ABSTRAK

Nikel aloi tanpa elektrik mempunyai banyak kelebihan khususnya dalam pelbagai bidang seperti industri kimia dan elektronik iaitu melalui pengurangan tindakbalas *Redox* dan pengoksidaan. Kajian ini ialah untuk mengkaji kesan daripada proses penyepuhlindapan pada ketiga-tiga aloi nikel tanpa elektrik. Penambahan bahan *Hypophosphite* digunakan untuk mengurangkan ejen dan menghasilkan Ni-P aloi. Dengan menambah elemen ketiga, iaitu Co, W dan Cu dalam proses penyaduran tanpa elektrik pada Ni-P akan menghasilkan Ni-Co-P, Ni-Cu-P dan Ni-W-P. Mikrostruktur aloi nikel tanpa elektrik akan berubah disebabkan oleh proses penyepuhlindapan, sekaligus memberi kesan kepada sifat-sifat mekanikal dan hakisan. Walau bagaimanapun, kesan penyepuhlindapan pada pelbagai komposisi masih kurang diketahui. Oleh itu, objektif daripada kajian ini ialah untuk mengkaji kesan penyepuhlindapan pada gabungan ketiga-tiga element salutan mikrostruktur dan kekerasan rintangan Corr. Sampel dikenanakn sepuhlindap menggunakan relau *Chemical Vapour Deposition* (CVD) dengan parameter yang diberikan. Sampel kemudiannya dianalisis melalui X-ray pendarfluor (XRF) iaitu untuk mengetahui tindak balas pada komposisi kakisan iaitu melalui polarisasi pengukuran lengkung dalam 3.5wt% dalam larutan NaCl. Ketahanan kakisan dalam larutan air garam aloi Ni tanpa elektrik berkurangkan selepas proses penyepuhlindapan. Walau bagaimanapun, kekerasan lapisan atom bertambah selepas rawatan haba kerana ia berhijrah dalam kekisi hablur dan bilangan kehelan berkurang. Kemudian, permukaan sampel yang diperhatikan menggunakan SEM. Suhu penyepuhlindapan adalah 350°C. Dengan meningkatnya suhu penyepuhlindapan, sifat-sifat pemendapan seperti saiz butiran mula bertmbah dan rintangan kakisan mula berkurangan.

ABSTRACT

Electroless nickel alloy deposition gain special interest in various fields such as chemical and electronic industries using only reduction Redox reaction and oxidation. This study is about the effects of an annealing process on ternary electroless nickel alloy. Electroless nickel deposition using hypophosphite as reducing an agent produces a binary Ni-P alloy. Furthermore, the addition of copper or tungsten in electroless plating bath will produce ternary alloy of Ni-Co-P, Ni-Cu-P and Ni-W-P respectively. The microstructure of the electroless nickel alloy will change due to annealing process, hence, affecting the mechanical and corrosion properties. However, the effect of annealing on various compositions of is still less known. In this study, the objective is to investigate the effect of annealing on various electroless ternary nickel alloy coating microstructure and hardness Corr resistance. The samples are annealed using the vacuum furnace Chemical Vapour Deposition (CVD) with a given parameter. The samples are then analyse via X-ray fluorescent (XRF) measurement to know the composition corrosion behavior is studied using polarization curve measurement in 3.5wt% in NaCl solution. Corrosion resistance in salt water solution of electroless Ni alloy reduces after annealing. However, the hardness of the coating increases after the heat treatment atoms because it migrate in the crystal lattice and the number of dislocations decreases. Next, the sample surface observed by SEM. The annealing temperature is 350˚C. With increasing annealing temperature, the properties of the deposition like grain size begin to grow, and corrosion resistance may reduce.

DEDICATION

To my beloved parents, friends and supporters.

ACKNOWLEDGEMENT

First of all, in a humble way I wish to give all the Praise to Allah, the Almighty God for with His mercy has given me the strength and time to complete this report.

I am deeply indebted to Dr. Muhammad Zaimi Bin ZainalAbidin, my supervisor, for her patience, supervision, encouragement and thoughtful guidance towards the completion of this report.

I am particularly grateful to Department of Material Engineering, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM) for financial support.

