EFFECT OF AGITATION TO ELECTROLESS NICKEL PLATING OF NiP/Ag NANOCOMPOSITE

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by

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Effect of Agitation to Electroless Nickel Plating of NiP/Ag Nanocomposite**". I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

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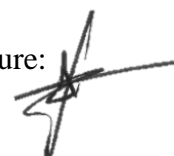
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Date: 13 AUGUST 2022

ACKNOWLEDGEMENT

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LIST OF SYMBOLS

º	Degree
Λ	Lambda
Θ	Theta
×	Multiply

LIST OF ABBREVIATIONS

XRD   X-ray diffraction

SEM   Scanning electron microscopy

AFM   Atomic force microscopy

NiP   Nickel phosphorus

NiP/Ag   Nickel phosphorus embedded with silver nanoparticles

EN   Electroless nickel

ENP   Electroless nickel plating

AgNPs   Silver nanoparticles

UBM   Under bump metallization

IMC   Intermetallic compound

SAC305   Lead-free alloy contains tin, silver and copper

rpm   Revolutions per minute

ICSD   Inorganic Crystal Structure Database

SPM   Scanning probe microscopy

PSPD   Position-sensitive photodetector

Ra   Roughness Average

RMS   Root Mean Square roughness

KESAN AGITASI KEPADA PENYADURAN NIKEL TANPA ELEKTRIK NANOKOMPOSIT NiP/Ag

ABSTRAK

Penyaduran nikel tanpa elektro (EN) adalah teknik metalisasi yang menarik untuk komponen elektronik yang disebabkan oleh sifatnya seperti ketebalan salutan seragam, kekasaran permukaan yang lebih rendah dan kestabilan haba yang baik. Nanokomposit telah menyediakan multifungsi dan kesan pengukuhan tambahan dalam matriks nikel-fosforus (Ni-P). Walau bagaimanapun, aglomerasi nanozarah dalam elektrolit EN telah menjadi cabaran utama kepada penyaduran komposit EN. Dalam kajian ini, 30 mg/L nanopartikel perak (AgNPs) dengan saiz 10 nm telah ditambah ke dalam elektrolit ENP untuk menghasilkan nanokomposit nikel-fosforus-perak (NiP/Ag) dengan bantuan pengacauan magnet dalam kadar kacau yang berbeza (0, 100, 200, 300, 400, dan 500 rpm) bertujuan untuk meningkatkan sentuhan elektrik permukaan NiP dan kebolehbasahan aliran semula pateri. Pelbagai kaedah pencirian telah digunakan untuk mencirikan nanokomposit NiP/Ag seperti pembelauan sinar-X (XRD), mikroskopi daya atom (AFM), mikroskop elektron pengimbasan (SEM), goniometer sudut sentuhan Ossila dan ujian rintangan sentuhan. Dalam analisasi XRD, nanokomposit NiP/Ag mempunyai puncak yang lebih tinggi berbanding dengan NiP dan 500 rpm NiP/Ag mempunyai puncak tertinggi pada satah (111). Seterusnya, keputusan menunjukkan kadar kacau magnet yang sesuai untuk salutan NiP/Ag dari segi ketebalan dan kebolehbasahan adalah 100 rpm yang telah memberikan salutan paling tebal (9.46 μm) dan sudut sentuhan terendah (22.84º). Walau bagaimanapun, 0 rpm adalah kadar kacau magnet yang sesuai untuk menghasilkan kekasaran permukaan terendah nanokomposit NiP/Ag dengan Ra 23.22 nm dan kerintangan terendah 0.1133 Ω-cm.

EFFECT OF AGITATION TO ELECTROLESS PLATING OF NiP/Ag NANOCOMPOSITE

ABSTRACT

Electroless nickel (EN) plating is an attractive metallization technique for electronic components due to its properties such as uniform coating thickness, lower surface roughness and good thermal stability. Nanocomposites have provided multifunctionality and additional strengthening effects in the nickel-phosphorus (Ni-P) matrix. However, agglomeration of nanoparticles in the plating solution has become a main challenge in EN composite plating. In this study, 30 mg/L of 10 nm silver nanoparticles (AgNPs) was added into EN plating solution to produce nickel-phosphorus-silver (NiP/Ag) nanocomposite under the assistant of magnetic stirring at different stirring rate (0, 100, 200, 300, 400, and 500 rpm) with target to improve electrical contact of NiP surface and wettability of solder reflow. Various characterization methods were used to characterize NiP/Ag nanocomposite such as X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), Ossila contact angle goniometer and contact resistance test. In XRD analysis, NiP/Ag nanocomposite has sharper peak compared to NiP coating and 500 rpm of NiP/Ag has the sharpest peak at plane (111). Next, the results showed that the suitable magnetic stirring rate for NiP/Ag coatings in terms of thickness and wettability is at 100 rpm which give the thickest coating of 9.46 μm and lowest contact angle of 22.84°. However, 0 rpm is a suitable magnetic stirring rate to produce the lowest surface roughness of NiP/Ag nanocomposite with Ra 23.22 nm and lowest resistivity of 0.1133 Ω-cm.

CHAPTER 1

INTRODUCTION

1.1   Background of the study

Miniaturization in this era has become an ongoing trend and the quality of the electronic devices must be ensured where they are appropriately integrated and packaged in a successful industrial product that can achieve the expectations of the consumer to be intelligent and multifunctional (Jiang et al., 2017). This has brought towards the thrust of research and development activities in metallization where it is a process that joins the semiconductor substrates together through a metal line. Metal line layers are deposited on the wafer to connect the circuits by forming conductive pathways where most common metals used includes aluminum (Al), nickel (Ni), chromium (Cr), gold (Au), germanium (Ge), copper (Cu), silver (Ag), titanium (Ti), tungsten (W), platinum (Pt), and tantalum (Ta), and their alloys (Sudagar et al., 2013).

