UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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ELECTROLESS QUATERNARY Ni-Co-Cu-P DEPOSITION ON Fe SUBSTRATE

This report is submitted with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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I hereby declare this report entitled **ELECTROLESS QUATERNARY Ni-Co-Cu-P DEPOSITION ON Fe SUBSTRATE** is the result of my own research except as cited in the references.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirement for the degree of Bachelor of Manufacturing Engineering (Engineering Material) (Hons.). The member of the supervisory is as follow:

………………………………

(Project Supervisor: Dr. Muhammad Zaimi Bin Zainal Abidin)

………………………………

(Project Co-Supervisor: Dr. Lau Kok Tee)

ABSTRAK

Kaedah pemendapan tanpa elektrik aloi terdiri dari empat unsur dibangunkan dengan tambahan dua tambahan logam ke dalam aloi nikel perduaan Ni-P untuk mempamerkan sifat-sifat unggul seperti kakisan dan rintangan. Dalam kajian ini, terdiri dari empat tanpa elektrik Ni-Co-Cu-P dihasilkan untuk mengkaji kesan tembaga dan kobalt di samping ketahanan kakisan dan kekerasan. Komposisi dan permukaan unsur morfologi mempunyai ciri-ciri dan dianalisis menggunakan X-Ray pendarfluor (XRF) dan Mengimbas Mikroskopi Elektron (SEM). Rintangan kakisan terdiri dr empat Ni-Co-Cu-P aloi dianalisis menggunakan pengukuran elektrokimia. Ujian kekerasan dilakukan menggunakan mikro-Vickers Hardness Tester untuk menunjukkan kekuatan terdiri dr empat tanpa elektrik Ni-Co-Cu-P aloi disimpan pada substrat Fe ini. Ni-Co-Cu-P mempunyai permukaan rata dan licin seperti meningkatkan pH mandi saduran. Kadar pemendapan tanpa elektrik Ni-Co-Cu-P meningkat dengan peningkatan pH mandi saduran. Peningkatan penyaduran pH mandi akan mengurangkan kandungan fosforus, tembaga dan kobalt. Potensi kakisan terdiri dari empat tanpa elektrik aloi Ni akan beralih kepada banyak potensi mulia berbanding Fe dan Ni.

ABSTRACT

Electroless quaternary alloys are developed with the addition of two metal additives into the binary nickel alloy of Ni-P to exhibit superior properties such as corrosion and wear resistances. In this study, the electroless quaternary Ni-Co-Cu-P is produced to study the effect of copper and cobalt addition on its corrosion resistance and hardness. The elemental composition and surface morphology is characterized and analyzed using X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). The corrosion resistance of the quaternary Ni-Co-Cu-P alloy is analyzed using electrochemical measurement. The hardness test is carried out using micro-Vickers Hardness Tester to indicate the strength of the electroless quaternary Ni-Co-Cu-P alloy deposited on the Fe substrate. The Ni-Co-Cu-P has flat and smooth surface as increasing plating bath pH. The deposition rate of electroless Ni-Co-Cu-P increases with increasing plating bath pH. The increase of plating bath pH will decrease the phosphorus, copper and cobalt content. The corrosion potential of electroless quaternary Ni alloy will be shift towards much noble potential compared to Fe and Ni.

DEDICATION

To my lovely mother, Latipah binti Samsuri and other family member for their continuous support throughout the study. To my supervisor, Dr. Muhammad Zaimi Bin Zainal Abidin for his guidance and advice to complete this research. To my friend for their support and all UTeM staff that cooperate directly or indirectly.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

