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Electroless and Immersion Plating Process towards Structures and IMC Formation

M.A. Rabiatul Adawiyah[1], O. Saliza Azlina *[1], Nor Akmal Fadil[2],
Siti Rabiatull Aisha [3], and M.A Azmah Hanim [4]

[1]Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, Batu Pahat, Johor, Malaysia
[2]Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia
[3]Faculty of Mechanical Engineering, Universiti Malaysia Pahang, Pekan, Pahang, Malaysia
[4]Faculty of Engineering, Universiti Putra Malaysia, Serdang, Selangor, Malaysia
[1] rabiatuladda90@gmail.com;[1*] salizaz@uthm.edu.my
[2]norakmal@fkm.utm.my
[3]rabiatull@ump.edu.my
[4]azmah@upm.edu.my

Abstract*-The selection of surface finish on printed circuit board is very important in soldering process because it can prevent the copper from oxidation and provide solderable surface. It is also will influence the cost, manufacturing, shelf life, surface quality, final product reliability and environment.Electroless and immersion plating process has now become an important and popular surface finish in electronic industry due to simple and low cost process. The application of electroless plating are widely used in electronic industry, however it also was used in various industries such as aerospace, automotive, oil and gas, chemical processing where the need on the complex shape, homogeneous and uniform layer are required. Besides, every surface finish has their strength and weakness. Immersion silver is one of the surface finishes frequently used on the printed circuit board due to their characteristics such as good solderability and wettability, easy assembly and low cost. Both of these two processes were acts as barrier layer between copper substrate and solder balls. This review was discussed about electroless nickel and immersion silver plated on copper substrate, coating process and parameters involved. The topic also covered include the morphology and thickness of the intermetallics formed during soldering as well as the isothermal aging process.

Keyword – Electroless plating, Electroless nickel, Immersion silver, Intermetallic compound, Reflow soldering

I. INTRODUCTION

The selection of surface finish on the printed circuit board could be the most important decision in electronic application. Currently, surface finish is used to protect the exposed copper surface from the oxidation when exposed to the environment which can reduce the strength of the solder joint and the wettability [1]. The electroless and immersion are widely used in electronic industry because both of them can enhanced the bond pad properties for electronic packaging [2]. The different between the electroless and immersion plating process are an auto-catalytic reaction [3-7] and displacement process [7], respectively. Electroless plating is a chemical reduction process [4,5], where the deposition process of the metal was not involved the electrical energy usage [6,7]. Typical surface finishes commonly used for electroless plating technique are electroless nickel/immersion gold (ENIG) and electroless nickel/electroless palladium/immersion gold (ENEPIG). In electronic industry, electroless nickel (EN) is a popular surface finish compared to other techniques such as electroplating. Many researchers have been issued about the advantages of the EN for the engineering and especially for printed circuit board (PCB) application [3,5,7-9]. Several advantages of EN include the quality of deposit such as physical and mechanical properties. There are some of the properties were usable as solderability, high hardness, magnetic properties, resistivity and low coefficient of friction. However, most applications of the auto-catalytic are depend on their wear and corrosion resistance [3,7]. The desired properties can be a range by choosing different temperature, pH value and composition of the bath [3] as shown in Table 1.

The immersion plating is a displacement process where the metallic ions in the solution will be reduced on the surface substrates [7]. Immersion silver (ImAg) is one of important surface finish for the electronic assembly and it was Restriction of Hazardous Substances (RoHS) compliant. ImAg also known as an alternative to HASL [10-12] and ENIG [13,14] because of their good solderability, wettability, co-planarity and bonding performance [10,15]. According to Wang *et al.* [10], the selection of immersion silver as a final surface finish is a good decision because it can eliminates the embrittlement of Au-Sn intermetallic layer (IMCs) as well as provides simpler operation and lower cost. Furthermore, immersion plating are not required to use reducing agent because the base material can behaves as reducing agent compared to electroless plating process [16]. In this review, the present work aims to study the electroless and immersion plating process towards structures and

intermetallic compound (IMC) formation including the coating process and its parameter, interfacial reaction between solder and substrates.

TABLE 1. Properties of Electroless Nickel Based Coatings [3]

Property	**Coating System**		
	Ni-3P	**Ni-8P**	**Ni-0.5B**
Composition range:			
Balance nickel	3-4 %P	6-9 %P	0.5-
Structure*	m-c	m-c-a	1.0 %B
Final melting point	1275	1000	c
Density (gm/cm^3)	8.6	8.1	1440
Electrical resistivity (mW-cm)	30	75	8.6
Thermal conductivity (W/cm-	0.6	0.05	10
K)	1000	ND	ND
Specific heat (J/kg-K)	10000	110	ND
Magnetic coercivity (A/m)	-10	+40	ND
Internal stress (MPa)	300	900	+500
Tensile strength (MPa)	0.7	0.7	ND
Ductility (%)	130	100-120	ND
Modulus of elasticity (GPa)			ND

