	11	9
Pits (pits/cm ²)	17	0	0	0	0

Pits counting were performed using an optical microscope at 40 x (objective lens) magnification and results are shown in Table 5.2. Under the optical microscope, every samples (except for *NA* stack) show little or no pitting. However the pits were not observed due to their minuscule size and were more apparent under SEM, which will be discussed in Chapter 5.3.4. Although the pits counting method thrives as a popular corrosion quantification technique, results can be misleading when executed with an optical microscope at low magnifications.

Figure 5.8 shows the surface and edges of a typical electrical contact, the surface denoting the top of a pin-out (of an electrical contact) and the edge denoting the region where the metal pin-out meets the carrier.

Figure 5.8 Uncoloured (a) and coloured (b) SEM micrographs showing the edge and surface of an electrical contact.

Pitting behaviour at both the surface and edges were observed using SEM, as shown in Figure 5.9. After an ultrasonic acid wash, *NA* displayed many small pits on the surface [Figure 5.9S(a)]. EDX scans indicated that Cu at the bottom was exposed. At the edge, pits were growing in a circular manner, reaching the carrier [Figure 5.9E(a)]. *PNA* samples displayed larger pits (than *NA*) and high surface pitting. The pits propagated in a circular manner with most pits revealing the Ni-P under-layer, some pits revealing Cu, and some pits rarely exposing the epoxy carrier [Figure 5.9S(b)]. Pitting at the edges were similar to surface pits [Figure 5.9E(b)]. Comparing the samples *NA* and *PNA*, the additional Ni-P underlayer (in *PNA*) increased corrosion resistance, inhibiting corrosive species from reaching the copper substrate. *PA* samples were untarnished and exhibited very few pits [Figure 5.9S(c)]; some edge corrosion was observed but in contrast to *NA*, the pits propagated in a vertical manner [Figure 5.9E(c)]. *NPA* displayed many surface pits that looked deep and propagated vertically [Figure 5.9S(d)]. There was considerable edge pitting similar to *PA* samples [Figure 5.9E(d)]. This again indicated that Ni-P arrests horizontal pit growth, but allows vertical pit propagation. *PNPA* displayed a high number of pits in varying sizes. Most pits exposed the Ni-P layer, indicating that the top two layers (of Ni and Ni-P) have been removed [Figure 5.9S(e)]. The edges show many pits which were almost circular with numerous pits formed at both the edges and surface [Figure 5.9E(e)].

Figure 5.9 SEM micrographs of samples: (a) Ni/Au (*NA*), (b) Ni-P/Ni/Au (*PNA*), (c) Ni-P/Au (*PA*), (d) Ni/Ni-P/Au (*NPA*), and (e) Ni-P/Ni/Ni-P/Au (*PNPA*) after a 10 day MFG test.

5.3.3 NSS corrosion test

The five stacks were exposed to 96 h NSS corrosion test and results are shown in Figure 5.10. Visually inspection of the samples indicated that *NA* (Figure 5.10a) and *NPA* (Figure 5.10d) samples were least affected by NSS. Heavy tarnishing was observed on the surface of *PNA* samples (Figure 5.10b). *PA* (Figure 5.10c) samples maintained the same lustre as prior to the corrosion test, but succumbed green corrosion residues at the edges of the module. *PNPA* samples (Figure 5.10e) displayed tarnishing, and green corrosion products formed at the centre of the modules.

Figure 5.10 Optical images of samples: (a) Ni/Au (*NA*), (b) Ni-P/Ni/Au (*PNA*), (c) Ni-P/Au (*PA*), (d) Ni/Ni-P/Au (*NPA*), and (e) Ni-P/Ni/Ni-P/Au (*PNPA*) after 96 h NSS.

According to the performed NSS tests, none of the analysed stacks demonstrated significant mass loss of samples, consistent with literature [173]. Thus weight loss measurement was unsuitable for quantifying corrosion in electrical contacts. Hence to quantify the extent of corrosion, the area of corroded surface to the total surface was assumed to be a reasonable gauge. Corrosion residues were found to be at the regions of pitting. For example, Figure 5.11a shows an area with green corrosion residue. After the corrosion residue was removed, the area exhibited heavy pitting corrosion coupled with Au delamination (as shown by progressively magnified SEM images: Figure 5.11b – c).

As such, the percentage of gold surface covered by corrosion residues quantifies the extent of corrosion. Colour measurements were used to quantify this percentage change; the results, as shown in Table 5.3, show that *NA* and *NPA* samples were least affected by NSS.

Table 5.3 Colour difference and pit counting data after 96 h NSS.

	<i>NA</i>	<i>PNA</i>	<i>PA</i>	<i>NPA</i>	<i>PNPA</i>
ΔE	2	7	3	2	7 ^a
Pits (pits/cm ²)	16 ^b	1	0	16 ^b	2

^aScattering of data ^bLarge scattering of data

Figure 5.11 SEM micrographs of (a) green corrosion product after 96 h NSS and (b-d) corrosion pits underneath the green corrosion product.

In addition, pits counting were performed using a microscope at 40 x (objective lens) magnification and results are given in Table 5.3. *PNA*, *PA* and *PNPA* samples displayed very low pitting densities and a small standard deviation (σ) between repeated samples. However, a large standard deviation was calculated between repeated samples for *NA* and *NPA* samples. Reproducibility can be a limitation with salt spray tests [174], likely due to the nature of the test. The corrosion is influenced by the cycling of water, which may not regularly remove the pit debris [175]. Debris that remains at a region encourages trapping of Cl^- which increased pitting at that region. Pits counting results deviated from visual inspections and spectrophotometric measurements; this would be further discussed in the Chapter 5.3.4.

Further analyses of the pitting behaviour of the five stacks were performed using SEM. The SEM micrographs of the Ni-based stacks after 96 h NSS test are shown in Figure 5.12. Sonication in a dilute HCl bath was essential in providing the necessary mechanical agitation to remove the corrosion residues that were wedged between crevices, as shown by *NA* [Figure 5.12S(a) cf. S(a)'] and *PA* [Figure 5.12S(c) cf. S(c)']. *NA* samples exhibited numerous small pits which either exposed Cu or Ni (Figure 5.12). Occasional corrosion at the edges was observed. *PNA* stack displayed many pits on the surface, exposing Ni-P (most frequently), Cu or the epoxy carrier (least frequently). Occasional corrosion at the edges was observed. *PA* samples exhibited some Au delamination. However, the Ni-P layer had inhibited corrosion reaching the Cu substrate. Most green corrosion residue was seen with the *PA* samples, particularly at the edges of the pinouts [Figure 5.10c & Figure 5.12E(c)]. SEM analysis on washed samples also revealed serious pitting at the edges. The *NPA* stacks exhibited pits through the Ni and sporadic delamination of the Ni-P/Au layer, as shown through EDX scans [Figure 5.12X (d)]. Most of the corrosion products were at the edges. *PNPA* samples exhibited heavy pitting, where the Ni/Ni-P/Au layer had been removed. Pits had also penetrated through the underlying Ni-P layer, revealing the Cu substrate.