$NiSO_4.6H_2O$	-	Nickel sulphate
NaH_2PO_2	-	Sodium Hypophosphite
$Na_3C_6H_5O_7$	-	Sodium Citrate
CH_3COONH_4	-	Ammonium Acetate
$CuSO_4$	-	Copper sulphate
$CoSO_4$	-	Cobalt sulphate
Fe	-	Ferum or Iron
M	-	Mol
NaCI	-	Sodium chloride
Mm	-	Millimeter
HCI	-	Hydrochloric Acid
Ni-P	-	Nickel-Phosphorus
Ni-Co-Cu-P	-	Nickel-Cobalt-Copper-Phosphorus
S	-	Second
Wt	-	Weight
K	-	Kelvin Celcius
%	-	Percent
μ	-	Micron
I_{corr}	-	Corrosion current
E_{corr}	-	Corrosion potential
A	-	Area

CHAPTER 1

INTRODUCTION

1.1 Background of study

Electroless nickel plating is widely uses as a coating in the industry due to their excellent properties such as corrosion resistance and hardness. Compare to Pressure Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) coating, electroless nickel plating produces uniform coating on any shape and type of substrate. Other than that, it does not need external current supply to produce coating and less porous deposited compared to electroplating. In electroless nickel plating bath, the reducing agent such as hypophosphite is to reduce the nickel ion into metallic nickel onto the substrate producing a binary Ni-P alloy. The Ni-P alloy is widely used in various industries such as chemical and electronic industry because of their excellent properties which depend on the phosphorus content. According to Balaraju et al., (2004), the presence of phosphorus in binary Ni-P alloy improves the properties of the metal to be plated such as corrosion and wear resistance, hardness, magnetic properties and electrical resistance.

Furthermore, the properties of Ni-P alloy is been such as corrosion resistance and hardness can been improved by developing ternary electroless nickel alloy with addition of another metallic element such as copper, cobalt, tungsten, molybdenum and becoming Ni-Cu-P, Ni-Co-P, Ni-W-P, and Ni-Mo-P alloy respectively. The inclusion of copper in Ni-P matrix has enhances the deposit characteristic such as corrosion resistance, brightness, and ductility (Balaraju et al., 2004).Other than that, the additions of tungsten in binary Ni-P alloy can improve the properties of the coating such as electrical resistance and thermal stability (Balaraju, et al., 2006). The operating parameter such as pH, temperature and metal ion concentration give significant effect to the metal additive content in electroless ternary nickel alloy. The deposition rate is increases and phosphorus content is decreased as increasing bath. The previous study of electroless Ni-Co-P by Aly et al. (2003) shows that the cobalt content increase as increasing in pH, temperature and copper sulphate concentration but decrease the phosphorus content.

Other than ternary nickel alloy, quaternary nickel alloy is developed with the addition of of another element as a fourth element for the purpose of further improvement properties such in corrosion and surface morphology. There are several quaternary nickel alloys that reported being produced using electroless methods such as Ni-W-Cu-P, Ni-Re-W-P, Ni-Mo-Cr-P, Ni-Fe-P-B, Ni-W-Cr-P, Ni-Zn-Cu-P and Ni-W-Sn-P. The previous study from Balaraju et al. (2004) proved that ternary Ni-W-P deposits are coarse whereas quaternary Ni-Cu-W-P deposits are smooth, nodule-free and quaternary nickel alloy increase the crystallinity of the alloy which also improved the corrosion resistance of the coating. The addition of copper and tungsten additive in Ni-P has improved the corrosion properties of the deposit. However, the corrosion resistance of electroless Ni-Zn-Cu-P alloy is the lowest compared with Ni-P, Ni-Zn-P and Ni-Cu-P alloy (Zaimi et al., 2012). The effect of zinc and copper addition produce a lowest corrosion while the effect of tungsten and copper addition produce excellent corrosion resistance. The effect of copper and cobalt additive in Ni-P matrix on its corrosion is still less known.

Hence, the effect of both copper and cobalt addition in electroless Ni-P alloy on its properties such as corrosion resistance and hardness is yet to be studied. In this study, the electroless quaternary Ni-Co-Cu-P is produced to study the effect of copper and cobalt addition on corrosion resistance and hardness. The elemental composition and surface morphology of electroless Ni-Co-Cu-P is been characterized and analyzed using X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM).The corrosion resistance of the quaternary Ni-Co-Cu-P alloy is being analyzed using electrochemical measurement. The hardness test is carried out using Vickers Hardness Tester to indicate the strength of the electroless quaternary Ni-Co-Cu-P alloy deposited on the Fe substrate.