Among the metals, Cu has been widely used in the under bump metallization (UBM) and as a substrate metallization for chip packaging. However, due to rapid formation of undesired intermetallic compound (IMC) at tin-based solder (SAC305 lead-free alloy) that will lead to reliability problem of this type of solder joint, Ni has better performance compared to Cu (Alam et al, 2002). Ni metallization has been acknowledged as good diffusion barrier for soldering on Cu substrate as it can effectively prevent the undesirable contamination from substrate materials into solder joints (Hsieh and Lin, 2011; Hare, 2017). Besides, development of Ni metallization has grown fast in plating industries included electroplating and electroless plating.

Electroless nickel (EN) plating is an attractive metallization technique as it allows the ability to metalize conductive and insulating substrates at low temperature where the processes and equipment involved are cost effective (Liu et al., 2019). Besides, the

properties of electroless nickel-phosphorus (Ni-P) coating such as high hardness, wear and corrosion resistance, uniform coating thickness, lower surface roughness, magnetic behavior, a higher fatigue limit and lower macroscopic deformation and good thermal stability allow it to have wide range of applications (Lelevic and Walsh, 2019). Consequently, many researchers are putting more efforts to seek for improvement on the properties of Ni-P coating.

Co-depositing another metallic (Cu, Pb and Mg) or non-metallic elements (C and ZrO) abrasive (CeO_2, SiC, SiO_2 and Al_2O_3) or lubricate (Ag and C) particles, or combination of them in binary Ni-P matrix can further enhance the properties was found (Agarwala and Agarwala, 2003; Ma et al., 2009; Alirezaei et al., 2013). Hence, this has led to a new generation of electroless composite platings. Ag that acts as a solid lubricant with its excellent chemical stability, oxidation resistance and thermal conductivity with the addition of higher electrical conductivity as comparing with Cu allows it to be used in high-temperature application (Caron, 2001). The very first research in co-depositing Ag nanoparticles (AgNPs) into Ni-P matrix by EN plating was done by Ma et al. (2009). The nanocrystalline nickel-phosphorus embedded with silver particles (NiP/Ag) composite coating has found to have higher hardness, better wear resistance after heat-treated, and higher thermal stability and good tribological performance at elevated temperatures (Ariffah et al., 2020; Shahbazi et al., 2019). However, the studies on electrical conductivity and wettability of NiP/Ag composite coatings are limited.

In this study, NiP/Ag coating was produced on copper sheet and the effect of AgNPs on the properties of the composite coating was characterized. Even though coatings produced by ENP give high uniformity of coating thickness, but in electroless plating of nanocomposite, where the addition of second phase Ag particles into Ni-P matrix lead to lower deposition rate, weak incorporation of AgNPs, non-uniform coating

and eventually affect the properties of the coating (Shahbazi et al., 2019). To overcome the problem, agitation is introduced into the EN plating solution to assist the plating process. Agitation can help to control the deposition rate, uniformity of thickness of the coating, and also enhance the stability of the EN plating solution and maintain the temperature throughout the solution in the tank (Ansari and Thakur, 2016). However, rate of agitation is important as it will affect the co-deposition of particles in two opposite ways such that increasing agitation will give a larger particles composite content but over agitation will decrease the particle composite content (Sen et al., 2011). Therefore, the rate of agitation must be well controlled to obtain the best quality of coating.

1.2   Problem Statement

Ni-P coatings offer a combination of good mechanical with good corrosion behavior and low surface roughness which is suitable to be used in electronic packaging device. All solder joints in electronic packaging devices require high thermal conductivity and electrical conductivity properties to give a necessary level of reliability of the application. However, Ni-P coatings has low conductivity which is required to be further improved in terms of conductivity. In this study, AgNPs are selected to be added into the EN plating solution to form a nanocomposite NiP/Ag as Ag has very high thermal and electrical conductivity. However, dispersion uniformity of the AgNPs in the NiP matrix main challenge in electroless composite coatings. In order to ensure the uniform dispersion of AgNPs, the electroless plating will run under the assistance of magnetic stirring agitation on the plating solution to enhance the properties of the coated material. This work will focus on finding suitable magnetic stirring rates for electroless plating of NiP/Ag nanocomposite to ensure the proper distribution of AgNPs and to give the best performance of coatings in terms of electrical contact and wettability of solder reflow.

1.3   Objectives

  i.   To investigate phases transform, surface morphology, coating thickness, surface roughness, contact resistance and wettability of NiP and NiP/Ag nanocomposite.

  ii.   To evaluate suitable magnetic stirring rates for NiP/Ag nanocomposite coating in terms of electrical contact and wettability.

1.4   Scope of work

The scope encompasses the following aspects of work:

- Preparation of copper substrate surface prior to electroless nickel coating include grinding, polishing, cleaning, acid etching and activation.

- Preparation of electroless nickel solution bath with pH5 with different stirring rate.

- Control and monitor the coating process.

- Preparation of coating characterization; cut sample to smaller pieces fit for testing, grind and polish cross-section sample, prepare sample for wettability test and contact resistance test.

- Characterization of coated sample using scanning electron microscope (SEM), x-ray diffraction (XRD) analysis, atomic force microscopy (AFM), and Ossila contact angle goniometer and contact resistance.

1.5   Thesis outline

The outline of thesis for this study is divided into 5 chapters. In Chapter 1, general background and significant issues with electroless plating of nanocomposite, the project's goals and possible methodologies to enhance the wettability and electrical conductivity of NiP/Ag nanocomposite are discussed. In Chapter 2, a comprehensive literature review on EN plating, electroless nanocomposite plating, application of EN plating, agitation mode, advantages and disadvantages are reviewed. Chapter 3 discusses the overall experimental methods and also the details of the materials and chemicals used to synthesize NiP/Ag nanocomposite. The experimental procedures for wettability and contact resistance test are also discussed in this chapter. Chapter 4 includes results and discussions of the characterization such as XRD, SEM, AFM, contact angle goniometer and contact resistance. Lastly, Chapter 5 summarizes the key findings of this study and provides suggestions for further research work related to magnetic stirring-assisted electroless NiP/Ag nanocomposite plating on supporting system.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

This chapter reviews the general properties of NiP/Ag nanocomposite. The synthesis techniques of NiP/Ag nanocomposite are also discussed. Particularly, magnetic stirring-assisted electroless nickel-phosphorus (NiP) plating technique and its synthesis factors that affect the morphology and electrical conductivity of NiP/Ag nanocomposite.