*a: amorphous; m-c: microcrystalline; m-c-a: mixed crystalline and amorphous;

c: crystalline; ND: not determined

II. ELECTROLESS NICKEL PLATING

A. *Introduction*

Electroless nickel (EN) is produced from chemical reaction which involves nickel salts and reducing agent. The properties of electroless nickel are depending on the quantity of phosphorus in the chemical solution[6,17]. Generally, electroless plating process comprising a source of metal ions, complexing agent, reducing agent, stabilizer, buffering agent, wetting agent, controlled pH and temperature [6,7] as represented in Table 2. EN is a continuous process of metal deposition. Uniform thickness [5] and thick layer is obtained (between 3 ~ 6 µm) as long as the metal substrates still in nickel solution [6]. By controlling the chemical reduction of nickel ion, it is necessary to change the metal ions to the metal in order to form a coating layer on the substrate [7]. Besides that, if the parameter is not properly controlled, the unintended results will be happened because the reduction of nickel ion can take place in all solutions. The electroless plating process usually used to deposit metal or its alloys such as nickel, palladium, silver, gold and etc. to the substrate. Besides, either the nickel containing phosphorous or boron also included in this category [18]. The additional metal elements used in electroless deposition process known as poly alloy [9,19]. Some of binary, ternary and quaternary diagram are referred as poly alloys. For example, binary alloys have Ni-P [19] and Ni-B [20], while ternary alloys have Ni-P-B [20], and Ni-W-P [21]. For quaternary alloys have Ni-W-Cu-P [9,22]. Tables 3 represent the types of electroless metallic alloy coatings and their features.

In additional, electronic micro-component and packaging need a convenient barrier layer between Cu, Ag, Al, Ni, Au, Pd and Co[7], as well as solder to perpetuate a long period of services. However, electroless nickel are found to be a suitable metal which can act as a barrier and protect the substrate due to it slowest pace rate dissolution of the solder and growth rate of the intermetallic compounds formation [24-28] compared to silver, gold or palladium. There are five types of EN coatings such as pure nickel, black nickel, electroless composite electroless nano-coatings and electroless nickel alloy coatings [7]. EN alloy coatings may consist four types, as follow [22]:

(1) Acid bath: Ni-P alloy, 3-5% P (low), 6-9% P (medium), 10-14% P (high).
(2) Alkaline bath: Ni-P alloy.
(3) Acid bath: Ni-B alloy, 0.1-2% B (low), 2.5% B (medium), 5-10% B (high).
(4) Alkaline bath: Ni-B alloy.

TABLE 2. Summary Parameter of the Electroplating Solution and Their Function

Parameter	Functions
Metal ions	Sources of metal. For examples nickel sulphate, nickel acetates and nickel chloride [7].
Reducing agent	To supply electrons to reduce the metal ions. For example sodium hypophosphite, amino boranes, sodium boron-hydride and hydrazine [3,6,7,18].
Complexing agent	To prevent access of free metal ions concentration, rapid pH change, retard the inclination for precipitation of nickel salts. For example EDTA, ammonia, dicarboxycarbo acids, alkanolamines, etc. [6,7,18].
Stabilizer	To stabilize the bath from decomposition by shielding. For examples Pb, Sn, As, Mo, Cd, thiourea, etc. [6,7]
Buffering agent	Sustain the pH for long time. For example sodium salt and to choice buffering agent depends on pH range used. For pH adjustment such as sulphuric and hydrochloric acids, soda ammonia [7,17,23].
Temperature	Energy for deposition [7].

TABLE 3. Features and Types of Electroless Metallic Alloy Coatings [7]

Consumption	Alloy types
Corrosion protection	Ni-P, Ni-P-Mo, Ni-Sn-P, Co-P, Co-P-Mo, Ni-Cu-P
Wear resistance	Ni-B, Ni-B-Tl, Ni-B-Mo, Ni-B-Sn, Co-P-W, Co-B; Ni-P-SiC, Ni-P-WC (dispersion)
Magnetic	Au-Ni, Au-Co; Ni-Co-P, Ni-Co-B, Ni-Fe-P
Solderability	Sn-Pb, Ni-P
High temperature	Co-W-B, Ni-Re-P
Diffusion barrier	Ni-P

B. Bath Chemistry

Reducing agent

Some of reducing agents have been widely used in electroless plating including sodium hypophosphite, amino boranes, sodium borohydride and hydrazine [3,6,7,18].

(1) Sodium hypophosphite
The most normally used to reduce agent was sodium hypophosphite. It is mainly used for electroless nickel plating because their characteristics can produce a nickel-phosphorus as a coating layer. Hypophosphite is capable to reduce nickel ions in solution to deposits nickel on metal substrate as well as on plastic substrates. More than 70% electroless nickel was deposited from solutions reduced by sodium hypophosphite [7,18].

(2) Amino boranes
Amino boranes are versatility which is can avoid some issues with other borane reducing agent. N-dimethyl amine borane (DMAB)-$(CH_3)_2NHBH_3$ and N-diethylamide borane (DEAB)-$(C2H_5)_2NHBH_3$ are two types of amine boranes was used in electroless nickel plating solutions [3].