1.2 Problem statement

Electroless Ni-Co-Cu-P deposition is still less known. In the previous research, electroless Ni-W-Cu-P deposition (Balaraju et al., 2004) and electroless Ni-Zn-Cu-P deposition (Zaimi et al., 2012) is produced to study the effect of both metal additive in Ni-P alloy on its corrosion properties. The copper and tungsten addition in Ni-P matrix shows the excellent corrosion resistance of deposit while copper and zinc addition shows the lowest corrosion resistance compare with binary and ternary nickel alloy. The effect of copper and cobalt additive in electroless Ni-P alloy corrosion behavior is salt solution is less known. Thus , the effect of various plating bath pH of electroless quaternary Ni-Co-Cu-P on deposition rate, coating composition, hardness and surface morphology are need to be studied.

1.3 Objective

The aim of this research is:

i. To investigate the effect of different plating bath pH on electroless quaternary Ni-Co-Cu-P deposited on Fe substrate microstructure, composition and hardness.
ii. To determine the correlation between corrosion behavior and composition of electroless quaternary Ni-Co-Cu-P alloy using electrochemical measurement method

1.4 Scope of study

The purpose of this study is to produce electroless quaternary Ni-Co-Cu-P alloy deposited on Fe substrate and determine its microstructure and composition by using different plating bath pH. Other than that, the elemental composition and surface morphology is characterized and analyzed using XRF and SEM analysis. The corrosion resistance of the quaternary Ni-Co-Cu-P alloy is being analyzed using electrochemical measurement. The hardness test is carried out using micro-Vicker Hardness Tester to indicate the hardness of the electroless quaternary Ni-Co-Cu-P alloy deposited on the Fe.

CHAPTER 2

LITERATURE REVIEW

This chapter contains literature review which based on the previous journal, books, technical document, report, thesis and also electronic media sources. The literature review is conducted based on the research which relates to the scope of the study.

2.1 Iron (Fe)

2.1.1 Definition and properties of Fe

Iron (Fe) is one of the most abundant elements that can be found in the earth's crust. The chemical symbol for iron is Fe that comes from the Latin word for iron namely ferum. Atomic number and atomic weight for Fe is 26 and 55.845. Iron is transition metal that can be found in group 8 of the periodic table. Iron is a shiny, greyish metal that easily identified, but usually discolored due to corrosion. Iron is in the form of ferrite and has a body-centered cubic crystalline structure at the room temperature. Iron is a good conductor of heat and easy to magnetized or demagnetized.

Iron is a metal that easily corroded if exposed to the moisture or air which cause the reaction between oxygen and Fe ion. However, iron is mostly used with combination of other alloying element such as chromium, molybdenum, nickel, tungsten, tin and vanadium to improve iron properties that known as steel.

2.1.2 Application of iron

Iron is widely uses due to its high strength properties and low cost. Iron is widely used in various applications such as automotive parts, machine tools, ship hulls, and building structure. Generally, iron is combined with others metal element to improve the ability of the iron in term of properties such as hardness and corrosion resistance which is useful in many application.

Besides, the iron compound also contribute many uses for example iron chloride is used to treat the sewage system and used in manufacturing printed circuit boards. Others iron compound such as iron sulfate, iron hydroxide and iron arsenate is uses to treat anemia, to purify water, and help prevents different type of pest attack in plants.

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2.2 Corrosion

2.2.1 Definition of corrosion

Corrosion is the degradation or deterioration of the material due to chemical reaction between it with the surrounding environment. According to Ahmad (2006), corrosion is the surface wastage that occurred when the metal surface is exposed to the reactive environments. Corrosion of metal is when metallic atom reacts with an oxygen atom in the air to form compound .Essentially, corrosion is always related with metal, but it also includes other materials such as polymer, ceramics and other non-metallic material.