2.2   Electroless Nickel-phosphorus Plating

Electroless plating has wide acceptance in the market due to the coatings' high hardness, uniform coating thickness, wear and corrosion resistance, magnetic behavior, a higher fatigue limit and lower macroscopic deformation (Lelevic and Walsh, 2019). It is also good for soldering and brazing purposes. Electroless plating is defined as a controlled autocatalytic deposition of a continuous layer on a catalytic surface by the reaction of a complex compound and a chemical reducing agent (Tarditi et al., 2017). In simple words, a superior metal will coat over the base metal by catalytic reduction using a reducing agent in the electrolyte containing the soluble salt of the coating metal without the use of electricity.

Coatings produced by electroless nickel plating method are more uniform in thickness where the plating solution composed of mainly nickel sulfate that acts as source of nickel, sodium hypophosphite as reducing agent, and chemicals to avoid the precipitation of insoluble nickel hydroxide (Sudagar et al., 2013). They are normally operated at about 85°C under low pH which is maintained in acid range for bath stability, but the evolution of hydrogen could lower the pH value. In order to prevent this condition, alkaline salts of sodium, Na and potassium, K or ammonium ions, N_4N^+ will be added to

maintain the pH (Tarditi et al., 2017).

Electroless nickel plating is categorized into 3 types which are illustrated in Figure 2.1. Materials produced from acidic plating solution has strong adhesion, high hardness, wear resistance and good corrosion resistance whereas materials produced from alkaline plating solution has weak binding force and low phosphorus content (Luo, 2016). Furthermore, electroless plating of metal matrix having particles as second phase materials have illustrated the composite systems, where the composite coating is written as Ni-P-X or Ni-B-X (X = particle) (Sudagar et al., 2013).

There are also other autocatalytic or chemical reduction methods without using external current, such as, immersion plating and homogenous chemical reduction process (Sudagar et al., 2013). Immersion plating refers to the copper deposited on the steel which is immersed into the copper sulfate solution, or the steel is immersed into the chloride and boric acid bath; homogenous chemical reduction process refers to silvering where normally is the process of making mirrors by coating glass with silver (Luo, 2016).
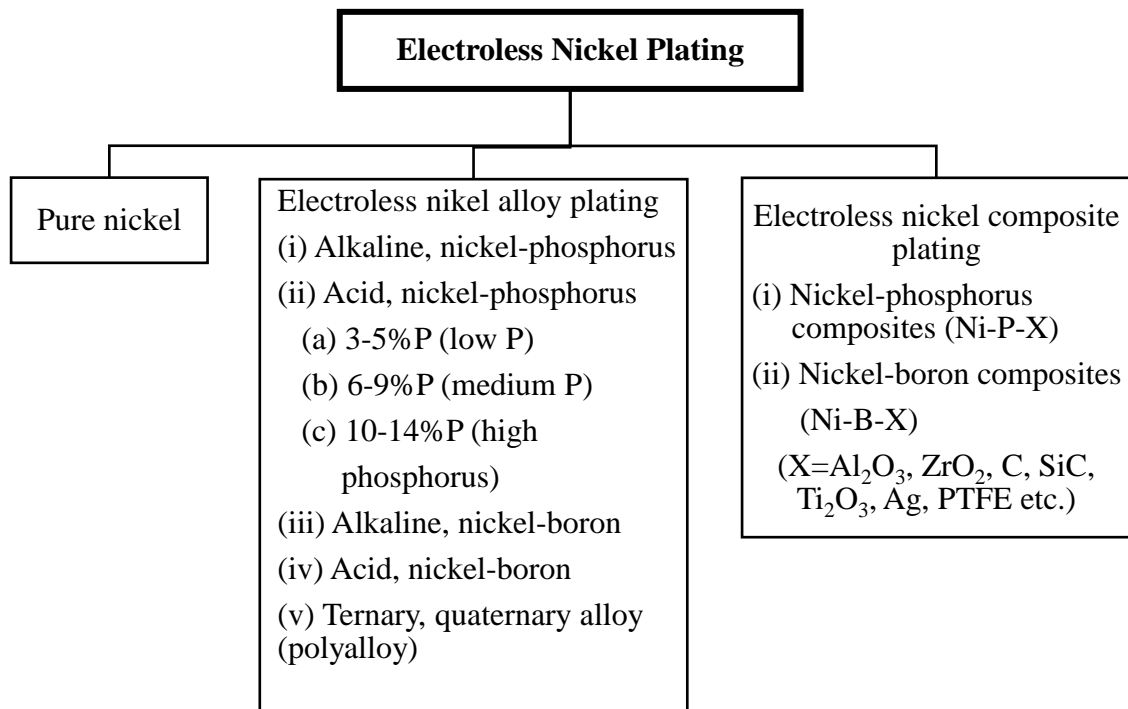
Figure 2.1: General categories of electroless nickel platings (Sudagar et al., 2013)

There are few several reasons for spontaneous decomposition of electroless nickel bath including local overheating, rapid addition of reducing agent (sodium hypophosphite), high concentration of phosphite, rapid addition of an alkali, excessive nickel deposits on tank walls or on heating coils, high pH during bath preparation that cause the precipitation of nickel compounds, incomplete removal of palladium after palladium activation, instability of fresh baths, low plating solution loadings, and overuse of plating solution that cause precipitation of phosphates (Krishnan et al., 2006).

