Electrolessly-plated ternary nickel alloys as metallization materials for lead-free soldering

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2014

Yang, Y. (2014). Electrolessly-plated ternary nickel alloys as metallization materials for lead-free soldering. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/59235>

<https://doi.org/10.32657/10356/59235>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**ELECTROLESSLY-PLATED TERNARY
NICKEL ALLOYS AS METALLIZATION
MATERIALS FOR LEAD-FREE SOLDERING**

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SCHOOL OF

MATERIALS SCIENCE AND ENGINEERING

2014

Electrolessly-plated Ternary Nickel Alloys as Metallization Materials for Lead-free Soldering

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A thesis submitted to the Nanyang Technological University in
partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2014

Acknowledgments

I would like to take this opportunity to acknowledge the guidance, support, and assistance received during this work.

First of all, I sincerely express my great gratitude to my supervisor, A/P Chen Zhong, for his invaluable guidance, advice, and encouragement throughout the course of this study. I would also like to thank Dr. J. N. Balaraju and Dr. K. Chen for their advices on electroless plating. Without their supervision and constant support, this work could not be accomplished.

I am thankful to all of my friends in the School of Materials Science and Engineering, Nanyang Technological University, for their friendship and inspiration. In particular, I thank Mr. Liu Hai for his help with FIB and TEM operation. I would like to thank Dr. Tay Yee Yan for his help with TEM operation as well. I am also thankful to the technical staff: Ms. Yeow Swee Kuan, Ms. Mastura, Ms. Irene Heng, Ms. Tay Poh Tin, Mr. Tan Yong Kwang, and Mr. Patrick Lai, for their great assistance. Moreover, special appreciation is due to TAC members-A/P Thirumany Sritharan, A/P Gan Chee Lip, and Asst/P Huang Yizhong. Last but not least, I would like to thank Dr. Nadeesh Singh Nobein for his help as second reader for my thesis.

I express my deepest gratitude to my parents for their great love and support at every moment of my life.

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List of Abbreviations

EDX	Energy Dispersive X-ray
FIB	Focused Ion Beam
IMC	Intermetallic Compound
I/O	Input/Output
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
UBM	Under Bump Metallization
ULSI	Ultra Large-Scale Integration

Abstract

To address the potential reliability challenges brought by the accelerated reaction with the adoption of lead-free solders, three electrolessly-plated ternary Ni-based metallizations (Ni-Sn-P, Ni-W-P and Ni-Co-P) were developed as the soldering metallization in this work. The interfacial reactions between lead-free Sn-3.5Ag solder and these ternary metallizations during reflow and thermal aging were investigated. The interfacial reaction between the same solder and electrolessly-plated binary Ni-P metallization was compared to understand the effect of the addition of the ternary element. Among all four types of metallizations, Ni-P is consumed at the fastest rate, while Ni-W-P is consumed at the slowest rate. Besides, Ni-Sn-P and Ni-Co-P are consumed at an equally slow rate close to that of Ni-W-P.

During the Ni-Sn-P/Sn-3.5Ag interfacial reaction, as predicted based on the limited available information on the Ni-Sn-P phase diagram, the formation of Ni_3P has been successfully avoided. Instead, two intermetallic compounds (IMCs), Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ are formed. Although no voids are observed at the Ni-Sn-P/Sn-3.5Ag interface, scattered cracking occurs in both the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ and the Ni-Sn-P metallization layers. Though the overall consumption rate of the Ni-Sn-P metallization is slow, the presence of scattered cracking leads to fast degradation of the Ni-Sn-P/Sn-3.5Ag solder joint strength.

In the case of Ni-W-P, two IMCs, Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ are formed. No voids are found at the reaction interface after prolonged reaction. The amorphous nature of the $(\text{Ni,W})_3\text{P}$ layer makes it an effective diffusion barrier for Ni, resulting in the slowest thickness reduction for Ni-W-P metallization. The growths of both Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers are found to be diffusion-controlled. The activation energies for the growth of

Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers during solid-state reaction are determined to be 62.3 kJ/mol and 58.2 kJ/mol, respectively.

In the case of Ni-Co-P, three IMCs, $(\text{Ni,Co})_3\text{Sn}_4$, $(\text{Ni,Co})_{12}\text{P}_5$ and $(\text{Ni,Co})_3\text{P}$ are formed. Nano-sized voids are visible in the $(\text{Ni,Co})_3\text{P}$ layer under TEM, but no large voids are found under SEM. $(\text{Ni,Co})_3\text{P}$ and $(\text{Ni,Co})_{12}\text{P}_5$ layers perform well as the diffusion barrier, which is proven by the slow consumption rate of the Ni-Co-P metallization.

The impact on the solder joint reliability was reported through the evaluation of the mechanical behavior of micro-tensile joints with these Ni-based metallizations. The tensile strength of Ni-P/Sn-3.5Ag solder joints decreases significantly after aging for 400 h and beyond. This is because the prolonged reaction has weakened the interface, making the fracture mode change from ductile failure inside the bulk solder to the brittle failure at the Ni_3Sn_4 /solder interface. The tensile strength of Ni-Sn-P/Sn-3.5Ag solder joints drops significantly after aging for 300 h and beyond. This is due to the scattered cracking occurred at the reaction interface. Such cracking is likely to be caused by the columnar structure of the metallization layer. On the other hand, even upon aging for 600 h, since the diffusion barriers in Ni-W-P/Sn-3.5Ag and Ni-Co-P/Sn-3.5Ag solder joints remain intact, the tensile strengths of these two types of solder joints remain high, with maintained ductile failure inside the bulk solder.

The current research has pointed out a new strategy to address the growing concerns over long-term reliability of solder joints in the miniaturized devices and under the harsh application environment, such as high temperature accumulated by long service period, high current density in high power applications, etc. In this work, although all Ni-Sn-P,

Ni-W-P and Ni-Co-P metallizations are found to be effective in slowing down the interfacial reaction, only Ni-W-P and Ni-Co-P can perform excellently as metallization materials. This is because the columnar structure of the Ni-Sn-P metallization causes the premature deterioration in the tensile strength of Ni-Sn-P/Sn-3.5Ag solder joints.

Chapter 1 Introduction

1.1. Background and Motivation

The most commonly used interconnect technologies in the packaging industry today are wire bonding and soldering. Between them, soldering is an area array technology which could potentially provide higher input/output (I/O) density, as opposed to wire bonding, which could only provide peripheral joining. Solder joints provide both electrical and thermal connection in an electronic device and their reliability is of critical importance. This is because the failure of a single solder joint will lead to the failure of the electronic device, or even the entire system. As the electronics industry continues to move towards higher I/O counts and smaller feature size, coupled with more strict restriction on materials toxicity (e.g. lead-free), the packaging industry faces ever greater challenges with regards to the interconnect reliability in the coming decades.

Compared to other past inventions, flip chip soldering technology has been proven to be a promising technology to cope with these challenges [1]. Fig. 1.1 shows a schematic illustration of the architecture of a typical flip chip solder joint. In the flip chip joint, the region on the surface of the chip, which is in direct contact with the solder, is named as under bump metallization (UBM). The UBM consists of a series of thin metal layers, which are deposited on the integrated circuit (IC) pads to protect the chip metallization from being attacked by the solder, and at the same time to provide a good wetting surface to the solder. Similarly, the solder pad on the substrate side is called substrate metallization. The interfacial reactions between solder and the metallizations on both IC and substrate occur not only during the reflow process, but also during service. During the reflow process, the solder undergoes a temperature cycle which causes liquid-

state reactions above the solder melting temperature. Such reaction proceeds very fast and its duration is short, i.e. around 60 s. During service, solid-state reactions occur at temperatures lower than the melting point of solder. Solid-state reaction proceeds slower than liquid-state reaction, but has a longer duration. In both liquid-state and solid-state reactions, intermetallic compounds (IMCs) form and continue to grow at the solder/metallization interface. Although the formation of IMCs is desirable to achieve good metallurgical bond, the excessive growth of IMCs has a tendency to degrade the mechanical reliability of the solder joint. Since UBM is typically very thin ($\sim 1 \mu\text{m}$), solder joint failure may occur when the thin UBM is fully consumed by soldering reaction. Therefore slow IMC growth is regarded to be beneficial for the solder joint reliability.

Fig. 1.1. Schematic illustration showing microstructure of a flip chip solder joint.

Among various metals, copper was previously the most popular choice for the surface layer of UBM due to its good wetting behavior with solders [2, 3], but its reaction with eutectic Sn-Pb solder was reported to be rapid and severe spalling of Cu-Sn IMCs was observed [3-5]. To slow down the reaction, graded Cu/Cr was adopted by IBM [6]

while other strategies were also taken up by other companies. However, with the push to implement lead-free solders since July 1st 2006, new challenges regarding the reliability of solder joints were encountered, as commonly used lead-free solders react much faster with UBM than eutectic Sn-Pb solder. This is because lead-free solders consist of mainly Sn (typically > 95 wt.%), and have higher melting temperatures (210-220 °C, compared with 183 °C for eutectic Sn-37%Pb solder). The reaction between Cu and lead-free solders is much faster than that between Cu and eutectic Sn-Pb solder. In such event, Cu will be completely consumed by lead-free solders very quickly, leaving only IMCs at the interface, and resulting in the degradation of mechanical strength of the solder joint [7-11]. This thereby suggests lead-free soldering with Cu-based metallizations may lead to some reliability concerns.

In order to improve the reliability of lead-free solder joints, a lot of research effort has been spent to find ways to slow down the interfacial reaction, while maintaining the good wetting between solder and the metallizations. One approach is to change the solder composition by adding of small quantities of additives into the solder alloy [12-14]. However, this approach is applicable only to solders in paste form and may sometimes lead to more complicated interfacial reactions. The other approach is to modify the metallization composition. Over the years, because Ni and Ni alloys were found to possess a much slower reaction rate with Sn as compared with Cu and Cu alloys [3, 15], Ni-based metallizations have received great attention in the lead-free era. Depending on the deposition techniques, there are several types of Ni-based metallizations, including sputtered nickel, electrolytic nickel, and electroless nickel. Among them, electroless nickel, which is effectively a Ni-P alloy, has been extensively studied [16-23] and widely

adopted in many applications because of its excellent uniformity, mask-less selective process, low residual stress, good solderability, and low processing cost. Electroless plating is carried out in an aqueous solution which contains metal ions, a reducing agent, complexing agents and stabilizers. Electroless Ni-P is an amorphous nickel alloy containing 12-19 at.% of P. The P content comes from the reducing agent in the plating solution. However, such P content makes the soldering reaction with the electroless Ni-P more complex than that with the pure nickel, resulting in the formation of multiple IMCs such as Ni_3P , Ni_2SnP , and Ni_3Sn_4 . It was found that the formed Ni_3P layer has a fine columnar structure, so the soldering reaction is accelerated since the grain boundaries of Ni_3P grains become the fast diffusion path. As a result, voids were observed in the Ni_3P layer after prolonged reaction [16], and the presence of these voids is suspected to degrade the reliability of the solder joint [24]. Therefore, electroless Ni-P metallization has certain limitation when long term reliability in the harsh application environment is required.

In order to slow down the interfacial reaction, the presence of the fast diffusion path, which is the Ni_3P layer formed in the case of using electroless Ni-P as metallization, should be ideally avoided. Or alternatively, its growth rate should be controllably slow. Based on the fundamental materials science, incorporation of a third element into Ni-P alloy during the electroless plating process could achieve the goal of avoiding or suppressing the formation of Ni_3P layer during soldering reaction. Based on the Ni-Sn-P phase diagram (Ni-rich part, available for high temperatures only) [25, 26], the formation of Ni_3P can be avoided by controlling the composition of Ni-Sn-P alloys. According to what have been reported so far, Ni-Sn-P alloys possess excellent thermal stability [27]

and good solderability [28]. Based on all of the above considerations, electroless Ni-Sn-P is hypothesized to be a promising diffusion barrier in lead-free soldering. However there has been no systematic investigation so far.

Besides Ni-Sn-P alloy, Ni-W-P alloy is considered as another good candidate in this work. This is because W is a refractory metal element, the diffusivity of other atoms in Ni-W-P would be low (compared with Ni-P), leading to a slower interfacial reaction with lead-free solders. In addition, it was reported that Ni-W-P alloys have improved characteristics, in terms of wear resistance [29], corrosion resistance [30], and thermal stability [31]. Electroless Ni-W-P coating was first made by adding salt of W into the electroless nickel bath by Pearlstein et al. [32] in 1968. More recently, Chen et al. first attempted to use the electroless Ni-W-P coating as the UBM for microelectronics packaging [33]. They found that the Ni-W-P coatings with higher W content have much longer service lifetime than the Ni-P coating in the case of using lead-free Sn-58Bi solder. After that, Jang et al. [34] studied the interfacial reaction between electroless Ni-W-P metallization and lead-free Sn-3.5Ag solder, and reported the drop impact test results of these solder joints as well. However, the growth kinetics of the IMCs formed at the Ni-W-P/solder interface and the mechanical properties of such solder joints have not been reported.

In addition to Ni-Sn-P and Ni-W-P alloys, Ni-Co-P is chosen as the third candidate for the interfacial reaction study in this work. It was reported that Ni-Co-P alloys have better corrosion resistance and thermal stability than Ni-P alloys [35, 36]. Moreover, Ni-Co-P alloys were found to have superior solderability and are able to reduce the electrical resistance of the interconnection [37]. In the early 1990s, Ni-Co-P alloy deposit was first

investigated as a diffusion barrier between an Al pad and a high-lead solder bump (95Pb-5Sn) by Lee and Lin [38]. In recent years, electrolessly-plated Ni-Co-P alloys have been investigated as a diffusion barrier layer in the ultra-large scale integration (ULSI) technology as well [36, 39, 40]. However, no work exists for its use as solder metallization for lead-free soldering.

1.2. Objectives

This thesis reports mainly an experimental study of the interfacial reactions during reflow soldering and thermal aging between lead-free Sn-3.5Ag solder and three types of electrolessly-plated ternary Ni alloys (Ni-Sn-P, Ni-W-P and Ni-Co-P alloys). Reaction mechanisms and IMC growth kinetics have been studied to understand the fundamental science behind the observed different phenomena. The impact on the solder joint reliability was reported through the evaluation of the mechanical behaviour of micro-tensile joints. Microstructural and fractographic analyses were carried out to understand the evolution of the joint mechanical performance. Based on the generated understandings, engineering solutions will be recommended for more reliable solder metallization materials than the currently used binary Ni-P alloys. The different research works discussed in this thesis are described as follows:

1.2.1. Soldering between Electroless Ni-Sn-P and Sn-3.5Ag

In this part of the work, an electroless Ni-Sn-P alloy with 6~7 wt.% of P and 19~21 wt.% of Sn was prepared, and its interfacial reaction with lead-free Sn-3.5Ag solder after

reflow and prolonged aging at 180 °C was studied. Tensile test of electroless Ni-Sn-P/Sn-3.5Ag solder joints upon reflow and aging at 180 °C was also performed. The interfacial reaction between the same solder and electroless Ni-P (6~7 wt.% of P) and the tensile strength of such solder joints under the same reflow and aging conditions were carried out again, and used as a benchmark for the study with electroless Ni-Sn-P. In addition, the fractographic analysis of both types of solder joints was conducted to investigate the failure modes upon aging.

1.2.2. Soldering between Electroless Ni-W-P and Sn-3.5Ag

An electroless Ni-W-P alloy with 6~7 wt.% of P and 14~16 wt.% of W was herein prepared, and its interfacial reaction with lead-free Sn-3.5Ag solder after reflow and prolonged aging at 180 °C was studied. Tensile test of electroless Ni-W-P/Sn-3.5Ag solder joints upon reflow and aging at 180 °C was performed. Similar to the Ni-Sn-P work, comparison with Ni-P (6-7 wt.% of P) benchmark samples were carried out. The fractographic analysis of both types of solder joints was also conducted to investigate the failure modes upon aging.

In addition, the growth kinetics of two IMCs - Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ formed at the electroless Ni-W-P/Sn-3.5Ag interface at three aging temperatures (140 °C, 160 °C and 180 °C) were investigated and the activation energies of their growths were determined.

1.2.3. Soldering between Electroless Ni-Co-P and Sn-3.5Ag

In this part of the work, an electroless Ni-Co-P alloy with 3~4 wt.% of P and 9~12 wt.% of Co was prepared, and its interfacial reaction with lead-free Sn-3.5Ag solder after reflow and prolonged aging at 180 °C was studied. In addition, tensile test of electroless Ni-Co-P/Sn-3.5Ag solder joints upon reflow and aging at 180 °C was performed. Similar to the work about Ni-Sn-P and Ni-W-P, comparison with Ni-P (6-7 wt.% of P) benchmark samples were carried out. Moreover, the fractographic analysis of both types of solder joints was conducted to investigate the failure modes upon aging.

1.3. Organization of the Thesis

This thesis is divided into 6 chapters and organized in the following manner:

Chapter 1 provides background, motivation, and objectives of this thesis report.

Chapter 2 presents a review on electroless nickel plating, interfacial reactions between electroless Ni-P and Sn-bearing solders, together with mechanical properties of such solder joints. The review of these interfacial reactions includes the formation, morphology, and growth kinetic of IMCs. In addition, other phenomena associated with these interfacial reactions, such as IMC grain spalling and void formation in the Ni₃P layer upon prolonged reaction are discussed.

Chapter 3 covers a study of electroless Ni-Sn-P/Sn-3.5Ag interfacial reaction upon reflow and aging at 180 °C and the tensile strength of such thermally-aged solder joints.

Chapter 4 presents a study of electroless Ni-W-P/Sn-3.5Ag interfacial reactions upon reflow and aging at 180 °C and the tensile strength of such thermally-aged solder joints.

Chapter 5 reports a study of electroless Ni-Co-P/Sn-3.5Ag interfacial reactions upon reflow and aging at 180 °C and the tensile strength of such thermally-aged solder joints.

Chapter 6 makes a comparison of all four types of Ni-based metallizations (Ni-Sn-P, Ni-W-P, Ni-Co-P and Ni-P), in terms of the metallization consumption rate during soldering and the mechanical performance of solder joints with these metallizations.

Chapter 7 concludes with the important findings from the experimental works, and provides recommendations for the future work.

Chapter 2 Literature Review

In microelectronic packaging, solder joints are known to be one of the weakest links in electronic products. The reliability of a single joint could determine the service life and functioning of an entire electronic device. Hence, the study of interfacial reactions and mechanical properties of solder joints is very important for reliability of electronic products. Sn-Pb solders were once widely used in the packaging industry. However, because of the new regulations related to the environmental concerns on toxicity of lead, the implementation of lead-free soldering has initiated since 1st July, 2006. Most lead-free solders are Sn-based eutectic alloys, and their eutectic alloying partners include noble metal elements such as Ag, Au, and Cu, and other elements such as In, Sb, Zn, Ge, and Bi. Ternary and higher order lead-free solders are most likely based on the binary eutectic Sn-Cu, Sn-Ag, Sn-Zn, or Sn-Bi alloys. Lead-free solders usually have a higher melting temperature than that of eutectic Sn-Pb solder, causing an increase of the dissolution rate of Cu or Ni in the molten solder, so the formation of IMC will be accelerated with lead-free solders. Besides having higher melting temperatures, lead-free solders usually have higher Sn content than that of eutectic Sn-Pb solder, so the soldering reactions with lead-free solders are more rapid as compared to that with eutectic Sn-Pb solder. In this chapter, a literature review of the electroless nickel plating and interfacial reactions between electroless Ni-P and Sn-bearing solders are discussed, together with mechanical properties of such joints.

2.1. Electroless Nickel Plating

Depending on the deposition techniques, there are several types of Ni-based metallizations, including sputtered nickel, electrolytic nickel, and electroless Ni-P. Among them, electroless Ni-P has the lowest manufacturing cost and it has been widely adopted in many applications. Compared with sputtered nickel, electroless Ni-P has lower residual intrinsic stress. Besides, although both electroless plating and electrolytic plating are aqueous reactions, electroless Ni-P is far superior to electrolytic nickel for coating application. First, electroless Ni-P has more uniform surface finish than electrolytic nickel. This is because electroless Ni-P provides a large flexibility of thickness and volume of the plating on metal surfaces, and can easily fill recesses or pits in the metal surface. This also allows electroless nickel plating to be applied for a wider variety of industrial parts, such as oil field valves, pumps, drive shafts, etc. Second, the electroless nickel plating process is simpler than electrolytic plating process. Electrolytic plating process requires complex filtration equipment and an external electrical source, while electroless plating process is an autocatalytic chemical reduction which requires no extra equipments. Thus, unlike the electrolytic plating process which requires electric connection to each soldering pad, electroless Ni-P can be applied to fine-pitch BGA substrates without complicating the design layout. Last but not least, electroless Ni-P has much better corrosion resistance than electrolytic nickel. This is because electroless Ni-P is normally an amorphous glass-like nickel phosphorous alloy and it has better thickness distribution than electrolytic nickel.

Brenner and Riddell [41] first used the term “electroless plating” to describe a method of plating metallic substrates with nickel or cobalt alloys without the help from

an external electrical source. Over the years, “electroless plating” has been broadened to describe any process that involving continuous deposition of metal from an aqueous solution. During electroless plating process, selective reduction of metal ions takes place at the surface of a catalytic substrate. This substrate is immersed into an aqueous solution containing metal ions that are desired to be deposited. Since the deposition continues through the catalytic action of the deposit itself, electroless plating is characterized as an autocatalytic process [42]. In the case of electroless nickel plating, reduction of Ni^{2+} ions from an ionic Ni solution occurs in the presence of a hypophosphite (H_2PO_2^-) reducing agent. The reactions occurred during electroless nickel plating are listed below:

The standard electrode potential (E°) for the reduction reaction is -25 mV, while the E° for the oxidation reaction is +50 mV, so the E° for the overall reaction is +25 mV. However, Reaction 2.3 does not represent the true electroless Ni plating reaction since hydrogen gas is also generated during the plating process [42].

The physical and chemical properties of electroless Ni-P depend on its composition, which is influenced by the composition and operating conditions of the plating solution. Typically, an electroless nickel plating solution contains a source of nickel ions, a reducing agent, complexing agents and stabilizers. In general, nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) is preferred as the nickel source. The choices for the reducing agent can be sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), sodium borohydride (NaBH_4), Dimethylamine borane ($((\text{CH}_3)_2\text{NHBH}_3)$), or hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). Among these

reducing agents, sodium hypophosphite is most popular because of its low cost, good stability and ease of preparation. Complexing agents have three functions. First, they can prevent the precipitation of nickel salts, such as basic salts or phosphites. Second, they can impede the fast decrease of the pH of the electroless nickel plating solution. Third, they can reduce the concentration of free nickel ions in the plating solution. The typical choices for complexing agents are lactic acid ($\text{C}_3\text{H}_6\text{O}_3$), ammonium ion (NH_4^+) or citrate ion ($\text{C}_6\text{H}_5\text{O}_7^{3-}$). In real practice, more than one complexing agents can be used to optimize the plating process. During electroless nickel plating process, an increase in the volume of the generated hydrogen gas and the presence of a black precipitate in the solution may lead to spontaneous decomposition of the plating solution. The black precipitate normally consists of nickel particles, and either nickel phosphide or nickel boride, which depends on the type of the employed reducing agent. Trace amount of stabilizers are used to prevent such decomposition of the plating solution. The choices for stabilizers are compounds of group VI elements (S, Se and Te), heavy metal cations (Sn^{2+} , Hg^+ , Pb^{2+} and Sb^{3+}), compounds containing oxygen (AsO_2^- , IO_3^- and MoO_4^{2-}), or unsaturated organic acids (maleic and itaconic) [42].