Lastly, I would like to acknowledge my family and my friends whose patient love enabled me to complete this report. Thank you.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

PVD	=	Physical Vapour Deposition
CVD	=	Chemical Vapour Deposition
W	=	Tungsten
Cu	=	Copper
Co	=	Cobalt
P	=	Phosphorus
Ni	=	Nickel
SEM	=	Scanning Electron Microscope
EDX	=	Energy Disperse X-ray Spectroscopy
XRD	=	X-ray diffraction
ECM	=	Electrochemical behaviour
d	=	Density
A	=	Sample area
EW	=	Equivalent weight
E_{corr}	=	Current potential
I_{corr}	=	Corrosion current density
Mpy	=	mils penetration per year
HCL	=	diluted hydrochloric acid
rpm	=	Rate per minute
ASTM	=	American Society for Testing and Materials
Sn	=	Tin
Fe	=	Ferum
Zn	=	Zinc
Ni^{2+}	=	Nickel ions
H^2	=	Hydrogen ions
$H_2PO_2^-$	=	Hypophosphite ions

CHAPTER 1

INTRODUCTION

1.1 Background study

Commonly, steel is widely used in a variety sector because of its high tensile strength and long lasting material. However, disadvantage of using this material is easy to form rust especially under moist condition. Coating is applied due to the application of high performance and unique properties especially in surface quality.

Surface protections are process of applying special coating that is a need to suitable for design and synthesis of advanced materials. Coating process can divide into two categories that are dry and wet process. There is a variety of process to produce coatings such as Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), electrodeposition and electroless deposition. Generally, dry process is expensive technique compared to wet process because there used additional equipment to coat the sample.

Suitable method introduced by Brenner and Riddell, 1946 chosen which electroless plating process is typically classified as a simple technique because no electric current

applied. Chemical reducing agent is used in this method by mix in order to reduce metallic ion.

Previous research has shown that electroless nickel is a suitable technique of coating which able to protect the surface and wear resistance Prasanta and Suman (2010). Compare to electroplating method, the advantage of electroless deposition is due to quality of the deposit which included for both physical and mechanical properties. Many difference examples can found in the works of electroless and electroplating. For example, electroless technique will coat more uniform in thickness compared to electroplating method. Ni-P alloys have higher corrosion resistance. It is because of its unique properties in ductility, lubricious and relatively brittle.

Electroless of the ternary alloy exhibit better performance than the binary. For example is by adding tungsten (W) into Ni-P will improve the deposit properties which are including of thermal stability, electrical resistance, and corrosion resistance. Supported by Ijeri, Bane, Shah, & Goradia (2014), the improvement of Ni-P properties can increase by adding a third element. In this ternary process, there have some changing in P grain size. It is because by adding P content will decrease and allows corrosion resistance to increase. Same goes when adding copper (Cu) to Ni-P. Based on the previous study by Abouchane *et. al.*(2010), there have improvement in corrosion resistance when adding Cu. Result from analysis by Xiaozhow (2010) show that strength of Co coating that applies to steel gear in increased.

Generally, the hardness and corrosion resistance of electroless nickel plating is improved by using heat treatment. This occurs because heat treatment produces finer microstructure and reduces the porosity of the coating. According to Ashassi-Sorkhabi, H. *et al*.(2004), the corrosion resistance of electroless Ni-P increase after being heat treated at the annealing temperature of 400˚C. Thus, it proved that the corrosion resistance of nickel plating increase after being heat treated. According to Sharma, A. K. *et at.,* (1999) the heat

treatment associated with structural transformation, precipitation and size of nickel phosphide particle which indicate that the hardness of Ni-P increase after being heat treated. But, the hardness of the coating is decrease after reach maximum annealing temperature. Previous study by Balaraju J. N. *et al*.,(2005) shows that the hardness of Ni-Cu-P increase as the annealing temperature increase from 200˚C to 400˚C and decrease at the temperature above 400˚C. The hardness of Ni-Cu-P decrease due to the grain size of plating become coarse after reach a maximum annealing temperature. The effect of annealing temperature on selected electroless ternary on its corrosion resistance and hardness is yet to be studied.

This study is the focus on the correlation between properties of Ni-W-P, Ni-Cu-P and Ni-Co-p when applying annealing treatment in a furnace. Annealing is referring to heat treatment where properties of the microstructure are changed at a particular time then slowly cooled. However, Ni-P alloy mostly in an amorphous phase and this is the main reason they easily crystallize when heated. In some cases, this condition able to increase mechanical behavior coating but create low corrosion resistance.

Annealing can affect corrosion behavior due to phase transformation of the alloy. In annealing, compound layers are produced during soldering. Ternary samples were applied until from 350˚C to obtain changing corrosion and changing microstructure. The correlation between corrosion and microstructure of the coating discussed.