In summary, the effects of the 96 h NSS corrosion test can be seen on the surface and edges of the electrical contact pinouts. From the SEM micrographs after NSS, there was a disparity between surface and edge corrosion. Single layer barrier layers such as *NA* and *PA* should provide better protection against pitting corrosion in this situation which is well corroborated with the results obtained. *NA* and *PA* samples could be improved for better corrosion resistance with regards to surface and edge pitting, respectively.

Figure 5.12 SEM-EDX images of samples: (a) Ni/Au (NA), (b) Ni-P/Ni/Au (PNA), (c) Ni-P/Au (PA), (d) Ni/Ni-P/Au (NPA), and (e) Ni-P/Ni/Ni-P/Au (PNPA) after 96 h NSS.

5.3.4 An overall perspective

Corrosion in all five stacks was driven by the small anode-large cathode phenomenon. Thicker gold films ($> 2 \mu\text{m}$) are accepted to be pore-free and corrosion resistant [176]. Gold films at $0.8 \mu\text{m}$ is known to be porous [176], and the porosity of thin films rises dramatically with decreasing thickness [177]. The corrosion mechanism seen in the electrical contact follows that proposed by Collins [4]. The bottom of a microscopic Au pore, which is the nickel-based barrier layer, acts as the small area (anode) and noble Au layer acts as the large area (cathode). Galvanic corrosion propagates the dissolution of the barrier layer allowing corrosive species to reach the Cu substrate.

Integrating MFG and NSS tests results highlights two main observations: (a) colour measurements were well-aligned with visual inspection and aided in quantifying the extent of corrosion in the functional area of the contact pads but (b) pits counting data and

observations from SEM analysis were incongruent. Regarding the latter, we have shown that conventional pits counting under light microscopy can only deliver limited information. Much important details could not be revealed; for example, pits that were seen in SEM images were not reflected in pits counting results under the conventional light microscope (e.g. MFG: *PNA* and *PNPA* – NSS: *PNA*, *NPA* and *PNPA*). The limitation in pits counting stems from the nature of this corrosion quantification technique. Requirements of pits counting over large areas lead to examinations at low magnifications. Hence smaller pits and larger pits filled with corrosion residues (blisters) go unnoticed. In this study we have used the two afore-mentioned inspection techniques to complement each other.

Generally corrosion that occurs in pure nickel spreads horizontally) while in Ni-P penetrates vertically. The reason for this can be understood by studying the corrosion behaviour of the triplex layer coating system in literature [159]. A coating of nickel containing 0.1 - 0.25 wt.% of sulfur (high-S) was applied between medium-S and low-S nickel layers, as shown in Figure 5.13a. The high-S nickel layer corroded preferentially even when pitting corrosion reaches the low-S nickel layer. This is because the high-S layer behaves as the anode while both the medium-S and low-S layers behave as cathodes, preventing vertical penetration.

Applying a similar concept, the direction of corrosion propagation (horizontal or vertical) depends largely on the arrangement of Ni and Ni-P within a stack. When Ni is deposited on Ni-P, Ni behaves as the anode and Ni-P behaves as the cathode; this is because the corrosion potential of Ni-P is more positive (more noble) than that of pure Ni [3]. As such, corrosion through the pure Ni layer is diverted horizontally when it reaches the Ni-P underlayer, as shown in Figure 5.13b. In contrast, when Ni-P is deposited on top of the Ni, the corrosion through the Ni-P penetrates quickly to the underlayer, as shown in Figure 5.13c. This can be termed as *vertical penetration*. Once the Ni-P layer is compromised, the galvanic coupling (battery effect) between the Ni and Ni-P/Au layers further catalyses the corrosion of Ni.

Thus, the interfaces of Ni-P and Ni behave as galvanic regions and accelerated corrosion. Removing these interfaces proved effective in preventing corrosion in NSS and MFG, as shown by *NA* and *PA* stacks. In contrast, increasing these interfaces intensified corrosion, as shown by the *PNPA* stacks which had double the Ni/Ni-P interface area as compared to *PNA* and *NPA* stacks. The tunnelling corrosion through the Ni-P layer became pronounced when the Ni-P layer thickness was reduced from 0.4 to 0.2 μm , possibly due higher percentages of discontinuities, i.e. porosity in thinner films of Ni-P. This differentiates this work from that of the Gu et al. [3] who reported highly corrosion resistant Ni-P/Ni/Ni-P coatings for steel substrates. They ensured pore-free, highly-dense and defect-free coatings through very thick coatings of 20 μm and electroless Ni-P deposition.

Figure 5.13 Models showing the proposed corrosion mechanism in the (a) triplex layer Ni coating (adapted from Schweitzer [159]); (b) Ni-P/Ni coating and (c) Ni/Ni-P coating arrangements.

5.4 Summary

Five stack arrangements Ni/Au (*NA*), Ni-P/Ni/Au (*PNA*), Ni-P/Au (*PA*), Ni/Ni-P/Au (*NPA*) and Ni-P/Ni/Ni-P/Au (*PNPA*) with a fixed total thickness were tested with 10 day mixed flowing gas (MFG) and 96 h neutral salt spray (NSS) corrosion tests. Pitting corrosion of all five stacks was driven by the small anode-large cathode phenomenon. Colour measurements were well-aligned with visual inspection which was instrumental in quantifying the degree of corrosion in the functional area of the contact pads. Conclusions made from results obtained from MFG and NSS, and combined perspectives are given below.

MFG caused tarnishing and brown specks on the contact surface. Each brown speck could be described as a ‘halo’ with a ‘bloom’ at the centre [4, 115]. A pit was seen in the centre of every brown speck but the reverse was not true. A dominant pit concept has been proposed which explains the coexistence of pits that result in the bloom, and the pits that do not. A new discovery associated with the difference in pitting behaviour of Ni and Ni-P layers has been highlighted and discussed in this report. Corrosion pits propagated vertically through Ni-P films and horizontally in Ni films and this was attributed to galvanic coupling between the two barrier layers.

NSS results show a disparity in edge and surface corrosion. *PA* and *NPA* did not succumb to surface pitting but displayed edge corrosion while *NA*, *PNA* and *PNPA* stacks produced more serious surface pitting. Research into this disparity would be reported in Chapter 6. Poor reproducibility of results was observed between batches of NSS tests; however the trend of corrosion was consistent within each batch. Removing the Ni and Ni-P interfaces effectively improved corrosion resistance in NSS and MFG. The tunnelling corrosion through Ni-P layer became pronounced as the thickness was decreased, likely due to higher percentages of discontinuities, i.e. porosity. This was worsened by interfaces of Ni and Ni-P multi-layers which accelerated corrosion through galvanic coupling. Therefore single layer barrier structures such as *NA* and *PA* should provide better resistance against pitting

corrosion. *NA* and *PA* stacks could be improved for better protection with regards to surface and edge pitting, respectively.