Besides the formulation of the plating solution, operating conditions also affect the properties of electroless Ni-P. The operating conditions of electroless nickel plating include process parameters, such as plating temperature and pH of the plating solution. With increasing the plating temperature, the electroless deposition rate increases due to the general endothermic nature of the deposition reaction. However, there is an upper limit for the plating temperature of electroless Ni-P since the plating solution may decompose at a temperature beyond 100 °C. With increasing the pH of the plating

solution, the deposition rate increases due to accelerated reduction of nickel ions. However, decomposition of the plating solution may happen when the reduction of nickel ions is too fast. Although lowering the pH of the plating solution can enhance the buffering action to prevent the decomposition, there is still a lower limit for the pH value since the deposition reaction will be retarded when the pH is too low [42].

2.2. Interfacial Reactions between Electroless Ni-P and Sn-bearing Solders

The interfacial reactions take place during both reflow soldering process and service. The liquid-state reactions take place during reflow soldering process, while the solid-state reactions occur during service. Both types of reactions result in the nucleation and growth of IMCs at the metallization/solder interface. It is because Ni-based metallizations have been reported to have a much lower reaction rate with Sn-bearing solders as compared to Cu-based metallizations [3, 15], extensive studies on Ni-based metallizations have been conducted over the past two decades. There are several types of Ni-based metallizations, such as sputtered nickel, electrolytic nickel, and electroless nickel. Among them, electroless Ni-P has been widely used as metallization for solder joint. Electroless Ni-P plating is carried out through autocatalytic chemical reduction of nickel ions. Unlike electroplating, electroless plating process does not require electrical source, so the coatings on non-conductive substrates can be achieved by this method. Moreover, another advantage of electroless plating is its ability to deposit the alloy coating uniformly on an irregular surface.

With the help of the equilibrium phase diagram of Ni-Sn binary alloy (Fig. 2.1), the IMC phases that can be possibly formed during interfacial reaction between certain type

of Ni-based metallization and the solder with a known composition under reflow and/or service condition can be listed. According to this phase diagram, three types of IMCs can be formed between Ni and Sn, which are Ni_3Sn_4 , Ni_3Sn_2 , and Ni_3Sn . Among these IMCs, Ni_3Sn_4 was reported to be the primary IMC formed by the interfacial reaction between electroless Ni-P and various Sn-bearing solders during normal reflow process with a temperature range of 200-260 °C [43-49]. Besides this predominant Ni_3Sn_4 layer, the formation of other Ni-Sn compounds, Ni_3Sn_2 [50] and $\text{Ni}_{48}\text{Sn}_{52}$ [51] was reported as well. However, both compounds were found to have a submicron thickness, which makes them difficult to be observed under SEM or even under TEM. The small thickness of these compounds may be attributed to their slow nucleation and/or growth.

Fig. 2.1. The equilibrium phase diagram of Ni-Sn binary alloy [52].

During electroless nickel plating, reduction of Ni^{2+} ions from an ionic Ni solution occurs in the presence of a hypophosphite (H_2PO_2^-) reducing agent [42]. Thus, the P

content in electroless Ni-P coating cannot be avoided since it comes from the hypophosphite reducing agent. However, the presence of P not only influences the microstructure of Ni-P, but also makes the soldering reaction with Ni-P more complicated than that with pure Ni. The complication of soldering reaction with Ni-P is because it results in the formation of both Ni-Sn and Ni-P compounds [16, 18, 53] while soldering reaction with pure Ni results in the formation of Ni-Sn compound alone [17, 54]. From past studies, electroless Ni-P has been found to have a microcrystalline structure when it contains less than 12.5 at.% of P, while it has an amorphous structure when its P content is higher [42, 55-57]. The electroless Ni-P used as metallization in electronic packaging normally has an amorphous structure since it contains more than 12.5 at.% of P. The crystallization of such amorphous Ni-P alloy can take place spontaneously during thermal treatment with a temperature that reaches its crystallization temperature. With the help of the equilibrium phase diagram of Ni-P binary alloy (Fig. 2.2), the phases that will form by the crystallization of electroless Ni-P can be predicted. According to this phase diagram, Ni and Ni₃P are the thermodynamics equilibrium phases that are present close to the composition of electroless Ni-P, so they may form during the crystallization of electroless Ni-P. In addition, it is worth noting that microstructure of amorphous electroless Ni-P changes into a fine crystalline structure during self-crystallization process [57].

Fig. 2.2. The equilibrium phase diagram of Ni-P binary alloy [58].

When electroless Ni-P reacts with Sn-based solder, the crystallization of amorphous Ni-P will be triggered at reflow temperature (200-260 °C), which is well below the self-crystallization temperature of Ni-P (350 °C) [59]. This phenomenon is denoted as “solder reaction-assisted crystallization” of electroless Ni-P, which leads to the transformation of amorphous Ni-P into Ni₃P [60]. This Ni₃P layer was reported to have a well-developed fine columnar structure [16, 48, 60, 61]. Although Ni₃P is widely reported to be the primary phase formed by solder reaction-assisted crystallization of electroless Ni-P, other Ni-P phases have also been found in the crystallized Ni-P layer. For example, Liu et al. has reported the formation of two separate layers of Ni₃P and Ni₁₂P₅ in electroless Ni-P/Sn-Pb solder joint after aging at 150 °C for 30 days [48]. Besides this, Sohn et al. has studied the interfacial reaction in the high P concentration (9 wt.%) electroless Ni-P/Sn-3.5Ag solder joint after 30 min of reflow at 250 °C [62]. They reported that only Ni₃P phase formed initially; however during extended reflow, a new Ni₂P phase formed. The

literature reveals that, when the P content in the Ni-P layer is less than 18 at.% (about 9 wt.%), Ni_3P phase would form first, on the other hand, when the P content in the Ni-P layer is more than 19 at.% (about 10 wt.%), other Ni-P phases, such as Ni_{12}P_5 and Ni_2P , might form first [63-68].

The solder reaction-assisted crystallization of electroless Ni-P is quite different from the self-crystallization of Ni-P. A. Kumar has summarized the differences between the two types of crystallization of electroless Ni-P with 12-19 at% of P (common composition of Ni-P alloys used as UBM) [69]. First, these two types of crystallized Ni-P have different compositions. The final products of the self-crystallization of Ni-P during thermal annealing were reported to be Ni_3P and Ni [57, 70], while the product of the solder reaction-assisted crystallization is either Ni_3P phase alone [60], or a mixture of Ni_3P phase and other Ni-P phases with a lower Ni to P ratio than that in Ni_3P [19, 22, 62, 71, 72]. This is because during soldering reaction, Ni atoms diffuse out of the electroless Ni-P layer to react with the Sn atoms from the solder to form Ni_3Sn_4 compound. Second, the self-crystallization of Ni-P is homogeneous, while the solder reaction-assisted crystallization occurs selectively at the surface of the Ni-P layer where is in contact with the solder. Third, the two types of crystallized Ni-P have quite different microstructures. The solder reaction-assisted crystallized Ni-P was reported to have a well-developed fine columnar structure [16, 48, 60, 61], while the self-crystallized Ni-P has coherent precipitates, which are observed as small evenly distributed dark particles [42].

Besides Ni-Sn and Ni-P compounds, a ternary Ni-Sn-P compound was also found in between the Ni-Sn and Ni-P compounds [20, 21, 50, 51, 62, 71-75]. The thin layer of Ni-Sn-P compound with a few hundred nano-meter thickness was found to consist of Ni_2SnP

phase [20, 21, 23, 51, 71-73] or Ni_3SnP phase [50, 62] by using TEM, while the thick layer of Ni-Sn-P compound with a few micron thickness was identified to be Ni_2SnP phase by using electron probe micro analyzer (EPMA) and SEM [74, 75]. All these studies suggest that in the interfacial reaction between electroless Ni-P and Sn-bearing solders, the Ni_2SnP phase is the primary phase formed in between the Ni-Sn and Ni-P compounds. From previous studies, the formation of this ternary Ni-Sn-P phase was found to significantly degrade the reliability of solder joints [76, 77]. This is because this Ni-Sn-P layer is flat and rather thin (less than 1 μm), it fails to play an interlocking role at the interface between metallizations and solders. As shown in Fig. 2.3, the fractured surfaces of the reflowed Ni-P/Sn-3.5Ag solders after ball shear test clearly reveal that fracture occurred along the interfaces of Ni-Sn-P/ Ni_3Sn_4 and Ni_3Sn_4 /solder, indicating that the thin Ni-Sn-P layer fails to play the interlocking role [77]. Moreover, in recent years, Duh et al. has studied the relationship between the formation of Ni_2SnP and the evolution of P-rich layer (Ni_3P , or Ni_{12}P_5 , or Ni_2P layers) [19, 22, 71, 72]. They found that in the Ni-13wt.% P/Sn-3.0Ag-0.5Cu solder joints after three reflows, as the Ni_2SnP phase formed, the P-rich layer would transform to some layer compounds, including Ni_3P , Ni_{12}P_5 and Ni_2P , probably influenced by the formation of Ni_2SnP phase (Fig. 2.4). According to the Ni-P phase diagram (Fig. 2.2), it is understood that Ni_3P , Ni_5P_2 and Ni_{12}P_5 are all thermodynamically stable. In a continuously varied composition profile, after Ni_3P , the next phase to be formed seems to be Ni_5P_2 , since it is the second P-rich phase. However, it was reported that with further reaction at the Ni-13wt.% P/Sn-3.0Ag-0.5Cu interface, Ni_3P would transform to Ni_{12}P_5 , which is the third P-rich phase in the Ni-P phase diagram. In such event, the formation of Ni_5P_2 was hindered. The

transformation of Ni_3P to Ni_{12}P_5 is attributed to their identical tetragonal structure, while Ni_5P_2 has a different structure, which is hexagonal [19, 22, 71, 72]. However, an opposite finding has been reported by V. Vuorinen et al. [78]. They found that the Ni_3P phase would transform into Ni_5P_2 rather than Ni_{12}P_5 at the Ni-9wt.% P/Sn-3.8Ag-0.7Cu interface after annealing at 170 °C for 64 h.

Fig. 2.3. The fractured surfaces after ball shear test for Ni-P/Sn-3.5Ag solder joints reflowed for: (a) 1 sec and (b) 10 min [77].

Fig. 2.4. Cross-sectional images at the Sn-3Ag-0.5Cu/Ni-13wt.% P interface after triple reflows: (a) Back-scattered image, and (b) TEM image with diffraction patterns for Ni_3P , Ni_{12}P_5 , Ni_2P , and UBM [72].

2.2.1. Morphology of Intermetallic Compound

The complicated interfacial reaction that takes place at the solder/metallization interface leads to the formation of intermetallic compounds. The morphology of intermetallic compounds tends to be affected by many factors, such as state of reactions (either liquid-state reaction or solid-state reaction [79]), material factors (the quantity of solute in Sn-matrix and the microstructure of solder and metallization [54, 62, 80]), and reflow parameters (the peak temperature, the dwell time over melting temperature of solder, and the post-reflow cooling rate [54, 81]).

The common IMC compound that has been found at the electroless Ni-P/Sn-bearing solders (eutectic Sn-Pb solder or lead-free solder without copper) is Ni_3Sn_4 . It was reported that during liquid-state reflow, Ni_3Sn_4 IMC has two types of morphologies, which are needle-type and chunky-type [17, 44, 54, 60, 82]. The formation of needle-type Ni_3Sn_4 grains dominates at the beginning of reflow; however, when the reflow time is extended, more chunky-type Ni_3Sn_4 grains form and grow by consuming of needle-type Ni_3Sn_4 grains due to the grain ripening during liquid-state reaction [17, 54, 60]. The driving force for the ripening of IMC grains has been reported to be the reduction of surface energy [83] and/or the gain of bulk free energy [84]. In addition, Hung et al. has reported that the morphology of Ni_3Sn_4 IMC is not affected by the variation of the P content in electroless Ni-P coating [44, 82]. As mentioned in the previous paragraph, the morphology of IMC can be affected by the state of reaction, so the morphology of Ni_3Sn_4 during solid-state aging will be quite different as compared to that during liquid-state reflow. Instead of needle-type and chunky-type grains, as shown in Fig. 2.5, a continuous wavy layer of Ni_3Sn_4 IMC is observed during solid-state aging [16].

Fig. 2.5. Cross-sectional images at the Ni-P/Sn-37Pb interface after aging at 170 °C for 625 h [16].

A few works have been conducted to study the effect of the post-reflow cooling rate on the morphology of IMCs, in terms of their size and shape [81, 85-88]. Among these works, Wang et al. [88] studied the as-reflowed electroless Ni-P/Sn-Pb interfacial microstructure with two types of cooling processes, which are air cooling and quenching by water. They concluded that faster cooling rate results in finer IMC grains, since the formed Ni_3Sn_4 IMC has a grain size of around 6 μm after air cooling, while it has a smaller grain size of around 2.5 μm after quenching by water. On the other hand, He et al. [81] studied the as-reflowed electroless Ni-P/Sn-3.5Ag interfacial microstructure with different cooling rates. They also reported that faster cooling rate leads to the formation of finer Ni_3Sn_4 grains. This is because although nucleation is favoured by faster cooling, the effective duration at high temperature zone that is favoured for IMC growth is shorter. It was observed that the fine grains formed by faster cooling are in needle shape. With decreasing cooling rate, the amount of needle-type grains decreases, while the amount of

chunky-type grains increases by consuming the needle-type ones. Moreover, He et al. [81] performed further annealing at 170 °C for these as-reflowed samples that have been undergone different cooling rates. Interestingly, they found that under the same annealing condition, thickening of Ni_3Sn_4 IMC is more rapid in the samples that have been undergone faster cooling rate (Fig. 2.6). They attributed this to the difference in size of Ni_3Sn_4 IMC grains under different cooling rates, i.e. the finer Ni_3Sn_4 grains formed by faster cooling rate have more grain boundaries, leading to easier elemental diffusion for the continued growth of IMC.

Fig. 2.6. Thickness of Ni_3Sn_4 layer in the annealed electroless Ni-P/Sn-3.5Ag solder joints, which undergo different cooling rates after reflow for 180 s (the annealing temperature is 170 °C) [81].

2.2.2. Spallation of Intermetallic Compound

During soldering reaction, IMC grains may detach from the reaction interface and move into the molten solder, this phenomenon is called spallation of IMC. Two reasons are commonly cited for this phenomenon: one is the mechanical stresses produced by the volumetric change between the reacting materials and the newly-formed IMC, and the other reason is the dewetting of IMC caused by either weak adhesion or complete consumption of the underlying metallization layer. These two reasons can be present together in most observed spallation.

From the literature, numerous studies have been carried out to understand the spallation of Ni_3Sn_4 IMC formed in electroless Ni-P/solder joints, and different explanations for this phenomenon were reported. For instance, some research groups have reported that the growth of the thin ternary Ni-Sn-P layer in between the Ni_3Sn_4 and Ni_3P layer causes the spallation of Ni_3Sn_4 grains [62, 75, 89]. Moreover, needle-type Ni_3Sn_4 compounds were found to have a larger propensity for spallation than chunky-type compounds, since the channels present among the needle-typed compounds behave as the short-circuit paths for Sn penetration [62].

2.2.3. Growth Kinetics of Intermetallic Compound

The factors that can determine and control the growth kinetics of the IMC layer include interfacial stress, IMC spallation, grain coarsening, diffusion through grain boundary and volume diffusion through the bulk layer. In order to determine the controlling mechanism and activation energy for IMC growth, it is necessary to obtain

the kinetic parameters of IMC growth. The relationship between the reaction time and the IMC layer thickness can be denoted by the following empirical power law:

$$\delta - \delta_0 = kt^{1/n}, \quad (2.4)$$

where, δ and δ_0 are the thickness of the IMC layer at time t and zero, respectively, n is the time exponent and k is the growth rate constant given by the following Arrhenius equation (2.5):

$$k = A \exp(-Q/RT), \quad (2.5)$$

Equation 2.5 shows the variation of the growth rate constant, k , with temperature, and A is a prefactor, R is the gas constant, T is the absolute temperature, and Q is the activation energy for IMC growth. The value for Q can be determined from the slope of the Arrhenius plot of $\ln k$ against $1/T$:

$$\ln k = \ln A - \frac{Q}{R} \cdot \frac{1}{T}, \quad (2.6)$$

The value of n in Equation 2.4 can be used to predict the growth-controlling mechanism of IMC. It is well-known that if n is 1, the IMC growth is controlled by the reaction rate, whereas if n is 2, the IMC growth is controlled by the diffusion of reacting element. However, 1 and 2 are ideal values for n . In practice, the value of n may be deviated from these ideal values. The factors, which cause such deviation, include different diffusion mechanisms, the formation of various IMC layers, and the time-dependent apparent diffusivity [90]. Besides, it was found that if the growth of IMC occurs along with the grain ripening or coarsening of IMC, the value of n can be close to 3 [84, 91]. In most studies about electroless Ni-P/solder interfacial reactions, the growth of IMC was assumed to follow diffusion-controlled mechanism [3, 16, 44, 60, 92-94]. Among these studies, the growth kinetics of either Ni_3Sn_4 or Ni_3P was reported, and this

is due to their inter-related growths. Moreover, the study of the growth kinetics of ternary Ni_2SnP compound was conducted recently. It was reported that the growth of Ni_2SnP is diffusion-controlled when the samples are aged at 140, 160, and 180 °C, but its growth becomes reaction-controlled when the samples are aged at 200 °C [90].

2.2.4. Diffusion and Reaction Mechanism at the Electroless Ni-P/Solder Interface

During soldering reaction, the formation and growth of a single compound is quite complicated since it involves several interfacial processes such as elemental dissolution in solder, elemental diffusion, phase nucleation, and creation and/or annihilation of defects. Since multiple compounds form in an electroless Ni-P/solder system, the interfacial elemental diffusion and reaction mechanism in this system becomes even more complicated.

In order to understand the interfacial elemental diffusion and reaction mechanism in electroless Ni-P/solder systems, it is necessary to find out the dominant diffusing species first. From the review of the previous studies, different elements, such as Ni or Sn or P, have been considered to be the dominant diffusing species. Jang et al. have proposed two possibilities of elemental diffusion mechanism in the interfacial reaction between electroless Ni-P and eutectic Sn-Pb solder [60]. As shown in Fig. 2.7, one possible mechanism is Ni atoms diffuse out of the electroless Ni-P layer and move through the grain boundaries of the Ni_3P layer to reach the $\text{Ni}_3\text{P}/\text{Ni}_3\text{Sn}_4$ interface. The other possibility is the Ni_3P compound decomposes into P and Ni at the $\text{Ni}_3\text{P}/\text{Ni}_3\text{Sn}_4$ interface, then P atoms move back by interstitial diffusion to the $\text{Ni}_3\text{P}/\text{electroless Ni-P}$ interface to grow Ni_3P layer. Based on their microstructural observation, no voids were found in the

Ni₃P layer, so there is no convincing evidence for the former mechanism because the grain boundary diffusion of Ni atoms has to be accompanied with the back diffusion of vacancies. Thus, they proposed the mechanism of Ni₃P dissociation and re-formation. However, subsequent results from other studies supported the Ni out-diffusion mechanism. Ahat et al. reported the diffusion of Ni from the electroless Ni-P to the solder at the SnAgCu/Ni-P/Cu joint [95]. Besides this, He et al. found voids in the Ni₃P layer at both of the electroless Ni-P/Sn-3.5Ag interface and the electroless Ni-P/Sn-Pb interface after prolonged aging at 150 °C, so they concluded that Ni is the main diffusing element in the Ni₃P layer [16]. However, V. Vuorinen et al. claimed that such voids could also be organic impurities since they found that the voids formed at the Ni-9 wt.% P/Sn-3.8Ag-0.7Cu interface contain organic material, which is most probably generated from the Ni-P plating bath solution [78].

Fig. 2.7. Schematic illustration showing the possible elemental diffusion mechanism in the interfacial reaction between electroless Ni-P and eutectic Sn-Pb solder [60].

Moreover, in order to verify the dominant diffusing species in Ni₃Sn₄, several marker experiments were performed. Lee and Lin (1994) used W marker in the electroless Ni-P/Sn-Pb solder joint, and their study concluded that Sn is the predominant

diffusing species that reaches the Ni-P layer, while Ni remains in the Ni-P layer or diffuses slowly relative to Sn [96]. Following on this study, a Ni-Sn diffusion couple with the patterned Ti stripes as marker was designed, as shown in Fig. 2.8. In this study, according to the location of the Ti stripes after aging, Sn was proven to be the dominant diffusing species in Ni_3Sn_4 [97].

Fig. 2.8. (a) Optical micrograph showing the plane-view of a Ni substrate with the deposited Ti stripes as markers, (b) cross-sectional view of the Ni/Sn diffusion couple prior to aging, and (c) after aging at 225 °C for 1000 h [97].

Based on all of these aforementioned studies, a partial but common understanding of elemental diffusion and reaction mechanism at the electroless Ni-P/Sn-bearing solders can be made, and elaborated as follows. Firstly, the growth of IMC requires not only Ni atoms from the electroless Ni-P layer but also Sn atoms from the solder [95, 96]. Secondly, P atoms remain in the Ni-P layer, rather than participating in the elemental diffusion [16, 95]. Thirdly, a Ni_3P layer which contains higher P content than Ni-P forms in between IMC and the remaining Ni-P layer [60]. Recently, the full understanding of elemental diffusion and reaction mechanism at the electroless Ni-P/Sn-3.5Ag interface was reported by Kumar and Chen [90]. As depicted in Fig. 2.9, three interfacial IMC layers, Ni_3Sn_4 , Ni_3P and Ni_2SnP , were found to form by the electroless Ni-P/Sn-3.5Ag interfacial reaction from their study. The Sn atoms diffuse out from the solder, first reach the solder/Ni-P interface to react with Ni atoms from the deposited Ni-P layer to form the Ni_3Sn_4 layer. The depletion of Ni from the Ni-P layer to form Ni_3Sn_4 leads to the formation of the Ni_3P layer within the Ni-P layer adjacent to the original Ni-P/ Ni_3Sn_4 interface. The formation of the crystalline Ni_3P follows the mechanism of solder reaction-assisted crystallization as explained before. Meanwhile, some Sn atoms from solder reach the $\text{Ni}_3\text{P}/\text{Ni}_3\text{Sn}_4$ interface, and react with Ni_3P to form Ni_2SnP . Moreover, the interdependent growth mechanisms and the related growth kinetics of these IMCs were revealed by Kumar and Chen (2011) [90]. They found that Ni_3Sn_4 and Ni_3P layers grow predominantly when the deposited Ni-P layer is not fully consumed. This is because at the beginning of reaction, most of the Sn atoms from the solder are consumed by the reaction with Ni atoms to form Ni_3Sn_4 , and only a small part of Sn atoms are consumed by the reaction with already-formed Ni_3P to form Ni_2SnP . However, when the deposited

Ni-P layer is fully transformed into Ni_3P , leading to the termination of Ni supply, all Sn atoms can only react with the already-formed Ni_3P to form Ni_2SnP , so Ni_2SnP layer grows rapidly at this stage. Kumar and Chen [90] also found that the growth of the Ni_2SnP layer is controlled by diffusion initially, but once the coated Ni-P layer is completely consumed, the growth of this layer is controlled by the reaction rate. In addition, voids were found in the Ni_3P layer, and the formation mechanism of such voids will be discussed in the following section.