2.2.1 Mechanism of deposition

The deposition of nickel in electroless nickel coating occurred when nickel ions in its aqueous salt solution is reduced and deposited on the catalytic surface of substrate immersed in the solution. Selective reduction of nickel ions only occur at the less noble surface of a catalytic substrate when immersed in an aqueous nickel ions solution containing a source of nickel ions, reducing agent and other components under prescribed conditions.

The reduction reaction is catalysed by the substrate surface and hence this process is also described as autocatalytic; once the reaction begins, the process will be continued on the entire substrate surface (Mallory et al., 2009). Therefore, the newly deposited nickel will then acts as a self-catalyst for further nickel deposition.

The electroless nickel coating process is so complicated that the exact mechanism of nickel-phosphorus deposition is still far from being fully understood. Since it was just discovered, there were several mechanism have been proposed for the chemical reactions that occur in the electroless nickel coating solutions (Agarwala & Agarwala, 2003; Baskaran et al., 2006; Beygi et al., 2012; Ijeri et al., 2014; Mainier et al., 2013; Meerakker, 1981; Sharma et al., 1998; Tarozaitë, 2005). However, the most widely accepted mechanism is the electrochemical mechanism.

For electroless nickel-phosphorus plating, since substrate is deposited by the nickel alloy from aqueous solutions without the use of electric current. The nickel ions is reduced to nickel metal by a reducing agent which is the sodium hypophosphite that is most commonly used due to its low cost and availability. A simple chemical reaction is written as below (Krishnan et al., 2006):

Anodic reaction:

The reducing agent is oxidized

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^- \text{ ----------- } (Equation\ 2.1)$$
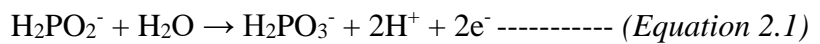
Cathodic reaction:

Ni^{2+} ions are reduced to Ni and deposited on the substrate

$$Ni^{2+} + 2e^- \rightarrow Ni \text{ ----------------------- } (Equation\ 2.2)$$

Net reaction:

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+ \text{-------- } (Equation\ 2.3)$$
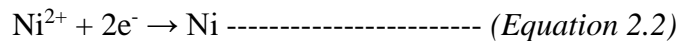
Furthermore, addition of additives such as complexing agent, stabilizer, and buffering agent also cause side-reaction in the coating solution bath and produce unwanted by-product. All this side-reactions occur in coating solution bath reduced the ability of co-deposition Ni-P coating as the concentration of the by-products increase (Mainier et al., 2013).

2.2.2 Electroless Coating Parameters

Generally, there are a source of metal ions, reducing agent, stabilizer, complexing agent, buffering agent, wetting agent in the electroless plating solution, together with the process parameters which include controlled temperature and pH. These components and parameters greatly affect the deposition rate and properties of the coating (Moniruzzaman

and Roy, 2011). Their role is briefly summarized in Table 2.1.

Table 2.1: Components and parameters of plating solution and their functions (Krishnan et al., 2006; Sudagar et al., 2013)

Component/Parameter	Function	Example
Metal ions	Source of metal.	Nickel sulfate, nickel chloride, nickel acetates.
Reducing agents	Supply electrons to reduce the metal (nickel) ions.	Sodium hypophosphite, aminoboranes, sodium borohydride, hydrazine.
Stabilizers (inhibitors)	Stabilize the plating solution from decomposition by shielding catalytically active deposition.	Pb, Sn, As, Mo, Cd, or Th ions, thiores, etc.
Complexants	Prevent excess of free metal ions concentration.	Monocarboxylic acids, dicarboxylic acids, hydroxycarboxylic acids, ammonia, alkanolamines, glycine, etc.
Wetting agents (Surfactant)	Increase wettability of surfaces to be coated.	Ionic and non-ionic surfactants.
Buffers	Maintain the pH for long time.	Sodium salt of complexants, choice depends on pH range used.
Accelerators (exultants)	Accelerate the reducing agent and increase the deposition.	Anions of some mono- and di-carboxylic acids, fluorides, borates.
pH regulators	pH adjustment	Sulphuric and hydrochloric acids, soda, caustic soda, ammonia.
Temperature	Energy for deposition.	-

2.2.2.(a) Nickel Metal Source

The common nickel salts such as nickel sulphate, nickel chloride, nickel formate, nickel fluoborate, nickel acetate, nickel hypophosphite, and nickel sulphamate are used as nickel source in electroless nickel solution. Generally, nickel salt such as nickel sulfate and nickel chloride are used in acid plating solution. In addition, among all of the nickel salts, nickel sulfate is preferred due to its cost effective and wide range of applications. As comparison, other nickel salts have limited applications and each of them have their own drawback such as no significant improvement in plating solution or the low coating quality (Parkinson, 2000; Mallory et al., 2009).

Besides, the concentration of nickel sulfate in the plating solution will affect the deposition rate and the phosphorus content. The deposition rate increase with increasing nickel concentration (Taheri, 2003) whereas the phosphorus content of coating may decrease if nickel sulfate is excessively added and will lead to instability of the plating solution. There was found that the phosphorus content remain unchange when the nickel concentration is more than 0.1M (Mallory et al., 2009).

2.2.2.(b) Reducing Agent

There are many reducing agents in the market such as sodium hypophosphite, amino boranes, sodium borohydride, and hydrazine. Sodium hypophosphite is widely used due to its lower cost, easier to control the process, and able to produce coatings with better corrosion resistance (Agarwala and Agarwala, 2003). There are two reactions occur in reduction mechanism of metal ions by hypophosphite which are the anodic and cathodic reactions as mentioned above. Gould et al. (1981) and Marshall (1983) found that the electrochemical mechanism will affect the deposition reaction but not the chemical reduction.

