UNIVERSITI TEKNIKAL MALAYSIA MELAKA (UTeM)

REACTION MECHANISM OF ELECTROLESS QUATERNARY NICKEL ALLOY DEPOSITION ON Fe SUBSTRATE

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

by

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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 Materials) (Hons.). The members of the supervisory committee are as follow:

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ABSTRAK

Pemendapan tanpa elektrik Ni-P aloi adalah satu daripada kaedah saduran untuk bahan-bahan salutan dengan aloi Nikel. Ia telah digunakan secara meluas dalam pelbagai industri seperti mekanikal, kimia dan industri elektronik. Hal ini disebabkan oleh ketahanan terhadap kehausan dan kakisan yang sangat baik dan juga meningkatkan kebolehan untuk mematri. Tambahan pula, penambahan unsur-unsur logam lain dalam aloi Ni-P seperti tembaga, kobalt dan tungsten didalam larutan Ni-P dapat meningkatkan sifat-sifat seperti kekerasan, kelancaran, kemuluran, kakisan dan ketahanan terhadap kehausan. Baru-baru ini, pemendapan tanpa elektrik terhadap aloi Ni dibangunkan yang terdiri daripada empat elemen dengan penambahan dua unsur logam lain ke dalam larutan aloi Ni-P. Sebagai contoh, menambah tungsten, W dan tembaga, Cu didalam larutan Ni-P yang menghasilkan larutan Ni aloi yang terdiri daripada empat elemen yang didepositkan. Walau bagaimanapun, kajian baru-baru ini tidak memberi tumpuan kepada mekanisme tindakbalas aloi Ni yang terdiri daripada empat elemen. Dalam kajian ini, mekanisme tindak balas terhadap pemendapan Ni aloi yang terdiri daripada empat unsur dikaji dengan menggunakan kaedah pengukuran elektrokimia. Larutan *plating* terhadap pelbagai pH dan bahagian-bahagian digunakan untuk mengkaji kesan pengukuran elektrokimia. Pengukuran elektrokimia dijalankan dengan menggunakan pengukuran *cyclic voltammetry*. Semakin tinggi pH larutan *plating*, *crossing potensial*, Ec bergerak ke arah potensi positif iaitu ke arah *noble potential*. Oleh itu, ion logam adalah lebih mudah untuk melakukan proses pendepositan. Dalam *cyclic voltammetry* yang dikaji, semakin tinggi nilai pH, lebih cepat yang pengurangan ion nikel. Selain itu, puncak pengoksidaan dan puncak pengurangan akan menjadi lebih rendah dan lebih luas apabila terdapat peningkatan nilai pH. Ini menunjukkan kelajuan tindak balas daripada larutan *plating* tersebut. Apabila puncak menjadi lebih rendah tindakbalas terhadap kadar pendepositan akan menjadi lebih cepa

ABSTRACT

Electroless deposition of Ni-P alloy is one of the plating methods for coating materials with nickel alloy. It has been widely used in many industries such as mechanical, chemical and electronic industries. This is due to their excellent wear and corrosion resistance and improves solderability properties. Furthermore, the addition of other metallic elements in the Ni-P alloy such as copper, cobalt and tungsten improves the properties of the binary Ni-P deposit such as hardness, smoothness, ductility, corrosion and wear resistance. Recently, the electroless quaternary Ni alloy deposition are developed by addition of two more metallic elements into the binary Ni-P alloy deposit. For example, adding tungsten, W and copper, Cu in the Ni-P that produces quaternary Ni alloy deposited. However, the recent studies are not focusing on the reaction mechanism of quaternary Ni alloy. In this study, the reaction mechanism of quaternary Ni alloy deposition is studied using electrochemical measurement method. The plating baths at various pH and components are used to study the effect of electrochemical measurement. The electrochemical measurements are conducted by using cyclic voltammetry measurement. The higher the plating bath pH the crossing potential, E_c shift to the positive potential which is towards much noble potential. Hence, metal ion is easier to be reduced. In the cyclic voltammetry studied, the higher the pH value, the faster the reduction of the Nickel ions. Besides, the oxidation peak and reduction peak will be lower and broader as pH value increase. This indicates the reaction speed of the plating bath solution. As the peaks become lower the reaction rate will be faster.

DEDICATION

This report is dedicated to my respective parents; Mr. Ahmad Bin Latek and Mrs. Kasipah Binti Kashdan, my supervisor; Dr. Muhammad Zaimi Bin Zainal Abidin and not forget my co-supervisor P.M. Dr. T. Joseph Sahaya Anand, my family's members and also to all my friends who have been supported and inspired me to do this research study whether direct or indirect way for completing this project.