Fig. 2.9. Schematic illustration of the interfacial elemental diffusion and reaction mechanism at the electroless Ni-P/Sn-3.5Ag interface [90].

2.2.5. Void Formation at the Electroless Ni-P/Solder Interface

The formation of voids is a severe reliability issue for solder interconnects, since with increasing reaction time, these voids become a short-circuit path for crack propagation, leading to brittle fracture of solder joint. The formation of voids in the solder joints with the electroless Ni-P metallization has been widely reported [16-18, 20, 21, 53, 61, 90, 98]. In the past literature, these voids are referred to as Kirkendall voids. However, it is realized more recently that this is not an appropriate depiction of the

phenomenon. By definition, the Kirkendall effect is the motion of the boundary layer between two metals that occurs when the faster diffusing element creates vacancies at a rate unmatched by vacancy filling with the other element. The voids formed at the boundary interface between these two metals due to Kirkendall effect are referred to as Kirkendall voids. By the formation mechanism, Kirkendall voids should only be present within the original side occupied by faster diffusing element. However, the voids formed due to the electroless Ni-P/solder interfacial reaction are observed inside the Ni_3P layer, and it is now understood that Sn is the fast diffusant in the Ni-Sn reaction couple. Therefore, it is not appropriate to refer to the voids formed at the electroless Ni-P/solder interface as Kirkendall voids.

More appropriate reason for the formation of the voids seen inside the Ni_3P layer could be explained by the schematics drawing in Fig. 2.9, and also the direct observation of interface layers in Fig. 2.10 [16]. Fig. 2.10 shows that the Ni_3P layer has a fine columnar structure, which makes it behave as a fast diffusion path for Ni atoms. The formation of the voids in the Ni_3P layer can be attributed to the net Ni flux that diffuses out through the Ni_3P layer to form Ni_3Sn_4 when the compensation from Sn to fill the vacant sites is made impossible because Sn element stops at the $\text{Ni}_3\text{Sn}_4/\text{Ni}_2\text{SnP}$ interface due to its slow yet favourable reaction with the Ni_3P layer.

Fig. 2.10. TEM micrograph showing the Ni_3P layer in a fine columnar structure [16].

2.3. Mechanical Properties of Solder Joints

Along with providing electrical connection and path for heat dissipation (sometimes), the solder joints also perform the main role of mechanical support between IC chip and substrate, their mechanical robustness is thus critical for reliability of soldered electronic devices. They must be able to bear the mechanical stresses that are present in electronic packages. Such stresses are mainly generated by two causes. The first cause is the thermal stress due to the coefficient of thermal expansion (CTE) mismatch between constituent materials, which in turn generates shear and tensile stresses in an electronic package. When the electronic package experiences thermal cycle during reflow or service, the fluctuating mechanical stresses may cause fatigue failure of solder joints. The second cause of mechanical stresses is from the direct external mechanical loading during service, for example, portable electronic devices are quite prone to accidental drops, leading to

the solder joint failures by brittle fracture at the IMC interfaces or by impact fatigue in the solder materials. Moreover, the excessive growth of IMCs generates intrinsic stresses in the solder joint, thus makes the solder joint more prone to failure. In addition to the IMC brittleness, excessive interfacial reaction may also induce severe defect formation between neighbouring layers at the solder joint interface region, leading to weakening or failure of the solder joints [99]. Therefore, in order to improve the reliability of electronic devices, slow interface reaction is generally beneficial, and it is important to understand all the factors that influence the mechanical properties of solder joints, before a solution can be proposed to enhance the reliability.

In order to study the mechanical properties of solder joints, various testing methods such as shear, tensile, indentation, and fatigue are employed. Among them, shear and tensile testing are used to evaluate the load-bearing capacity of the solder joint. The indentation testing is used to determine the micro-mechanical properties of the solder joint, such as hardness and modulus of solder, metallization, and IMCs. Fatigue testing is helpful to determine the lifetime of the solder joint since the electronic devices usually experience thermal or mechanical cycles during service. In this work, only tensile testing was employed to investigate the mechanical properties of solder joints formed by the interfacial reaction between lead-free Sn-3.5Ag solder and novel ternary Ni-based metallizations, thus a brief discussion of tensile properties of the conventional electroless Ni-P/Sn-3.5Ag solder joints is given in the following section.

2.3.1. Tensile Properties of Electroless Ni-P/Sn-3.5Ag Solder Joints

Although the packaging industry routinely performs the shear testing because of its ability to more closely replicate the actual stress state encountered in service in a real package, tensile testing is preferred in research. This is because it preserves the fractured surface better for the fractographic analysis to reveal the weakest link (within a layer or at an interface) in the solder joints. The tensile strength of a solder joint is given as the maximum load experiences in the testing divided by the cross-sectional area of the solder joint. It is because the solder joint tensile strength is sensitive to the changes that occur at various interfaces in the solder joint, tensile testing is an appropriate method to evaluate the degree of degradation of the solder joint.

During a tensile test, if the cohesive strength of the bulk solder is weaker than the cohesive strength of the interfacial IMC layer itself and its adhesion to the solder, strain energy can be accommodated by the deformation and the gradual ductile rupture of the solder. Ductile deformation and ultimate failure thus occur inside the bulk solder rather than in the IMC layer, or at the solder/IMC interface. On the other hand, if the cohesive strength of the bulk solder is stronger than the cohesive strength of the interfacial IMC layer itself and its adhesion to the solder, the solder can only accommodate a limited amount of strain energy whereas the rest of the energy has to be transferred to the IMC layers. The deformation thus takes place in the IMC layer, or at the solder/IMC interface rather than inside the bulk solder. The nature of IMC layer or interface failure is typically brittle, as they are unable to take up much deformation so that energy accommodation is limited. Therefore, the tensile behaviour of a solder joint mainly depends on the changes of its interfacial microstructure upon interfacial reactions. As discussed before, interfacial

reaction could induce stress concentration, de-wetting of interface layers, and formation of voids. All these could be effectively assessed by observing the stress-strain curve of the tensile test.

The reported solder joint tensile strength is affected by the thickness of solder in between the metallizations. If the solder layer is too thin, the tensile strength of solder joint will be greater than that of the cohesive strength of the bulk solder [100]. This is due to the effect of geometric constraint, i.e. solder with confinement induces 3-D stress state that makes it more stiff and brittle. Another important factor which can influence the tensile strength of solder joints is the strain rate. A low strain rate is usually preferred for evaluating the tensile strength of solder joints, as they normally experience slow deformation in real practice. Generally, comparison of solder joint strength should ideally be made with the same solder joint geometry and size, and under the same strain rate.

A number of studies focused on the tensile properties of electroless Ni-P/Sn-3.5Ag solder joints have been conducted in the past [18, 33, 53, 99-101]. From these studies, it was found that the tensile strength of the electroless Ni-P/Sn-3.5Ag solder joints drops with increasing aging time and aging temperature. In general, the decrease of the tensile strength of solder joints upon aging is primarily attributed to the extended interfacial reaction, and the degree of joint strength degradation could be well correlated to the thickening of the Ni_3Sn_4 IMC layer. In addition, Kumar et al. have reported that not only the thickness of electroless Ni-P [53], but also its P content [101] affects the tensile properties of Ni-P/Sn-3.5Ag solder joints. Moreover, He et al. have identified four types of failure modes in the electroless Ni-P/Sn-3.5Ag solder joints upon aging [100]. Detailed description of these failure modes are given in the following section.

2.3.2. Fractographic Analysis of Electroless Ni-P/Sn-3.5Ag Solder Joints

He et al. have summarized four typical types of fracture patterns of electroless Ni-P/Sn-3.5Ag solder joints upon aging, namely Mode I, II, III and IV [100]. As shown in Fig. 2.11, Mode I is the ductile failure occurred inside the bulk solder, Mode II is the interface failure between the bulk solder and the neighbouring Ni_3Sn_4 layer, Mode III is the failure through the interfacial layers (Ni_3Sn_4 , Ni_2SnP , and/or Ni_3P), and Mode IV is the failure between the coated Ni-P layer and the underlying Ni substrate. The authors reported that with increasing aging time and aging temperature, the tensile strength of the electroless Ni-P/Sn-3.5Ag solder joints drops while the fracture mode of solder joints changes from Mode I to Mode IV. In many instances, instead of a single mode, mixed modes of fracture were observed.

Fig. 2.11. Schematic illustration showing the fractured surface in the electroless Ni-P/Sn-3.5Ag solder joints, indicating four typical types of fracture modes [100].

In Mode I, fracture occurs inside the bulk solder for the as-reflowed solder joints. In this case, since the cohesive strength of the bulk solder is weaker than the cohesive strength of the interfacial IMC layer itself and its adhesion to the solder, the deformation can be accommodated by the bulk solder. When the solder is under deformation, necking takes place with an increase of plastic strain. In addition, the work hardening around the neck together with the dimension restrictions increases the resistance to deformation. Such strain energy can be accommodated by deformation in the bulk solder, leading to the ductile rupture of the bulk solder eventually.

In Mode II, the failure path shifts from the bulk solder to the solder/ Ni_3Sn_4 interface for the thermally-aged solder joints. In this case, the cohesive strength of the bulk solder and the cohesive strength of the interfacial IMC layer are both stronger than the adhesion of interfacial IMC layer to the solder, the solder can only accommodate a limited amount of strain energy whereas the rest of the energy has to be transferred to the interfacial IMC layers. The deformation thus takes place at the solder/ Ni_3Sn_4 interface rather than inside the bulk solder. The weakening of the solder/ Ni_3Sn_4 interface might be attributed to the stress originated by the volume mismatch between neighbouring layers, and such stress increases with the growth of the Ni_3Sn_4 layer. Besides, the morphology of the Ni_3Sn_4 IMC changes from needle-type and chunky-type grains (in the as-reflowed solder joints) to a continuous wavy layer in the thermally aged solder joints, such flattened solder/ Ni_3Sn_4 interface could be a contributing factor for the shift of failure mode from inside the bulk solder to be at the solder/ Ni_3Sn_4 interface.

In Mode III, failure occurs in one of, or through all of the interfacial IMC layers (Ni_3Sn_4 , Ni_2SnP , and Ni_3P) in the thermally-aged solder joints. In this case, the cohesive

strength of the bulk solder and the adhesion between the interfacial IMC layers and solder are both stronger than the cohesive strength of the interfacial IMC layers, deformation takes place in one of, or through all of the interfacial IMC layers. The reason for weakening of the cohesive strength of the interfacial IMC layers could be the stress generated by the volume mismatch among the interfacial IMC layers during their growth. Besides, since the interfacial IMC layer is brittle in nature, it may fracture by itself when it becomes too thick with increased defects within the layer.

In Mode IV, the failure occurs between the coated Ni-P layer and the underlying Ni substrate. In this case, the cohesive strength of the bulk solder, the adhesion between the interfacial IMC layers and solder, and the cohesive strength of the interfacial IMC layers are all stronger than the adhesion between the coated Ni-P layer and the underlying substrate, deformation takes place at the Ni-P/substrate interface rather than elsewhere. The stress produced by the volume change during transformation of Ni-P coating into crystallized Ni_3P phase is most probably responsible for the weakening of the Ni-P/substrate interface. It was reported that the volume shrinks by 12% after Ni-P coating is transformed into Ni_3P phase [102], hence, such large shrinkage in volume could produce high tensile stress to delaminate the Ni-P layer away from the underlying Ni substrate.

2.4. Summary and Remarks

From the review of different literatures published from previous studies, it is apparent that the interfacial reactions between electroless Ni-P metallization and Sn-bearing solders are very complex because of the P content in Ni-P. Multilayered interfacial IMCs, such as Ni_3Sn_4 , Ni_3P (Ni_{12}P_5 and Ni_2P may form first in some cases),

and Ni-Sn-P (Ni_3SnP or Ni_2SnP) form during interfacial reactions, and the growth kinetics of Ni_3Sn_4 , Ni_3P , and Ni_2SnP IMCs has been studied. Needle-type and chunk-type Ni_3Sn_4 grains were observed in the as-reflowed Ni-P/solder joint, whereas a continuous layer of Ni_3Sn_4 IMC was observed during solid-state aging. The formation of voids in the Ni_3P layer has been reported in many studies. In addition, mechanical properties of Ni-P/Sn-bearing solder joints have been widely studied. All these available literatures indicate despite the advantages of adopting electroless Ni-P metallization, there is still plenty of room for improvement in terms of long-term solder joint reliability.

In order to improve the behaviour of Ni-P alloy as diffusion barrier in lead-free soldering, incorporation of a third element into Ni-P alloys to form ternary Ni-based alloys by electroless plating is considered as a potential approach to slow down the interfacial reaction. In the current work, three types of Ni-based ternary alloys, namely, Ni-Sn-P, Ni-W-P, and Ni-Co-P are obtained by electroless plating. The reasons for choosing these ternary alloys are discussed in detail in section 1.1. Systematic investigations have been carried out on the microstructure, morphology, growth kinetics, and the mechanical performance of the solder joints with the objectives stated in Section 1.2.

In what follows, electroless Ni-Sn-P metallization will be studied first as a diffusion barrier in lead-free soldering in chapter 3. Its interfacial reaction, together with tensile properties of such solder joints upon reflow and aging are investigated. This will be followed by the study of Ni-W-P metallization in chapter 4. In the literature, a few preliminary results about using the electroless Ni-W-P metallization as a diffusion barrier in lead-free soldering have been reported, including the interfacial reaction and drop

impact test of such solder joints. Thus, in the current work, the growth kinetics of IMCs formed in the Ni-W-P/Sn-3.5Ag solder joint, and tensile properties of such solder joints upon reflow and aging are investigated to further complete the study of the barrier behavior of electroless Ni-W-P in lead-free soldering. In the current work, electroless Ni-Co-P metallization is used for the first time as a diffusion barrier in lead-free soldering, and its interfacial reaction, together with tensile properties of such solder joints upon reflow and aging are studied in chapter 5. The comparison of all four types of metallizations (ternary Ni-based metallizations together with the binary Ni-P as a reference) is made in Chapter 6, in terms of their consumption rates upon aging and the long-term reliability of solder joints with these metallizations. The conclusions about the important findings from the experimental works and the recommendations for the future work are provided in Chapter 7.

Chapter 3

Soldering between Electroless Ni-Sn-P and Sn-3.5Ag

3.1. Introduction

As highlighted in the literature review, in order to slow down the interfacial reaction with lead-free solders, it is necessary to avoid the formation, or suppress the growth of the fast diffusion path, which is the Ni_3P layer with a columnar structure. According to the Ni-Sn-P phase diagram at 550 °C [25, 26], the formation of Ni_3P will be avoided when the Sn concentration is greater than 10 wt.% (5 at.%) and P content is around 6-7 wt.%. Instead, the composition falls into the region of $(\text{Ni} + \text{Ni}_3\text{Sn} + \text{Ni}_{21}\text{P}_6\text{Sn}_2)$ at 550 °C [25]. Unfortunately the phase diagram for Ni-Sn-P is not available for lower temperatures below 550 °C due to a number of practical difficulties [103]. In such event, no thermodynamic data can be obtained at the solder reflow temperature around 260 °C. Nevertheless the author could hypothesize that if the ternary phase $(\text{Ni}_{21}\text{P}_6\text{Sn}_2)$ is stable at lower temperatures, the three-phase equilibrium $(\text{Ni} + \text{Ni}_3\text{Sn} + \text{Ni}_{21}\text{P}_6\text{Sn}_2)$ could be maintained without the presence of Ni_3P . This principle is true, even if the three phases are not exact as what they are at 550 °C.

To test the above hypothesis, Ni-P alloy with incorporation of a high concentration of Sn was prepared for soldering reaction with Sn-3.5Ag. Interfacial reaction and tensile properties of the Ni-Sn-P/Sn-3.5Ag solder joints after reflow and prolonged aging, as well as the diffusional formation mechanism were studied. For comparison, the interfacial reaction and tensile properties of solder joints between the same solder and a binary electroless Ni-P metallization under the same reflow and aging conditions were

carried out. This was followed by fractographic analysis of both types of solder joints to investigate the failure modes of tensile test samples.

3.2. Experimental Procedures

3.2.1. Preparation of the Metallizations by Electroless Plating

Cu plates (99.98 wt.%) with a thickness of 6 mm were used as substrate for electroless plating of both Ni-P and Ni-Sn-P. Prior to Ni-P plating, the Cu plates were well-polished and then etched with 35 vol.% nitric acid for 30 s. After that, the Cu surface was activated using a commercial ruthenium-based pre-initiator. Electroless Ni-P plating was carried out in a commercial acidic sodium hypophosphite bath (from MacDermid) with a pH level of 5.3 (adjusted by 28% ammonia hydroxide). The plating temperature was 88 ± 2 °C and the plating time was 30 minutes.

On the other hand, electroless Ni-Sn-P plating was carried out in an alkaline bath with a pH of 9.0 for 45 min. The plating temperature was maintained at 85 °C. As listed in Table 3.1, this alkaline bath contained nickel sulphate and tin chloride as nickel and tin sources respectively, sodium hypophosphite as a reducing agent along with sodium citrate, lactic acid and ammonium sulphate as the complexing agents.

Table 3.1. Composition of the plating bath for electroless Ni-Sn-P.

Constituents of plating bath	Concentration
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	20 g/L
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	1 g/L
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	20 g/L
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	35 g/L
$(\text{NH}_4)_2\text{SO}_4$	30 g/L
Lactic acid	4 mL/L

3.2.2. Solder Joints Formation

The electrolessly-coated Cu plates were joined by lead-free Sn-3.5Ag solder to form Ni-P/Sn-3.5Ag and Ni-Sn-P/Sn-3.5Ag solder joints. A thin layer of no-clean paste flux was first applied on top of the plated surface of Cu to remove any oxides during soldering, before small pieces of Sn-3.5Ag solder wires were orderly arranged on the plated surface. The schematic arrangement of the coated Cu plates and solder wires used to form solder joints is shown in Fig. 3.1. As illustrated, the arrangement comprised of alumina spacers (around 650 μm thick), which were hired to maintain a fixed and uniform thickness of solder in between the joined Cu plates. The reflow soldering process was carried out in an IR reflow oven (ESSEMTEC RO-06E), involving an initial preheating at 190 °C for 100 s, followed by reflowing at a peak temperature of 260 °C for 60 s, and finally cooling down to 120°C in the oven.

Fig. 3.1. Schematic illustration of joining the electrolessly-coated Cu plates.

3.2.3. Solid-state Thermal Aging

Solid-state thermal aging at 150 °C for 1000 h is a typical test requirement to study the reliability of solder joints. In the current work, solid-state aging was conducted at a higher temperature (180 °C) to shorten the aging duration. Both Ni-P/Sn-3.5Ag and Ni-Sn-P/Sn-3.5Ag solder joints were thermally-aged at 180 °C for 600 h to study their interfacial reactions and tensile properties upon aging. After aging, these solder joints were taken out from the oven and cooled down to room temperature in air.

3.2.4. Tensile Test Sample Preparation

The joined plates were then cut along the Cu plate thickness direction into a number of small test samples having cross-sectional area of around $650\ \mu\text{m} \times 650\ \mu\text{m}$ dimension using a diamond precision cutter. Fig. 3.2 shows the schematic diagram of a sample prepared for the tensile testing.

Fig. 3.2. Schematic diagram of the sample for tensile testing.

3.2.5. Tensile Testing

Tensile testing was performed using INSTRON 5567 tensile tester. For both types of solder joints, five to ten samples from each reflow or aging condition were tested to obtain the average tensile strength. The tensile test was carried out with a constant crosshead speed of 0.05 mm/min to a complete fracture at room temperature.

3.2.6. Morphological and Microstructural Observations

The surface morphologies and the thicknesses of both Ni-P and Ni-Sn-P coating layers were observed under scanning electron microscope (SEM), along with the interfacial microstructures of both types of solder joints after prolonged aging at 180 °C. The compositions of the coating layers, and the compositions of the interfacial compounds formed in the as-reflowed and the aged solder joints were analyzed using energy dispersive X-ray (EDX) incorporated in the SEM. For the cross-sectional SEM study, the samples were mounted into epoxy and then mechanically ground with SiC abrasive papers, followed by polishing with diamond pastes, to a 1 μm finish. After polishing, chemical etching was performed to reveal the microstructure of the interface compounds. The etchant used was 4 vol% of hydrochloride acid. The samples were

immersed into the etchant for 30 s at room temperature, and then a thin gold film was sputtered on the surface of the etched samples to prevent electrical charging during SEM observation. Moreover, the newly-formed interfacial compounds in the Ni-Sn-P/Sn-3.5Ag solder joint were identified by using transmission electron microscope (TEM). The TEM sample was prepared by focused ion beam (FIB) technique. The model of FIB used in this study is FEI NOVA nanolab 600i.

3.3. Results

3.3.1. As-deposited Metallizations

The composition of the deposited Ni-P layer was measured to be 6~7 wt.% of P by EDX. As shown in Fig. 3.3(a), the surface of the deposited Ni-P layer had smooth nodules with uneven size. The thickness of the deposited Ni-P layer was measured to be around 9.7 μm (Fig. 3.3(b)). This layer was seen to closely adhere to the Cu substrate since no pores were found at the interface.

Fig. 3.3. As-deposited Ni-P layer: (a) surface morphology, (b) cross-sectional micrograph.

On the other hand, the composition of the deposited Ni-Sn-P layer was measured to be 6~7 wt.% P and 19~21 wt.% Sn by EDX. As shown in Fig. 3.4(a), the surface of the deposited Ni-Sn-P layer also contained smooth nodules with uneven size. The thickness of the deposited Ni-Sn-P layer was measured to be around 11.5 μm (Fig. 3.4(b)). As in the case of the deposited Ni-P layer, the Ni-Sn-P layer also closely adhered to the Cu substrate. Moreover, Fig. 3.4(b) reveals that the Ni-Sn-P coating has a unique “tree-like” structure, as a result of columnar growth during the electroless plating.

Fig. 3.4. As-deposited Ni-Sn-P layer: (a) surface morphology, (b) cross-sectional micrograph.

3.3.2. Interfacial Microstructure Analysis of As-reflowed Solder Joints

Fig. 3.5(a) shows the cross-sectional micrograph of the as-reflowed Ni-P/Sn-3.5Ag solder joint. Chunky-type Ni_3Sn_4 is the primary IMC formed at the joint interface, and some of them spalled into the bulk solder. The formation of Ni_3Sn_4 is due to the reaction between Sn from the solder and Ni from the Ni-P metallization. A dark layer of Ni_3P formed within the top region of the Ni-P metallization, with a few voids present inside. The formation of these voids has been explained in previous study [16]. A very thin

ternary Ni_2SnP layer was also noticed to form in between the Ni_3Sn_4 and Ni_3P layers [73, 90].

For the as-reflowed Ni-Sn-P/Sn-3.5Ag solder joint, chunky-type Ni_3Sn_4 was formed, as shown in the cross-sectional micrograph of the solder joint in Fig. 3.5(b). Unlike in the as-reflowed Ni-P/Sn-3.5Ag solder joint, there was neither Ni_3P layer nor voids formed in the as-reflowed Ni-Sn-P/Sn-3.5Ag solder joint. Thus, the hypothesis is confirmed that the formation of Ni_3P layer could be avoided through the design of the metallization composition. From Fig. 3.5(b), a thin ternary Ni-Sn-P compound layer was also observed to form in between the Ni_3Sn_4 layer and the unconsumed Ni-Sn-P coating. EDX result indicates that the newly-formed ternary Ni-Sn-P compound contains ~51 at.% Ni, ~34 at.% Sn and ~15 at.% P (Fig. 3.6). It is a different IMC from the Ni_2SnP compound formed in the Ni-P/Sn-3.5Ag solder joint.