(3) Sodium borohydride
One of the powerful reducing agent was sodium borohydride, where avai1able for the electroless nickel plating. Nickel boride will formed because of the presence of nickel ions. Borohydride is catalytically decomposed if the pH value above than 13 for alkaline solution and the reaction product is principally containing nickel. In general, 5 kg of hypophosphite is required while 0.6 kg of sodium borohydride is needed to reduce 1 kg of nickel [7]. However, complexing agents such as ethylenediamine must be used to prevent nickel hydroxide precipitation [3].

(4) Hydrazine
Using reducing agent such as hydrazine can produce pure electroless nickel deposition, which is contain up to 90% of nickel [7], with oxygen and 10% of nitrogen [22]. For the example, nickel chloride hexahydrate contain $4.8gL^{-1}$, $32gL^{-1}$ of hydrazine and $4.6gL^{-1}$ of sodium tartrate dehydrate at 10 pH values and 95^oC of deposition.

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Complexing agent

Complexing agents are an organic acids. The function of this agent are to maintain stability of pH level, help to prevent precipitation of nickel salt such as phosphates and to reduce the concentration of free nickel ions [22]. Besides, this agent alsobuffer the solution that prevents a rapid pH change and retard the precipitation of nickel phosphate [6]. However, ammonia, hydroxides, carbonates may also have to be added periodically to neutralize the hydrogen [7].

Stabilizer

In general, stabilizer can control the plating reaction with added inhibitor (also known as stabilizer) in nickel plating bath solution. This additives have four types of stabilizer's concentration usually used in industries such as oxygen containing compounds (AsO^{-2}, MoO_2, etc.), Compound of group IV elements (Se, Te, etc.), heavy metal cations (Sn^{+2}, Pb^{+2}, etc.) and unsaturated organic acids (maleic, etc.) [6].

Buffering agents

Another family of additives is known as buffers. Buffers is a substance or joining of substance in solution. It is able to neutralizing both acids and base without changing the original of solution's pH [23]. The amount of acid was required to change the pH value to measure of buffer quantity. The common acids that used as buffer in electroless plating are including acetic, propionic, glutaric, succinic and adipic [17].

TABLE 4. Effect of pH Change on Electroless Nickel Plating Process [23]

pH change	Effect on solution	Effect on deposition
Raise pH	Lower phosphate solubility, increased deposition rate. Decreased stability with resultant plate-out	Decreased P content, shift in stress to tensile direction. Poorer adhesion on steel.
Lower pH	The improvement of phosphate solubility, the deposition rate is decrease.	Increased P content, shift in stress to compressive direction. Improved adhesion on steel.

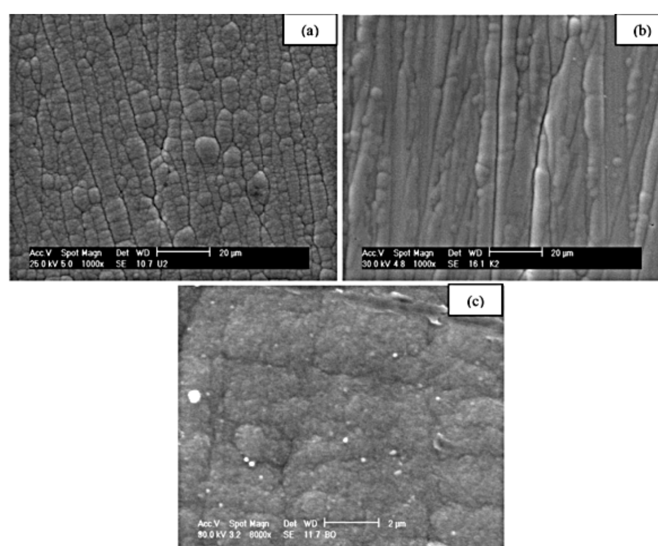

Fig. 1. SEM image top view of Ni-P with different P content (a) high Ni-P, (b) medium Ni-P and (c) low Ni-P [24]

Maintaining an EN solution begins with an understanding the chemical and physical process variable involved where it can influenced the bath process performance. These variablesalso can affect the quality of final deposition on copper board. Besides that, the condition of plating and sample preparation process also will influence the performance and quality of the EN plating.A consistent andstable solution during plating process is very important to provide high quality and uniform layer of nickel deposition on copper or PCB board.

C. Nickel phosphorous

Nickel phosphorous (Ni-P) alloy are commonly used for the deposition because it can let the thick coating onto the metal or substrates. Besides that, the bath solution is more stable during plating and better quality of coating

can obtained [29]. The content of phosphorous in EN can influence the behaviour of the physical, mechanical and corrosion resistance properties of the coating. Oduoza and Khan [30] mentioned that the phosphorous content in EN can give effect on the internal stress because the existing internal stress depends on the microstructure Ni-P deposited. The parameter such as pH and temperature also can influence the rate of Ni-P deposition. It is an important to control the deposition rate of Ni-P or bath composition because when the pH decrease, the rate of deposition also decrease [31]. Table 4 shows the effect of pH change on EN plating process. According to Baldwin *et al.*[32], the temperature of plating bath will increased to the normal operating range when the content of phosphorous is decreased. Due to their properties, the phosphorous content may easy to control. The value of temperature also influences the rate of deposition. When the temperature increase, the plating rate also exponentially increases [23]. The increasing temperature more than 90˚C make the pH value difficult to control [31,5].