The adding of sodium hypophosphite will reduce the content of nickel deposited on the substrate and the percentage of the deposited phosphorus will greatly affect the properties of a product such as corrosion and wear resistance, and hardness (Parkinson, 2000). In general, 1 kg of sodium hypophosphite able to reduce 200 g of nickel with an average efficiency of 37% (Mallory, 1974). The properties of coatings vary with the phosphorus content in a wide range, typically 3% to 12%. They are sub-classified into:

(i)   2-5% P (low phosphorus). These coatings have high hardness, excellent wear resistance and high corrosion resistance against alkaline or caustic environments.

(ii)   6-9% P (medium phosphorus). These coatings have sufficient corrosion protection and abrasion resistance for most applications. The plating solution works economically.

(iii)   10-13% P (high phosphorus). These coatings are very ductile and have corrosion resistance against acidic environments, chlorides, and simultaneous mechanical stress.

For medium phosphorus coatings, they can be either fully amorphous or consist of a mixture of amorphous and nanocrystalline nickel phase which will give a broadening effect in X-ray diffraction (XRD) analysis. Low phosphorus coatings that consist of nanocrystalline nickel with a small amount of amorphous phase or simply crystalline nickel phase will result in a sharper peak in XRD analysis. Therefore, the phosphorus content is important in determining the phase and the properties of the coatings.

Aminoboranes as the reducing agent in electroless nickel plating are limited to two compounds which are the N-dimethylamine borane (DMAB)-$(CH_3)_2NHBH_3$ and H-diethylamine borane (DEAB)-$(C_2H_5)_2NHBH_3$. The solubility of DMAB is spontaneous in water while DEAB needs to be mixed with other substances such as ethanol before

added into the plating solution. Also, the pH after adding amineboranes into nickel content plating solution shows positive value in the range between 6 and 9 and hence, they are suitable to be used in acidic baths under 50°C to 80°C. However, they also can be used at low temperatures of 30°C (Aliofkhazraei et al., 2021). In general, 1 kg of DMAB able to reduce 1 kg of nickel (Sudagar et al., 2013).

Sodium borohydride ($NaBH_4$) has very strong reducing power where it can provide up to eight electrons for reduction of metals as compared to sodium hypophosphite that can only provide two electrons for the reduction of metals. Moreover, it is also more cost effective and cheaper than dimethylamine borane to be used in alkaline solution. Also, 600 g sodium borohydride able to reduce 1 kg of nickel with more than 92.97% purity (Sudagar et al., 2013). However, spontaneous decomposition will happen in acid or neutral borohydride-based plating solutions and produce nickel boride. This makes the control of pH becomes important where it has to be maintained in the range of 12 to 14 in order to prevent the formation of nickel boride. Therefore, sodium borohydride is normally used as alkaline plating solution (Aliofkhazraei et al., 2021).

Hydrazine baths normally operate in alkaline solution within pH 10 to 11 at 90°C to 95°C. It can produce high purity of electroless nickel coating over 99%. However, it is less commonly used in industries due to its instability at high temperatures and difficult to control. Moreover, the coating produced is highly stressed and brittle which is not desirable for applications (Agarwala and Agarwala, 2003). Also, it is costly and hazards (Sudagar et al., 2013).

Concentration of reducing agent influence the amount of nickel reduction and thus the nickel and phosphorus content in the coating. Generally, increasing the sodium hypophosphite concentration, increased the hypophosphite ion concentration in the Ni-P solution and thus results in an increase in the phosphorus content of the coating (Marshall,

1983; Aliofkhazraei et al., 2021). Increment in deposition rate is also observed when sodium hypophosphite concentration is increased (Jiang et al., 2017; Krishnan et al., 2006; Balaraju et al., 2006).

Unlike electrolytic nickel coating, the electroless nickel coating is not pure nickel but contains phosphorus, boron or nitrogen, depending on the reducing agent used. Sodium hypophosphite will yield electroless nickel coating containing phosphorus (Ni-P). Nickel-boron (Ni-B) coating was produced when sodium borohydride and amineboranes were used as reducing agent while hydrazine yields nitrogen-containing nickel coating (Ni-N) Sudagar et al., 2013).

2.2.2.(c) Stabilizers

Stabilizers also known as inhibitors where they can be harmful as well as beneficial effects on the plating solution and the coating. The concentration of the stabilizer in the plating solution can be very critical (Mallory et al., 2009). Small amount of stabilizer can increase the rate of deposition and the brightness of the coating. However, there are by-products of the reduction such as orthophosphate or borate and hydrogen ions will accumulate in the solution. These by-products will affect the deposition rate in such a way that the concentration of orthophosphate increases, the plating solution may decompose spontaneously, and the coating produced have roughened surface (Sudagar et al., 2013). It has been observed that the stabilizers have minor effect on the phosphorus content and a major effect on the morphology of the coating (Krishnan et al., 2006). The addition of the stabilizers also affecting the nanograin size of the electroless nickel coating (Cortés et al, 2010).

Stabilizers also are the chemical agents that are able to avoid homogeneous reaction that triggers the subsequent random decomposition of the whole plating solution.

The most effective stabilizers are divided into four classes (Mallory et al., 2009):

(I)   Compounds of Group VI elements (S, Se, Te)

(II)   Compounds containing oxygen (AsO_2^-, IO^{3-}, MoO_4^{2-})

(III) Heavy metal cations (Sn^{2+}, Pb^{2+}, Hg^+, Sb^{3+})

(IV)   Unsaturated organic acids (Maleic, itaconic)

Class I or Class II stabilizers can function effectively at low concentration around 0.10 ppm but in many cases, they are added beyond 2 ppm. As for Class III and IV stabilizers, they are conveniently defined in terms of molar concentrations such that Class III stabilizers is from range of 10^{-3} M to 10^{-3} M, whereby for class IV stabilizers is usually in the range of 10^{-3} M to 10^{-1} M (Mallory et al., 2009).

The type and concentration of stabilizers have significant effect on the quality of the coating and the microstructure. Some of the stabilizers also have the similar function as an accelerator and complexing agents (Cheong et al., 2004).