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$Ag/AgCl/KCl_{sat}$ - Silver/silver chloride/ Potasium Chloride

Co - Cobalt

Co-P - Cobalt Phosphorus

Cu - Copper

Cu-P - Copper Phosphorus

CVD - Chemical Vapor Deposition

E_c - Crossing Potential

EN - Electroless nickel

i_{pa} - Anodic Current Peak

i_{pc} - Cathodic Current Peak

NaOH - Sodium hydroxide

Ni - Nickel

Ni-Co-Cu-P - Nickel cobalt copper Phosphorus

Ni-Co-P - Nickel cobalt phosphorus

Ni-Cu-P - Nickel copper phosphorus

Ni-P - Nickel phosphorus

PVD - Physical Vapor Deposition

CHAPTER 1

INTRODUCTION

1.1 Background of study

Electroless plating is one of the coating methods which are the process for covering the material with an additional layer to improve their performances such as increase corrosion and wear resistant. Electroless plating also known as autocatalytic is the process involves the presence of chemical reducing agent such as hypophosphite used in the solution to reduce the metal for deposited onto substrate (Mallory and Hadju, 1990). One of the advantages of electroless deposition is it can deposit on any type and shape of substrate unlike electroplating that requires external current that is limiting the area of deposition. In electroless deposition, there is no external current source used during the reaction instead, the reaction only relies on the redox reaction (Schlesinger, 2010). Electroless nickel alloy depositions have been applied in many industries such as chemical, mechanical and electronics industries. This is due to their better physical and mechanical properties. In electroless deposition, the plating bath is important in order to coat a material. There are some parameters that are being used in the plating bath such as pH, temperature and the use of additives. According to Mordechay Schlesinger (2010), by rising a bath's pH value it will increases the deposition rate. In addition, when the bath temperature increased, the deposition rate will also increase exponentially. The additives such as complexing agents and buffering agents are used in the plating bath to prevent free nickel ions that is available for the reactions and also avoiding the precipitation of Nickel salts such as phosphites. Moreover, it is also used for maintaining a stable pH level of the plating bath solutions.

The electroless metal deposits are mainly using a binary alloy such as addition of phosphorus or boron. Reducing agent such as hypophosphite ions used in the Ni-P plating bath solutions is important to reduce the nickel into nickel ions and to being deposited on the substrate surface. According to Yu, Luo, & Wang, (2001), the electroless Ni-P alloy have extensive application in industries because of their excellent wear and corrosion resistance and also increase physical properties performances such as magnetic property, solderability and polishability.

Furthermore, the addition of another metallic element in Ni-P matrix such as copper, cobalt, tungsten and molybdenum makes the Ni-P alloy deposition becomes Ni-Cu-P, Ni-Co-P, Ni-W-P and Ni-Mo-P. This will improve the binary nickel alloy properties with the development of electroless ternary nickel alloy (Balaraju & Rajam, 2005). According to Balaraju & Rajam (2005), the codepositing of another element in Ni-P matrix enhances the properties such improve the hardness, electrical properties, wears and corrosion resistances. Besides, addition of tungsten in Ni-P matrix improves the properties of the coating material such as wear and corrosion resistance, thermal stability and electrical resistance. Other than that, the smoothness, brightness, ductility and corrosion resistance increase when copper is being deposited on the electroless Ni-P matrix

Recently, addition of others element in the electroless ternary alloy deposit give better improves the properties of coating materials. According to Balaraju & Rajam (2005), the surface morphology electroless quaternary Ni-W-Cu-P alloy deposit show very smooth and nodule-free structure compare to electroless ternary Ni-W-P alloy deposit which exhibits coarse nodular structure. This shows that without affecting the hardness in Ni-W-P ternary alloy, the addition of copper has improved the morphology that results in more bright and smooth quaternary Ni-W-Cu-P alloy (Balaraju & Rajam, 2005).

However, the reaction mechanisms of electroless quaternary Ni alloy depositions on Fe substrates are still less known. Besides that, the effect of various plating bath pH and plating bath components on the reaction mechanism of electroless quaternary Ni alloy deposition with copper and cobalt as ion additives are also not very well-known.

The purpose of this study is to analyze the reaction mechanisms of the electroless quaternary Ni alloy depositions on Fe substrates by using electrochemical measurements. Other than that, this research is done to investigate the effect of various plating bath condition on the reaction mechanism of electroless quaternary nickel alloy with copper and cobalt as ion additives. This experiment is carried out with various plating bath pH and components. Besides that, the reaction mechanism is analyzed using cyclic voltammetry measurement.

1.2 Problem Statement

The reaction mechanism of electroless quaternary Ni alloy deposition on Fe substrates is still less known. In this research study, the reaction mechanisms of electroless quaternary Ni alloy depositions are study with different plating bath components and pH. The effect of various plating bath pH and various bath components on the reaction mechanism of electroless quaternary Ni alloy deposition with cobalt and copper ion additives are also still less known.