Fig. 3.5. Back-scattered SEM images showing IMCs formed in (a) as-reflowed Ni-P/Sn-3.5Ag solder joint and (b) as-reflowed Ni-Sn-P/Sn-3.5Ag solder joint. The ternary Ni-Sn-P layer consists of ~51 at.% Ni, ~34 at.% Sn and ~15 at.% P.

Fig. 3.6. EDX compositional results of the newly-formed ternary Ni-Sn-P layer.

The crystal structure of the ternary Ni-Sn-P compound was identified using electron diffraction under TEM. The cross-section sample was prepared by focused ion beam (FIB) from the Ni-Sn-P/Sn-3.5Ag interface after reflow for 25 cycles (reflow at 260 °C for 60 s as one cycle). Fig. 3.7 shows the TEM micrograph of the FIB sample and the lattice image of the Ni-Sn-P compound. The EDX result of this compound from TEM is consistent with the result obtained from SEM. The lattice image of the Ni-Sn-P compound with the Fourier reconstructed pattern (Fig. 3.7(b)) is matched to $\text{Ni}_{13}\text{Sn}_8\text{P}_3$, combined with the composition result from EDX as a secondary evidence, this new compound was identified as $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ having a triclinic lattice ($P1$, $a = 6.456 \text{ \AA}$, $b = 21.291 \text{ \AA}$, $c = 13.247 \text{ \AA}$, $\alpha = 81.052^\circ$, $\beta = 56.260^\circ$, $\gamma = 68.221^\circ$) [104].

Fig. 3.7. (a) TEM micrograph of the FIB sample from Ni-Sn-P/Sn-3.5Ag interface after reflow for 25 cycles, and (b) lattice image and Fourier reconstructed pattern of region A in (a) with $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ [44, 2, -6].

3.3.3. Interfacial Microstructure Analysis of Aged Solder Joints

Fig. 3.8 shows the growth of various compounds at the Ni-P/Sn-3.5Ag interface aged at 180 °C for up to 600 h. The Ni_3Sn_4 layer grew much thicker during prolonged aging, and some Ag_3Sn particles accumulated inside this layer. From Fig. 3.8(c), the deposited Ni-P layer was seen to be fully consumed and transformed into Ni_3P layer after 300 h of aging. The thickness of the Ni_3P layer after 300 h of aging ($\sim 4.9 \mu\text{m}$) is much smaller than that of the as-deposited Ni-P layer ($\sim 9.7 \mu\text{m}$). Such 50% shrinkage indicates that, Ni atoms diffuse out from Ni-P to form Ni_3Sn_4 during reflow and aging. It was noted that after 600 h of aging (Fig. 3.8(f)), the thickness of the Ni_3P layer ($\sim 4.4 \mu\text{m}$) reduced by about 10% as compared to that after 300 h of aging ($\sim 4.9 \mu\text{m}$), while the thickness of the Ni_2SnP layer ($0.34 \mu\text{m}$) increased by about 17% as compared to that after 300 h of aging ($0.29 \mu\text{m}$). This indicates that, once the Ni-P layer is fully consumed, the Ni_2SnP layer grows at the expense of the Ni_3P layer. Interestingly, after the Ni-P layer was fully consumed (Fig. 3.8(c)-(f)), instead of $(\text{Ni,Cu})_3\text{Sn}_4$, only Ni_3Sn_4 formed and no voids were observed at the Cu/ Ni_3P interface, indicating that Cu atoms still remained in the substrate even after aging for 600 h. Moreover, there were very few voids present in the Ni_3P layer at the as-reflowed state (Fig. 3.5(a)); however, as the reaction proceeded upon aging, the voids in the Ni_3P layer grew both in size and number (Fig. 3.8).

Fig. 3.8. Back-scattered SEM images showing IMCs at Ni-P/Sn-3.5Ag interface after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, (e) 500 h, and (f) 600 h.

The growth of various compounds at the Ni-Sn-P/Sn-3.5Ag interface aged at 180 °C for up to 600 h is shown in Fig. 3.9. It was observed that some Ag_3Sn particles also accumulated inside the Ni_3Sn_4 layer. Unlike at the aged Ni-P/Sn-3.5Ag interface (Fig.

3.8), the thickness of the Ni_3Sn_4 layer only increased a little during prolonged aging. After 300 h of aging, the deposited Ni-Sn-P layer was only consumed by around 29% (around $8.2\ \mu\text{m}$ remains as compared to the original thickness of around $11.5\ \mu\text{m}$). As a comparison, the Ni-P layer with an original thickness of around $9.7\ \mu\text{m}$ was fully consumed after aging for 300 h (Fig. 3.8(c)). Even after 600 h of aging, the remaining Ni-Sn-P layer was almost unchanged, indicating that the Ni-Sn-P layer was consumed much slower than the Ni-P layer. Fig. 3.10 shows the consumption of Ni-P and Ni-Sn-P metallizations upon aging for 600 h. It was clearly seen that the consumption rate of the Ni-Sn-P layer is much slower. The significantly retarded consumption rate of the Ni-Sn-P layer is consistent with the much reduced growth rate of the Ni_3Sn_4 layer as compared to that at the Ni-P/Sn-3.5Ag solder interface. It is worth mentioning that no Ni_3P was observed at the Ni-Sn-P/Sn-3.5Ag interface with extended aging for up to 600 h (Fig. 3.9), indicating that this phase is thermodynamically avoidable. This is a further evidence of the successful application of phase diagram in the alloy design. As shown in Fig. 3.9, the growth of the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer was negligible during aging. Interestingly, the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer began to break at some weak locations after aging for 300 h. The EDX elemental mapping results (Fig. 3.11) confirm that the Ni_3Sn_4 compound formed at these broken locations. The scattered cracking in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer is believed to be due to the weakness of the underlying Ni-Sn-P metallization layer, which will be elaborated in Section 3.4.3 later.

Fig. 3.9. Back-scattered SEM images showing IMCs at Ni-Sn-P/Sn-3.5Ag interface after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, (e) 500 h, and (f) 600 h.

Fig. 3.10. Consumption of Ni-P and Ni-Sn-P metallizations upon aging for 600 h. Notice that the Ni-P metallization with an original thickness of 9.7 μm was fully consumed after 300 h of aging.

Fig. 3.11. EDX elemental mapping analysis of Ni-Sn-P/Sn-3.5Ag interface after aging at 180 °C for 300 h: (a) Back-scattered SEM image, (b) mapping for Ni, (c) mapping for Sn, (d) mapping for P, (e) mapping for Cu, and (f) mapping for Ag. Elemental concentration decreases with decreasing colour intensity.

Moreover, some cracks were observed to originate inside the unconsumed Ni-Sn-P metallization layer after aging for 300 h (Fig. 3.9(c)-(f)). The formation of such cracks may be attributed to the intrinsic tensile stress inside the Ni-Sn-P coating layer. This type of tensile stress is brought about by the electroless plating process itself [42]. Prior to aging, the magnitude of such tensile stress is insufficient to cause the formation of cracks, so no cracks were observed in either the as-deposited Ni-Sn-P layer or this layer after reflow. However, the aging process can increase such tensile stress [42]. As a result of prolonged aging, cracks began to initiate inside the Ni-Sn-P metallization layer, followed by propagation along the weak regions inside this layer.

3.3.4. Tensile Strength of Solder Joints

Table 3.2 shows the average tensile strengths obtained from both Ni-Sn-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag solder joints upon aging at 180 °C for up to 600 h. Fig. 3.12 depicts the tensile strengths of both types of solder joints as a function of aging time up to 600 h. Both types of as-reflowed solder joints had similar tensile strength. The strength of Ni-P/Sn-3.5Ag solder joints dropped significantly after aging for 400 h and beyond, while the strength of Ni-Sn-P/Sn-3.5Ag solder joints dropped significantly after aging for 300 h and beyond. The significant drop in tensile strength is believed to be due to the shift of fracture path upon prolonged aging, so it is necessary to perform fractographic analysis for both types of solder joints under different aging durations.

Table 3.2. Tensile strengths of Ni-P/Sn-3.5Ag and Ni-Sn-P/Sn-3.5Ag solder joints upon aging at 180 °C for 600 h.

Aging Time (hour)	Tensile Strength (MPa)	
	Ni-P/Solder Joint	Ni-Sn-P/Solder Joint
As-reflowed	35.41 ± 2.85	32.48 ± 1.28
100	32.75 ± 1.38	30.00 ± 0.89
200	31.75 ± 1.36	30.07 ± 0.81
300	31.32 ± 0.43	23.42 ± 0.71
400	22.69 ± 1.36	23.26 ± 1.07
600	22.46 ± 0.99	22.61 ± 0.77

Fig. 3.12. Tensile strengths of both Ni-Sn-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag solder joints after aging for up to 600 h.

3.3.5. Failure Analysis of Solder Joints

The fractographic analysis of both Ni-P/Sn-3.5Ag and Ni-Sn-P/Sn-3.5Ag solder joints were conducted under SEM to study the fracture mechanism in tensile testing upon aging. Fig. 3.13 (a) and (b) show the cross-sectional view and fractured surface of the as-reflowed Ni-P/Sn-3.5Ag solder joints, respectively. As shown in Fig. 3.13(a), an obvious necking occurred in the bulk solder, and the fracture surface inclined at about 45° to the tensile-stress axis. Fig. 3.13(b) shows the fractured surface of this solder joint, and the EDX results indicates that Sn was the dominant element at the fractured surface, confirming the fracture occurs completely in the bulk solder.

Fig. 3.13. (a) Cross-sectional view and (b) fractured surface of the as-reflowed Ni-P/Sn-3.5Ag solder joint.

Fig. 3.14 shows that Ni-P/Sn-3.5Ag solder joints still experienced complete ductile failure inside the bulk solder after aging at 180°C for up to 300 h. The entire fracture path is inside the bulk solder in the as-reflowed Ni-P/Sn-3.5Ag solder joints and this type of joints after aging for up to 300 h. This indicates that the cohesive strength of the bulk solder is weaker than the cohesive strength of each interfacial layer and the adhesion of

the Ni_3Sn_4 IMC layer to the solder in the as-reflowed condition and after aging for up to 300 h.

Fig. 3.14. Cross-sectional view of Ni-P/Sn-3.5Ag solder joint after aging at 180 °C for (a) 100 h, (b) 200 h, and (c) 300 h.

However, as shown in Fig. 3.15, in the Ni-P/Sn-3.5Ag solder joints aged at 180 °C for 400 h and 600 h, the failure occurred completely at the interface. As shown in Fig. 3.15(a) and (c), the entire fracture path in both samples was quite flat, indicating macroscopic brittle behaviour in the prolonged aged Ni-P/Sn-3.5Ag solder joints. At the fractured surfaces of the solder joints aged for 400 h and 600 h, SEM morphological observation and EDX compositional analysis indicated the presence of Ni_3Sn_4 and solder

materials on the fractured surface, revealing that the brittle fracture occurred at the $\text{Ni}_3\text{Sn}_4/\text{Sn-3.5Ag}$ interface. This means that in the Ni-P/Sn-3.5Ag solder joints after aging for 400 h and beyond, the cohesive strength of the bulk solder and the cohesive strength of each interfacial layer are stronger than the adhesion of the Ni_3Sn_4 IMC layer to the solder. The weakening of the $\text{Ni}_3\text{Sn}_4/\text{solder}$ interface is believed to be attributed to the stress originated by the volume mismatch between the Ni_3Sn_4 IMC and the solder, and such stress increases with growth of the Ni_3Sn_4 layer. Besides, as shown in Fig. 3.8, upon aging with longer duration, the $\text{Ni}_3\text{Sn}_4/\text{solder}$ interface became more flat due to the tendency of reducing the interface area. The smoothed $\text{Ni}_3\text{Sn}_4/\text{solder}$ interface loses the mechanical interlocking as compared with the uneven $\text{Ni}_3\text{Sn}_4/\text{solder}$ interface in the as-reflowed solder joints and the solder joints undergoing shorter aging durations. Thus, such flattened $\text{Ni}_3\text{Sn}_4/\text{solder}$ interface could be a contributing factor towards the shift of failure path from inside the bulk solder to the $\text{Ni}_3\text{Sn}_4/\text{solder}$ interface. It was noted that the voids in the Ni_3P layer grew both in number and size upon aging (Fig. 3.8), and the presence of voids should in theory weaken the Ni_3P layer itself. However, the Ni_3P layer was not observed to be the weakest connection at the entire joint interface region, one of the possible solutions is because other locations degrade much faster than the Ni_3P layer.

Fig. 3.15. (a) Cross-sectional view and (b) fractured surface of the Ni-P/Sn-3.5Ag solder joint after aging at 180 °C for 400 h. (c) Cross-sectional view and (d) fractured surface of the Ni-P solder joint after aging at 180 °C for 600 h.

Fig. 3.16(a) and (b) show the cross-sectional view and fractured surface of the as-reflowed electroless Ni-Sn-P/Sn-3.5Ag solder joint, respectively. As shown in Fig. 3.16(a), an obvious necking occurred in the bulk solder, and the fracture surface inclined at about 45° to the tensile-stress axis. Fig. 3.16(b) shows the fractured surface of this solder joint, and the EDX results indicates that Sn was the dominant element at the fractured surface, confirming the fracture occurs completely in the bulk solder. This is very similar with the as-reflowed Ni-P/Sn-3.5Ag solder joint.

Fig. 3.16. (a) Cross-sectional view and (b) fractured surface of the as-reflowed Ni-Sn-P/Sn-3.5Ag solder joint.

Fig. 3.17 shows that Ni-Sn-P/Sn-3.5Ag solder joints still experienced complete ductile failure inside the bulk solder after aging at 180 °C for up to 200 h. The entire fracture path is inside the bulk solder, similar to the as-reflowed case. Therefore the interface remains stronger than the bulk solder in the as-reflowed condition and after aging for up to 200 h.

Fig. 3.17. Cross-sectional view of Ni-Sn-P/Sn-3.5Ag solder joint after aging at 180 °C for (a) 100 h, and (b) 200 h.

However, as shown in Fig. 3.18, after the Ni-Sn-P/Sn-3.5Ag solder joints were aged at 180 °C for 300 h, 400 h and 600 hours, the failure path shifted to the interface. It was seen that the entire fracture path is relatively flat, indicating macroscopic brittle behaviour in these prolonged aged solder joints.

Fig. 3.18. Cross-sectional view of Ni-Sn-P/Sn-3.5Ag solder joint after aging at 180 °C for (a) 300 h, (b) 400 h, and (c) 600 h.

Figs. 3.19, 3.20, and 3.21 show the fractured surfaces of the Ni-Sn-P/Sn-3.5Ag solder joints after aging at 180 °C for 300 h, 400 h and 600 h, respectively. At these fractured surfaces, Ni_3Sn_4 , solder and the unconsumed Ni-Sn-P layer were detected by EDX compositional analysis and SEM morphological observation, revealing that the

brittle fracture occurred not only at the Ni_3Sn_4 /solder interface, but also through all of the interfacial layers (Ni_3Sn_4 , $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ and Ni-Sn-P metallization layers). This indicates that, in the Ni-Sn-P/Sn-3.5Ag solder joints after aging for 300 h and beyond, the cohesive strength of the bulk solder is stronger than the adhesion of the Ni_3Sn_4 IMC layer to the solder and the cohesive strength of each interfacial layer. The weakening of the Ni_3Sn_4 /solder interface might be attributed to the stress originated by the volume mismatch between the Ni_3Sn_4 IMC and the solder, and such stress increases with growth of the Ni_3Sn_4 layer. The fracture that occurred through the other interfacial layers could be contributed by the similar factor of volume mismatch induced stress. In addition, Fig. 3.9 reveals that as a result of prolonged aging in the Ni-Sn-P/Sn-3.5Ag solder joints, some cracks began to initiate inside the Ni-Sn-P metallization layer, and then propagated along the weak regions inside this layer. The presence and propagation of these cracks in the direction paralleled to the tensile-stress axis make it more prone for the fracture to pass through all of the interfacial layers.

Fig. 3.19. (a) Fractured surface of Ni-Sn-P/Sn-3.5Ag solder joint after aging at 180 °C for 300 h, (b) the magnified region A, (c) the magnified region B, and (d) the magnified region C.

Fig. 3.20. (a) Fractured surface of Ni-Sn-P/Sn-3.5Ag solder joint after aging at 180 °C for 400 h, and (b) the magnified region A.

Fig. 3.21. (a) Fractured surface of Ni-Sn-P/Sn-3.5Ag solder joint after aging at 180 °C for 600 h, (b) the magnified region A, and (c) the magnified region B.

3.4. Discussion

3.4.1. Diffusional Formation Mechanism of IMCs at the Ni-Sn-P/Solder Interface

As discussed previously, there are only two interfacial compounds, Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ that are formed during the electroless Ni-Sn-P/Sn-3.5Ag interfacial reaction. Since the Ni-Sn-P coating contains both Ni and Sn, in order to find out whether the formation of Ni_3Sn_4 is caused by the soldering reaction between Sn from the solder and Ni from the metallization or reaction between the existing Ni and Sn within the Ni-Sn-P metallization at the reflow temperature, XRD was carried out on the as-deposited Ni-Sn-

P and such deposit after annealing at 260 °C (the same as the reflow temperature). Fig. 3.22 shows XRD patterns of the Ni-Sn-P deposit before and after annealing at 260 °C for 2 h. The XRD spectra were recorded between 2-theta from 30 ° to 80 ° with a fixed glancing angle of 2 °. It was observed that the pattern for the as-deposited Ni-Sn-P consisted of only one broad peak with highest intensity belonging to Ni; hence, the as-deposited Ni-Sn-P has an amorphous structure. After annealing at 260 °C for 2 h, the XRD result shows that no peaks from Ni_3Sn_4 were present, and the Ni-Sn-P still has an amorphous structure, proving that the formation of Ni_3Sn_4 cannot occur by the reaction between the Sn and Ni composition within the Ni-Sn-P coating itself at the reflow temperature. Since the formation of Ni_3Sn_4 compound was also found during the Ni-P/Sn-3.5Ag interfacial reaction, the formation of Ni_3Sn_4 during reflow at the Ni-Sn-P/Sn-3.5Ag interface is due to the reaction between the Sn atoms diffusing out from the solder and the Ni atoms diffusing out from the Ni-Sn-P coating layer. The continuous formation of Ni_3Sn_4 during soldering reaction leads to the depletion of Ni from the surface of the Ni-Sn-P layer.

Fig. 3.22. XRD patterns of the Ni-Sn-P coating before and after annealing at 260 °C (the same as the reflow temperature) for 2 h.

The $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound has never been reported in any literatures relating to soldering reaction before, thus its formation mechanism requires some focused attention in the current work. Since the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer thickens during the soldering reaction, a certain type of diffusional formation mechanism is deduced based on several observations in the current work, and detailed analysis is provided below.

From the review of various publications, there is no convincing evidence reporting the out-diffusion of P atoms from the Ni-P layer during soldering reaction. In the current work, the P atoms in the Ni-Sn-P are also believed to remain in the deposited layer during soldering reaction. This is probably best confirmed by comparing the compositions of the as-deposited Ni-Sn-P layer (77 at.% Ni, 10 at.% Sn and 13 at.% P) and the newly-formed $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer (54 at.% Ni, 33 at.% Sn and 13 at.% P). Since both layers have the same

P concentration, it is most likely that the Ni-Sn-P deposit is transformed into the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound during soldering reaction. As the Ni and Sn concentrations in the two neighbouring layers are different, the author needs to explain what the diffusion paths for these two elements are.

It is obvious that the formation of Ni_3Sn_4 causes depletion of Ni from the surface of the Ni-Sn-P layer, so the top region of the Ni-Sn-P layer can be transformed into a phase with lower Ni content, which is in agreement with the fact that the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound has a lower Ni content than the Ni-Sn-P deposit. Since the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound has a higher Sn concentration than the Ni-Sn-P deposit, it is speculated that the transformation of the Ni-Sn-P deposit into the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound requires Sn supply from the solder, which is similar to the formation of the Ni_2SnP compound during Ni-P/Sn-3.5Ag interfacial reaction. Based on the above arguments, the author believes that the nanocrystalline $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound is formed by transforming the amorphous Ni-Sn-P with the aid of Ni (outward) and Sn (inward) diffusion during the Ni-Sn-P/Sn-3.5Ag soldering reaction.

EDX line scan and elemental mapping were conducted to study the diffusion profile at the Ni-Sn-P/Sn-3.5Ag interface. Fig. 3.23 illustrates the EDX line scan results at the Ni-Sn-P/Sn-3.5Ag interface after aging at 180 °C for 300 h. It was noted that at the interface between the deposited Ni-Sn-P layer and the newly-formed $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer, the Sn intensity started to increase. This indicates that the Sn atoms from the solder diffuse into the deposited Ni-Sn-P layer to form the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound. It was clearly seen that the Ni intensity began to drop at the Ni-Sn-P/ $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ interface, indicating that Ni atoms diffuse outward from the deposited Ni-Sn-P layer to react with Sn atoms from the solder

to form Ni_3Sn_4 . These are in agreement with the proposed diffusional formation mechanism of Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compounds at the Ni-Sn-P/Sn-3.5Ag interface. Moreover, it was observed that the intensities for Ni, Sn, and P fluctuated inside the unconsumed Ni-Sn-P layer. Such fluctuation is believed to be caused by the elemental segregation in the Ni-Sn-P coating.

Fig. 3.23. Elemental distribution at the Ni-Sn-P/Sn-3.5Ag interface after aging at 180 °C for 300 h.

From the mapping result of the as-reflowed Ni-Sn-P/Sn-3.5Ag interface (Fig. 3.24), it was clearly seen that P remained in the Ni-Sn-P and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layers. In contrast, Ni atoms diffused out from the Ni-Sn-P layer to form Ni_3Sn_4 . The signal from Sn atoms was detected in all layers, except the Cu substrate. These are in agreement with the findings from the line scan (Fig. 3.23) and the aforementioned diffusional formation mechanism of Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compounds at the Ni-Sn-P/Sn-3.5Ag interface.

Fig. 3.24. EDX element mapping analysis of the as-reflowed Ni-Sn-P/Sn-3.5Ag interface: (a) SEM image, (b) mapping for Ni, (c) mapping for Sn, (d) mapping for P, (e) mapping for Cu, and (f) mapping for Ag. Elemental concentration decreases with decreasing colour intensity.

Fig. 3.25 schematically illustrates the diffusional formation mechanism of Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layers between Ni-Sn-P metallization and Sn-3.5Ag solder. The Sn atoms that diffuse out from the solder react with the Ni atoms that diffuse out from the Ni-Sn-P layer to form the Ni_3Sn_4 layer. Meanwhile, the top region of the Ni-Sn-P metallization becomes Ni-depleted due to the out-diffusion of Ni to form the Ni_3Sn_4 . Since Sn is the faster diffusant in Ni_3Sn_4 [97], some Sn atoms will also reach the Ni_3Sn_4 /Ni-Sn-P interface for the formation of $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound. The continued growth of Ni_3Sn_4 requires Ni supply from the Ni-Sn-P layer, so Ni atoms have to diffuse through the formed $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer to react with the Sn atoms from the solder. Thus, the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer acts as barrier for Ni diffusion.