2.2.2.(d) Complexing Agents

During plating process, the Ni ions are being continuously reduced, and this will cause the precipitation of nickel and decomposition of plating solution as plating time passes. To avoid decomposition and to control the deposition rate, complexing agents are required to be added into the plating solution to form a stable complex and results in better stability of the plating solution. At the meantime, stabilizer should be added together as well in order to control the reduction of nickel ions and to allow the reduction occurs only on the surface of the substrate (Luo, 2016). Generally, there are three main roles of complexing agents in the nickel plating solution (Jin et al., 2010):

(i)   Acting as pH buffer agents to prevent the pH from dropping rapidly

(ii)   Prevent nickel salt precipitation

(iii)   Decrease the concentration of 'free' nickel ions

Complexing agents prevent the decomposition of solutions and also to control the reaction by ensuring the reactions only occurs on the catalytic surface. Examples of complexing agents are the acetic acid, citric acid, amber acid, malic acid and their salts. They are organic acids or their salts which is to control the amount of free electron from Ni available for reaction (Agarwala and Agarwala, 2003). In plating solution, the positive nickel ions will interact with and bound to the negative end of the dipole oxygen of the water molecules to form octahedral hexaquonickel ion $[Ni(H_2O)_6]^{2+}$ (Figure 2.2a). After adding of complexing agent, the water molecules that are coordinated to the nickel ion are replaced by complex ions or molecules where the resulting compound is known as a nickel complex (Figure 2.2b) and the combining, or donor group is so-called the complexing agent or ligand (Mallory et al., 2009).
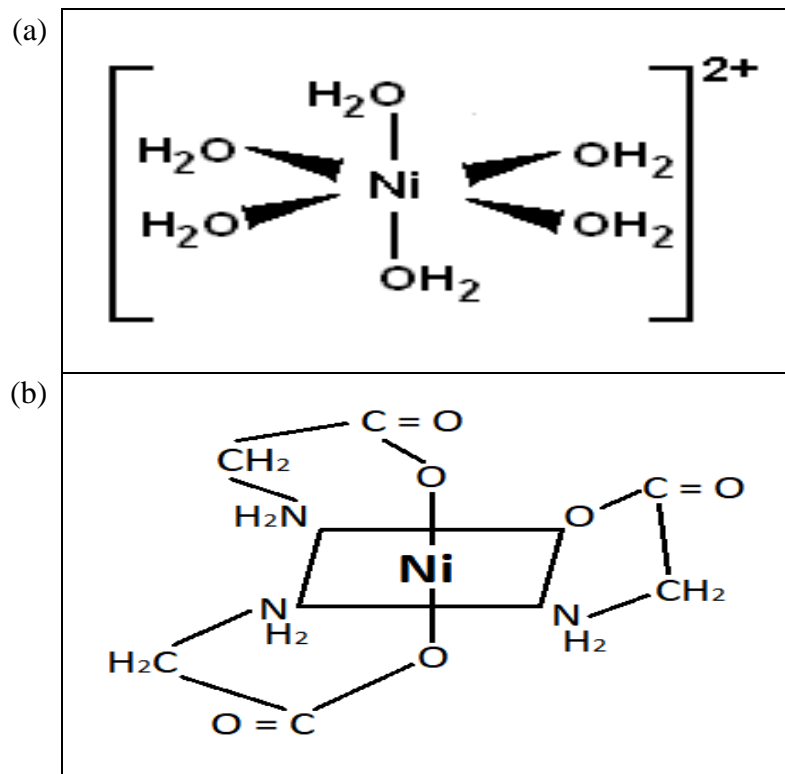

Figure 2.2: Schematic diagram of structure of (a) nickel bound to water molecule; (b) nickel complex (nickel-glycine molecules) (Martyak et al., 1996)

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In addition, complexing agents also buffer the solution and slow down the precipitation of nickel phosphite. This is due to the complexing agents have a considerable affinity for hydrogen ions as electron donors. When plating solution that contains free metal ions, M^{2+} is added with complexing agents, equilibrium is established as shown schematically (Mallory et al., 2009):

$M^{2+} + mL^{n-} = ML_m^{-(n-2)}$ ------------------------------- *(Equation 2.4)*
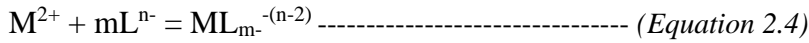
where M^{2+} = Metal

mL^{n-} = Ligand

$ML_m^{-(n-2)}$ = Metal-Ligand Complex ------------ *(Equation 2.5)*

In order to maintain the pH, the plating solution can be added with ammonia, hydroxides, or carbonates periodically to neutralize hydrogen (Sudagar et al., 2013).

The addition of complexing agents not only affecting the mechanism but also affecting the properties of the coating such as corrosion resistance, morphology, magnetic properties, and hardness. It was found that the amount of complexing agents have no significant effect on phosphorus content but it results in different surface morphology. Nanocrystalline phase is found after adding lots of complexing agents that eventually gives high hardness and high thermal stability of the coating (Cheng et al., 2008). However, excess complexing agents in the plating solution will increase the coating stress and thus produced low ductility and high porosity coating (Mallory et al., 2009).