Chapter 6

The disparity of corrosion resistance between Ni/Au and Ni-P/Au electrical contacts in mixed flowing and salt spray tests

Single layer barrier systems such as Ni/Au and Ni-P/Au (the function of the ultra-thin Au top layer is not considered as a barrier), compared to bi-layer stacks like Ni/Ni-P/Au, have reportedly enhanced corrosion resistance. However when assessed using neutral salt spray (NSS) and acidic mixed flowing gas (MFG) tests, the corrosion resistance of Ni/Au showed better corrosion resistance in the NSS test and the Ni-P/Au stacks in the MFG tests. To explain this disparity, factors that could influence corrosion resistance, such as internal stress, surface wettability and sulfur co-deposition were examined. Interestingly, none of these factors could reason for the disparity. Corrosion product analysis was then executed to understand the corrosion mechanisms in the NSS and MFG tests. Detailed pits analysis revealed that the disparity was due to edge porosity and corrosion product migration. These new concepts were further supported by purposely designed experiment. This study brings in new insights which will help in the designing of corrosion resistant metallic coatings in the future.

6.1 Introduction

The scope of this paper covers two Ni based systems and the disparity in corrosion performance seen between two different corrosion tests. Single barrier layer systems such as Ni/Au and Ni-P/Au (compared to bi-layer stacks such as Ni/Ni-P/Au) have been reported to display enhanced corrosion resistance [167]. However, when the corrosion resistance of Ni-P/Au stacks and Ni/Au stacks was assessed NSS and MFG tests, each stack was only superior in one test. Ni/Au stacks were more corrosion resistant to the NSS test and weaker in the MFG test, while Ni-P/Au stacks displayed an opposite trend [167]. Similar observations were cited in another study where increasing the thickness of Ni-P resulted in more corrosion after NSS and less corrosion after MFG [43].

Despite the novel research devoted to new structures of nickel based barrier layers, the performance of these new structures has not been distinguished from that of pure Ni films. Hence the actual enhancement of corrosion resistance relative to pure Ni films cannot be fully determined. Moreover, little has been done to compare the corrosion resistance of such systems in more than one corrosion test. Even lesser has been done in providing an explanation for the disparity in corrosion performance. Herein, this chapters explores the cause for the disparity in corrosion performance attained between two different corrosion tests for Ni/Au and Ni-P/Au barriers.

6.2 Experimental

Ni/Au and Ni-P/Au stacks were prepared through electrodeposition. The methods of substrate preparation, description of the electrolytic baths, material characterization methods and choice of corrosion tests have already been mentioned in great detail in Chapter 3.

6.3 Results and Discussion

To affirm the disparity in corrosion performance between Ni-P/Au and Ni/Au contacts in NSS and 2-gas MFG tests, as observed previously [167], samples were prepared and assessed. Figure 6.1 shows the optical images of Ni/Au and Ni-P/Au samples after NSS and MFG test. The inverse corrosion performance of Ni-P/Au and Ni/Au in SS and MFG test was visibly evident. Hence the properties of the electrodeposits were studied to determine the root cause for this disparity of corrosion resistance.

Figure 6.1 Optical images of (a) Ni/Au and (b) Ni-P/Au contacts after 96 h NSS and, (c) Ni/Au and (d) Ni-P/Au contacts after MFG tests.

6.3.1 Internal Stress

Nickel sulfamate baths [178], compared to Watts-type (sulfate-chloride) baths, reportedly produce deposits with lower internal stress [58, 179]. Internal stress has been claimed to

be influenced by current density [180-182] which in turn affects corrosion resistance [183, 184].

To ascertain the internal stress of Ni-P and Ni electrodeposits, the bent strip test was adopted. Figure 6.2 depicts the relationship between residual internal stress and current density for these electrodeposits. The internal stress of Ni-P deposits reduced to 9.5 MPa when current density was increased to 50 mA cm⁻²; and remained tensile at both 25 and 50 mA cm⁻². Conversely, internal stress of Ni deposits turned from compressive to tensile with the increase of current density.

The disparity in corrosion resistance was observed in electrodeposits of Ni-P and Ni plated at 50 and 100 mA cm⁻² (Figure 6.1). At these current densities, the internal stress of both Ni-P and Ni electrodeposits were close to zero (Figure 6.2). Moreover, when these results were compared with literature, we understand that Ni electrodeposits with a difference of around 25 MPa reportedly displayed a meagre 1 % difference in percentage corroded area [185]. In comparison, in this study the difference in internal stress between Ni-P (50 mA cm⁻²) and Ni (100 mA cm⁻²) was around 6 MPa. Therefore, the disparity in corrosion resistance was deemed not to be direct influence of the internal stresses within the films.

Figure 6.2 A plot of internal stress against current density of Ni and Ni-P electrodeposits.

6.3.2 Wettability

Atmospheric corrosion of metal initiates at the interface between a metal surface and water vapour. This process is quickened by dissolution of soluble corrosive ions, such as chlorides and sulfides, at a certain relative humidity (RH) [186-189]. Theoretically, the presence of a water droplet or a finite film of water over a metal surface changes the electrochemical behaviour at the surface from homogeneity to heterogeneity [190]. As the surface of a material serves as the first line of defence against corrosion, the corrosion performance of a material corresponds to its surface wettability [191-193].

In the NSS test, samples are typically placed on jigs that are angled at 30° from the vertical, while samples are hanged vertically (0°) inside a MFG chamber. Hence, the difference in corrosion performance in NSS for Ni-P/Au and Ni/Au samples might stem from the difference in propensity for water to roll off these surfaces. Static and dynamic contact angles (CA) were measured to determine the wettability of the surfaces.

The static CA of the Ni/Au and Ni-P/Au surfaces were 68 and 71°, respectively. The receding and advancing angles of a 5 µL water droplet were the contact angles measured as the stage was tilted from 0-90°. These dynamic contact angles of Ni/Au and Ni-P/Au contacts are depicted in Figure 6.3. The absence of acute changes of the advancing contact angle (ACA) and receding contact angle (RCA), as the stage was tilted from 0 to 90°, indicate that the water droplet did not roll off, even at an angle of 90°. Based on the negligible difference in static and dynamic contact angles, the wettability of the surfaces could not be the root cause for the disparity in corrosion resistance.

Figure 6.3 A plot of advancing (ACA) and receding (RCA) contact angles of 5 μL water droplet on Ni/Au and Ni-P/Au contacts as the base was tilted from 0 to 90°.

6.3.3 Sulfur Co-deposition

Elemental sulfur is arguably co-deposited with nickel due to the presence of sulfur in the Ni and Ni-P electrolytic baths [194, 195]. Sulfur has been claimed to reduce the corrosion resistance of electrodeposits because of the activating effect of sulfur [196]. While the electrolytic nickel bath was sulfamate-based, the Ni-P bath was sulfate-based with proprietary complexing agents. Hence the degree of S co-deposition might be different due to the bath used.

Figure 6.4 displays the elemental maps of a Cu/Ni-P electrical contact obtained through electron probe microanalysis (EPMA). The copper substrate was detected at moderate levels. The nickel elemental map reflected the back-scattered electron image (BEI) and lighter elements (carbon) were observed at the edges. The phosphorus elemental map reflected the secondary electron image (SEI) showing that phosphorus was uniformly deposited; the electrons scattered by sulfur were heavily influenced by the overall topography owing to the EPMA technique. Most importantly, no significant sulfur inclusion was detected.