1.2 Problem statement

The introduction of the selected third elements may improve the corrosion resistance of Ni-P alloy. The ternary electroless exhibit better characteristic such as in corrosion resistance, magnetic properties and thermal stability than the binary. Applying heat treatment able to change the hardness of the deposited because based on Sudagar, Lian, & Sha (2013), by applying annealing at 200˚C until 500˚C able to increase the hardness while decrease corrosion resistance of Ni-P. The analysis of the hardness can refer from size of grain structure of microstructure. The annealing parameter and temperature for ternary nickel alloy of Ni-Co-P and Ni-W-P are less known to ensure optimum hardness and corrosion resistance in NaCl solution. The effect of the annealing on the microstructure of the electroless nickel ternary alloy at various composition need to be investigated.

Another problem faced in this study is hard to control the composition of electroless ternary Ni alloy in 3.5wt % NaCl solution. Effect of the corrosion behavior of various annealed of ternary need to studied and compared because size of the microstructure becomes more complicated. According to Zhao, Zou, Zhang, & Zou (2014), Ni-P alloys of electroless plating show that different cluster size of microstructures is because of changing temperature when the annealed process. It proved when the temperature is high, and it will create new crystalline from the coating and grain size may also increase.

1.3 Objective

This research was aimed to study the effect of ternary alloy when applied to substrate composition. This research is carried out under certain objectives as follows:

a) To investigate the effect of annealing temperature on various electroless ternary nickel alloy coating microstructure and hardness.
b) To study the effect of various annealed electroless ternary nickel alloy corrosion behavior in 3.5 wt% NaCl solution.

1.4 Scope

The ternary alloy of Ni-Cu-P, Ni-W-P and Ni-Co-P are deposit on low carbon steel substrate at various plating bath condition. The coating is then undergo heat treatment process with temperature of 350°C. The effect of annealing temperature on the ternary nickel alloy microstructure is studied using SEM and XRF. Furthermore, the hardness and corrosion behavior of ternary nickel alloy is studied using micro Vickers hardness and electrochemical measurement method respectively.

CHAPTER 2

LITERATURE REVIEW

This part gives by and large review concerning the theory and information based on previous research. The source of research focused on books, journals, articles, case study, theory and electronic media. Ultimately, the element will be narrow down and based on the analysis, measurement methods for further processing determined.

2.1 Introduction to coating

Nowadays, almost of entire metal product are applying coating technology. It is due to their excellent properties especially in producing high-quality surface mainly to provide corrosion resistance. Coating is the process of applying the material to the surface of an object. According to Nazier, & Arafa (2008), coating material will produce great application because it will improve equipment protection. Therefore, to obtain the quality of the results, coating must be sufficiently strongly bonded to the substrate so that able to prevent the occurrence of spall. Metal coating technique is widely use compared to another method. It is because of the metal to metal bond that produce is strongly enough.

2.1.1 Substrate

Substrate is the base layer which is applied process of cleaning, degreasing, etching and rinse before applying electroless process. Low carbon steel is type of material used as substrate. This type of steel has an alloying element with carbon content is less than 0.3%. The reason of choosing this type of material is because of the surface hardness can increase through carburizing besides it is easy to shape. Commonly, the use of low carbon steel is widely used in the variety sector because of its workable and easy to form into certain shapes. By applying plating process, surface hardness can increase.

2.1.2 Method

Industrial field has two types of technique that include wet and dry coating. Both of the methods consist of Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD) electroless and electroplating technique. The method discussed below.

2.1.2.1 Dry process

In dry process, vapor deposition is important in PVD and CVD. Advantage of dry process is both of the technique able to create a thin layer onto a substrate. A vacuum technology used in the process. However, the difference between both methods is the material used.

a) PVD

PVD coating has high quality in coating. There are four steps to complete PVD process. They are evaporation, transportation, reaction, and deposition. According to Sproul (1996), the process can harm the environment because the bombardment of energetic charged ion will dense when produced thin film.

The suitable temperature used is in a range of 450ºc to 500ºc. Pressure applied to operating is low which 0.5-1Pa with speed of 0.1μm/min. Additional, DC diode, RF, and magnetron also used in order to ionize the gas.

b) CVD

CVD is the same process with PVD. However, the difference is on material used. Based on William and Sproul (1996) research, CVD become more efficient compared to PVD. Due to the temperature applied, temperature of CVD is higher which reach to 1000 º C. CVD is bond a coating by combination of metal vaporizing and chemical reaction. CVD is thicker than PVD. The influence of the difference come from temperature applied, types of material and career gas used.