Fig. 3.25. A schematic illustration of the diffusional formation mechanism of Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layers between Ni-Sn-P metallization and Sn-3.5Ag solder.

3.4.2. The Mass Conservation of Ni Atoms at the Ni-Sn-P/Solder Interface

In order to verify the proposed diffusional formation mechanism of the Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layers at the Ni-Sn-P/Sn-3.5Ag interface, law of mass conservation of Ni atoms across the metallization/solder interface was carried out. According to Fig. 3.25, the following reactions should occur at the Ni-Sn-P/Sn-3.5Ag interface:

The mass conservation is applied to samples aged for 100 h (Fig. 3.9(a)) and 400 h (Fig. 3.9(d)), i.e. the number of moles of Ni in the Ni-Sn-P layer consumed within this aging duration must be equal to the sum of the number of moles of Ni in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer and the number of moles of Ni in the Ni_3Sn_4 layer grown within this duration. The number of moles of Ni in a layer of thickness t_{layer} per unit area can be determined by:

$$Ni_{\text{layer}} = m \times \frac{\rho_{\text{layer}} t_{\text{layer}}}{M_{\text{layer}}}, \quad (3.3)$$

where m is the number of moles of Ni in one mole of the layer, M_{layer} is the molecular weight of the layer, and ρ_{layer} is the density of the layer.

As shown in Fig. 3.9, the thickness of the unconsumed Ni-Sn-P layer after aging for 100 h and 400 h was 8.9 μm and 8.2 μm , respectively. Due to lack of the density information for the coated Ni-Sn-P layer in the literature, the density of this layer has to be estimated based on rule of mixtures by known density data of Ni-P and Sn. This layer consists of 73.5 wt.% of Ni, 6.5 wt.% of P, and 20 wt.% of Sn, so it can be treated as a mixture of 20 wt.% of Sn and 80 wt.% of Ni-P (with 8.1 wt.% of P). By rule of mixtures, density of the Ni-Sn-P coating layer is estimated as:

$$\rho_{\text{Ni-Sn-P}} = \frac{1}{\frac{f_{\text{Ni-P}}}{\rho_{\text{Ni-P}}} + \frac{f_{\text{Sn}}}{\rho_{\text{Sn}}}} = \frac{1}{\frac{0.8}{8.1 \text{ g/cm}^3} + \frac{0.2}{7.17 \text{ g/cm}^3}} = 7.90 \text{ g/cm}^3, \quad (3.4)$$

where f stands for the fraction of each constituent. The density of the Ni-P with 8.1 wt.% of P and Sn is found to be 8.1 g/cm^3 [42] and 7.17 g/cm^3 [105], respectively. The coated Ni-Sn-P layer contains 77 at.% of Ni, so the value of m (for Ni) in this layer is 77. The molar weight of this layer is 6108.64 g/mol . Substituting these values into Equation 3.3, the number of moles of Ni in the unconsumed Ni-Sn-P layer after aging for 100 h and 400 h is $8.86 \times 10^{-5} \text{ mol/cm}^2$ and $8.17 \times 10^{-5} \text{ mol/cm}^2$, respectively. Thus, the number of moles of Ni in the Ni-Sn-P layer consumed within the aging duration of 300 h, labelled as $Ni_{\text{Ni-Sn-P}}$, is calculated as $0.69 \times 10^{-5} \text{ mol/cm}^2$.

Also from Fig. 3.9, the thickness of the Ni_3Sn_4 layer after aging for 100 h and 400 h was 5.399 μm and 6.986 μm , respectively. The density of the Ni_3Sn_4 layer is 8.64 g/cm^3 [60]. The molar weight of this layer is 650.83 g/mol , and the value of m (for Ni) is 3. Substituting these values into Equation 3.3, the number of moles of Ni in the Ni_3Sn_4 layer after aging for 100 h and 400 h is $2.15 \times 10^{-5} \text{ mol/cm}^2$ and $2.78 \times 10^{-5} \text{ mol/cm}^2$, respectively.

Thus, the number of moles of Ni in the Ni_3Sn_4 layer grown within the aging duration of 300 h, labelled as $N_{i_{\text{Ni}_3\text{Sn}_4}}$, is determined to be $0.63 \times 10^{-5} \text{ mol/cm}^2$.

Based on the same figure, the thickness of the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer after aging for 100 h and 400 h was 1.422 μm and 1.528 μm , respectively. The molar weight of this layer is 1805.40 g/mol, and the value of m (for Ni) is 13. The density of the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer can be calculated by its molar weight divided by its molar volume. The molar volume of a compound can be calculated by:

$$V_m = V_c N_a / Z, \quad (3.5)$$

where V_c is the volume of the compound unit cell, N_a is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), and Z is the number of formula weight per unit cell. For $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound, since its V_c is 1403.07 $\text{\AA}^3$, and Z is 4 [104], V_m of it is calculated to be 211.23 cm^3/mol . Thus, the density of this compound is determined to be 8.55 g/cm^3 . Substituting these values into Equation 3.3, the number of moles of Ni in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer after aging for 100 h and 400 h is $0.88 \times 10^{-5} \text{ mol/cm}^2$ and $0.94 \times 10^{-5} \text{ mol/cm}^2$, respectively. Thus, the number of moles of Ni in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer grown within this aging duration, labelled as $N_{i_{\text{Ni}_{13}\text{Sn}_8\text{P}_3}}$, is calculated as $0.06 \times 10^{-5} \text{ mol/cm}^2$.

Therefore, from these values it is clear that $N_{i_{\text{Ni-Sn-P}}} = N_{i_{\text{Ni}_3\text{Sn}_4}} + N_{i_{\text{Ni}_{13}\text{Sn}_8\text{P}_3}}$. This proves the mass balance of Ni during reaction at the Ni-Sn-P/Sn-3.5Ag interface, i.e. all of the Ni atoms diffused out from the Ni-Sn-P layer take part in the reaction to form Ni_3Sn_4 , and the depletion of Ni from the surface of the Ni-Sn-P layer leads to the formation of the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer.

3.4.3. The Success in Avoiding Ni₃P Formation and Related Problems with Ni-Sn-P Metallization

It has been discovered that at the Ni-P/Sn-3.5Ag interface, the presence of voids is attributed to the formation of Ni₃P layer with a fine columnar structure [16], since it is relatively easy for the Ni atoms from the deposited Ni-P layer to diffuse along the columnar grain boundaries of Ni₃P to form Ni₃Sn₄. When the compensation from other elements to fill the vacant sites left by Ni atoms is insufficient, voids will form inside the Ni₃P layer [16]. The interface elemental diffusion becomes easier through the free surface of the voids, thus the presence of these voids can further accelerate the diffusion of Ni atoms through the Ni₃P layer, leading to a rapid consumption rate of the Ni-P layer in the Ni-P/Sn-3.5Ag solder joint (e.g. Fig. 3.8). Therefore, the formation of Ni₃P layer should be avoided to slow down the interfacial reaction. The current work to choose an electroless Ni-Sn-P as metallization for lead-free soldering is based on the limited thermodynamic data with reasonable assumption that the formation of Ni₃P layer could be avoided altogether when the Sn concentration is high enough. Indeed, in the current work with Ni-Sn-P metallization, the formation of Ni₃P has been successfully avoided, and there are no voids observed at the Ni-Sn-P/Sn-3.5Ag interface even after prolonged reaction. The author has also shown that when the Ni₁₃Sn₈P₃ layer is continuous, it behaves as a very effective barrier for Ni diffusion.

However, the Ni₁₃Sn₈P₃ layer was observed to contain cracks at some locations after prolonged aging (Fig. 3.9(c)-(f)). The presence of these broken locations seriously deteriorates the diffusion barrier performance of this layer. As a consequence, although the overall consumption rate of the Ni-Sn-P metallization is still much slower than that of

Ni-P (Fig. 3.10), as elaborated in Section 3.3.4 and 3.3.5, the long-term reliability of Ni-Sn-P/Sn-3.5Ag solder joint becomes slightly inferior to the one of Ni-P/Sn-3.5Ag solder joint. The scattered cracking in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer is likely due to the weakness of the underlying Ni-Sn-P layer. The author has explained earlier that the Ni-Sn-P metallization layer has contained intrinsic tensile stress in the as-plated state [42]. Coupled with the unique “tree-like” morphology of the Ni-Sn-P layer, which is as a result of columnar growth during the electroless plating, it is not unexpected to see the cracking through the weak boundary between the neighbouring columns (Figs. 3.9 (c)-(f)).

As observed previously, when the reaction at the Ni-Sn-P/Sn-3.5Ag interface proceeds upon aging, the Ni_3Sn_4 grows into the gaps at the broken locations in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer. This might have led to the accelerated crack formation in the Ni-Sn-P metallization layer because the “invasion” of the Sn through gaps in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer will attract more Ni atoms from the metallization. The depletion of Ni that is likely to occur preferably along the columnar boundary will further weaken the metallization layer.

Once Sn reaches the Cu substrate through the cracks, the interfacial reaction becomes more complicated. Fig. 3.26(a) shows the consequence when the Sn diffusion through the opening in the metallization layer and the formed Ni_3Sn_4 IMC have reached the Cu substrate after aging at 200 °C for 400 h. It was observed that Cu_3Sn , Cu_6Sn_5 , $(\text{Ni}_{0.84}\text{Cu}_{0.16})_3\text{Sn}_4$, and $(\text{Cu}_{0.55}\text{Ni}_{0.45})_6\text{Sn}_5$ compounds formed after the Ni_3Sn_4 compound is in contact with the Cu substrate. Fig. 3.27 shows the EDX elemental mapping of the Ni-Sn-P/Sn-3.5Ag interface at the location shown in Fig. 3.26(a). The mapping results indicate that due to lacking of the deposited Ni-Sn-P layer as a diffusion barrier, Cu atoms managed to diffuse out from the substrate, and incorporated into the compound

formation. As a result, the originally formed Ni_3Sn_4 was transformed into ternary $(\text{Ni}_{0.84}\text{Cu}_{0.16})_3\text{Sn}_4$ and $(\text{Cu}_{0.55}\text{Ni}_{0.45})_6\text{Sn}_5$ compounds. Meanwhile, the Sn atoms from the solder diffuse through these ternary compounds to react with Cu to form Cu_3Sn and Cu_6Sn_5 compounds within the Cu substrate.

At the locations where the formed Ni_3Sn_4 had reached the Ni-Sn-P/Cu interface, the deposited Ni-Sn-P layer was almost totally consumed after aging at 200 °C for 400 h (Fig. 3.26(a)). In contrast, at the locations where Ni_3Sn_4 had not reached the Ni-Sn-P/Cu interface, the Ni-Sn-P layer still had a thickness of about 6.7 μm after aging at 200 °C for 400 h (Fig. 3.26(b)). Therefore, it was found that the consumption of the deposited Ni-Sn-P layer is significantly accelerated at the locations where diffusion barriers, which are the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound and the Ni-Sn-P metallization layers, both break down. The original Ni_3Sn_4 compound contains 43 at.% of Ni, but after it reaches the Cu substrate, Cu atoms diffused out of the substrate, and are incorporated into the compound formation. As a result, the original Ni_3Sn_4 compound adjacent to the Ni-Sn-P layer was transformed into $(\text{Cu}_{0.55}\text{Ni}_{0.45})_6\text{Sn}_5$ compound which contains 25 at.% of Ni.

Fig. 3.26. Back-scattered SEM images showing Ni-Sn-P/Sn-3.5Ag interface after aging at 200 °C for 400 h: (a) at the location where Ni_3Sn_4 had reached the Ni-Sn-P/Cu interface, and (b) at the location where Ni_3Sn_4 had not reached the Ni-Sn-P/Cu interface.

Fig. 3.27. EDX elemental mapping analysis of Ni-Sn-P/Sn-3.5Ag interface after aging at 200 °C for 400 h at the location shown in Fig. 3.26(a): (a) Back-scattered SEM image, (b) mapping for Ag, (c) mapping for Ni, (d) mapping for P, (e) mapping for Sn, and (f) mapping for Cu. Elemental concentration decreases with decreasing colour intensity.

Based on the above results and analyses, the significantly retarded soldering reaction at the Ni-Sn-P/Sn-3.5Ag interface as compared with that at the Ni-P/Sn-3.5Ag interface is due to the elimination of fast diffusion path, which is the Ni_3P phase. The introduced

Ni-Sn-P metallization would have been a perfect solution in slowing down the interface reaction while maintaining the high level of solder joint strength after a long duration of thermal treatment. Unfortunately, cracks are formed in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound and the Ni-Sn-P metallization layers, which in turn promote non-uniform IMC growth along the reaction interface (e.g. Fig. 3.26). Such highly non-uniform interfacial reaction, coupled with the cracking, is the cause for the premature deterioration in the tensile strength of Ni-Sn-P/Sn-3.5Ag solder joints (Fig. 3.12). If the cracking could be prevented, the Ni-Sn-P/Sn-3.5Ag solder joint is expected to be much more thermally durable than the Ni-P/Sn-3.5Ag counterpart. This requires some adjustment in the bath formulation and operating conditions of plating to avoid the “tree-type” morphology of the metallization. The work could be an interesting piece of future research.

3.5. Summary

The interfacial reaction and tensile properties of solder joints between Sn-3.5Ag solder and electroless Ni-Sn-P metallization with a composition of 6~7 wt.% of P and 19~21 wt.% of Sn were studied after reflow and prolonged aging, with interfacial reaction and tensile properties of solder joints between the same solder and electroless Ni-P metallization (6~7 wt.% of P) as a benchmark. The following conclusions can be made based on the investigation:

1. There are two interfacial compounds, Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$, formed during the Ni-Sn-P/Sn-3.5Ag solder reaction. The Sn atoms from the solder react with the Ni atoms from the Ni-Sn-P layer to form Ni_3Sn_4 , and as a result, the top surface of the Ni-Sn-P layer becomes Ni-depleted. The Sn atoms from the solder also diffuse

through the formed Ni_3Sn_4 layer to reach the $\text{Ni}_3\text{Sn}_4/\text{Ni-Sn-P}$ interface, and react with the Ni-depleted region of the Ni-Sn-P layer to form the second IMC, $\text{Ni}_{13}\text{Sn}_8\text{P}_3$. The reaction mechanism has been proven by the mass balance of Ni during Ni-Sn-P/Sn-3.5Ag interfacial reaction, which confirms that all of the Ni atoms diffused out from the Ni-Sn-P layer take part in the reaction to form Ni_3Sn_4 .

2. It was found that probably due to the weakness of the Ni-Sn-P metallization layer, the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer broke at some weak locations. The Ni_3Sn_4 compound was observed to form at these broken locations, as a consequence of the direct contact between the Sn atoms from the solder and the Ni atoms from the Ni-Sn-P layer. Such intrusion of Ni_3Sn_4 IMC into the metallization layer might have contributed to the metallization cracking and facilitated Sn-Cu reactions as a result of barrier breakdown.
3. The tensile strength of the as-reflowed Ni-Sn-P/Sn-3.5Ag solder joints was found to be comparable to that of the as-reflowed Ni-P/Sn-3.5Ag solder joints. Both types of as-reflowed solder joints experience ductile failure in the bulk solder. The strength of Ni-P/Sn-3.5Ag solder joints drops significantly after aging for 400 h and beyond, while the strength of Ni-Sn-P/Sn-3.5Ag solder joints drops significantly after aging for 300 h and beyond. The Ni-P/Sn-3.5Ag solder joints aged for 400 h and beyond experience brittle fracture at the $\text{Ni}_3\text{Sn}_4/\text{solder}$ interface. The Ni-Sn-P/Sn-3.5Ag solder joints aged for 300 h and beyond experience brittle fracture not only at the $\text{Ni}_3\text{Sn}_4/\text{solder}$ interface, but also through all of the interfacial layers (Ni_3Sn_4 , $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ and Ni-Sn-P layers).

4. Despite the weak locations, the overall consumption rate of the Ni-Sn-P metallization layer is much slower than that of Ni-P during soldering reaction. This is due to the elimination of fast diffusion path for Ni atoms at the Ni-Sn-P/Sn-3.5Ag interface. The elimination of fast diffusion path is advantageous in maintaining the tensile strength of the Ni-Sn-P/Sn-3.5Ag solder joint after long-term aging treatment. However on the other hand, the sporadic cracking occurred at the Ni-Sn-P/Sn-3.5Ag interface brings in a detrimental effect on the joint strength. The combined effect makes the long-term reliability of Ni-Sn-P/Sn-3.5Ag solder joint comparable with or slightly inferior to the one of Ni-P/Sn-3.5Ag solder joint. Further research is needed to eliminate the detrimental effect while keeping the beneficial factor.

Chapter 4

Soldering between Electroless Ni-W-P and Sn-3.5Ag

4.1. Introduction

In Chapter 3, Ni-Sn-P was studied as a candidate for soldering metallization with success: the addition of Sn into Ni-P alloy successfully prevented the formation of columnar-structured Ni_3P , and the overall consumption rate of the metallization was indeed significantly slowed down. However, unexpected cracking in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ and metallization layers has eradicated the benefit in solder joint strength that would have been derived from the success. The likely reason for such cracking, as revealed in the previous chapter, is the columnar structure of the Ni-Sn-P metallization. Tensile stress usually exists in electrolessly-plated nickel alloys, and such stress increases upon aging. Thus, upon prolonged reaction, cracking occurs through the weak boundary between the neighbouring columns. The scattered cracking in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer is believed to be caused by the weakness of the underlying Ni-Sn-P metallization. As the reaction proceeds, the Ni_3Sn_4 compound grows into the gaps at the broken locations in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer, which will attract more Ni atoms from the metallization. In such event, the depletion of Ni occurs preferably along the columnar boundary, which further weakens the metallization layer. Upon further reaction, at the locations where the formed Ni_3Sn_4 IMC reaches the Ni-Sn-P/Cu interface, the consumption of Ni-Sn-P metallization is significantly accelerated at these “leakage” points. At such locations, due to out-diffusion of Cu atoms from the substrate, the originally formed Ni_3Sn_4 compound is transformed into the ternary $(\text{Ni,Cu})_3\text{Sn}_4$ and $(\text{Cu,Ni})_6\text{Sn}_5$ compounds. Meanwhile, the Sn atoms from the solder manage to diffuse through these ternary compounds to react with

Cu to form Cu_3Sn and Cu_6Sn_5 compounds within the substrate (Fig. 3.26). Such highly non-uniform interfacial reaction, along with the scattered cracking, making the long-term reliability of Ni-Sn-P/Sn-3.5Ag solder joint slightly inferior to that of Ni-P/Sn-3.5Ag solder joint (Fig. 3.12). The author believes that if the cracking could be prevented, the Ni-Sn-P/Sn-3.5Ag solder joint would be much more thermally durable than the Ni-P/Sn-3.5Ag counterpart. The disadvantage of the Ni-Sn-P metallization is due to its columnar structure. One possible way to avoid such structure is to adjust the bath formulation and operating conditions of plating, which could be an interesting work for future.

The lesson learnt from Ni-Sn-P has clearly demonstrated that in order to fully benefit from slow interfacial diffusion, structure of the metallization is also an important consideration. In this thesis work, two other choices for the ternary alloying element, namely W and Co, have been attempted. The work regarding to Ni-W-P and Ni-Co-P will be reported in this chapter and Chapter 5, respectively. From the literature, neither of Ni-W-P and Ni-Co-P was reported to have the similar columnar structure as Ni-Sn-P.

Ni-W-P alloy is considered as a good candidate for soldering metallization since W is a refractory metal. Duh's group has reported that the crystallization temperature of Ni-P compounds in electroless Ni-P (8.5 wt.% of P) and electroless Ni-W-P (7.6 wt.% of P and 10.9 wt.% of W) coatings were 337 °C and 406 °C, respectively [59], indicating the addition of W into Ni-P can effectively retard the crystallization of Ni-P compounds. Thus, it is possible to slow down the interfacial reaction with adoption of Ni-W-P as the soldering metallization by retarding the formation of fast diffusion path, which is the Ni_3P compound layer with voids in the case of Ni-P metallization. Electroless Ni-W-P film was first made by Pearlstein et al. [32] by adding salt of W into the electroless nickel

bath. Attempts to use the Ni-W-P coating as the soldering metallization in microelectronic packaging were first made by Chen et al. [33], and they reported that the Ni-W-P coating (7 wt.% of P and 14 wt.% of W) with a high W content has a much longer service lifetime than the Ni-P coating by studying long-term interfacial reaction between Ni-W-P and molten Sn-58Bi solder at 200 °C. After that, the Ni-W-P films with three different levels of W at two fixed levels of P (5 and 9 wt.%) were prepared by Jang et al. [34], and the interfacial reaction between Sn-3.5Ag solder and these Ni-W-P films, as well as the drop impact test results of these solder joints were studied. However, the growth kinetics of the IMCs formed in the Ni-W-P/solder joints and the mechanical properties of such solder joints have not been reported.

In this thesis work, the interfacial reaction between Sn-3.5Ag solder and electroless Ni-W-P metallization containing 14~16 wt.% of W was studied. Again the diffusional formation mechanism of the interfacial IMCs was proposed. The growth kinetics of the Ni_3Sn_4 and $(\text{Ni},\text{W})_3\text{P}$ compounds formed at the Ni-W-P/Sn-3.5Ag interface was also investigated with their activation energies reported for the first time in this system. In addition, the tensile testing performed on Ni-W-P/Sn-3.5Ag solder joints after reflow and prolonged aging is also reported. Comparison with conventional binary Ni-P metallization was carried out. The fractographic analysis of the failed Ni-W-P/Sn-3.5Ag solder joints was also conducted to investigate the evolution of the failure mode upon extended aging.

4.2. Experimental Procedures

Similar to the work reported in Chapter 3, Cu plates (99.98 wt.%) with a thickness of 6 mm were used as the substrate for Ni-W-P plating. The surface treatment for Cu substrate was the same as described in Section 3.2.1. The electroless Ni-W-P plating was conducted in an alkaline bath with a pH level of 9.0 (adjusted by 25% sulphuric acid) at 85 ± 2 °C for 2 h. As listed in Table 4.1, this alkaline bath contained nickel sulphate and sodium tungstate as nickel and tungsten sources respectively. Sodium hypophosphite was used as a reducing agent along with sodium citrate as the complexing agent.

Table 4.1. Composition of the plating bath for electroless Ni-W-P [106].

Constituents of plating bath	Concentration (g/L)
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	26
$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	33
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	12
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	75

Following the electroless plating process, the Ni-W-P/Sn-3.5Ag solder joints were formed, and then thermally-aged at 180 °C for 600 h to study their interfacial reactions, tensile strengths and fracture behaviour. The procedures for forming the Ni-W-P/Sn-3.5Ag solder joints are the same as detailed in Section 3.2.2. Moreover, in order to study the growth kinetics of the IMCs formed at the Ni-W-P/Sn-3.5Ag interface, solid-state aging was also conducted at three different temperatures (140 °C, 160 °C, and 180 °C) for 625 h. For the tensile testing, the steps to prepare the micro-joints for the test are the same as described in Section 3.2.4, while the testing procedures can be referenced in Section 3.2.5. On the other hand, the morphological and microstructural observations

were conducted according to the procedures similar to those detailed in Section 3.2.6. The newly formed interfacial compounds in the Ni-W-P/Sn-3.5Ag solder joints were also identified using transmission electron microscope (TEM). The TEM sample was prepared using focused ion beam (FIB) technique.