Figure 6.4 Backscattered electron image (BEI), secondary electron image (SEI) and elemental maps of Cu, Ni, P and S obtained from electron probe microanalysis (EPMA) of a Cu/Ni-P electrical contact.

6.3.4 Crystallinity

The crystallinity of nickel alloys has been widely reported to affect the corrosion resistance of materials [78, 85]. The lack of grain boundaries and triple junctions in amorphous alloys enhances the corrosion resistance, when compared to crystalline nickel films [78, 79]. The microstructure of Ni-P transitions from crystalline to amorphous as the P content increases. An intermediate nano-crystalline stage has also been reported [81]. The scientific community remains divided over the accurate ratio of Ni : P, which determines the structural state of the Ni-P deposit; amorphous Ni-P deposits have been obtained at 6 wt.% P by Rofagha [78], at > 8 wt.% by Lo [82], Lewis [83] and Parente [84], at > 9 at.% by McMahon [81], and at >10 wt.% by Krolkowski [85]. Therefore it is pertinent to study the microstructure of the Ni-P electrodeposits in this experiment.

X-ray diffraction (XRD) analyses of Ni and Ni-P alloy films were performed to determine crystallinity. Figure 6.5a depicts the XRD patterns obtained from a Ni/Au electrical contact, with the conventional Bragg-Brentano geometry. Nickel (111) and (200) peaks show a crystalline microstructure for pure Ni films. Peaks due to the Cu substrate were also present due to the penetration of X-rays through the 2 μm thin Ni layer. Figure 6.5b shows the XRD patterns obtained from a Cu/Ni-P/Au electrical contact, with the Bragg-Brentano geometry. The absence of Ni peaks indicated that Ni-P was amorphous. However, the grazing incidence XRD (GIXRD) patterns obtained from Ni-P/Au electrical contacts, as

shown in Figure 6.5c, revealed a broad max with a sharp Ni peak at $2\theta = 44.5^\circ$. This shows that there were both crystalline and amorphous phases within the Ni-P film. This observation is consistent with works by Benje [197] and Crousier [198], where the film was hypothesised to be composed of small nickel crystals supersaturated with phosphorus embedded in an amorphous matrix. However, these nickel crystals result in a very small degree of crystalline region, evidenced by the weak intensity of the Ni peak (due to the $2\ \mu\text{m}$ Ni-P) which was lower than both the Au topcoat and the underlying Cu substrate. In short, the Ni films prepared were crystalline, and the Ni-P films were considered (predominantly) amorphous due to the high content of elemental phosphorus. The impact of the crystal structure on corrosion will be discussed later.

Figure 6.5 XRD patterns of (a) Cu/Ni films obtained through Bragg-Brentano geometry and XRD patterns of Ni-P alloy films obtained through (b) Bragg-Brentano and (c) Grazing incidence (GI) geometries.

6.3.5 Corrosion Product Analysis and Mechanism

6.3.5.1 MFG Corrosion

XPS analysis of the corrosion products was conducted to identify the corrosion products and understand the corrosion mechanism of the copper based contacts under MFG. Figure 6.6a shows the optical image of a corroded electrical contact (a) and the XPS spectra of $\text{Cu}_{2p_{3/2}}$ for the corrosion product formed on Cu/Ni-P/Au electronic contact after exposure to 2-gas MFG for 10 days before (Figure 6.6b) and after sputtering (Figure 6.6c). The sputtering process has been described in the experimental section. The peak located approximately at 934.3 eV, 932.7 eV and 360.0 eV were assigned to CuO [199, 200], Cu_2S [201] and CuSO_4 [202], respectively. Notably, the corrosion products at the surface of bloom were similar to that at surface of the halo.

Figure 6.6 (a) Optical image of a Ni-P/Au electrical contact exposed to MFG and the XPS spectra of $\text{Cu}_{2p_{3/2}}$ of the corrosion product formed at (b) point 1 – before sputtering, (c) point 2 – before sputtering, (c) point 1 – after sputtering and, (c) point 2 – after sputtering.

The major corrosion products at the bloom and halo were Cu_2O , Cu_2S and CuS while the minor corrosion products were CuO and CuSO_4 . It is widely accepted that gases such as H_2S , SO_2 , in the presence of water, react with metals forming sulfides, sulfites, sulfates or even oxides. The oxidation of copper to Cu_2O has been hypothesised and shown to be the first corrosion product to be formed [55-57]. Subsequently, sulfides begin to form faster [108, 203, 204] and usually form a thicker layer of corrosion product than Cu_2O as the former has significantly higher mobility than the latter [115, 205]. This explains the major product of Cu_2S . Hence, the corrosion products on the surface of electrical contacts should be stacked in the following arrangement: $\text{Cu}_2\text{O}/\text{Cu}_2\text{S}$. With time, and in the presence of SO_2 and H_2O , further oxidation to CuO (peak located approximately at 934.5 eV was assigned to CuO) and CuSO_4 can be expected in a 10 day MFG corrosion test, consistent with reported corrosion products in literature [162]. Works by Reid et al. [57] also support this concept of further oxidation as their 1 day class II MFG test performed on copper electrical contacts only formed Cu_2O and Cu_2S . With the inclusion of CuO and CuSO_4 , the corrosion products stacked on the surface of electrical contacts should reflect as such: $\text{Cu}_2\text{O}/\text{Cu}_2\text{S}/\text{CuO}+\text{CuSO}_4$. Within the topmost layer of corrosion, the XPS spectra (Figure 6.6) show that the CuO and CuSO_4 were likely the major and minor corrosion products, respectively.

Nickel corrosion products were in undetectable amounts. This is because once the relatively thin layer (2 μm) of Ni had been compromised, the corrosion of the underlying Cu substrate is accelerated through galvanic coupling with the gold topcoat or passivated Ni layer. Since the Cu substrate is around 20 μm thick, the overwhelming concentrations of copper corrosion products had made that of nickel insignificant.

Herein, based on the corrosion products observation and analysis by the authors of this paper, and references from literature [172, 206] the copper corrosion model and chemical equations for an electrical contact after MFG corrosion test have been discussed from Eq. 6.1 – 6.14.

Formation of Cu_2O :

After the dissolution of the nickel upper coat, the anodic reaction of copper initiates with the dissolution of itself to its ionised state (Eq. 6.1) [172, 207]. This oxidative process is coupled with oxygen reduction, as given in Eq. 6.2. As the potential for Eq. 6.1 is much lower than Eq. 6.2 ($\Delta E^0_{\text{cell}} = +0.89 \text{ V}$), copper continues to corrode until either all the oxygen is depleted or a precipitated copper oxide film inhibits corrosion. The combination of the these reductive and oxidative processes produce Cu_2O , where the copper cations react with moisture to form copper (I) oxide (Eq. 6.3) [208]. The direct path for the formation of Cu_2O may be through the oxidation of $\text{Cu}(0)$ in the presence of oxygen, especially with high temperature [209]. However, the presence of the high humidity within the MFG corrosion chamber should be more influential in generating voluminous corrosion products in alignment to Eq. 6.3.