The corrosive environment such as air and humidity, fuel gases, soils, salt water, alkalies and acids is lead to the material corrosion. These environments are unable to control because of it is a necessities of life, so the corrosion reaction is difficult to be avoided. However, there are many preventive methods is being applied such as material selection, corrosion inhibitors, protective coating, design and cathodic protection (Ahmad, 2006)

2.2.2 Form of metallic corrosion

There are several types of metallic corrosion that discovered such as uniform corrosion, intergranular corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, erosion corrosion, stress corrosion cracking and biological corrosion (Schweitzer, 2006).

2.2.3 Corrosion of iron

Corrosion is usually related to metal which commonly happen to iron metal. The corrosion of iron is usually related to metal that commonly happen to iron metal. The corrosion of iron is an oxidation-reduction process between iron ion and oxygen to form iron oxide that called as rust. Iron is one of the most widely used metals in the worldwide because it is cheap and strong. But, iron is a metal that easy to corrode when exposed to air or water. The figure below shows the corrosion of iron in contact with water.

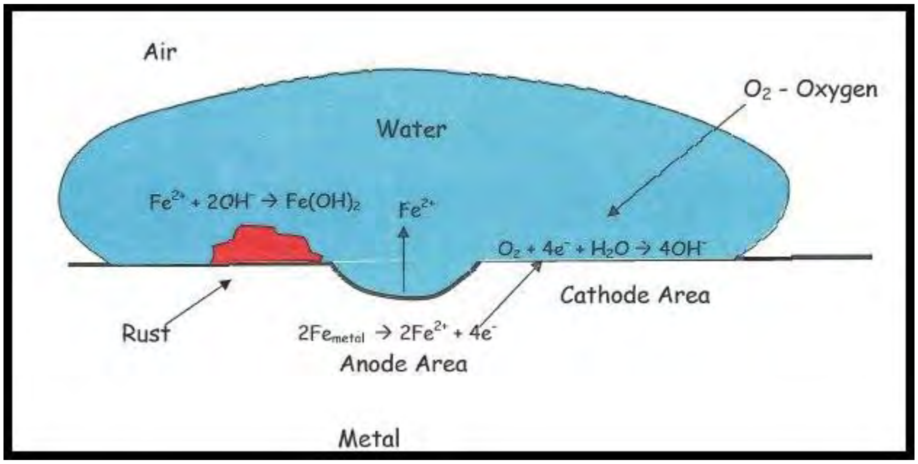

Figure 2.1: Corrosion of a metal, iron in contact with water (http://www.corrosionist.com/Iron_Corrosion.htm)

The corrosion process consists of several steps. First, the iron is oxidized to form iron (II) ions, Fe^{2+}. Next, the oxygen from the air is reduces with water to form hydroxide ion, OH^{-}. This oxidation-reduction half reaction is shown in Equation 1 and 2.

Oxidation half-reaction: $Fe(s) \rightarrow Fe^{2+} (aq) + 2e^{-}$ (1)

Reduction half-reaction: $O_2 (g) + 2H_2O (l) + 4^{-}- \rightarrow 4OH^{-}(aq)$ (2)

The overall reaction for this reaction after combining both half reactions is in equation 3.

$2Fe(s) + O_2 (g) + 2H_2O(1) \rightarrow 2Fe^{2+}(aq) + 4OH\text{-}(aq)$ (3)

These overall reaction form iron(II) hydroxide precipitates is in Equation 4

$Fe^{2+}(aq) + 2OH\text{-}(aq) \rightarrow Fe(OH)_2(s)$ (4)

The iron(II) hydroxide then react with oxygen to form iron oxide: Fe_2O_3 (red) and Fe_3O_4 (black). These both iron oxide combination is called as rust.