4.3. Results

4.3.1. As-deposited Metallizations

As shown in Fig. 3.3, the thickness of the Ni-P coating was measured to be around $9.7\ \mu\text{m}$, and this coating was found to contain 6~7 wt.% of P. With regarding to the Ni-W-P coating, its thickness was measured to be around $10.7\ \mu\text{m}$ (Fig. 4.1 (b)), and its composition was found to be 6~7 wt.% of P and 14~16 wt.% of W. As shown in Fig. 4.1(a), the surface of the Ni-W-P coating contained smooth nodules with uneven size, and this coating layer closely adhered to the Cu substrate as no pores were observed at the interface (Fig. 4.1(b)).

Fig. 4.1. As-deposited Ni-W-P layer: (a) surface morphology, (b) cross-sectional micrograph.

4.3.2. Crystallization Behavior of Electroless Ni-P and Ni-W-P Coatings

The XRD patterns of electroless Ni-P and Ni-W-P coatings after 2 h of annealing at different temperatures are illustrated in Fig. 4.2. All the XRD patterns were recorded between 2-theta from 40 ° to 60 ° with a fixed glancing angle of 2 °. Both the as-deposited Ni-P and Ni-W-P coatings were found to have an amorphous structure, as their XRD patterns consisted of only one broad peak with highest intensity belonging to Ni (Fig. 4.2). As shown in Fig. 4.2(a), precipitation of Ni₃P phase was observed in the Ni-P coating after heating at 350 °C for 2 h. Besides the Ni₃P phase, no precipitation of meta-stable phases was observed. This result is consistent with the previous studies which revealed that if P content in Ni-P is less than 9 wt.%, the precipitation of Ni-P compound would directly transfer to the final stable Ni₃P phase [107, 108]. The presence of the sharpened diffraction peaks in the Ni-P coating after annealing at 350 °C indicates that the crystallization of the coating is complete. Thus the crystallization temperature of Ni-P compound in the Ni-P coating in the current work is 350 °C, which is in agreement with the literature [59]. Moreover, in the Ni-P coating after heating above 350 °C, all the well-defined diffraction peaks belonged to the Ni and Ni₃P phases, so no other phases were formed. On the other hand, the Ni-W-P coating still had an amorphous structure even after annealing at 400 °C. It is only after annealing at 450 °C that small diffraction peaks corresponding to the Ni and Ni₃P phases were noticed. From this work, the crystallization temperature of Ni-P compound in the Ni-W-P coating is thus found to be 450 °C. With increasing annealing temperature from 450 °C to 600 °C, the diffraction peaks belonging to the Ni and Ni₃P phases became more prominent; however, no peaks belonging to W were observed even after heating at 600 °C.

It is thus shown that the crystallization temperature of the Ni-W-P coating in the current work is 100 °C higher than that of Ni-P. Both Ni-P and Ni-W-P coatings have the similar P content, so it is the incorporation of W into Ni-P that retards the crystallization of Ni-P compound. As discussed earlier, W is a refractory metal element, so the elemental diffusion rate will be reduced in the Ni-W-P alloys as compared to that in the Ni-P alloys, and will result in a higher crystallization temperature of Ni-P compound in the Ni-W-P coating.

Based on Fig. 4.2(a), the Ni(111) and Ni(200) XRD peaks are located at 44.6 ° and 52.0 ° respectively in the crystallized Ni-P alloy. In contrast, the Ni(111) and Ni(200) peaks in the Ni-W-P coating shift to the lower angles at 44.0 ° and 51.3 °, respectively (Fig. 4.2(b)). The dilation of Ni lattice in the Ni-W-P coating indicates the dissolution of W into the Ni matrix because W has a larger atomic radius than Ni. However, no shift of the Ni₃P peaks was observed in the case of Ni-W-P coating (Fig. 4.2). These observations are similar with the findings reported by Jang et al. [34]. Such observation indicates that the solubility of W in Ni₃P lattice is limited. It is reasonable to believe that the reason for the delay in crystallization of Ni-W-P alloy is due to the good solubility of W in Ni matrix and low solubility of W in Ni₃P lattice. In order to form a crystalline Ni₃P, W has to be expelled from the matrix. Since this calls for a long range diffusion of W, a high temperature (higher than that in the case of Ni-P) is needed. Alternatively, W could be incorporated into Ni₃P in a non-crystalline state at lower temperatures. This explains why the amorphous (Ni,W)₃P compound forms during the interfacial reaction between Ni-W-P and Sn-3.5Ag solder, which will be discussed later in this chapter.

Fig. 4.2. XRD spectra of (a) Ni-P and (b) Ni-W-P coatings after annealing at various temperatures [109].

4.3.3. Interfacial Microstructure Analysis of As-reflowed Solder Joints

As shown in Fig. 3.5(a), at the as-reflowed Ni-P/Sn-3.5Ag interface, Chunky-type Ni_3Sn_4 compound was formed, and some of the faceted Ni_3Sn_4 particles spalled into the bulk solder. A dark layer of Ni_3P was formed adjacent to the coated Ni-P layer. There was a very thin layer of Ni_2SnP present between the Ni_3Sn_4 and the Ni_3P layer. It was noticed that a few voids were clearly formed inside the Ni_3P layer.

The cross-sectional micrograph of the as-reflowed Ni-W-P/Sn-3.5Ag solder joint is shown in Fig. 4.3. It was observed that a layer of Ni_3Sn_4 compound clearly formed, and there was no significant spallation of this compound as noticed in the reaction between Sn-3.5Ag solder and binary Ni-P metallization. Underneath the Ni_3Sn_4 layer, there was a thin ternary layer consisting of Ni, W, and P elements. As illustrated in Fig. 4.4, the composition of this ternary layer was measured to be ~65 at.% of Ni, ~10 at.% of W and ~25 at.% of P. Such composition suggests that the compound is $(\text{Ni,W})_3\text{P}$. Jang et al. [34] have conducted the XRD analysis for the heat-treated Ni-W-P films with different W levels. Their XRD results showed that the Ni_3P lattice parameter seems to be unaffected by the W addition, thereby concluding that the W solubility in Ni_3P lattice is very limited or the $(\text{Ni,W})_3\text{P}$ stoichiometry is quite stable. Our XRD results presented in last section also support their findings. Moreover, Fig. 4.3 shows that the interface between this $(\text{Ni,W})_3\text{P}$ layer and the unconsumed Ni-W-P layer was uneven, implying the consumption of the Ni-W-P layer is non-uniform during reflow soldering.

Fig. 4.3. Back-scattered SEM images showing IMCs formed in as-reflowed Ni-W-P/Sn-3.5Ag solder joint.

Fig. 4.4. EDX compositional results of the newly-formed ternary Ni-W-P layer.

Fig. 4.5 shows SEM and TEM micrographs from the Ni-W-P/Sn-3.5Ag solder joint aged at 180 °C for 625 h, along with diffraction patterns from the Ni_3Sn_4 and $(\text{Ni},\text{W})_3\text{P}$

layers. As shown in Fig 4.5(a), no distinct interface between the $(\text{Ni,W})_3\text{P}$ layer and unconsumed Ni-W-P layer was observed under TEM. The total thickness of the $(\text{Ni,W})_3\text{P}$ and the unconsumed Ni-W-P layers was found to be 7.8 μm . The SEM micrograph of the same aged solder joint at the location where the TEM sample was prepared is illustrated in Fig. 4.5(d). The interface between the $(\text{Ni,W})_3\text{P}$ layer and the unconsumed Ni-W-P layer was clearly distinguishable, and the $(\text{Ni,W})_3\text{P}$ layer had a thickness of around 1 μm . Moreover, the total thickness of the $(\text{Ni,W})_3\text{P}$ layer and the unconsumed Ni-W-P layer was measured to be around 7.8 μm . This thickness is the same as the total thickness of the $(\text{Ni,W})_3\text{P}$ and the unconsumed Ni-W-P layers measured in the TEM micrograph (Fig. 4.5(a)). Thus, the $(\text{Ni,W})_3\text{P}$ layer in Fig. 4.5(a) had the same thickness ($\sim 1 \mu\text{m}$) as that shown in Fig. 4.5(d). Based on this, Location 1 in Fig. 4.5(a) was confirmed to be within the $(\text{Ni,W})_3\text{P}$ layer, and the diffraction analysis from this location showed a typical ring pattern of the amorphous structure (Fig. 4.5(c)). Thus, the $(\text{Ni,W})_3\text{P}$ layer was found to be amorphous, which is in agreement with the literature [34]. As explained in the last section, due to the low solubility of W in the crystalline form of Ni_3P , W has to be excluded when Ni_3P crystallizes. However during the soldering-induced phase transformation, the temperature is not high enough, therefore W is incorporated in the amorphous structure of $(\text{Ni,W})_3\text{P}$. Besides, as shown in Fig 4.5(b), the phase above the $(\text{Ni,W})_3\text{P}$ layer was confirmed to be Ni_3Sn_4 ($C12/m1$, $a = 12.214 \text{ \AA}$, $b = 4.060 \text{ \AA}$, $c = 5.219 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 105.0^\circ$) [110].

Fig. 4.5. (a) Cross-sectional TEM micrograph of the Ni-W-P/Sn-3.5Ag solder joint aged at 180 °C for 625 h (TEM sample preparation was done by focused ion beam (FIB) technique), diffraction patterns from (b) Ni_3Sn_4 and (c) $(\text{Ni,W})_3\text{P}$ layers, (d) SEM image showing the same aged solder joint at the location where the TEM sample was prepared.

4.3.4. Interfacial Microstructure Analysis of Aged Solder Joints

Fig. 3.8 in the previous chapter summarizes the growth of various compounds at the Ni-P/Sn-3.5Ag interfaces aged at 180 °C for up to 600 h. The deposited Ni-P metallization layer was fully consumed and converted into Ni_3P after 300 h of aging (Fig. 3.8(c)). After that, the Ni_2SnP layer grew at the expense of the Ni_3P layer. The voids in the Ni_3P layer grew both in size and number with extended aging.

The growth of various compounds at the Ni-W-P/Sn-3.5Ag interface after aging at 180 °C for up to 600 h is shown in Fig. 4.6. It was found that during aging, the $(\text{Ni,W})_3\text{P}$

layer grew very slowly. The thickness increase of the Ni_3Sn_4 layer is much slower than that formed at the Ni-P/Sn-3.5Ag interface (Fig. 3.8). Unlike the Ni-P layer which was fully consumed after 300 h of aging (Fig. 3.8(c)), the Ni-W-P layer after 600 h of aging still had around 8.0 μm left (Fig. 4.6(f)), which is 75% of its original thickness. This indicates that the Ni-W-P layer was consumed much slower than the Ni-P layer. The consumption of Ni-P and Ni-W-P metallizations upon aging for 600 h is shown in Fig. 4.7. It was clearly seen that the consumption of the Ni-W-P metallization is significantly retarded as compared to that of Ni-P. Moreover, it is interesting to note that even after 600 h of aging, no voids were found in the Ni-W-P/Sn-3.5Ag solder joint (Fig. 4.6(f)). After comparing the two reaction couples, it is reasonable to attribute the slow IMC growth and slow consumption rate of the Ni-W-P metallization to the amorphous nature of the $(\text{Ni,W})_3\text{P}$ layer which can effectively hinder the diffusion of Ni from the underneath layer. This point will be elaborated later in conjunction with diffusion profile analysis.

Fig. 4.6. Back-scattered SEM images showing IMCs at Ni-W-P/Sn-3.5Ag interface after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, (e) 500 h, and (f) 600 h.

Fig. 4.7. Consumption of Ni-P and Ni-W-P metallizations upon aging for 600 h. Notice that the Ni-P metallization with an original thickness of 9.7 μm was fully consumed after 300 h of aging.

4.3.5. IMC Growth Kinetics at the Ni-W-P/Solder Interface

The growth kinetics of both Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ compounds is presented in the current work. Three aging temperatures (140, 160, and 180 $^{\circ}\text{C}$) were selected for this study. The average thicknesses of the Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers were obtained from at least 10 SEM images of different locations of each sample by measuring the cross-section area of the layer over a certain length on the SEM image with the help of an image analyzer. The thickness of the Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers formed in the Ni-W-P/Sn-3.5Ag solder joint as a function of aging time at different temperatures is depicted in Fig. 4.8. It was observed that both layers grew with aging at all three temperatures, but the growth of the $(\text{Ni,W})_3\text{P}$ layer was much slower than that of the Ni_3Sn_4 layer.

Fig. 4.8. Thickness of the Ni_3Sn_4 and $(\text{Ni},\text{W})_3\text{P}$ layers formed in the Ni-W-P/Sn-3.5Ag solder joint as a function of aging time at temperatures of (a)140 °C, (b)160 °C, and (c)180 °C.

The thickness of the IMC layer in the solder joint can be generally expressed by Equation 2.1 and repeated here for convenience:

$$\delta - \delta_0 = kt^{1/n}, \quad (2.4)$$

where δ and δ_0 are the thickness of the IMC layer at time t and zero, respectively, k is the growth rate constant, and n is the time exponent. Fig. 4.9 shows the thickness of the Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers as a function of the square root of the aging time (i.e. assuming $n = 2$) at different aging temperatures.

The thickness increment of both layers was found to increase linearly with the square root of aging time, suggesting that the growths of these two layers at the Ni-W-P/Sn-3.5Ag interface are both controlled by diffusion. The growth rate constant is calculated from a linear regression analysis of $(\delta - \delta_0)$ versus $t^{0.5}$, where the slope is equal to k , and the values of k for both layers at each aging temperature are listed in Table 4.2. The growth rate constants of Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers increase with increasing aging temperature, indicating that the growths of both layers were faster at higher aging temperatures.

Fig. 4.9. Thickness increment of the (a) Ni_3Sn_4 and (b) $(\text{Ni,W})_3\text{P}$ layers formed in the Ni-W-P/Sn-3.5Ag solder joint as a function of square root of aging time at temperatures of 140, 160, and 180 °C [106].

Table 4.2. IMC growth rate constants at the Ni-W-P/Sn-3.5Ag interface at various aging temperatures [106].

Temperatures (°C)	k of Ni_3Sn_4 ($\times 10^{-8} \text{ cm/s}^{1/2}$)	k of $(\text{Ni,W})_3\text{P}$ ($\times 10^{-8} \text{ cm/s}^{1/2}$)
140	6.13	2.13
160	8.78	2.20
180	13.7	2.30

To calculate the activation energy for the interfacial compound growth, the Arrhenius equation is used:

$$k^2 = A \exp(-Q/RT), \quad (4.1)$$

where k^2 is the square of the growth rate constant, A is a prefactor, T is the absolute temperature, R is the gas constant, and Q is the activation energy. The value for Q is obtained from the slope of the Arrhenius plot, as shown in Fig. 4.10. The activation energy for the Ni_3Sn_4 growth in the solid-state reaction between the Ni-W-P and Sn-3.5Ag solder is obtained to be 62.3 kJ/mol, along with a prefactor of $2.75 \times 10^{-7} \text{ cm}^2/\text{s}$. Table 4.3 lists the values of the activation energies for the growth of Ni_3Sn_4 in the Ni-based metallization/Sn-3.5Ag solder systems obtained from previous works [16, 90, 93, 94]. Our result lies within the range of values obtained by previous works on Sn-3.5Ag/Ni-P reactions.

Fig. 4.10. Arrhenius plot of the growth of (a) Ni_3Sn_4 and (b) $(\text{Ni,W})_3\text{P}$ layers in the Ni-W-P/Sn-3.5Ag solder joint [106].

Table 4.3. Activation energy for the growth of Ni_3Sn_4 in the Ni-based metallization/Sn-3.5Ag solder systems obtained in different studies [106].

Solder/substrate	Experimental Conditions (Temperature/Time)	Q (kJ/mol)	Reference
Sn-3.5Ag/Ni-W-P	140-180 °C / up to 625 hours	62.3	Present work
Sn-3.5Ag/Ni-P	130-170 °C / up to 625 hours	110.0	[16]
Sn-3.5Ag/Ni-P	100-170 °C / up to 60 days	49.0	[93]
Sn-3.5Ag/Au/Ni-P	70-170 °C / up to 100 days	72.5	[94]
Sn-3.5Ag/Ni-P	140-200 °C / up to 400 hours	98.9	[90]

Despite the possible discrepancy, the activation energy is an important parameter as it reflects the magnitude of the critical barrier for the compound growth. The comparable activation energy value with other reported Sn-3.5Ag/Ni-P soldering systems indicates that the controlling mechanism for the Ni_3Sn_4 IMC formation might remain the same, which is likely to be the diffusion of Sn in the Ni_3Sn_4 IMC. As cited in a review article by Ho et al. [97], Ti marker experiment in a Ni/Sn reaction couple has proven that Sn diffuses faster than Ni through Ni_3Sn_4 IMC, therefore the IMC growth activation energy is likely related to the Sn diffusivities in the Ni_3Sn_4 IMC. Unfortunately, data for Sn diffusivities in Ni_3Sn_4 are unavailable, which could be an interesting topic for future studies.

The activation energy for the $(\text{Ni,W})_3\text{P}$ growth in the solid-state solder reaction is found to be 58.2 kJ/mol, along with a prefactor of $2.46 \times 10^{-15} \text{ cm}^2/\text{s}$. It is worth noting that the prefactors for growths of both the Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers are many orders of magnitude lower than the prefactor of Ni_3Sn_4 formation in soldering with Ni-P [16], which is due to the presence of W in the metallization that decreases the availability of Ni at the soldering interface. Although the activation energy of $(\text{Ni,W})_3\text{P}$ growth is similar to

that of Ni_3Sn_4 growth, the prefactor of $(\text{Ni,W})_3\text{P}$ growth is much lower, so $(\text{Ni,W})_3\text{P}$ grew much slower than Ni_3Sn_4 , under the same aging conditions.

4.3.6. Tensile Strength of Solder Joints

Table 4.4 shows the average tensile strengths obtained from both Ni-W-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag solder joints upon aging at 180 °C for up to 600 h. Fig. 4.11 depicts the tensile strengths of both types of solder joints as a function of aging time up to 600 h. Both types of as-reflowed solder joints had similar tensile strength. Upon aging for 600 h, there was no significant drop in strength of Ni-W-P/Sn-3.5Ag solder joints. However, the strength of Ni-P/Sn-3.5Ag solder joints dropped significantly after aging for 400 h and beyond. The reasons for the drop, as discussed in Chapter 3, include the accumulated interface flaws generated during the continued interfacial reactions, as well as the stresses caused by phase transformation. Therefore, Ni-W-P metallization has an advantage over Ni-P in terms of resistance to joint strength deterioration upon aging.

Table 4.4. Tensile strengths of both Ni-P/Sn-3.5Ag and Ni-W-P/Sn-3.5Ag solder joints upon aging at 180 °C for 600 h.

Aging Time (hour)	Tensile Strength (MPa)	
	Ni-P/Solder Joint	Ni-W-P/Solder Joint
As-reflowed	35.41 ± 2.85	32.72 ± 1.40
100	32.75 ± 1.38	31.78 ± 0.36
200	31.75 ± 1.36	30.47 ± 0.84
300	31.32 ± 0.43	30.37 ± 0.65
400	22.69 ± 1.36	30.05 ± 0.85
600	22.46 ± 0.99	30.02 ± 0.84

Fig. 4.11. Tensile strengths of both Ni-W-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag solder joints after aging for up to 600 h.

4.3.7. Failure Analysis of Solder Joints

The fractographic analysis of both Ni-P/Sn-3.5Ag and Ni-W-P/Sn-3.5Ag solder joints were conducted under SEM to study the fracture mechanism in tensile testing upon aging. The fracture behaviour of Ni-P/Sn-3.5Ag solder joints upon aging was discussed in Section 3.3.5. The entire fracture path was found to be inside the bulk solder in the as-reflowed Ni-P/Sn-3.5Ag solder joints (Fig.3.13) and the ones aged for up to 300 h (Fig.3.14). Samples aged for 400 h and beyond failed at the Ni_3Sn_4 /solder interface (Fig. 3.15), indicating the deterioration of the interface region due to the extended compound growth.

Fig. 4.12 (a) and (b) show the cross-sectional view and fractured surface of the as-reflowed Ni-W-P/Sn-3.5Ag solder joints, respectively. As shown in Fig. 4.12(a), an obvious necking occurred in the bulk solder, and the fracture surface occurred at an inclined angle to the tensile-stress axis. Fig. 4.12(b) shows the fractured surface of this solder joint. As expected, EDX result indicates that Sn is the dominant element at the fractured surface, confirming the fracture occurs completely in the bulk solder.

Fig. 4.12. (a) Cross-sectional view and (b) fractured surface of the as-reflowed Ni-W-P solder joint.

From Fig. 4.13, it can be depicted that the Ni-W-P/Sn-3.5Ag solder joints still experienced complete ductile failure inside the bulk solder after aging at 180 °C for up to 600 h. This indicates that the interface remained stronger than the cohesive strength of the bulk solder even upon aging for 600 h. In contrast, the fracture path shifted from inside the bulk solder to the Ni_3Sn_4 /solder interface in the Ni-P/Sn-3.5Ag solder joints aged for 400 h and beyond. The retained high Ni-W-P/Sn-3.5Ag interface strength is clearly related to the much slower interfacial reaction compared to that in the Ni-P/Sn-3.5Ag solder joints.

Fig. 4.13. Cross-sectional view of Ni-W-P solder joint after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, and (e) 600 h.

4.4. Discussion

4.4.1. Diffusional Formation Mechanism of IMCs at the Ni-W-P/Solder Interface

EDX line scan and elemental mapping were conducted to study the diffusion profile at the Ni-W-P/Sn-3.5Ag interface. The elemental distribution at the Ni-W-P/Sn-3.5Ag interface after aging at 180 °C for 300 h is depicted in Fig. 4.14. It was noted that Ni intensity started to decrease at the interface between the Ni-W-P layer and the $(\text{Ni,W})_3\text{P}$ layer. This indicates that Ni atoms diffused outward from the deposited Ni-W-P layer during the interfacial reaction, leading to the formation of Ni_3Sn_4 . On the other hand, the sudden drop of the Sn intensity observed at the $(\text{Ni,W})_3\text{P}/\text{Ni}_3\text{Sn}_4$ interface was attributed to the fact that Sn atoms did not diffuse into the $(\text{Ni,W})_3\text{P}$ layer.

Fig. 4.14. (a) Back-scattered SEM image and (b) elemental distribution at Ni-W-P/Sn-3.5Ag interface after aging at 180 °C for 300 h.

The area mapping (Fig. 4.15) supports the line-scan results that W and P atoms remained in the Ni-W-P and (Ni,W)₃P layers. In contrast, Ni atoms diffused out from the Ni-W-P layer to form Ni₃Sn₄. The signal from Sn was found to terminate in the Ni₃Sn₄, and no Sn was present in the (Ni,W)₃P layer. It was also noted that after such a prolonged aging, Cu atoms still remained in the substrate, and neither (Cu,Ni)₆Sn₅ nor (Ni,Cu)₃Sn₄

compounds were detected, suggesting that Ni-W-P is a good diffusion barrier preventing the inter-diffusion between Cu and Sn.

Fig. 4.15. EDX elemental mapping analysis of the as-reflowed Ni-W-P/Sn-3.5Ag interface: (a) SEM image, (b) mapping for Ni, (c) mapping for W, (d) mapping for P, (e) mapping for Sn, (f) mapping for Cu, and (g) mapping for Ag. Elemental concentration decreases with decreasing colour intensity.