Formation of Cu_2S :

The scientific community, although united that Cu_2O formation is the primary step, remains divided with regards to the formation mechanism of Cu_2S . Graedel [210] and Reid [8] suggest that Cu_2S originates from Cu . To begin with, Cu_2O layer forms on the surface.

Subsequently Cu_2S form on the Cu_2O layer through the dissolution and migration of ionic species through the Cu_2O layer (likely via the grain boundaries of Cu_2O). This mechanism, reflected in Eq. 6.4, might only be dominant in the very initial stages where Cu_2O layer on Cu is thin. As the thickness of Cu_2O increases, it is conceivable that, the direct sulfidation of Cu_2O would be preferred to the sulfidation of migrated copper.

A more probable reaction (Eq. 6.5) was proposed by Yang et al. [211]. They claimed that Cu_2S directly originates from Cu_2O . First the oxygen adsorbed on the surface of Cu_2S is reduced, producing electron holes and Cu^+ vacancies. The electron holes and Cu^+ vacancies migrate by diffusion through the Cu_2S and Cu_2O layers and get annihilated at the Cu/ Cu_2O interface. The Cu_2O species formed at the top is subsequently converted to Cu_2S through the reaction with H_2S . A similar mechanism resonating with Yang's has also been proposed by Smith et al. [212]. Interestingly, these reactions appear as the half-cell reactions of Yang's overall reaction. Smith suggests that an intermediate Cu (0) state reacts with the ionized species of H_2S to form Cu_2S (Eq. 6.6 – 6.7).

More recently, Kristiansen et al. [213] has proposed that Cu_2S forms from CuO . The authors suggested that the Cu^+ ions formed through the comproportionation reaction between the Cu^{2+} ions (from the CuO layer) and the $\text{Cu}(0)$ atoms (from the Cu underlayer), as stated in Eq. 6.8. Subsequently Cu^+ ions react with the ionised species of H_2S to form Cu_2S , as stated in Eq. 6.9. However, Eq. 6.8 – 6.9 are less probable to occur as these require the formation of Cu^{2+} and the migration of Cu^+ ions through the corrosion product film; when the Cu^+ generated through Eq. 6.8, may revert to Cu_2O instead of forming Cu_2S . Hence, the more probable pathway for the formation of Cu_2O might be through Eq. 6.5 or Eq. 6.6 – 6.7.

Formation of CuO :

CuO may result from Cu₂O as shown in Eq. 6.10. The cathodic reaction can again be the reduction of oxygen in the environment (Eq. 6.2) [214, 215]. Although the overall reaction (Eq. 6.11) appears as a direct reaction with oxygen, the half-cell reaction shows the need for acidic and humid environment.

Formation of cupric sulfate:

The formation of CuSO₄ is believed to be due to the presence of SO₂. Water adsorbs onto metal or metal-oxide surfaces forming a thin layer of water film, even under non-condensing atmospheric conditions. The thickness of the water film primarily depends on the relative humidity (RH) and the nature of substrate's surface. At 20 % RH, it is expected that around one monolayer of water form on a metal surface [216]. In the case of MFG the typical RH is at 75 %, at which the thickness is increased to about five monolayers [216]. This layer thickness at time can be non-uniform as often water layers cluster, resulting in increased localized thickness. SO₂ dissolves into this water films, forming sulfurous acid (H₂SO₃) as shown in Eq. 6.12 [217]. Subsequently, the oxidation of sulfurous acid in air results in sulfuric acid (Eq. 6.13) [217]. The reaction between sulfuric acid and the CuO film forms cupric sulfate (Eq. 6.14).

6.3.5.2 NSS corrosion

The elements in the corrosion products matched those reported in our previous work [43]. The green corrosion products covered regions with heavy pitting while the brown stains were linked to less serious pitting [43]. The brown corrosion products were observed below the green corrosion product, therefore former were deemed to be the produced before the later. These observation were well aligned with the XPS analysis.

Figure 6.7a shows an optical image of the brown corrosion product on the surface on an electrical contact. XPS analysis performed on the corroded sample, as shown in Figure 6.7b, revealed peaks (fitted) at 935.8 eV, 933.9 eV and 932.4 eV. The peak located approximately at 933.9 eV was assigned to major product: CuO [199]. Peak at 932.4 eV was assigned to Cu₂O [199]. The peak at 935.8 eV was characteristic of Cu²⁺ (in Cl-Cu-Cl bonds present in CuCl₂) and the OH-Cu-OH bonds in Cu(OH)₂. These characteristic peaks indicate a mixed Cu²⁺ bonding structure which is consistent with Cu₂(OH)₃Cl [218]. After sputtering to remove the top layers of the brown corrosion product, Cu₂O was revealed as the major product (Figure 6.7c). This meant that the brown corrosion product consisted on a thick base of Cu₂O which was covered by a film of CuO (major) and Cu₂(OH)₃Cl (minor).

Figure 6.7 XPS (Cu₂p_{3/2}) spectra of the brown corrosion product formed corrosion on a Ni-P/Au electrical contact exposed to NSS (a) before and (b) after Ar sputtering.

Similar analyses were done to understand the components of the green corrosion product. XPS analysis of the green corrosion product, as shown in Figure 6.8a, revealed Cu₂(OH)₃Cl (major) and Cu₂O (minor). After sputtering to remove the top layers of the green corrosion product, the major product was revealed to be Cu₂O (Figure 6.8b). This indicates that the

green corrosion product consists of a base of Cu_2O , covered by a film of $\text{Cu}_2(\text{OH})_3\text{Cl}$. Nickel corrosion products were undetectable due to the aforementioned reasons.

Figure 6.8 XPS ($\text{Cu}2p_{3/2}$) spectra of the green corrosion product formed corrosion on a Ni-P/Au electrical contact exposed to NSS (a) before and (b) after Ar sputtering.

Herein, based on the corrosion products observed and analysis by the authors of this paper, and references from literature [151, 207, 219-223] the copper corrosion model and chemical equations for an electrical contact after NSS corrosion test are proposed, as shown in Figure 6.9.

Initially the nickel layer is compromised as the porous gold layer acts as the cathode and nickel as the anode. When corrosion reaches the copper underlayer, the copper begins to corrode (Eq. 6.15), coupled with the reduction of water (Eq. 6.16). The formation of CuCl_2^- can occur through three different proposed mechanisms which has been critically reviewed by Kear et al. [224]; hence it shall not be discussed here. The authors of this report have adopted the widely accepted two step mechanism (Eq. 6.17 – 6.18). Copper ions react with the abundant chloride species and form CuCl and subsequently CuCl_2^- . CuCl_2^- migrates

along the insides of the pit and reach the ‘mouth’ of the pit and reacts with water forming Cu_2O (Eq. 6.19). With time, Cu_2O further reacts with water to form CuO (Eq. 6.20) and with water and chloride ions to form $\text{Cu}_2(\text{OH})_3\text{Cl}$ (Eq. 6.21). The detailed chemical equations of processes mentioned above are given in Eq. 6.15 – 6.21.

Figure 6.9 Simplified model of copper corrosion in an electrical contact after NSS test.