2.2.2.(e) Wetting Agents/Surfactant

Wetting agents are also called as surfactant. Surfactants are the surface active agents that are made of organic compounds which are amphiphile. They will lower the surface tension of the liquid to ease the spreading and reduce the interfacial tension between two liquids by absorbing at the liquid-liquid interface, and thus, increase its

wettability (Assadi et al., 2012). In principle, the main role of surfactant molecules is to remove the tiny hydrogen bubbles from the surface of the substrate via adsorption at the hydrogen-liquid interface as shown in Figure 2.3. The addition of surfactants that lower the surface tension, it reduces the adsorption of particulates, hydrogen gas, and colloidal impurities and eventually lead to reducing of micro defects in the coating (Chen et al., 2002).
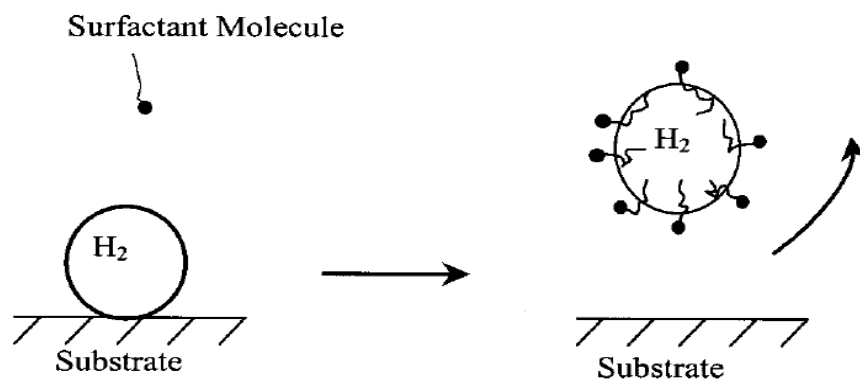

Figure 2.3: Schematic diagram shows the adsorption of surfactant molecules on the hydrogen bubble (Chen et al., 2002)

Also, surfactant molecules consists of two parts which are the head and tail (Muraliraja and Elansezhian, 2014). The head of surfactant is water soluble (hydrophilic) whereas the tail is oil soluble (hydrophobic). Surfactant is classified according to the presence of formally charged groups in its hydrophilic head as tabulated in Table 2.2.

Table 2.2: Different types of surfactants (Muraliraja and Elansezhian, 2014)

Type of surfactant	Type of charge	Example
Anionic surfactant	Hydrophilic head carries negative charge	Sulfonate salts, alcohol, sulfates, alkyl benzene, phosphoric esters, carboxylic acid salts

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Cationic surfactant	Hydrophilic head carries positive charge	Poliamide and their salt, quartenary ammonium salts and amine oxides, salt of long chain amine)
Non-ionic surfactant	Hydrophilic head has no charge	Polyethylenated alkyl phenols, alcohol ethoxylates and alkanolamides
Zwitterionic surfactant	Has both positive and negative charges	Long chain amino acid, betains and sulfobetain

2.2.2.(f) pH regulator and pH buffer

pH is a very important parameter in electroless nickel plating as it can decide the properties of the coating and the application of it (Mallory et al., 2009). Therefore, pH of the plating solution must be controlled in order to provide a suitable environment for the reaction to occur where the pH regulators act as the main role of adjusting the pH of the plating solution. Most common pH regulators are the sulphuric and hydrochloric acids, ammonia hydroxide and caustic soda that were compatible with electroless nickel bath (Krishnan et al., 2006).

During plating, pH of the plating solution is lowered due to the generation and accumulation of hydrogen ions (H^+). The direct effect of the drop pH is the decreasing in deposition rate where a very low deposition rate is observed when pH drop below 4.0. The amount of pH changes due to the generation of hydrogen ions is related to the buffer capacity of the complexing agents and buffers that are present in the plating solution. The greater the amount of acid needed, the better the buffer (Mallory et al., 2009).

Buffer is a solution that prevent pH change upon the addition of an acidic or basic components. A good buffer will neutralize the addition of small acid or base and maintain the pH of the plating solution (Mallory et al., 2009). Therefore, in order to obtain a reliable and repeatable results, it is vital that a constant-solution pH have to be maintained during the entire plating process (Schlesinger and Paunovic, 2010).

2.2.2.(g) Temperature

Temperature is one of the crucial parameters in electroless nickel plating process that particularly influences the deposition rate. Electroless nickel plating is a catalytic reactions which is depending on the energy in order to continue where the energy is supplied in the form of heat. Since the electroless plating reactions are endothermic, further increase the temperature of plating solution will increase the deposition rate (Mallory et al., 2009). The dependence of deposition rate on solution temperature is illustrate in Figure 2.4.
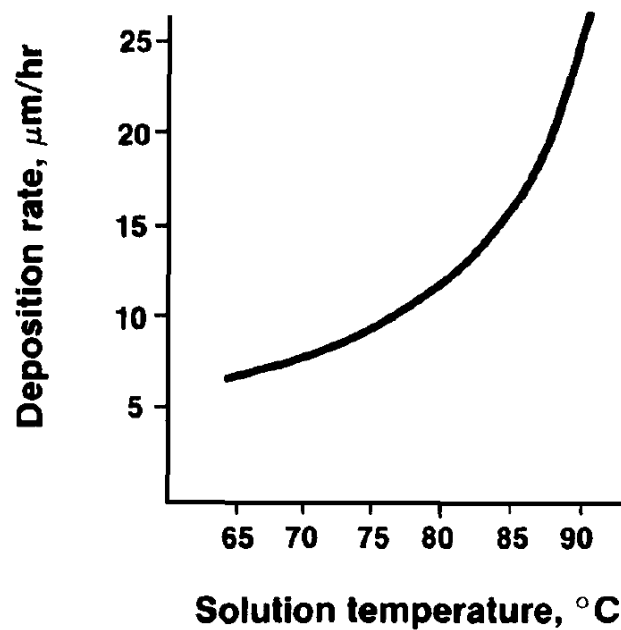
Figure 2.4: Effect of temperature on plating rate (Mallory et al., 2009)

For electroless Ni-P plating, ideal temperature for the plating solution is within the range of 85°C to 95°C at pH 4.5 to 5.0 (McKeen, 2016). However, pH is difficult to control and the plating solution may spontaneously decompose when temperature above 90°C (Sudagar et al., 2013).