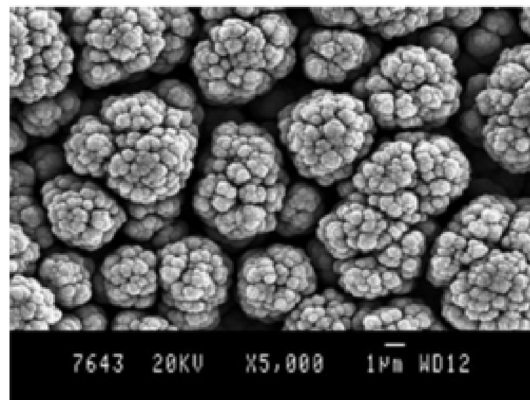

Fig. 2. SEM image of Ni-P morphology [34].

The growth structure of electroless nickel by using hypophosphate as reducing agent can be amorphous or liquid-like [18,33]. The amount of Ni-P can determine the microstructure of the coating either crystalline, amorphous, or both combination of microstructure [36]. Currently, electroless nickel process at low and medium phosphorus level has a mixture amorphous and microcrystalline nickel. While, the structure will be fully amorphous when the phosphorus content is high [7,35,36] as showing in Fig. 1. Low Ni-P has created nodular shape (Fig. 1(c)), where it happened from combination granular type with grain boundaries. The grain boundaries affected the efficiency of low P as a diffusion barrier. These grain boundaries can be eliminated by using high P content nickel [24]. Schlesinger [22] also mentioned that the higher sizes of the nickel crystallites making up when the phosphorus content is lower. Thus, phosphorus can act as an inhibitor of crystal formation. At the temperature above 220-260˚C, the structure of Ni-P begins change and the deposits starts to crystalline and also lose its amorphous structure. Fig. 2 shows the microstructure of electroless Ni-P plating. Besides, the morphology of the structure is cauliflower-like and crystalline structure. Based on low phosphorous content, these coating have better wear resistant and excellent corrosion resistance in concentrated caustic soda. The abrasion resistance and corrosion protection are better enough as well as economical in plating bath work, if medium phosphorous was used. For the high phosphorous, the coatings have good corrosion resistant, very ductile [39], low porosity, low internal intrinsic stress and non-magnetic is as plated state [23].

Solder Joint Microstructure of Ni-P coating

During plating process, intermetallic compound (IMC) will never form because the phosphorus atoms are trapped between nickel atoms in random way. It is because, they can lessen the possibility of contact among nickel atoms [18,38]. After the plating process, the intermetallic layer will be formed as Ni_3P within the alloy. Ni_3P is a first intermetallic layer that forms after plating process. This formation will happen when the temperature raises 320˚C as well as the crystallized structures will reach a maximum after heating at 400˚C for 1 hour. Before the formation of Ni_3P phase in stable condition, NiP_2 and $Ni_{12}P_5$ can be form with medium and high phosphorous contents [7].

From the previous researchers [39,40], the polycrystalline columnar structure of Ni_3P has a contain defects. Kirkendall voids are defects that form on P-rich layer formation and these voids will be affected the joint reliability that cause brittle fracture. Alam *et al.* [43] reported that the content of P and thickness Ni-P layer probably effect the performing shear test. Normally, a new layer such as Ni-P rich is formed between interfacial IMC and pure electroless Ni-layer during reflow process [44].

Normally, the type of IMC that formed after reflow soldering between substrates and solder balls was $(Cu,Ni)_6Sn_5$. The formation of intermetallic compound between solder and Ni-P are depending on Cu concentration. If the Cu concentration in the solder was lower than 0.2 wt%, only $(Ni,Cu)_3Sn_4$ appeared at the interface. Meanwhile, when the high concentration of Cu is more than 0.6w% the IMC layer was $(Cu,Ni)_6Sn_5$.

However, when the Cu concentration between 0.2 wt% and 0.6 wt%, both $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$ IMC was detected [24,43-46]. Azlina *et al*. [49] was investigated about effect nickel doping on interfacial reaction between lead-free solder and Ni-P substrate. They found that only $(Cu,Ni)_6Sn_5$ was appeared at the interface after reflow soldering. Similar findings was reported by [24,48,51]. In addition, the formation of IMC at interface will be changed with reflow condition [45]. Fig. 3 shows the IMC $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$ at interface between Ni-P with different content and Sn-4.0Ag-0.5Cu solder after reflow process. The typical structure of the IMC morphology is fine needle-type and boomerang-type [24].