Oxidation of copper at the anode:

Cathodic reaction:

Reaction to form cuprous chloride:

Formation of cuprous dichloride anion:

Formation of cuprous oxide:

Formation of cupric oxide:

Formation of dicopper chloride trihydroxide:

6.3.6 Cause of Disparity

Various properties of Ni and Ni-P electrodeposits were measured and compared; however only the crystallinity of the deposits varied significantly. Moving from a perspective of overall corrosion to one that focuses on the location of corrosion products was needed to understand the disparity in corrosion resistance.

Upon closer scrutiny of samples after NSS and MFG, corrosion products were seen at the edges (edge corrosion, [225]) for Ni-P/Au stacks but at random locations (surface and edge) for Ni/Au stacks. To further investigate, the locations of pits were studied under SEM. The edge is termed as the region of metal contact which meets the epoxy glass tape carrier. The surface is termed as the region away from the edge, closer to the middle of a pin-out pad. As the definitions of the edge and surface have been well-described in Chapter 5 [167], it shall not be further described here.

The size and number of pits at the surface and edges of Ni/Au and Ni-P/Au electrical contacts, after exposure to NSS or MFG environments, were counted. The results are shown in Figure 6.10. The x-axis indicates the size of pit and the y-axis indicates the arbitrary number given to each pit. For example, in Figure 6.10a each symbol represents a pit and its corresponding pit area; as such the total number of surface pits was around 40. Figure 6.10a depicts the pits on a Ni/Au electrical contact after exposure in NSS environment. A total of 45 pits were observed on the surface and 8 pits at the edges; the largest pits at the surface and edge were approximately 79 and 61 μm^2 , respectively. As the area of the surface was much larger than that of the edges, the pitting at the surface is proportionally higher. Figure 6.10b portrays the pits on a Ni-P/Au electrical contact after exposure in NSS environment. Only one pit was observed on the surface and 53 pits at the edges; the largest pits at the surface and edge were approximately 2 and 2755 μm^2 , respectively. In short, the disparity becomes apparent as the both number of pits and area of pits were higher at the edges for Ni-P based stacks.

The pits analysis of Ni/Au and Ni-P/Au electrical contacts after MFG test led to similar deductions as mentioned above. Countless small pits (>2000) were observed on the surface of the Ni/Au contact (Figure 6.10c). At the edge, only 17 pits were observed. Figure 6.10d portrays the pits on a Ni-P/Au electrical contact after exposure in MFG environment. Fifteen pits were observed on the surface and 87 pits at the edges; the largest pits at the surface and edge were approximately 62 and 344 μm^2 , respectively.

Therefore, *edge corrosion* [225] was overwhelmingly dominant in the Ni-P/Au stack; the ratio of area of pits at the edge to surface was approximately 700:1 after NSS test and 32:1 after MFG test. Edge corrosion has been defined corrosion of metals at the edges of traces which result in exposing the base materials [225]. In contrast, pitting at the surface was dominant for the Ni/Au stack; the ratio of area at the edge to surface pit area was approximately 1:3 after NSS test and 1: 6 after MFG test. In short, Ni-P (compared to pure Ni) displayed weaker and stronger corrosion resistance at the edges and surface, respectively. An explanation for this observation is proposed.

With Ni-P electrodeposition, low current efficiency, and in turn an overvoltage [226, 227]), was observed, which was consistent with literature [228]. The overvoltage is higher at the edge of the pads as current tends to concentrate at edges and points [229, 230]. The higher overvoltage at the edges causes extensive gas evolution, mostly hydrogen discharge. This results in deposits with higher defects i.e. porosity, forming at the edges of the module in alloy electrodeposits. This was termed as *edge porosity*. Edge porosity reduces the corrosion resistance of Ni-P at the edges. Therefore, Ni-P was repeatedly seen to be corroded at the edges, both in MFG and NSS. To prove this explanation experimentally, Ni-P based stacked were prepared with different current densities. The thickness of Ni-P and the Au topcoat was kept constant at 2 μm and 0.05 μm , respectively. As the effects of edge porosity are apparent after NSS, these samples were exposed to 96 h NSS test and optical images of the sample after the test are shown in Figure 6.11. As expected, with increasing current density, the corrosion along the edges increased. In comparison, the superior corrosion resistance of Ni-P at the surface was credited to its amorphous microstructure.

Figure 6.10 Plots showing the comparison of pits against their corresponding size, that occur at the edges and surfaces of (a) Ni/Au stacks after exposure to NSS, (b) Ni-P/Au stacks after exposure to NSS, (c) Ni/Au stacks after exposure to MFG, (b) Ni-P/Au stacks after exposure to MFG.

The effects of edge porosity are magnified by *corrosion product migration*. The corrosion products which originate from an edge pit, ‘flow’ through the channels between pin-out pads. This magnifies the perceived degree of corrosion. In contrast, MFG corrosion residues do not ‘flow’ through the channel but solely creep over the metal surface (described as the halo). This magnifies the perceived degree of corrosion. Corrosion

product migration also explains the limitation of spectrophotometric techniques used to quantify corrosion (particularly to MFG corrosion) on electrical contacts [167]. Colour measurements detect the spectrophotometric changes that are perpendicular to the corroding surface. As MFG corrosion residues do not ‘flow’ through the channels between the pin-out pads, spectrophotometric measurements cannot measure the colour change (and in turn the corrosion) at the edges.

Figure 6.11 Optical images of Ni-P/Au electrical contacts, which were electrodeposited at (a) 100 A/m² (b) 400 A/m² (c) 800 A/m², exposed to 96 h NSS test.

In contrast to Ni-P, pure Ni forms denser (relative to Ni-P) deposits at the edges, due to the absence of high overvoltage. Therefore the quality of deposits at the surface and edge are almost similar. Hence, the likelihood of corrosion at the edges is similar to that at the surface. The crystalline nature of pure Ni (as opposed to amorphous Ni-P) presents line (dislocation), planar (grain boundaries & stacking faults) and bulk (voids) defects. These defects expose pure Ni to pitting corrosion randomly across surface and edge. It can be seen that Ni/Au contacts display pitting corrosion in both NSS and MFG. In NSS, shallow pits were generated. After the MFG test, countless pits were generated in MFG test, but in this instance due to the more aggressive environment of MFG (lower pH) and length of exposure (10 d in MFG c.f. 4 d in NSS), these pits appeared deeper.

In summary, corrosion resistance of Ni-P electrodeposits (to both NSS and MFG) can be improved by employing very low current densities. However this method has its own disadvantages as low current densities result in low deposition rates which will inhibit industrial adoption.

6.4 Summary

Corrosion resistance of Ni/Au and Ni-P/Au stacks were assessed using neutral salt spray (NSS) and acidic mixed flowing gas (MFG) tests. As each stack emerged superior in only one test, the cause of such phenomenon was studied. Factors that could influence corrosion resistance, such as internal stress, surface wettability and sulfur co-deposition were examined. However, none of these factors could explain for the disparity in corrosion performance.