2.1.2.2 Wet process

(a) Electroplating

Electroplating is the process of applying coating on the substrate by immersed in a solution of the composition. The plating covered by deposited metal through catalytic substrate. The outer surface added to other element according to the application required. Based on this analysis, nickel substrate used because it ability to dissolve in water. Because of the process is complex, cost of the process is expensive. Figure 2.8 show the process of coating.

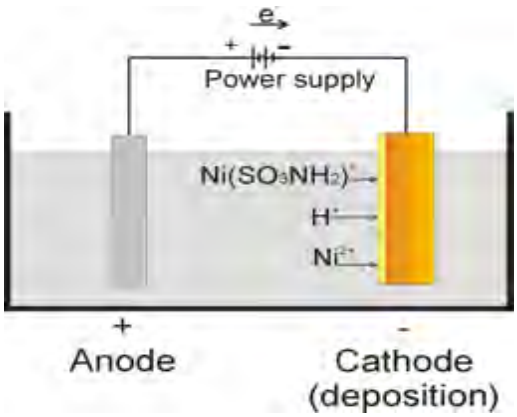

Figure 2.1: Oxidation and reduction process of electroplating method

(b) Electroless plating

Electroless is used chemical solution same as electrodeposition. However, the difference is no electrical applied which means the process is self-catalyzing. By altering heat in bath composition, properties of resultant layer of hardness is increase. According to Delaunois (2000), electroless nickel is used because it is high corrosion resistance.

Advantage of applying this process is because it is direct plating. Compare to the electroplating process, this process have no extra equipment required. The solution which is contain of chemicals used to replenish automatically and the result is a smooth surface is create. Electroless process is to study the chemical reaction that deposit the coating on the surface.

2.2 Element

In this research, element of metals and alloys can be used as plating materials. According to periodic table, zinc, gold and nickel are some example that commonly deposited materials. Every metals has certain advantages that make it selected to specific application.

2.2.1 Nickel

Nickel that familiar with symbol Ni is synonym to electroless. Its density is 8.90 grams per cubic centimeter with atomic number of 28. So, it can beat into extremely thin sheets. Nickel classified as transition metal that is in the periodic table is in group 10. Appearance of this material can resist corrosion even in high temperature because the melting point of nickel is 1455˚C.

Nickel is commonly used because of their ability in plating process. This element is good in corrosion resistance, long service life and many more. Besides, it is also good in adhesion between base metals and surface layers.

Nickel is considered as good corrosion resistance because it reacts slowly with the oxygen in the air at room temperature making it an excellent choice as a final layer. If compare to chrome, nickel have better properties based on its ability to beaten into the small part because chrome density is 7.19 grams per cubic. Table 2.1 represents the advantages and disadvantage of both materials.

Table 2.1: Advantages and disadvantages of nickel compare to chrome. (Balseal, 2010)

	NICKEL	CHROME
ADVANTAGE	i. High corrosion resistance in the as-deposited condition. ii. Plate small diameters and deep bores.	i. Harder than electroless nickel plating. ii. Relatively easy to plate.
DISADVANTAGE	i. Requires high standards of quality control of surface preparation and plating solution. ii. Softer than chrome plating.	i. Coarser surface finish after plating. ii. Small bores and intricate shapes difficult to plate.

2.2.2 Binary Nickel-alloy

Nickel phosphate forms through process known as precipitation hardening. Adding a new element will produce unique properties. Phosphate is one of the examples that usually added to nickel and its function as reducing agent. Co-deposited of reducing agent must be controlled and based on Sudagar *et. al.,* (2013) lower the density will increase amorphous structure of the corrosion resistance. In addition, high deposit of phosphorus will decrease the hardness with high corrosion resistance. Figure 2.2 are showing graph hardness versus heat treatment temperature. Another study by Ghuanglian et. al., (2014) show that increasing annealing time will increase the cluster size of Ni-P.

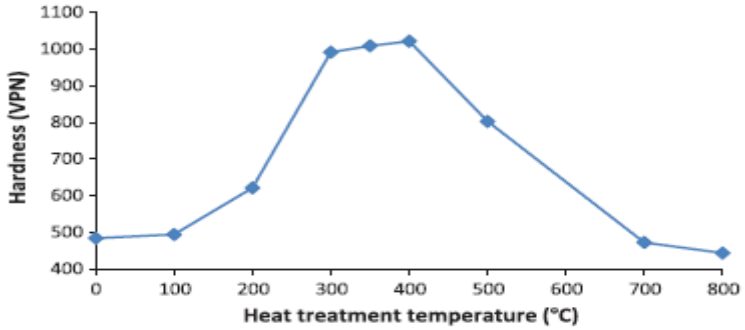

Figure 2.2: Effect of heat treatment temperature on the hardness ofNickel – phosphorus coatings. (Sudagar *et. al.*,2013)

Commonly, nickel is added to phosphorus and boron. The combination of alloy content will change mechanical and physical properties. Changing the physical depended on temperature applied and content of added material. Ni-P is starting to amend its structure above 250˚C while Ni-B is above 320˚C. Then, the sample hardness is higher but its corrosion resistance reduced. The selecting of binary Ni-P is because according to Claeys (2003) even though the boron is very hard, but it is ten times more expensive if compared to phosphorus.