Fig. 4.16 schematically illustrates the diffusional formation mechanism of the Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers at the Ni-W-P/Sn-3.5Ag interface. Based on elemental analysis, P atoms in the Ni-W-P remained in the deposited layer during soldering reaction. The deposited Ni-W-P layer contains 82.5 at.% of Ni, 5 at.% of W and 12.5 at.% of P, while the newly-formed $(\text{Ni,W})_3\text{P}$ layer contains 65 at.% of Ni, 10 at.% of W and 25 at.%

of P. Thus, the ratio of W to P in the $(\text{Ni,W})_3\text{P}$ layer is the same as that in the deposited Ni-W-P layer, suggesting that Ni was the only element to diffuse outward from the Ni-W-P coating layer during soldering reaction. As depicted in Fig. 4.16, Ni atoms diffuse out from the Ni-W-P layer towards solder and react with Sn atoms from the solder to form Ni_3Sn_4 . Meanwhile, the formation of Ni_3Sn_4 causes the depletion of Ni from the surface of the Ni-W-P layer, leading to continued growth of the newly-formed ternary $(\text{Ni,W})_3\text{P}$ layer.

Fig. 4.16. A schematic illustration of the diffusional formation mechanism of Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers between the Ni-W-P metallization and Sn-3.5Ag solder [106].

It was reported that the Ni_3P layer formed at the Ni-P/Sn-3.5Ag interface has a fine columnar structure, and this layer acts as a fast diffusion path for Ni atoms during the interfacial reaction [16]. As a result, the rapid diffusion of Ni atoms through the Ni_3P layer leads to the formation of voids inside this layer while the compensation from other elements to fill the vacant sites left by Ni atoms is insufficient. In the case of Ni-W-P, the $(\text{Ni,W})_3\text{P}$ layer has an amorphous structure. Such structure is free of the fast diffusion channel such as grain boundaries and void surfaces, thus it is more difficult for Ni atoms

to diffuse out through this layer. This is evidenced by observation that no voids are formed inside this layer after prolonged reaction (Fig. 4.6). As a result, the interfacial Ni_3Sn_4 IMC growth rate was much slower than that at the Ni-P/Sn-3.5Ag interface. This is also proved by the much slower consumption rate of the Ni-W-P metallization as compared to the binary Ni-P (Fig. 4.7).

4.4.2. The Mass Conservation of Ni Atoms at the Ni-W-P/Solder Interface

In order to verify the proposed diffusional formation mechanism of the Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers at the Ni-W-P/Sn-3.5Ag interface, law of mass conservation is applied on the Ni atoms across the metallization/solder interface. The mass conservation is applied to the as-reflowed sample (Fig. 4.3) and the sample aged for 400 h (Fig. 4.6 (d)), i.e. the number of moles of Ni in the Ni-W-P layer consumed within this aging duration of 400 h must be equal to the sum of the number of moles of Ni in the $(\text{Ni,W})_3\text{P}$ layer grown within this duration and the number of moles of Ni in the Ni_3Sn_4 layer grown within this duration. The number of moles of Ni in a layer of thickness t_{layer} per unit area can be determined by Equation 3.3 and repeated here for convenience:

$$Ni_{\text{layer}} = m \times \frac{\rho_{\text{layer}} t_{\text{layer}}}{M_{\text{layer}}}, \quad (3.3)$$

where m is the number of moles of Ni in one mole of the layer, M_{layer} is the molecular weight of the layer, and ρ_{layer} is the density of the layer.

The thickness of the unconsumed Ni-W-P layer in the as-reflowed state and after aging for 400 h was found to be 9.1 μm and 8.3 μm , respectively. Due to lack of the density information for the coated Ni-W-P layer in the literature, the density of this layer

has to be estimated based on rule of mixtures by known density data of Ni-P and W. This layer consists of 78.7 wt.% of Ni, 6.3 wt.% of P, and 15 wt.% of W, so it can be treated as a mixture of 15 wt.% of W and 85 wt.% of Ni-P (with 7.4 wt.% of P). By rule of mixtures, density of the coated Ni-W-P layer is given by:

$$\rho_{Ni-W-P} = \frac{1}{\frac{f_{Ni-P}}{\rho_{Ni-P}} + \frac{f_W}{\rho_W}} = \frac{1}{\frac{0.85}{8.2 \text{ g/cm}^3} + \frac{0.15}{19.3 \text{ g/cm}^3}} = 8.97 \text{ g/cm}^3, \quad (4.2)$$

where f stands for atomic fraction of each constituent in the Ni-W-P coating. The density of the Ni-P with 7.4 wt.% of P and W is found to be 8.2 g/cm³ [42] and 19.3 g/cm³ [105], respectively. Since the coated Ni-W-P layer contains 82.5 at.% of Ni, 5 at.% of W and 12.5 at.% of P, the molar weight of this layer is 6148.30 g/mol, and the value of m is 82.5. Substituting these values into Equation 3.3, the number of moles of Ni in the unconsumed Ni-W-P layer in the as-reflowed state and after aging for 400 h is 10.95×10^{-5} mol/cm² and 9.99×10^{-5} mol/cm², respectively. Thus, the number of moles of Ni in the Ni-W-P layer consumed within the aging duration of 400 h, labelled as Ni_{Ni-W-P} , is calculated to be 0.96×10^{-5} mol/cm².

The thickness of the (Ni,W)₃P layer in the as-reflowed state and after aging for 400 h was found to be 0.851 μm and 1.192 μm , respectively. Due to lack of the density information for the (Ni,W)₃P layer in the literature, the density of this layer has to be estimated based on rule of mixtures by known density data of Ni-P and W. This layer consists of 59.4 wt.% of Ni, 12.0 wt.% of P, and 28.6 wt.% of W, so it can be treated as a mixture of 28.6 wt.% of W and 71.4 wt.% of Ni-P (with 16.8 wt.% of P). By rule of mixtures, density of the (Ni,W)₃P layer is given by:

$$\rho_{(Ni,W)_3P} = \frac{1}{\frac{f_{Ni-P}}{\rho_{Ni-P}} + \frac{f_W}{\rho_W}} = \frac{1}{\frac{0.714}{7.4 \text{ g/cm}^3} + \frac{0.286}{19.3 \text{ g/cm}^3}} = 8.98 \text{ g/cm}^3, \quad (4.3)$$

where f stands for atomic fraction of each constituent in the $(\text{Ni,W})_3\text{P}$ layer. The density of the Ni-P with 16.8 wt.% of P and W is found to be 7.4 g/cm^3 [42] and 19.3 g/cm^3 [105], respectively. The $(\text{Ni,W})_3\text{P}$ layer contains 65 at.% of Ni, 10 at.% of W and 25 at.% of P. so the molar weight of this layer is 6427.60 g/mol , and the value of m is 65. Substituting these values into Equation 3.3, the number of moles of Ni in the $(\text{Ni,W})_3\text{P}$ layer in the as-reflowed state and after aging for 400 h is $0.77 \times 10^{-5} \text{ mol/cm}^2$ and $1.08 \times 10^{-5} \text{ mol/cm}^2$, respectively. Thus, the number of moles of Ni in the $(\text{Ni,W})_3\text{P}$ layer grown within the aging duration of 400 h, labelled as $Ni_{(\text{Ni,W})_3\text{P}}$, is determined to be $0.31 \times 10^{-5} \text{ mol/cm}^2$.

The thickness of the Ni_3Sn_4 layer in the as-reflowed state and after aging 400 h was found to be $2.055 \text{ }\mu\text{m}$ and $3.701 \text{ }\mu\text{m}$, respectively. The density of the Ni_3Sn_4 layer was found to be 8.64 g/cm^3 [60]. The molar weight of this layer is 650.83 g/mol , and the value of m is 3. Substituting these values into Equation 3.3, the number of moles of Ni in the Ni_3Sn_4 layer in the as-reflowed state and after aging for 400 h is $0.82 \times 10^{-5} \text{ mol/cm}^2$ and $1.47 \times 10^{-5} \text{ mol/cm}^2$, respectively. Thus, the number of moles of Ni in the Ni_3Sn_4 layer grown within the aging duration of 400 h, labelled as $Ni_{\text{Ni}_3\text{Sn}_4}$, is determined to be $0.65 \times 10^{-5} \text{ mol/cm}^2$.

Therefore, from these values it is clear that $Ni_{\text{Ni-W-P}} = Ni_{\text{Ni}_3\text{Sn}_4} + Ni_{(\text{Ni,W})_3\text{P}}$. This proves the mass balance of Ni during reaction at the Ni-W-P/Sn-3.5Ag interface, i.e. all of the Ni atoms diffused out from the Ni-W-P layer take part in the reaction to form Ni_3Sn_4 , and the depletion of Ni from the surface of the Ni-W-P layer leads to the formation of the $(\text{Ni,W})_3\text{P}$ layer.

4.5. Summary

The interfacial reaction and tensile properties of solder joints between Sn-3.5Ag solder and electroless Ni-W-P metallization with a composition of 6~7 wt.% of P and 14~16 wt.% of W were studied after reflow and prolonged aging. The interfacial reaction and tensile strength of such solder joints were compared with the solder joints between the same solder and electroless Ni-P metallization (6~7 wt.% of P) to understand the role of W. The following conclusions can be made based on the investigation:

1. There are only two interfacial compounds, Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$, formed during Ni-W-P/Sn-3.5Ag interfacial reaction. Ni atoms diffuse out from the Ni-W-P layer towards solder and react with the Sn atoms from the solder to form Ni_3Sn_4 . Meanwhile, the formation of Ni_3Sn_4 causes the depletion of Ni from the surface of the Ni-W-P layer, leading to continued growth of the ternary $(\text{Ni,W})_3\text{P}$ layer. This reaction mechanism has been supported by the mass balance of Ni during Ni-W-P/Sn-3.5Ag interfacial reaction.
2. After prolonged aging, unlike at the Ni-P/Sn-3.5Ag interface, no voids were found at the Ni-W-P/Sn-3.5Ag interface. The Ni_3Sn_4 compound grows much more slowly. In addition, the consumption of the Ni-W-P layer was found to be much slower than that of the Ni-P layer. These facts indicate a significantly slow out-diffusion of Ni atoms at the Ni-W-P/Sn-3.5Ag interface; hence, Ni-W-P layer stands out as an impressive diffusion barrier for lead-free soldering.
3. Both growths of the Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers at the Ni-W-P/Sn-3.5Ag interface are diffusion-controlled. The activation energies for the growths of Ni_3Sn_4 and

(Ni,W)₃P layers during solid-state reaction are calculated to be 62.3 kJ/mol and 58.2 kJ/mol, respectively.

4. Prior to aging, the tensile strength of the Ni-W-P/Sn-3.5Ag solder joints was found to be comparable to that of the Ni-P/Sn-3.5Ag solder joints. Both types of as-reflowed solder joints experienced ductile failure in the bulk solder. Unlike the strength of Ni-P/Sn-3.5Ag solder joints, which dropped significantly after aging for 400 h and beyond due to the brittle fracture at the Ni₃Sn₄/solder interface, there was no significant drop in strength of Ni-W-P/Sn-3.5Ag solder joints upon aging for up to 600 h. Ductile failure inside the bulk solder was maintained till such prolonged aging condition.

Chapter 5

Soldering between Electroless Ni-Co-P and Sn-3.5Ag

5.1. Introduction

So far the experiment to incorporate a third element into electroless Ni-P has shown good success with Ni-W-P, and mixed success and disappointment with Ni-Sn-P. In this chapter, the potential application of another alloy, namely Ni-Co-P, will be explored. Similar to Ni, Co is also reactive with Sn, and based on the Co-Sn phase diagram, a few IMCs may form between Co and Sn. However, Ni-Co-P phase diagram is not available. In other studies, it was reported that Ni-Co-P alloys can be a better protective coating than Ni-P due to their improved corrosion resistance and thermal stability [35, 36]. Ni-Co-P alloys were also explored as the plug contact on the silicide transistor gate [37]. In the early 1990s, Ni-Co-P alloy deposit was first investigated as a diffusion barrier between an Al pad and a high-lead solder bump (95Pb-5Sn) [38]. In recent years, the electrolessly-deposited Ni-Co-P alloys have been investigated as a diffusion barrier layer in the ultra large-scale integration (ULSI) technology as well [36, 39, 40]. However, no work on the application of electroless Ni-Co-P metallization as a diffusion barrier in lead-free soldering has been conducted so far.

The objective of this work is to study the interfacial reaction and tensile strength of solder joints between lead-free Sn-3.5Ag solder and electroless Ni-Co-P metallization after reflow and prolonged aging. Attention is laid on the interfacial IMC formation mechanism and how the reaction affects the solder joint strength. Again, the observed interfacial reaction and the tensile properties of Ni-Co-P/Sn-3.5Ag solder joints were compared with the solder joints between the same solder and electroless Ni-P

metallization. Fractographic analysis on both types of failed solder joints was conducted to assist the understanding of the joint strength degradation.

5.2. Experimental Procedures

Similar to the work reported in Chapter 3 and 4, Cu plates (99.98 wt.%) with a thickness of 6 mm were used as the substrate for Ni-Co-P plating. The surface treatment for Cu substrate was the same as described in Section 3.2.1. The electroless Ni-Co-P plating was conducted in an alkaline bath with a pH level of 10.0 at 88 °C for 1 h. As listed in Table 5.1, this alkaline bath contained nickel chloride and cobalt chloride as nickel and cobalt sources, respectively. Sodium hypophosphite was used as a reducing agent along with sodium citrate, lactic acid and ammonium chloride as the complexing agents.

Following the electroless plating process, the Ni-Co-P/Sn-3.5Ag solder joints were formed, and then thermally-aged at 180 °C for 600 h to study their interfacial reaction, tensile strengths and fracture behaviour. The procedures for forming this type of solder joints are the same as detailed in Section 3.2.2. For the tensile testing, the steps to prepare the micro-joints for the test are the same as described in Section 3.2.4, while the testing procedures can be referenced in Section 3.2.5. On the other hand, the morphological and microstructural observations were conducted according to the procedures similar to those detailed in Section 3.2.6. The newly formed interfacial compounds in the Ni-Co-P/Sn-3.5Ag solder joints were also identified using transmission electron microscope (TEM). The TEM sample was prepared using focused ion beam (FIB) technique.

Table 5.1. Composition of the plating bath for electroless Ni-Co-P.

Constituents of plating bath	Concentration
NiCl_2	10 g/L
CoCl_2	4 g/L
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	16 g/L
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	40 g/L
NH_4Cl	30 g/L
Lactic acid	4.5 ml/L

5.3. Results

5.3.1. As-deposited Metallizations

The composition of the as-deposited Ni-Co-P layer, measured by EDX, was found to be 3~4 wt.% of P and 9~12 wt.% of Co. As shown in Fig. 5.1(a), the surface of the deposited Ni-Co-P layer contained smooth nodules with uneven size. The deposited Ni-Co-P layer was observed to adhere closely to the underlying copper substrate, with a thickness around 9.9 μm (Fig. 5.1 (b)).

Fig. 5.1. As-deposited Ni-Co-P layer: (a) surface morphology, (b) cross-sectional micrograph.

5.3.2. Interfacial Microstructure Analysis of As-reflowed Solder Joints

The cross-sectional micrograph of the as-reflowed Ni-Co-P/Sn-3.5Ag solder joint is shown in Fig. 5.2. It was observed that a layer of compound was clearly formed, and such compound consisted of Ni, Co and Sn. Unlike the case in Ni-P/Sn-3.5Ag reaction (Fig. 3.5), there was no significant spallation of this compound into the bulk solder. Under this Ni-Co-Sn compound layer, two unknown thin layers were noticed, one is grey and the other one is dark in colour. The grey layer partially spalled into the Ni-Co-Sn compound layer.

Fig. 5.2. Back-scattered SEM images showing IMCs formed in the as-reflowed Ni-Co-P/Sn-3.5Ag solder joint.

5.3.3. Interfacial Microstructure Analysis of Aged Solder Joints

The microstructure at the Ni-Co-P/Sn-3.5Ag interface after aging at 180 °C for up to 600 h is shown in Fig. 5.3. It was found that during aging, the unknown dark and grey

layers grew very slowly. The thickness increase of the Ni-Co-Sn compound layer was much slower than that of the Ni_3Sn_4 layer formed at the Ni-P/Sn-3.5Ag interface (Fig. 3.8). Unlike the Ni-P metallization with an original thickness of $9.7\text{ }\mu\text{m}$ was fully consumed after 300 h of aging, the Ni-Co-P metallization has only reacted away $3.4\text{ }\mu\text{m}$ after 600 h of aging (Fig. 5.3(f)). Fig. 5.4 shows the consumption of Ni-P and Ni-Co-P metallizations upon aging for 600 h. It was clearly seen that the consumption rate of the Ni-Co-P layer is much slower than that of the Ni-P layer. The magnified image of the Ni-Co-P/Sn-3.5Ag interface aged at $180\text{ }^\circ\text{C}$ for 600 h is depicted in Fig. 5.5. It was observed that both thicknesses of unknown dark and grey layers were still less than $1\text{ }\mu\text{m}$ after 600 h of aging. Moreover, it was noted that even after 600 h of aging, no voids were found in the Ni-Co-P/Sn-3.5Ag solder joint (Fig. 5.3(f) and Fig. 5.5).

Fig. 5.3. Back-scattered SEM images showing IMCs at Ni-Co-P/Sn-3.5Ag interface after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, (e) 500 h, and (f) 600 h.

Fig. 5.4. Consumption of Ni-P and Ni-Co-P metallizations upon aging for 600 h. Notice that the Ni-P metallization with an original thickness of 9.7 μm was fully consumed after 300 h of aging.

Fig. 5.5. Magnified back-scattered SEM image showing IMCs at Ni-Co-P/Sn-3.5Ag interface after aging at 180 °C for 600 h.

From the EDX elemental mapping of the Ni-Co-P/Sn-3.5Ag interface after aging at 180 °C for 600 h (Fig. 5.6), it was found that the unknown dark and grey layers both consisted of Ni, Co and P elements. The composition of the unknown dark layer was measured to be 58.9 at.% of Ni, 16.2 at.% of Co, and 24.9 at.% of P by EDX (Fig. 5.7). This composition is suggestive of $(\text{Ni,Co})_3\text{P}$ compound. On the other hand, the composition of the unknown grey layer was measured to be 47.4 at.% of Ni, 22.1 at.% of Co, and 30.5 at.% of P by EDX (Fig. 5.8). Such composition is suggestive of either $(\text{Ni,Co})_5\text{P}_2$ or $(\text{Ni,Co})_{12}\text{P}_5$ compound. For the Ni-Co-Sn layer, its composition was measured to be 41.3 at.% of Ni, 3.6 at.% of Co, and 55.1 at.% of Sn by EDX (Fig. 5.9), which is suggestive of $(\text{Ni,Co})_3\text{Sn}_4$ compound. However, the quantitative composition result from EDX is regarded to be not very accurate, especially for both the unknown dark and grey layers due to their sub-micron thickness. In such event, diffraction analysis by TEM was also conducted to identify the interfacial IMCs formed at the Ni-Co-P/Sn-3.5Ag interface.

Fig. 5.6. EDX elemental mapping analysis of the Ni-Co-P/Sn-3.5Ag interface aged at 180 °C for 600 h: (a) SEM image, (b) mapping for Ni, (c) mapping for Co, (d) mapping for P, (e) mapping for Cu, (f) mapping for Ag, and (g) mapping for Sn. Elemental concentration decreases with decreasing colour intensity.

Fig. 5.7. EDX compositional result of the unknown dark layer.

Fig. 5.8. EDX compositional result of the unknown grey layer.

Fig. 5.9. EDX compositional result of the Ni-Co-Sn compound layer.

The TEM sample was prepared by focused ion beam (FIB) technique from the Ni-Co-P/Sn-3.5Ag solder joint aged at 180 °C for 600 h. Fig. 5.10 shows the TEM micrograph of the FIB sample and the diffraction patterns from all interfacial layers formed at the Ni-Co-P/Sn-3.5Ag interface. Layer A in Fig. 5.10(a) is the unknown dark layer, whose diffraction pattern is given in Fig. 5.10(b). The diffraction analysis from this layer indicates a ring pattern of the polycrystalline tetragonal structure similar to Ni_3P . In

conjunction with the composition result from EDX (Fig. 5.7), the unknown dark layer is confirmed to be $(\text{Ni,Co})_3\text{P}$, where Co is dissolved into the Ni sublattice. Moreover, it was noted that nano-sized voids formed inside the $(\text{Ni,Co})_3\text{P}$ layer (Fig. 5.10(a)). The formation of these voids is believed to be caused by the out-diffusion of Ni and Co atoms. Layer B in Fig. 5.10(a) is the unknown grey layer, whose diffraction pattern is given in Fig. 5.10(c). The diffraction analysis from this layer indicates a ring pattern of the polycrystalline tetragonal structure similar to Ni_{12}P_5 . In conjunction with the composition result from EDX (Fig. 5.8), the unknown grey layer is confirmed to be $(\text{Ni,Co})_{12}\text{P}_5$, where Co is dissolved into the Ni sublattice. Layer C in Fig. 5.10(a) is the Ni-Co-Sn layer, whose diffraction pattern is given in Fig. 5.10(d). The diffraction analysis from this layer indicates a superlattice pattern of $(\text{Ni,Co})_3\text{Sn}_4$, with a series of sharp satellite spots around the fundamental Bragg ones. In conjunction with the composition result from EDX (Fig. 5.9), the Ni-Co-Sn layer is confirmed to be $(\text{Ni,Co})_3\text{Sn}_4$, where Co is dissolved into the Ni sublattice.

Fig. 5.10. (a) Cross-sectional TEM micrograph of the Ni-Co-P/Sn-3.5Ag solder joint aged at 180 °C for 600 h (TEM sample preparation was done by focused ion beam (FIB) technique), diffraction patterns from (b) $(\text{Ni,Co})_3\text{P}$, (b) $(\text{Ni,Co})_{12}\text{P}_5$, and (d) $(\text{Ni,Co})_3\text{Sn}_4$ layers.

5.3.4. Tensile Strength of Solder Joints

The average tensile strengths obtained from both Ni-Co-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag solder joints upon aging at 180 °C for up to 600 h are tabulated in Table 5.2. The tensile strength of both types of solder joints as a function of aging time up to 600 h is shown in Fig. 5.11. Both types of as-reflowed solder joints had similar tensile strength. Upon aging for 600 h, there was no significant drop in strength of Ni-Co-P/Sn-3.5Ag solder joints, while the strength of Ni-P/Sn-3.5Ag solder joints dropped significantly after aging for 400 h and beyond. Therefore, Ni-Co-P metallization possesses an advantage over Ni-P in terms of resistance to joint strength deterioration during aging.

Table 5.2. Tensile strengths of Ni-P/Sn-3.5Ag and Ni-Co-P/Sn-3.5Ag solder joints upon aging at 180 °C for 600 h.

Aging Time (hour)	Tensile Strength (MPa)	
	Ni-P/Solder Joint	Ni-Co-P/Solder Joint
As-reflowed	35.41 ± 2.85	36.26 ± 1.12
100	32.75 ± 1.38	33.64 ± 1.39
200	31.75 ± 1.36	33.51 ± 1.07
300	31.32 ± 0.43	33.99 ± 0.71
400	22.69 ± 1.36	33.64 ± 0.93
600	22.46 ± 0.99	33.52 ± 1.27

Fig. 5.11. Tensile strengths of both Ni-Co-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag solder joints after aging for up to 600 h.