Ni-P has been repeatedly claimed to be more corrosion resistant than pure Ni. The enhanced corrosion resistance for Ni-P lies in its amorphous microstructure; its homogeneity and absence of dislocations and grain boundaries are advantageous over pure Ni. Crystalline pure nickels have defects such as grain boundaries and dislocations that serve as preferred corrosion paths. However, from our observations heavy corrosion was seen with Ni-P after NSS test. We have proposed the edge porosity and corrosion product migration concepts to rationalise this phenomenon.

Ni-P (compared to pure Ni) shows weaker and stronger corrosion resistance at the edges and surface, respectively. The weaker corrosion resistance at the edge due to porous deposits (edge porosity) and stronger corrosion resistance at the surface credit to its amorphous structure. Ni (compared to Ni-P) shows similar corrosion resistance in MFG and NSS at both surface and edge, due to its uniform crystalline microstructure. This coupled with the non-migratory nature of the MFG corrosion products (corrosion product migration) resulted in the overall disparity in corrosion.

Chapter 7

Conclusion on the impact, limitations, and recommendation for future work

This chapter concludes the thesis by discussing the extent to which the engineering target was achieved. Key achievements include a more detailed understanding on the effects of various plating parameters on corrosion protection of industrially practiced Ni/Ni-P/Au stacks. Increasing the thickness of Ni consistently improves the corrosion resistance in both neutral NSS and MFG corrosion tests. However, the influence of Ni thickness on corrosion is overshadowed by the Ni-P thickness. Increasing the thickness of Ni-P deposits results in higher corrosion in the NSS environment and decreased corrosion under the MFG environment. The results (from Chapter 4) point towards a disparity that Ni-P may not be suitable for corrosion protection in environments with heavy chlorine concentration but appropriate for sulfur-containing corrosion media. However, subsequent in-depth studies (discussed in Chapter 6) reveal that the early findings regarding the disparity in corrosion resistance of Ni-P in MFG and NSS was due to the high edge porosity caused by fast plating. It also highlights the implications and limitation of the work. It suggests opportunities, such as reduction of edge porosity passivation of Ni underlayer, hydrophobic coatings and new plating systems, and associated challenges that might be useful for future work.

7.1 Discussions

7.1.1 Achievements

This study focused on nickel and nickel phosphorus electrodeposits as barrier coatings to enhance the corrosion resistance of electrical contacts.

First Ni/Ni-P/Au stacks were studied as they were presently used in the industries. Although the processing parameters (such as current density) were linked to the some properties (such as thickness and P content) of the film, the effect of these parameters and properties were not related to corrosion resistance. This study served as a systematic study to bridge this knowledge gap. The corrosion resistance of the Ni/Ni-P plating metallurgy was studied as a function of current density and electrodeposit thickness. Among other revelations, the discrepancy between NSS and MFG corrosion test results was a novel discovery. Increasing the thickness of Ni-P electrodeposits increased corrosion in NSS tests but increasing the thickness of these deposits decreased corrosion in MFG test.

Breaking away from the traditional Ni/Ni-P stack arrangement, other arrangements were explored. The corrosion performance of single layer stacked and multi-layered stacks were studied. Ni/Au (*NA*), Ni-P/Ni/Au, was studied. The pits formed due to the MFG tests were explained using a proposed novel dominant pit concept. Among other findings, single layered stacks (*NA* and *PA*) showed relatively better corrosion performance in the NSS and MFG tests, respectively. The pitting in multi-layered stacks, and as a consequence their lower corrosion resistance, was explained through galvanic coupling.

Most importantly, the last study was designed to study the similar disparity that was observed in the first two parts of the thesis. When the corrosion resistance of Ni/Au and Ni-P/Au stacks was assessed using NSS and MFG, each stack emerged superior to the other in one test. This observation was hypothesized to be due to the properties of the electrodeposits. Hence, properties such as internal stress, surface wettability, sulfur co-deposition and structural state. However, except for the structural state, other properties showed no difference. Ni was crystalline and Ni-P was predominantly amorphous. These

did impact the corrosion resistance of the electrodeposits whereby Ni-P electrodeposits, compared to Ni electrodeposits, showed excellent corrosion resistance, but solely at the surface. This excellent corrosion resistance was due to the amorphous microstructure of Ni-P which is free from defects such as grain boundaries and dislocations that serve as preferred corrosion pathways. However the disparity in corrosion resistance exists due to the weak resistance of Ni-P to corrosion at the edges. This was explained with novel concepts such as edge porosity and was experimentally proven. In addition, the perceived corrosion was larger with NSS due to the migratory nature of the NSS corrosion product, as compared to the MFG corrosion product.

7.1.2 Implications and Limitations

This research has shown the research community the downfalls of using the popular pits counting method as a means of corrosion quantification techniques. As shown in Chapter 6, pits counting might be misleading in many cases, as the total numbers of pits do not truly reflect the severity of corrosion. Figure 7.1 shows a pictorial representation of pits on an electrical contact surface. Under pits counting technique the total numbers of pits are normalized over the total surface area of an electrical contact. Based on this technique, both Figure 7.1a and Figure 7.1b show a single pit hence suggesting similar corrosion resistance. Fundamentally, the size of the pit varies and so should the corrosion performance. The ideal method would be to count the volume of the pits; however, this may not be practical. Three-dimensional X-ray mapping of the surface pits may be useful for this purpose, but can be time-intensive to map large surfaces.

In addition, this research has shown that pits counting at the edges are clearly not sufficient. The edges cannot be discounted. Although proportionate corrosion at the edges to the surface could be seen for Ni/Au stacks, corrosion was disproportionately higher for Ni-P/Au stacks. Hence, the assumption that the edges and surfaces corrode proportionately can result in erroneous conclusions.

Figure 7.1 Pictorial representation of pits depicting the limitation of pits counting.

The quantification technique, i.e. spectrophotometry, adopted in Chapter 5 and Chapter 6 has its limitations. The migratory nature of corrosion products produced at the edges in the NSS test, flow through the channels between pinouts. The amount of corrosion is worsened with materials such as Ni-P which may have high edge defects. This can be picked up by the spectrophotometer. However, the corrosion products that form in MFG do not flow through the channels between the pinouts hence cannot be picked up by the spectrophotometer. Hence, the intense corrosion, or the lack of it, cannot be measured accurately by a spectrophotometer. However, the spectrophotometer still serves as a quick guide to quantify the corrosion which cannot be done visually. This research has shown that the results obtained by the spectrophotometer follow the same trend that was reached when samples were rated visually. Hence, it can be stated that the use of the spectrophotometer might be useful to quantify *cosmetic corrosion*.

Another limitation exists whereby the corrosion resistance of the electrical contacts could only be optimised or improved for one test, but not both MFG and NSS. Results from Chapter 6 show that Ni-P/Au stacks display lower corrosion resistance in NSS (compared to Ni/Au stacks) due to its high edge porosity. In contrast Ni/Au stacks display lower corrosion resistance in MFG (compared to Ni-P/Au stacks) due to its intrinsically lower corrosion resistance. This exists as an engineering problem which will be discussed further in the later section under future work.

7.1.3 Opportunities for Future Work

There is much scope for studies in the topic of corrosion (and especially corrosion of electrical contacts), albeit much progress has been made by current literature.