2.2.3   Advantages and Disadvantages of Electroless Nickel Plating

Major advantages over the electrodeposition process including the formation of a uniform coating on any substrate geometry and direct deposition on surface activated non-conductors. Coatings produced from electroless nickel plating have better thickness distribution compared with electrodeposited coatings where it can be seen from Figure 2.5. The advantages of electroless nickel plating include the quality of coating that will result in a good physical and mechanical properties. During the process, the sharp edges also gain same thickness of coatings as a blind hole do where the coatings are extremely bright. Also, the desirable properties can be varied by adjusting the parameters such as pH, temperature and the composition of the bath (Krishnan et al., 2006). The coating produced by electroless normally has excellent corrosion resistance, excellent wear and abrasion resistance, high hardness (especially after heat-treated), good ductility, lubricity, good electrical properties, and good solderability (Krishnan et al., 2006; Sudagar et al., 2013; Kaya et al., 2008).
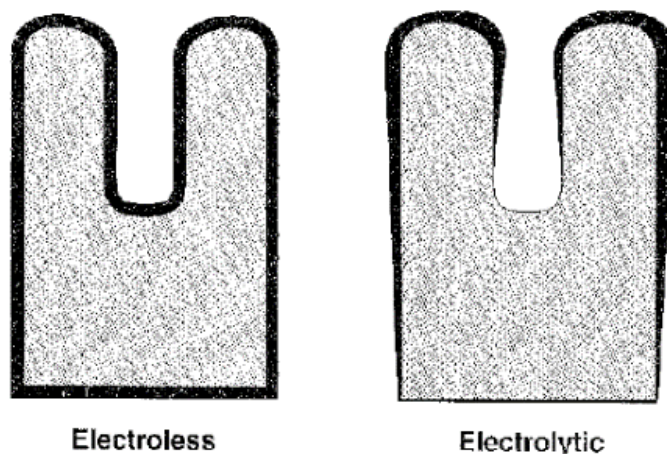
Figure 2.5: Comparison of coatings uniformity (Parkinson, 2000)

The disadvantages of electroless plating process including that the plating solution needs to monitor for the entire process to ensure the temperature and pH is within the range to avoid decomposition (Agarwala and Agarwala, 2003). Besides, the plating solution may have short lifespan due to the accumulation of contaminants and eventually leads to high chemical cost (Jendrzynski, 1959).

2.2.4 Applications of Electroless Nickel Plating

There are many applications in chemical process industry due to the properties of electroless nickel coating. Generally, low phosphorus coating has better corrosion resistance in strong alkaline environments whereas high phosphorus coating has better resistance to chemicals that may hydrolyze to produce weak acid environments (Tulsi, 1986). Examples of the products in the applications of processing, storage and transportation of chemicals are steel compressors, control valves, cooling towers, cooling tower water pumps, and the nuts and bolts. Other components on rail cars used for transporting chemicals such as safety vents, unloading connections, air connection valves and bottom outer valve assemblies that are coated with low phosphorus that results in excellent corrosion resistance and able to prevent the discoloration of the product

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(Parkinson, 2000).

Besides that, food industry also widely applies electroless nickel plating technology in the packaging equipment such as bearings, conveyer systems, rollers, hydraulics and gears in meat processing, bakeries, fast food restaurants and etc. This is due to electroless nickel can act as a protective layer for different components and would not direct contact and contaminate the food (Parkinson, 2000).

Furthermore, electroless coating also provided excellent service in oil and gas industry. The most valued properties to the industry are the thickness uniformity of the coating, excellent corrosion resistance (high phosphorus type), and the abrasion or erosion resistance. Examples of the product are the valves and flow control devices, compressors, gas turbines, pump housings, tubing, blowout preventors, heat exchangers and riser connectors. Therefore, the equipment produced from electroless nickel can sustain longer in a severe environmental condition that contain chlorides, hydrogen sulphide, carbon dioxide, brines, sea water and reef water (Strafford et al., 1982; Tulsi, 1986).

In automotive industry, the companies focus on the quality, performance, efficiency and the extended warranties. Consequently, electroless nickel coating gives great advantage in the industry such as corrosion resistance, wear resistance, lubricity and uniform coating thickness. Typical applications in automotive industries are the heat sinks, pistons, engine bearings, shock absorber, fuel injectors, exhaust system components, carburetor parts and gear assemblies. Also, high hardness of the coating can be obtained after heat treatment for the components to support the vehicles (Tulsi, 1986).

Moreover, electroless nickel plating has a combination of excellent functional properties like wear, corrosion and erosion resistance, uniformity of coating thickness on complex components that considered as an interest to be applied in aerospace industry as

well. Examples application are the compressor section of gas turbine, high pressure compressor stator assemblies, compressor case components, variable vanes, bearing housing, flexible bearing support, oil and fuel lines, airframe assemblies, landing gear, navigational systems and metallic optics, manual locking system and connecting link for the rotor head (Strafford et al., 1982).

Next, electronics industry also utilizes the properties of electroless nickel coating such as magnetic properties, corrosion and wear resistance, solderability and appearance. In memory disc making, aluminium substrate is plated with non-magnetic, hard and high phosphorus electroless nickel at thickness of 10 to 15 microns. Also, electroless nickel with good thermal conductivity properties allows the use of heat sinks devices to cool semiconductor components (Tulsi, 1986). Thin and uniform surface mount components also can be produced by electroless nickel. Other components like connectors, microwave components, transistor chips and etc also produced by electroless nickel coating due to its uniformity, good solderability and electrical conductivity of the coating. There are also other applications used in different industries such as foundry tooling, mold protection, printing industry and textile industry (Parkinson, 2000).

2.3   Electroless NiP Nanocomposite Coatings

According to many researchers, co-depositing another metallic or non-metallic elements or abrasive/lubricate particles or combination of them in binary Ni-P matrix can further enhance the properties (Ma et al., 2009; Allahkaram et al., 2012; Sudagar et al., 2013; Lelevic and Walsh, 2019). Electroless Ni-P based composite coatings that is coated with second phase particles in micron size like Al_2O_3, B, SiC, B_4C, MoS_2, C, PTFE, Si_3N_4, etc. have been co-deposited successfully. These composites that are produced from different types of particles which were added into Ni-P coatings exhibits different