5.3.5. Failure Analysis of Solder Joints

Fig. 5.12(a) and (b) show the cross-sectional view and fractured surface of the as-reflowed Ni-Co-P/Sn-3.5Ag solder joints, respectively. As shown in Fig. 5.12(a), an obvious necking occurred in the bulk solder, and the fracture surface inclined at about 45° to the tensile-stress axis. The fractured surface of this solder joint is shown in Fig. 5.12(b), and from EDX analysis, Sn was found to be the dominant element at the fractured surface, confirming the fracture occurs completely in the bulk solder.

Fig. 5.12. (a) Cross-sectional view and (b) fractured surface of the as-reflowed Ni-Co-P/Sn-3.5Ag solder joint.

Fig. 5.13 shows that the Ni-Co-P/Sn-3.5Ag solder joints still experienced complete ductile failure inside the bulk solder after aging at 180 °C for up to 600 h. This means there is no serious damage to the interfacial IMC layers and the adhesion between solder and the neighbouring IMC. As a comparison, it was shown earlier in Chapter 3 that the fracture path shifted from inside the bulk solder to the Ni_3Sn_4 /solder interface in the Ni-P/Sn-3.5Ag solder joints aged for 400 h and beyond.

Fig. 5.13. Cross-sectional view of Ni-Co-P/Sn-3.5Ag solder joint after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, and (e) 600 h.

5.4. Discussion

5.4.1. Diffusional Formation Mechanism of IMCs at the Ni-Co-P/Solder Interface

EDX elemental mapping was conducted to study the diffusion profile at the Ni-Co-P/Sn-3.5Ag interface. From the area mapping result of the Ni-Co-P/Sn-3.5Ag interface aged at 180 °C for 600 h (Fig. 5.6), it was clearly seen that P atoms remained in the Ni-Co-P, $(\text{Ni,Co})_{12}\text{P}_5$ and $(\text{Ni,Co})_3\text{P}$ layers. In contrast, Ni and Co atoms both diffused out from the Ni-Co-P layer to form $(\text{Ni,Co})_3\text{Sn}_4$. The signal from Sn was found to terminate at the $(\text{Ni,Co})_3\text{Sn}_4/(\text{Ni,Co})_{12}\text{P}_5$ interface, and no signal from Sn was detected in the $(\text{Ni,Co})_{12}\text{P}_5$ layer, indicating that Sn atoms did not diffuse through the $(\text{Ni,Co})_{12}\text{P}_5$ layer. It was also noted that after such a prolonged aging, Cu atoms still remained in the substrate as neither $(\text{Cu,Ni})_6\text{Sn}_5$ nor $(\text{Ni,Cu})_3\text{Sn}_4$ compounds were detected. This suggests that Ni-Co-P is a good diffusion barrier to prevent the inter-diffusion between Cu and Sn.

Fig. 5.14 schematically illustrates the diffusional formation mechanism of the interfacial layers at the Ni-Co-P/Sn-3.5Ag interface. Based on elemental analysis, P atoms in the Ni-Co-P remained in the metallization during soldering reaction. The continuous growth of the $(\text{Ni,Co})_3\text{Sn}_4$ IMC attracts Ni and Co to diffuse out from the Ni-Co-P metallization layer. The depletion of Ni and Co from the surface of the Ni-Co-P metallization leads to the formation of $(\text{Ni,Co})_3\text{P}$ compound which has been explained before as the solder reaction-assisted crystallization [60]. In this case, instead of forming the Ni_3P -type compound alone, Ni_{12}P_5 -type compound also forms, and due to the presence of Co, the compound takes the form of $(\text{Ni,Co})_{12}\text{P}_5$. This is because $(\text{Ni,Co})_3\text{P}$ forms at the very beginning of the reaction, then as a consequence of the continued out-

diffusion of Ni and Co atoms from the already formed $(\text{Ni,Co})_3\text{P}$ layer, part of this layer is transformed to $(\text{Ni,Co})_{12}\text{P}_5$.

Fig. 5.14. A schematic illustration of the diffusional formation mechanism of IMCs between the Ni-Co-P metallization and Sn-3.5Ag solder.

According to the Ni-P phase diagram (Fig. 2.2), it is understood that all three types of compounds, namely Ni_3P , Ni_5P_2 and Ni_{12}P_5 , are thermodynamically stable. After Ni_3P , the next phase to be formed seems to be Ni_5P_2 in a continuously varied composition profile, since it is the second P-rich phase. However, Duh's group reported that with further reaction at the Ni-P/Sn-3Ag-0.5Cu interface, Ni_3P would transform to Ni_{12}P_5 which is the third P-rich phase in the Ni-P phase diagram, whereas the formation of Ni_5P_2 was hindered [19, 22, 71, 72]. Both Ni_{12}P_5 and Ni_3P have the identical tetragonal structure, while Ni_5P_2 has a hexagonal structure. Based on this, Duh's group argued that the transformation of Ni_3P to Ni_{12}P_5 is attributed to their similar crystal structures. The formation of Ni-Co-P compounds, which is due to the dissolution of Co atoms into the Ni sublattice of the Ni-P compounds, should not alter the original crystal structures of the

Ni-P compounds because Ni and Co have very similar atomic radius. Hence, both $(\text{Ni,Co})_{12}\text{P}_5$ and $(\text{Ni,Co})_3\text{P}$ should have identical tetragonal structure, while $(\text{Ni,Co})_5\text{P}_2$ should have a hexagonal structure. Therefore, with further reaction at the Ni-Co-P/Sn-3.5Ag interface, $(\text{Ni,Co})_3\text{P}$ transforms to $(\text{Ni,Co})_{12}\text{P}_5$ due to their similar crystal structures, while the formation of $(\text{Ni,Co})_5\text{P}_2$ is hindered.

At the Ni-P/Sn-3.5Ag interface, micro-sized voids were observed inside the Ni_3P layer under SEM observation (Fig. 3.8). In contrast, at the Ni-Co-P/Sn-3.5Ag interface, no voids were observed under SEM. However, nano-sized voids were observed inside the $(\text{Ni,Co})_3\text{P}$ layer at the Ni-Co-P/Sn-3.5Ag interface under TEM (Fig. 5.10(a)). It is reasonable to attribute the difference in the size of voids that formed in these two reaction couples, to the different structures of $(\text{Ni,Co})_3\text{P}$ and Ni_3P layers. The Ni_3P layer formed at the Ni-P/Sn-3.5Ag interface has a fine columnar structure, which makes it behave as fast diffusion path for Ni atoms during the interfacial reaction [16]. As a consequence, when the net Ni flux diffuses out from the Ni-P layer to form Ni_3Sn_4 , the compensation from other elements to fill the vacant sites left by Ni atoms will be insufficient, leading to formation of voids with a micro-size inside the Ni_3P layer after prolonged reaction. Unlike the Ni_3P layer formed at the Ni-P/Sn-3.5Ag interface, as shown in Fig. 5.10(a), the $(\text{Ni,Co})_3\text{P}$ layer formed at the Ni-Co-P/Sn-3.5Ag interface does not have a columnar structure. Thus, the $(\text{Ni,Co})_3\text{P}$ layer does not act as fast diffusion path for Ni and Co atoms during the interfacial reaction. As a result, a much reduced growth rate of the $(\text{Ni,Co})_3\text{Sn}_4$ IMC and slow metallization consumption rate were observed, and the void growth inside the $(\text{Ni,Co})_3\text{P}$ layer may have to take much longer time.

5.5. Summary

The interfacial reaction and tensile properties of solder joints between Sn-3.5Ag solder and electroless Ni-Co-P metallization with a composition of 3~4 wt.% of P and 9~12 wt.% of Co were investigated after reflow and prolonged aging. The interfacial reaction and tensile properties of solder joints between the same solder and electroless Ni-P metallization (6~7 wt.% of P) were studied as a benchmark. The following conclusions can be made based on the investigation:

1. Three types of interfacial IMCs, $(\text{Ni,Co})_3\text{Sn}_4$, $(\text{Ni,Co})_3\text{P}$ and $(\text{Ni,Co})_{12}\text{P}_5$, are formed during the Ni-Co-P/Sn-3.5Ag interfacial reaction. Both Ni and Co atoms diffuse out from the Ni-Co-P layer towards solder and react with the Sn atoms from the solder to form $(\text{Ni,Co})_3\text{Sn}_4$. Meanwhile, the formation of $(\text{Ni,Co})_3\text{Sn}_4$ causes the depletion of Ni and Co from the surface of the Ni-Co-P layer, leading to the formation of $(\text{Ni,Co})_3\text{P}$ at the very beginning of the reaction. As a consequence of the continued out-diffusion of Ni and Co atoms from the already formed $(\text{Ni,Co})_3\text{P}$ layer, part of this layer is transformed to $(\text{Ni,Co})_{12}\text{P}_5$.
2. At the prolonged aged Ni-Co-P/Sn-3.5Ag interface, although nano-sized voids were found inside the $(\text{Ni,Co})_3\text{P}$ layer, the $(\text{Ni,Co})_3\text{Sn}_4$ compound grew much slower than the Ni_3Sn_4 compound formed at the Ni-P/Sn-3.5Ag interface. In addition, the consumption of the Ni-Co-P layer was found to be much slower than that of Ni-P. These facts indicate a significantly slow out-diffusion of Ni and Co atoms from the Ni-Co-P layer, so Ni-Co-P layer stands out as a promising diffusion barrier for lead-free soldering.

3. Prior to aging, the tensile strength of the Ni-Co-P/Sn-3.5Ag solder joints was found to be comparable to that of the Ni-P/Sn-3.5Ag solder joints. Both types of as-reflowed solder joints experienced ductile failure in the bulk solder. Unlike the strength of Ni-P/Sn-3.5Ag solder joints, which dropped significantly after aging for 400 h and beyond due to the brittle fracture at the Ni_3Sn_4 /solder interface, there was no significant drop in strength of Ni-Co-P/Sn-3.5Ag solder joints after aging for up to 600 h. Ductile failure inside the bulk solder was maintained till such prolonged aging condition.

Chapter 6

Comparison of the Four Types of Ni-based Metallizations

6.1. Consumption Rates during Aging

Fig. 6.1 shows the consumption of all four types of metallizations as a function of aging at 180 °C for up to 600 h. Among the different metallizations, it is clearly seen that during soldering reaction, Ni-P is consumed fastest, while the consumption of Ni-W-P is the slowest. Besides, Ni-Sn-P and Ni-Co-P metallizations are consumed at an equally slow rate, which is slightly faster than that of Ni-W-P.

Fig. 6.1. Consumption of all four types of Ni-based metallizations as a function of aging at 180 °C for up to 600 h. Notice that the Ni-P metallization with an original thickness of 9.7 μm was fully consumed after aging for 300 h.

The fastest consumption rate of the Ni-P metallization is attributed to the formation of the Ni_3P layer, which has a fine columnar structure. This is because the columnar grain boundaries of this layer act as fast diffusion path for Ni atoms. During soldering, Ni atoms diffuse out through the Ni_3P layer to form Ni_3Sn_4 , while there is insufficient compensation from other elements to fill the vacant sites left by Ni. As a result, micro-sized voids are formed in the Ni_3P layer, which further reduce its ability as a diffusion barrier since diffusion along the free surfaces of voids is relatively easier.

In the case of Ni-W-P metallization, its slowest consumption rate is due to the formation of the $(\text{Ni,W})_3\text{P}$ layer, which is amorphous in nature (Fig. 4.5). During soldering, such amorphous structure can effectively hinder the out-diffusion of Ni atoms from the underlying metallization layer. The formation of Ni_3Sn_4 IMC requires Ni supply from the metallization layer, so the formation of the amorphous $(\text{Ni,W})_3\text{P}$ layer results in not only the slow metallization consumption but also the much reduced growth of Ni_3Sn_4 as compared with that at the Ni-P/Sn-3.5Ag interface.

The slow overall consumption rate of the Ni-Sn-P metallization (slightly faster than that of Ni-W-P) is likely to be caused by the formation of $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer. Although the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer is polycrystalline in nature (Fig. 3.7), it does not have a columnar structure as the Ni_3P layer formed at the Ni-P/Sn-3.5Ag interface does, so the overall consumption rate of Ni-Sn-P metallization is only slightly higher when compared to that of the Ni-W-P metallization. However, the consumption rate of this metallization layer is significantly accelerated at the locations where diffusion barriers, which are the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ compound and the Ni-Sn-P metallization layers, both break down (Fig. 3.26). The root cause of such breakdown is the columnar structure of the Ni-Sn-P metallization layer.

The metallization layer prepared by electroless plating has contained intrinsic tensile stress at the as-deposited state, and such stress increases with thermal treatment. Hence, because of the columnar structure of the Ni-Sn-P metallization, it is not surprised to form cracking along the weak boundaries between the neighbouring columns of this metallization upon prolonged aging. Such weakness of the metallization layer causes the scattered cracking in the adjacent $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer as well. The Ni_3Sn_4 compound grows into the gap at the broken locations of the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer. As reaction proceeds, the invaded Ni_3Sn_4 compound manages to make direct contact with the Cu substrate. Under this circumstance, the Cu atoms from the substrate manage to incorporate into the interfacial reaction, as a result, the formed Ni_3Sn_4 compound transforms into $(\text{Cu},\text{Ni})_6\text{Sn}_5$ and $(\text{Ni},\text{Cu})_3\text{Sn}_4$ compounds, along with the formation of Cu_6Sn_5 and Cu_3Sn compounds within the substrate. Such highly non-uniform interfacial reaction is responsible to the fast local consumption rate of the Ni-Sn-P metallization.

For Ni-Co-P metallization, its slow consumption rate (equally slow as the overall consumption rate of Ni-Sn-P) is probable due to the formation of $(\text{Ni},\text{Co})_{12}\text{P}_5$ and $(\text{Ni},\text{Co})_3\text{P}$ layers. These two layers are both polycrystalline in nature (Fig. 5.10); however, unlike the Ni_3P layer formed at the Ni-P/Sn-3.5Ag interface, neither of $(\text{Ni},\text{Co})_{12}\text{P}_5$ and $(\text{Ni},\text{Co})_3\text{P}$ layers has a columnar structure, so the consumption rate of Ni-Co-P metallization is much slower than that of Ni-P.

6.2. Correlation with Long-term Solder Joint Strength

In general, the choices of the three elements, namely Sn, W, and Co, to be incorporated into Ni-P metallization in the effort to slow down the interfacial reaction,

have been successfully demonstrated. The next critical question is whether the slow reaction will be translated into the retained high solder joint strength after prolonged aging. Fig. 6.2 shows the tensile strengths of all four types of solder joints as a function of aging at 180 °C for up to 600 h. Among these solder joints, it was clearly seen that no significant drop in strength was experienced by solder joints with Ni-W-P and Ni-Co-P metallizations. In contrast, the strength of Ni-P/Sn-3.5Ag solder joints dropped significantly after aging for 400 h and beyond, while the strength of Ni-Sn-P/Sn-3.5Ag solder joints dropped significantly after aging for 300 h and beyond. Therefore, among all four types of solder joints, Ni-W-P/Sn-3.5Ag solder joints and Ni-Co-P/Sn-3.5Ag solder joints have superior mechanical reliability to other two types of solder joints.

Fig. 6.2. Tensile strengths of all four types of solder joints as a function of aging at 180 °C for up to 600 h.

The fast degradation of the Ni-P/Sn-3.5Ag solder joint strength has been well studied in Chapter 3. The drop of strength in this type of solder joint is accompanied by the shift of the fracture mode from the ductile failure inside the bulk solder to the brittle failure at the Ni_3Sn_4 /solder interface. The weakening of this interface is caused by the stress generated by the volume mismatch between solder and the neighbouring Ni_3Sn_4 IMC.

Among the solder joints with ternary metallizations, strength of the solder joint with Ni-Sn-P metallization does not maintain at the high level as the other two counterparts. The reliability of this type of solder joint is even slightly inferior to that of solder joint with Ni-P metallization. The drop of strength in solder joint with Ni-Sn-P metallization is along with the shift of the fracture mode from the ductile failure inside the bulk solder to the brittle failure not only at the Ni_3Sn_4 /solder interface but also through all interfacial layers. Initially it might be a surprise to see such premature degradation in the strength of this type of solder joint. Through the detailed analyses in Chapter 3, the author now understands that the reason is due to the scattered cracking occurred at the Ni-Sn-P/Sn-3.5Ag interface. If the cracking could be prevented, the solder joint with Ni-Sn-P metallization is expected to be much more thermally durable than the solder joint with Ni-P. The solution to avoid such cracking requires further research in the future.

6.3. Recommended Engineering Solutions for More Reliable Solder Metallization Materials

Based on the above analyses, it is recommended that electrolessly-plated ternary Ni-W-P (14~16 wt.% of W and 6~7 wt.% of P) and Ni-Co-P (9~12 wt.% of Co and 3~4 wt.%

of P) alloys could be used to replace the binary Ni-P alloy that has been widely used in the packaging industry. The Ni-Sn-P (19~21 wt.% of Sn and 6~7 wt.% of P) alloy could be a good candidate if the problem of its high tendency of cracking could be solved, as discussed in Chapter 3.

Chapter 7 Conclusions and Recommendations

7.1. Conclusions

This work has investigated the interfacial reactions between lead-free Sn-3.5Ag solder and three types of electrolessly-plated ternary Ni-based metallizations (Ni-Sn-P, Ni-W-P, and Ni-Co-P). The influence of interfacial reactions on the solder joint reliability was reported through the evaluation of the mechanical behaviour of micro-tensile joints. The interfacial reaction between Sn-3.5Ag solder and electrolessly-plated binary Ni-P metallization and tensile properties of such solder joints were compared to understand the effect of addition of a ternary alloying element. Based on this work, the following conclusions can be made:

Soldering with Ni-Sn-P metallization:

- As predicated by Ni-Sn-P phase diagram, the formation of Ni_3P is successfully avoided.
- Two IMCs, Ni_3Sn_4 and $\text{Ni}_{13}\text{Sn}_8\text{P}_3$, are formed.
- The $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer is formed by the depletion of Ni from the surface of the Ni-Sn-P layer in conjunction with the Sn supply from the solder.
- After prolonged reaction, no voids are observed at the reaction interface, but scattered cracks are found in both the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ and Ni-Sn-P metallization layers.

Soldering with Ni-W-P metallization:

- Two IMCs, Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$, are formed.
- The $(\text{Ni,W})_3\text{P}$ layer is formed by the depletion of Ni from the surface of the Ni-W-P layer.

- After prolonged reaction, no voids are observed at the reaction interface.
- The growths of both the Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers are diffusion-controlled.
- The activation energies for the growth of Ni_3Sn_4 and $(\text{Ni,W})_3\text{P}$ layers during solid-state reaction are 62.3 kJ/mol and 58.2 kJ/mol, respectively.

Soldering with Ni-Co-P metallization:

- Three IMCs, $(\text{Ni,Co})_3\text{Sn}_4$, $(\text{Ni,Co})_{12}\text{P}_5$ and $(\text{Ni,Co})_3\text{P}$, are formed.
- The $(\text{Ni,Co})_3\text{Sn}_4$ layer is formed due to the reaction of Sn from the solder with Ni and Co from the Ni-Co-P metallization.
- The $(\text{Ni,Co})_3\text{P}$ layer is formed by the depletion of Ni and Co from the surface of the Ni-Co-P layer.
- Due to the continued out-diffusion of Ni and Co atoms from the already formed $(\text{Ni,Co})_3\text{P}$ layer, part of this layer transforms to $(\text{Ni,Co})_{12}\text{P}_5$.
- Nano-sized voids are visible in the $(\text{Ni,Co})_3\text{P}$ layer under TEM.

Consumption rates comparison:

- Ni-P is consumed at the fastest rate (9.7 μm of its original thickness was fully consumed after 300 h of aging at 180 °C).
- Ni-W-P is consumed at the slowest rate (only 2.7 μm was consumed after 600 h of aging at 180 °C).
- Ni-Sn-P and Ni-Co-P are consumed at an equally slow rate (3.3 μm of Ni-Sn-P and 3.4 μm of Ni-Co-P were consumed after 600 h of aging at 180 °C), but slightly faster than that of Ni-W-P.

Tensile behaviour comparison:

- Tensile strengths of the as-reflowed solder joints with all four types of Ni-based metallizations (Ni-P, Ni-Sn-P, Ni-W-P and Ni-Co-P) are very similar to each other, which are around 30~37 MPa.
- Tensile strength of Ni-P/Sn-3.5Ag solder joints decreases significantly to around 22 MPa after aging for 400 h at 180 °C when the fracture mode changes from the ductile failure inside the bulk solder to the brittle failure at the Ni₃Sn₄/solder interface.
- Tensile strength of Ni-Sn-P/Sn-3.5Ag solder joints drops significantly to around 23 MPa after aging for 300 h at 180 °C when the fracture mode changes from the ductile failure inside the bulk solder to the brittle failure not only at the Ni₃Sn₄/solder interface, but also through all of the interfacial layers.
- Tensile strengths of Ni-W-P/Sn-3.5Ag and Ni-Co-P/Sn-3.5Ag solder joints remain high (above 30 MPa) after aging for 600 h at 180 °C, and the fracture mode in these two types of solder joints remains to be ductile failure inside the bulk solder.

Correlation between soldering reaction and retention of joint strength:

- Evidenced from the excellent performance of Ni-W-P and Ni-Co-P metallizations, slow interfacial reaction is clearly beneficial to retention of joint strength.
- Ni-Sn-P metallization is an exception since diffusion is very fast at the scattered locations, where the diffusion barrier breakdown occurs. The root cause of such breakdown is the columnar structure of the Ni-Sn-P metallization. In this case, future work is needed to avoid the formation of the weak columnar structure in this type of metallization.

- Therefore, besides slow interfacial reaction, the structure of the metallization itself is also an important factor for retention of joint strength.

Based on the above observation and analysis, it is recommended that Ni-W-P (14~16 wt.% of W and 6~7 wt.% of P) and Ni-Co-P (9~12 wt.% of Co and 3~4 wt.% of P) alloys could be used to replace the conventional Ni-P alloy as solder metallization material. The Ni-Sn-P (19~21 wt.% of Sn and 6~7 wt.% of P) alloy requires further improvement to eliminate the weak columnar structure before it can be recommended as a promising replacement.

7.2. Recommendations for Future Work

Based on the understandings and conclusions from the current work, future scopes for additional in-depth works exist and are as follows:

1. To fully benefit from the slow overall interfacial reaction in the Ni-Sn-P system, cracking at the Ni-Sn-P/solder interface has to be avoided. By adjusting the bath formulation and the operating conditions of plating, the columnar structure of the Ni-Sn-P metallization can be avoided to reduce its cracking tendency. Meanwhile, this will also hinder the cracking in the $\text{Ni}_{13}\text{Sn}_8\text{P}_3$ layer.
2. In this work, the author has studied the interfacial reactions between three ternary Ni-based metallizations (Ni-Sn-P, Ni-W-P and Ni-Co-P) and lead-free Sn-3.5Ag solder, more work should be done by using other common lead-free solders, such as Sn-Cu and Sn-Ag-Cu, etc.
3. The present work limits the investigation of solder joint strength to monotonic tensile test. However, in the industrial reliability test and/or under the service condition,

solder joints are subjected to cycling stress. Thus, fatigue behaviour of solder joints formed between these ternary Ni-based metallizations and lead-free solders worth studying in the future.

4. It was reported that electromigration influences the interfacial reaction and mechanical performance of solder joints formed between binary Ni-P metallization and Sn-3.5Ag solder [111-113]. More work can be done in this area to study the effect of electromigration on the interfacial reaction and mechanical performance of the solder joints formed between the ternary Ni-based metallizations and lead-free solders.

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