Besides, according to Gray *et. al*., (1996), first eutectic point is at 11.0wt% P reach to 880˚C. Figure 2.3 describes phase obtained by cooling of composition from the binary melt. Low phosphorus deposited coating consists of the β phase which represent as crystalline solid solution. The phosphorus content makes the deposit somewhat self-lubricating.

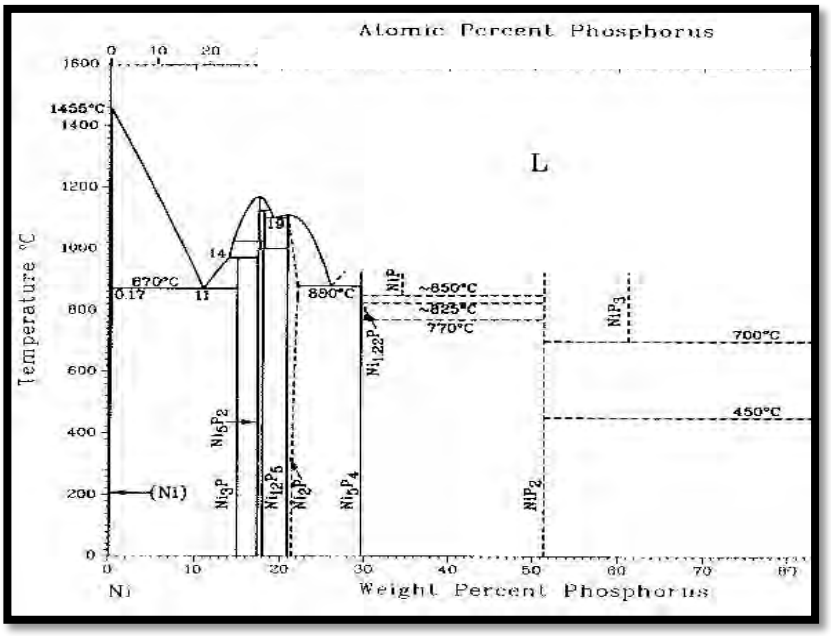

Figure 2.3: Ni-P phase diagram. (Gray, 1996)

2.2.2.1 Ternary Nickel-alloy

Ternary alloy is addition of a third element such as Cobalt, Copper and Tungsten into Ni-P. The choice of material are based on desired properties of the deposit. The combination of ternary element able to improve on corrosion resistance and hardness. Process preparing deposited is studied using alkaline bath by electroless process.

a) Electroless Ni-Cu-P alloy

Commonly, the copper element is added to Ni-P. Symbol for copper is Cu and present atomic number of 29 with the density of 8.96 g cm^{-3}. The highlight advantages of this element are easily joined because it is ductile metal and corrosion resistance. Combination of nickel is to improve wear resistance of nickel. Effect from it is service life of the material is also increase.

In addition, they are essentially immune to corrosion because its ability is low in the reactivity series because it is readily oxidize. The combination of Ni-Cu-P produces smooth and bright surface. Amorphous will show in the phase diagram. If applied to electroless, it tends to become more hard and resistance to oxidation.

b) Ni-Co-P

Cobalt with the chemical element of Co always added to Ni-P. Atomic number for cobalt is 27 with the density of 8.90 $g.cm^{-3}$ and melting point of 1495˚C. Cobalt can resistance to stress and corrosion at high temperature. If the cobalt is added to other material, very strong magnet will produced.

The process were studied based on relation of magnetic to the others. However, the properties are based on both thickness and microstructure resulted.

c) Ni-W-P

Tungsten with symbol of W that come from group 6 and its atomic number of 74 is also known as wolfram. It has highest melting point compared to copper and cobalt melting point which is 3422 °C. Corrosion resistance of tungsten is excellent and attacked only slightly by most mineral acids.

A survey from literature show that by addition of tungsten in binary Ni-P marked change the properties of corrosion resistance. Corrosion resistance of the alloy is increase due to the grain boundary on the surface of substrate.