1.3 Objectives

The purpose of doing this research is to investigate the reaction mechanism of electroless quaternary nickel alloy deposition on Fe substrate. This study is carried out with certain objectives which are:

i. To study the effect of various plating bath component which are binary, ternary and quaternary on the reaction mechanism of electroless quaternary nickel alloy deposition on Fe substrate.
ii. To study the reaction mechanism of electroless quatenary Nickel alloy with different plating bath pH deposition on Fe substrate.

1.4 Scope of study

This research project is to study the reaction mechanism of electroless quaternary nickel alloy deposition. This experiment is carried out with different plating bath pH and components of binary, ternary and quaternary electroless Ni alloy deposition. The reaction mechanism of electroless Ni-Co-Cu-P alloy deposition is analyzed using the cyclic voltammetry measurement. The conditions to run the electrochemical measurements are by fixed the scanning range at -1V to +1V and the scanning rate at 10mV/s. This electrochemical measurement is done by using three electrode systems which are reference electrode, counter electrode and working electrode. After that, the cyclic voltammetry result is correlated with the actual electroless quaternary Ni-Co-Cu-P deposition.

CHAPTER 2

LITERATURE REVIEW

This chapter provide with overall overview about all the research related to the scope. This research is conducted based on the previous journal, thesis, technical document, books, reports and also electronic-media sources.

2.1 Coating Method

2.1.1 Definition of Coating

Coating is the process of covering the material with an additional layer to the surface of an object which referred as substrate. Coating is importance because it forms an effective barrier which can enhance the material properties such as corrosion resistance, wear resistance, hardness and abrasion. There are many types of coating method such as vapor deposition, electro-deposition and electroless deposition

2.1.2 Process of coating

2.1.2.1 Dry Process

Dry process of coating consists of physical vapor deposition (PVD) and also chemical vapor deposition (CVD). Physical Vapor Deposition (PVD) is a process where the material is vaporized from solid or liquid sources in the form of atom or molecules. It is being transported to the substrate in the form of vapor or low pressure gaseous environment (Mattox, 2010). It has been widely used in the industry due to the improvement of hardness, wear resistance and oxidation resistance including in aerospace industries, automotive industries, cutting tools and medical equipment. According to Mattox (2010), the PVD process can be used for deposits film from a few nanometers to thousands of nanometers thickness and can form multilayer coating with a very thick deposited. Besides that, the substrates can be from a small to a very large size and from flat in shape to the complex geometries. According to Holmberg and Matthews (2009), PVD methods can be divided into two which are evaporation and sputtering. The evaporation involves in thermal vaporization of deposition material sources while sputtering is a kinetic controlled process which the source material is made cathodic and bombarded with ion usually inert gas. Thus, it will result in the transfer of momentum to the atom in the target that leads to the ejection of coating atoms (Holmberg and Matthews, 2009).

The advantages of using this PVD method are more variety of coating can be produced, coating thickness can be precisely produced, high wear resistance and low friction coefficient. On the other hands, their limitations are corrosion resistant only for under a certain condition and the part need to be rotated during processing in order to achieve uniform coating thickness.

Besides that, Chemical Vapor Deposition (CVD) is a deposition of a solid material on a heated surface from a chemical reaction in the vapor phase (Pierson, 1999). According to Holmberg and Matthews (2009), CVD is a process where gasses containing material to be deposit is placed into the reaction chamber and it will condense onto substrate to form a coating. Generally, it requires deposition temperatures in the range of 800°C to 1200°C. CVD is normally used for tool coating with titanium nitrade and titanium carbide (Holmberg and Matthews, 2009). Other than that, it has been widely used in semiconductor industries to make thin film.

The advantages of CVD process method is it is not restricted only to a line sight of deposition which means deep recesses, holes and other difficult configuration can relatively be coated. Besides, the deposition rates for CVD are high and thick coating can be readily obtained. On the other hand, the disadvantages of CVD are high processing temperatures and for some metal they are not possible to be coated. Besides that, the chemical precursor's requirements with high vapor pressure are normally hazardous and extremely toxic (Hugh Pierson, 1999).

2.1.2.2 Wet Process

a) Electro-deposition method

According to Pandey (1996), electrodeposition is also known as electroplating and has been well known and used for preparing metallic mirrors and corrosion resistant on the surface of the material. The electroplating process requires plating bath that consists of an electrolyte which containing metal ions, an electrode or substrate and counter electrode. In this process, it requires an external current source. When a current flows through the electrolyte, the cations and anions move towards the cathode and anode respectively. This may be deposited on the electrodes after undergoing a charge transfer reaction and a coating will be formed (Pandey, 1996). According to Mellor (2006), the rate of deposition of the cations is controlled by the proportions of the cations in the plating bath and also by the complexants used in the bath. The anode used in this process is made of by the material which is being plated to be maintaining in the bath chemistry (Mellor, 2006). The plating bath has to be electrically conductive and it can be in the form of aqueous, non-aqueous or molten and also must contain suitable salt. Besides