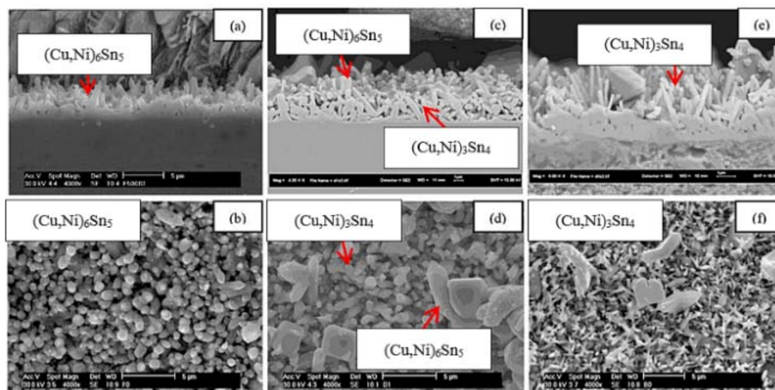

Fig. 3. Types of IMC at the interfaces between Ni-P and Sn-4.0Cu solder after reflow process: (a and b) high-P, (c and d) medium-P and (e and f) low-P [24].

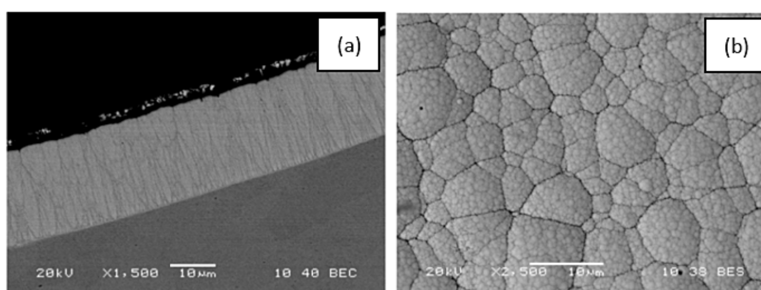

Fig. 4 The structure of Ni-B coating on top view (a) cross section columnar and (b) cauliflower-like surface [52].

To achieve a good performance standard of Ni-P deposition depends on the proper handling and correct operation. Surface preparation, operating parameter and chemistry solution are the main variables that influenced deposition rate, smoothness and uniform layer. The better understanding about the Ni-P plating process and their structure, it is easier to examine the crystallisation kinetic of the process with different phosphorous content. The different crystalline structure and IMC formation is depends on phosphorous content and reflow condition respectively. The first reaction between Ni-P deposits and subtracts is Ni_3P layer. Ni_3P layer is a thin layer that formed after plating process regardless of the phosphorous content. Currently, the type of IMC formationhas been determined by the type of lead-free solder, temperature, time and copper concentration. $(Cu,Ni)_6Sn_5$, and $(Ni,Cu)_3Sn_4$are normally IMC that formed and found after reflow soldering process.

D.Nickel-Boron

The advantages of electroless Nickel-Boron (Ni-B) has gained the attention from manufacturer. This surface finish become popular in industry because of its ability to provide a high hardness, high wear, abrasion resistance and lubricity as well as excellent solderability [21,50,51]. The properties of electroless Ni-B found a significant interest in aerospace, automotive, chemical industries and electronics [49,52,53]. Besides that, the ability of Ni-B can act as capping layer to avoid the diffusion of Cu substrates and it is necessary in the Cu interconnects technology [57]. Commonly, reducing agent such as sodium borohydride or dimethyl-amine borane was used in Ni-B alloy. These reducing agent has superior mechanical and chemical properties compared with Ni-P deposits [49,51-53,55].

In general, the phase of Ni-B consider as a mix amorphous and nano-crystalline because it is depending on boron content [55,56]. Similar reported by Delaunois and Lienard [60]. The structure of Ni-B present a typical cauliflower-like [49,58] as showing in Fig. 4. The formation of deposition Ni-B is begins by nodules, and then it was grows in columnar morphology. According to Rao *et al*. [56], the columnar morphology formed caused by the effect of the thickness of diffusion layer as illustrated in Fig. 5. These researchers also mentioned that the

thicker of diffusion layer, growth at the edge of the columns where it is likely to be disturbed by convection than on their tops. Therefore, the morphology leads to the typical cauliflower-like surface.

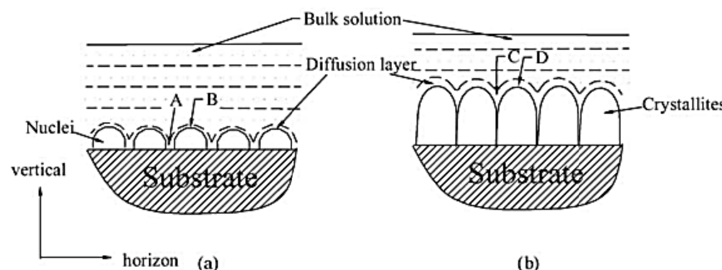

Fig. 5 The illustration for the effect of diffusion layer on top of Ni-B deposition (a) nucleation period and (b) crystallite growing period [56].