First the opportunity lies closest to the content of the thesis. As mentioned in the earlier Section 7.1.2, stacks that display better corrosion resistance to both MFG and NSS need to be formulated. The corrosion resistance exhibited by these new stacks need to be better than that of Ni/Au and Ni-P/Au stacks. One direct method to achieve this goal may be by reducing the defects at the edges in the Ni-P layer. This can be realised by employing very low current densities where hydrogen gas evolution would be suppressed. However a low current density has its disadvantage, as it implies slower deposition rate which discourages industries to adopt this method.

Another method of enhancing the corrosion resistance of Cu/Ni/Au electrical contacts may be through passivation of nickel layer. Presently, high cost of gold has led to thinner and porous gold layers, which expose the nickel underlayer to the corrosive environment. This leads to pitting corrosion. Therefore by intentionally thickening the passive layer of the Ni underlayer, the corrosion rate of Ni can theoretically be retarded. However this method may have its limitation as the passive layer cannot be indefinitely increased, as it should plateau at some point.

A quick method to enhance the corrosion resistance of these electrical contacts may stem from hydrophobic coatings. Much work has been done of hydrophobic coatings [149, 193, 231, 232] for anti-corrosion applications. These may be applied to electrical contacts but with some limitations. The hydrophobic contacts should be transparent, and surface-selective if conductive or extremely thin if non-conductive. This is because individual pinouts must be electrically disconnected and the coatings should not drastically increase the contact at the pinouts.

New plating systems can be introduced as barrier layers for electrical contacts as such initiatives are lacking within the industry. This reluctance to explore new systems might result from large scale production challenges that some newer baths pose. For example, electrodeposits like Ni-Al₂O₃ [31], Ni-SiO₂ [37], Ni-SiC [40-42] and Ni-TiO₂ [233] have been shown to possess good corrosion resistance properties. However these baths typically suspend micro and nano particles in a Watts or sulfamate baths, and this poses a problem of electrolyte homogeneity. In large plating cells, particles tend to accumulate at low agitation areas and the electrolyte lacks homogeneity leading to uneven deposition. Moreover, filters placed to remove sludge (due to the decomposition and by-product formation in the electrolytic bath) may filter out micro particles or aggregated nanoparticles. Therefore, plating systems without such limitations could be viable for exploration.

Lastly, as mentioned in the Chapter 2, the mechanism of P co-deposition needs more research involving a deeper scrutiny into the direct and indirect mechanisms. Although many lean towards the indirect mechanism, indications are present that the direct mechanism cannot be ruled out.

7.2 Conclusion

Reliability of a smart card can be defined as the likelihood that the device retains functional performance for a given time period under certain operating condition without failure. The electrical contacts of smart cards are important parts of the device as these contacts are exposed to the environment. Hence corrosion of these contacts become pertinent and this thesis has focused on electrical contacts that employ nickel based barrier layers.

Presently Ni/Ni-P/Au stacks are being employed for corrosion resistance against NSS and MFG corrosion test but these stacks have not been studied in detail. The performance of such stacks under MFG and NSS tests has not been well established. The engineering challenge was to derive at improved stacks within the boundaries of allowable change via

a detail study to understand the science behind the corrosion behaviour of such electrical contacts.

Key achievements include a more detailed understanding into the effects of various plating parameters on corrosion protection of industrially practiced Ni/Ni-P/Au stacks. Increasing the thickness of Ni consistently improved the corrosion resistance in both neutral NSS and MFG corrosion tests. However, the influence of Ni thickness on corrosion was overshadowed by the Ni-P thickness. Increasing the thickness of Ni-P deposits resulted in higher corrosion in the NSS environment and decreased corrosion under the MFG environment. The results (from Chapter 4) point towards a disparity that Ni-P may not be suitable for corrosion protection in environments with heavy chlorine concentration but appropriate for sulfur-containing corrosion media. However, subsequent in-depth studies (discussed in Chapter 7) reveal that the early findings regarding the disparity in corrosion resistance of Ni-P in MFG and NSS was due to the high *edge porosity* caused by fast plating.

Varying the electrodeposition parameters of Ni/Ni-P stacks shed important information but served as a limited solution to fulfil the engineering challenge. Hence, different single, bi- and tri-layered stacks of Ni and Ni-P were studied. Different stacks such as Ni/Au (*NA*), Ni-P/Ni/Au (*PNA*), Ni-P/Au (*PA*), Ni/Ni-P/Au (*NPA*) and Ni-P/Ni/Ni-P/Au (*PNPA*) stacks were examined. Results showed that multi-layer stacks, such as *PNA*, *NPA*, *PNPA*, displayed worse corrosion protection than single-layered stacks (*NA*, *PA*). Removing Ni and Ni-P interfaces was effective in inhibiting corrosion in NSS and MFG environments as Ni/Ni-P interfaces accelerate corrosion due to galvanic coupling. Corrosion pits propagated horizontally and vertically through Ni and Ni-P films, depending on the arrangement of Ni and Ni-P within a stack. Tunnelling corrosion through Ni-P turned distinct with a reduction in Ni-P thickness. This was attributed to possibly higher percentages of discontinuities (i.e. porosity) with decreasing thickness. The reducing thickness coupled with the galvanic coupling between Ni and Ni-P layers further worsened the corrosion in stacks such as Ni-P/Ni/Ni-P/Au.

The disparity in corrosion resistance of Ni and Ni-P barrier layers under NSS and MFG corrosion tests was a recurring observation in Chapters 4 and 5. When corrosion resistance of Ni/Au and Ni-P/Au stacks was assessed using NSS and MFG corrosion tests, each stack emerged superior in only one test. To explain this disparity, factors that could influence corrosion resistance were examined first, namely: internal stress, surface wettability and sulfur co-deposition. None of these factors could explain for the disparity in corrosion performance. Corrosion product analysis was then performed to understand the corrosion product formation due to NSS and MFG. Detailed pits analysis revealed that the disparity was caused by the porosity and corrosion product migration. These concepts were supported by purposely designed experiments.

This thesis offers some engineering solutions to improve the corrosion resistance of electronic contacts under the MFG and NSS corrosion tests. Optimisation of various parameters to generate the current stacking arrangement (i.e. Ni/Ni-P/Au) offer important but limited solution to enhance corrosion protection as individuals layers behave differently when coupled. Different stacking arrangements studied in this thesis show that single-layered stacks such as Ni/Au or Ni-P/Au offer better corrosion protection. The failure of bi-layered and tri-layered stacks does not necessarily stem from the design of such stacks but stem from the industrial practice to layer very thin coatings (such as Ni-P at 500 nm) on Ni under-layers. The increased defects in such thin Ni-P coatings accelerate galvanic corrosion due to difference in corrosion potentials and the small-anode-large-cathode phenomenon. The study on single layered stacks points to the most important aspect of this thesis. Ni-P as a single barrier layer deposited at lower current densities (≤ 1 ASD) and at higher thicknesses (≥ 2 μm) can improve overall pitting corrosion resistance in both NSS and MFG corrosion tests.

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