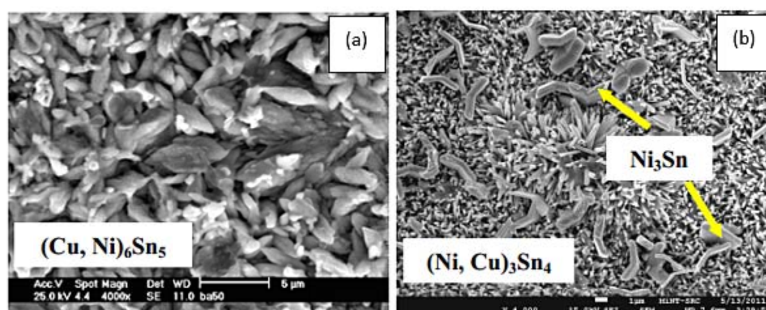

Fig. 6: SEM image top view of Sn-4Ag-0.5Cu between Ni-B after reflow soldering (a) near center area and (b) near outside area [62].

Solder Joint Microstructure of Ni-B coating

The first IMC layer of Ni-B will be leads to the crystallization of the Ni_3B phase and it happened after plating process [7,49]. When temperature above 250˚C, the structures of Ni-B start crystalline and Ni_3B will form at temperature 370-380˚C as well as Ni_2B [7]. Many researchers have been studied about interfacial reaction between lead-free solders and Ni-P [24,47,48,43-46]. Several of researcher also investigated about joint reliability and interfacial reaction between lead-free solder and Ni-B, but the knowledge about the structure and crystallization behaviour are still not yet clear [6,7,21,50,51,61]. The microstructure of the Ni-B is not too much different with Ni-P. Aisha *et al*. [64] was investigated about interfacial reaction of lead free solder on electroless Ni-P/ImAu and Ni-B/ImAu. They found that the formation of IMC layer after reflow process were $(Cu,Ni)_6Sn_5$ for both electroless Ni-P and Ni-B respectively. However, the IMC layer of $(Ni,Cu)_3Sn_4$ wasdetected at interface between $(Cu,Ni)_6Sn_5$ and Ni_3P after exposure in isothermal aging process. According to Azlina *et al*. [62], there are two types of IMC was formed between SAC405/EN(B)EPIG after reflow soldering. $(Ni,Cu)_3Sn_4$ was observed at the near outside area of the solder ball meanwhile, $(Cu,Ni)_6Sn_5$ was found at the near center area as can be seen in Fig. 6. Both IMC was continuously growth when subjected to isothermal aging.

III. PLATING PROCESS OF IMMERSION SILVER

A. Introduction

The immersion plating is a process where the chemical displacement reaction will be deposited into the bare copper. During the reaction, the base metal donates the electrons that can reduce the positive charge metal ions which present in solution. During the reaction, once the metal is plated, there is no any source of electrons and the reaction will automatically stopped. Therefore, this reaction is considered as a self-timing process [65]. The ImAg process consist the cleaning, micro-etching, pre-dipping, immersion silver deposition. The function of each steps of ImAg process has been presented in Table 5. During ImAg process, the operating parameter such as pH, temperature and solution very important to get the best surface finish. These parameters will be affected to the transfer dynamics at the plating surface [66].

TABLE 5. The Function of Each Steps Immersion Silver [10]

Process	Function
Cleaner	To clean the copper surface before the next process. Removes surface oils, oxides, any organic material and to ensure the copper surface will be in good condition and to be uniformly micro-etch.
Micro-etching	To produce a plating surface that promotes good deposit adhesion. Remove any chemical contaminant and metal oxides by lightly etching the exposed copper surface. The example of etchant types are sodium per-sulphate, peroxide / sulphuric.
Pre-dipping	To prevent any chemical residues from the previous rinsing step and remove any surface oxidation that may happen in the previous rinsing stage.
Immersion silver deposition	To deposits a layer of silver onto all of the exposed copper surface and protect copper from oxidation.
Drying process	To ensure the copper with silver surface finish are completely dry. Remove any leftovers moisture from the board to prevent discolour and to ensure metal quality.

B. Characteristics of the Immersion Silver Surface Finish

Immersion silver (ImAg) is one of an alternative finish where it was designed as protective surface finish to ensure the solderability of the underlying substrate [10,15]. The advantages of ImAg finish including good co-planarity, wire bondable [15], and suitable for fine-pitch of electronic applications [67]. According to Barbetta [67], ImAg also has good solderability, and it can maintained through the multiple reflow cycles. Besides that, it is also can maintaining thesolderability or wettability until 12 months before assembly process [12].

During soldering process, ImAg will be dissolved into the molten solder during assembly process because of liquidation of silver into the tin (Sn) based in the solder [10,15] as shown in Fig 7 (a). The thickness of Ag layer is typically less than 1 µm. It is happen because the deposition of Ag process will be stopped when the substrate surface is fully covered with the Ag solution [15]. Furthermore, Cullen [68] stated that the ImAg consist of 0.15-0.55µm thickness layer and it is 100 times thinner than the traditional electroplated silver deposits. In addition, Wang *et al*. [10] found that in order to get the 0.5 µm Ag layer in range [69], the duration of plating time is around 1 minute to 4 minutes. The Association Connecting Electronics Industrial standard (IPC-4553) [70] stated that the recommended thickness of Ag layer as minimum 0.13µm and typically 0.2µm-0.3µm can be obtained by using 60 x 60 mil pad. The standard also indicated that the possibility to obtain Ag thickness from 0.07µm to 0.12µm is possible, but it may limited for general purpose application only [10,66]. Some researchers reported that the thickness of immersion silver must be not too thick due to brittle solder joint in lead-free soldering, and not too thin to ensure a lifespan of this surface finish during storage [70–72].

C. Solder Joint Microstructure of Immersion Silver

During reflow soldering, the interfacial reaction will occur between ImAg and solder. As the result, the layer of intermetallic compound (IMC) will be formed between them and provides a good metallurgical bonding [10]. The type of IMC layer will be formed at the interface is depends on the metal surface and solders were used. Thus, a selection of surface finish and solder type are playing an important role.

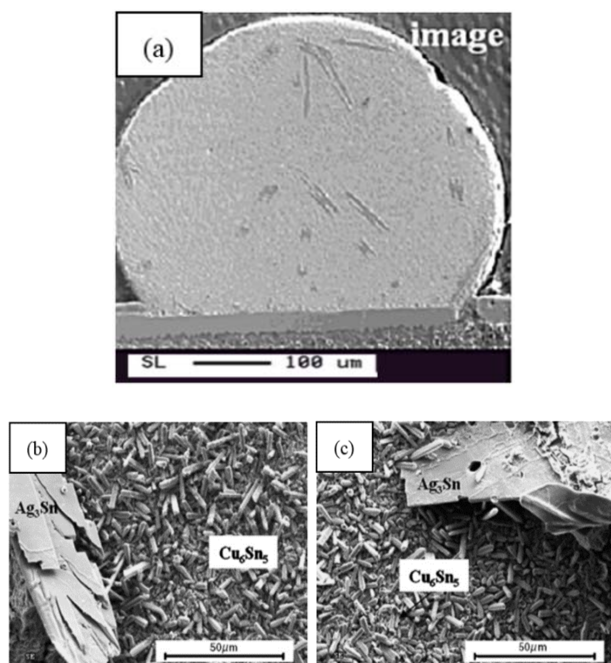

Fig. 7 SEM images of the Sn-3.5Ag-0.7Cu/ImAg plated joint reflowed at 250˚C at 60 s: (a) solder joint surface, (b) and (c) top view of the interface between solder and substrate [72].

The Formation of Intermetallic Growth

Generally, the formation of IMCs such as Cu_6Sn_5 and Cu_3Sn form at the interfaces. While, Ag_3Sn compounds was appearedat the bulk solder. According to Yoon and Jung[72], the layer of Cu_6Sn_5 has been observed at the interface when reflowed the Sn-3.5Ag-0.7Cu with ImAg finish at 250˚C for 60 seconds. The microstructure of the IMC layer in solder matrix comprised of a β-Sn matrix. A typical shape-type of the Cu_6Sn_5 was formed between the solder and ImAg interface after reflow process (Fig. 7 (b) and (c)). The morphology of Cu_6Sn_5 is rods-like, while Ag_3Sn is plates-like [72]. Zheng *et al.* [65] was investigated the similar surface finish with Sn-3.8Ag-0.7Cu. They also found a large Ag_3Sn platelet or needles are currently above the Cu_6Sn_5 layer after reflow process. Wiese *et al.*[73] was studied about the microstructure of Sn-4.0Ag-0.5Cu, they found that the formation of Ag_3Sn and Cu_6Sn_5 in a matrix of tin. Similar results have obtained by Lee *et al.*[74]. However, the Ag_3Sn platelet will be disappeared from the interface after exposed to high temperature aging and a new thin layer Cu_3Sn will be appeared between the interface substrate and Cu_6Sn_5. It was happened because of atomic diffusion between copper atoms and tin atoms from the solder [10,75].

Based on Cu-Sn phase diagram, IMC phase of Cu_6Sn_5 is form from the liquid solder state and the Cu_3Sn phase will be formed during inter-diffusion between interface copper and the Cu_6Sn_5 layer. Prior to aging process, the morphology of IMC is scalloped, but after exposed to aging it becomes thicker and uniform [69]. The different of aging times can influence the thickness of IMC layers either Cu_6Sn_5 or Cu_3Sn because the increasing of IMC layers with increasing aging time. Korhonen *et al.*[76] also investigated the thickness of the IMC layer. These researchers stated that the thickness of IMCs is depends on the solder sizes. The small solder balls will produced thicker IMC compared to the bigger solder balls. This is because the small solder will saturates quickly and caused the fast growth of IMCs.

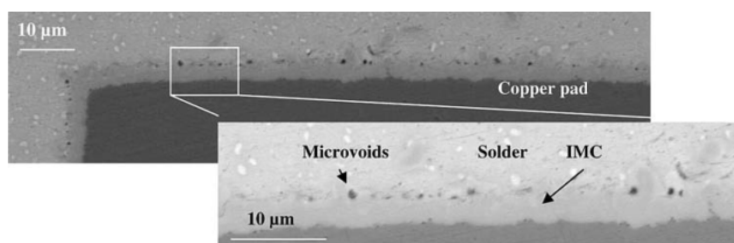

Fig. 8 Immersion silver pad finish with Sn-3.0Ag-0.5Cu solder joint; microvoids were found at the interface of solder and IMC layer [10].

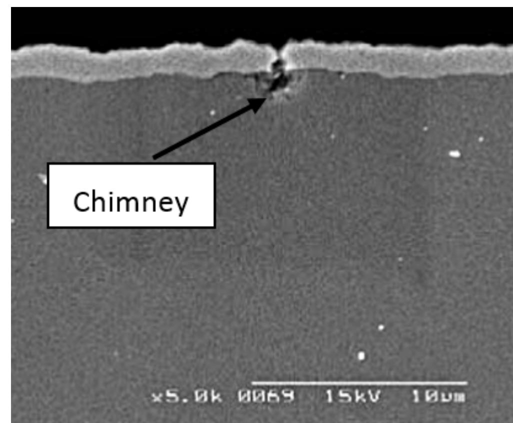

Fig. 9 The formation of chimney at a pathway between caves and silver surface [77].

The Formation of Microvoiding

A small holes (smaller than 50 µm) that form in a solder joint knows as microvoids (champagne voids) [78] as showing in Fig. 8. These voids caused by the unbalanced inter-diffusion ofcopper and tin at the interface between substrates and solder [10]. According to Schueller [79] and Yau *et al*. [78], the formation of microvoids caused by cavities or empty bubbles in the copper (the source of the microvoids upon reflow) It is happened because of the interaction between silver and copper during silver plating process [11,75,76].

Furthermore, the thicker silver layer can influence microvoid formation [78]. Typically, voids will form at near the surface of the copper pad, where the silver layer was used. The size of microvoids can separated into two groups which are small microvoids for the diameter less than the thickness of IMC layer (about 5 µm), while large microvoids for diameter greater than the thickness of IMC layer (less than 25 µm) [78]. The existence of microvoids can affect the solder joint strength [80], reliability and lead to crack propagation [10]. Besides that, the chemical solution during plating process has to be maintained, followed the specifications and guidelines to prevent the possibility of microvoid formation [80].

Previous researcher has found the "caves" under the immersion silver coating (Fig. 9). The formation of cave happened due to contaminant of inorganic residues material on the copper substrates during plating process [78]. Once the cave will be appeared at the surface, the microvoids formation have high tendency to occur during assembly. Besides that, Cullen *et al.* [78] discussed that a chimney formation was detected between caves and silver layer. Chimney is a micro pore that connecting the cave to the surface. However, the formation of cave can be reduced by modify the pre-sulphate micro etches solution.

ImAg finish proves to be high performing and low cost and allowed as alternative to both of HASL and ENIG because of a simpler process. Using the immersion process, the layer was uniform and met the thickness criteria and very stable process because the reaction only based on replacement process. It is also a better choice for lead-free electronics application that has good wettability and solderability compared to other lead free surface finishes. During reflow process, the layer of Cu_6Sn_5 and Ag_3Sn are growing into the solder. When the solder exposed to the aging process, Cu_3Sn_4 layer was appeared and Ag_3Sn platelet disappeared (with the high temperature aging) from the interface of solder. However, the defect known as microvoid and cave formation has been observed at near surface of copper substrate under silver layer coating, however the prevention can be made by maintained and controlled the chemical plating during the immersion silver process.

IV. CONCLUSION

Plating process involves covering outer layer of the copper or PCB board by deposition process. It is act as barriers to prevent corrosion and to improve the surface finish appearance. Every plating process required advantages from process control because it is very important to achieve the desired properties such as physical and mechanical properties as well as to getting quality of deposits. Besides, two crucial parameter such as pH value and temperaturewere affectedthe performance of plating process. This review paper has presented two plating process namely electroless nickel and immersion silver plating including their structures and IMC formation, by various researchers are reviewing the variety of informations.ENhas two types namely Ni-P and Ni-B. Both of Ni-P and Ni-B crystalline structures formation depended on the amount of P and B content. The different both of these content, the different structures will be appeared either the structure are amorphous, crystalline or amorphous and crystalline.While, the ImAg surface finish is an alternative to both HASL and ENIG due to excellent wettability, simple process and economical. There are several types of IMC that formed after reflow soldering for EN and ImAg such as $(Cu,Ni)_6Sn_5$, $(Ni,Cu)_3Sn_4$ and Cu_6Sn_5, Cu_3Sn_4 for respectively. The thickness and size of microstructure of IMC layer influenced by reflow condition, solder size and aging

time. The increasing of aging duration made IMC layer also increased. Meanwhile, the bigger solder ball sizes produced a thinner IMC layer compared with smallest solder ball sizes where produced thicker IMC layer.

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