THE INFLUENCE OF GALLIUM ADDITION ON THE PROPERTIES OF Sn3.0Ag0.5Cu LEAD FREE SOLDER

By

MOHAMAD FADLEY BIN ZAKARIA

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TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO : LITERATURE REVIEW

CHAPTER THREE : EXPERIMENTAL

CHAPTER FOUR : RESULTS AND DISCUSSION

CHAPTER FIVE : CONCLUSIONS AND SUGGESTIONS

LIST OF TABLES

LIST OF FIGURES

List of Abbreviations

Ag_4Sn – argentum stanum

BSE – Back Scattered Electron

Ca – calcium

Ce – cerilium

CTE – Coefficient of Thermal Expansion

Cu – copper

$Cu_{10}Sn_3$ – copper stanum

DSC – Differential Scanning Calorimetry

DTA – Differential Thermal Analysis

EDX – Electron Diffraction X-ray

Ga – gallium

Ge – germanium

IMC – Intermetallic Compound

P – phosphorus

Pb – lead/plumbum

RE – Rare Earth

SAC – stanum argentum copper

SE – Secondary Electron

SEM – Scanning Electron Microscopy

Sn – stanum/tin

TE – Transition Element

TG – Thermogravimetry

TGA – Thermogravimetry Analysis

UTS – Ultimate Tensile Strength

XRD – X-ray Diffraction

Zn – zinc

KOH – potassium hydroxide

KESAN PENAMBAHAN GALIUM KE ATAS SIFAT-SIFAT PATERI Sn3.0Ag0.5Cu BEBAS PLUMBUM

ABSTRAK

Kajian ini menekankan ke atas kesan penambahan gallium (Ga) ke atas sifat-sifat fizikal, mekanikal dan metalurgi bagi pateri bebas plumbum Sn3.0Ag0.5Cu (berdasarkan peratus berat). Sepuluh sampel yang berlainan dihasilkan dengan mencampurkan gallium mengikut peratusan yang berbeza dari julat 0.1% hingga 1.0% (peratus berat) kepada pateri Sn3.0Ag0.5Cu. Dari kajian, didapati penambahan gallium ke atas aloi ini sehingga 1.0 wt% telah mengurangkan kerintangan elektrik. Tiada sebarang perubahan ketara ke atas sifat kebolehbasahan sampel, nilai bagi daya pembasahan, F_{max} berada dalam julat 4.00mN hingga 5.9mN. Secara purata, sudut pembasahan yang terhasil adalah di antara 40^O hingga 60^O, sementara kawasan penyebaran berkurang dengan peningkatan kandungan gallium. Begitu juga suhu lebur untuk kesemua sampel, penambahan 0.1 hingga 1.0%Ga berada dalam julat 216-217^{O}C. Berdasarkan pemerhatian ke atas mikrostruktur, terdapat tiga fasa utama iaitu (i) fasa Sn yang berwarna putih; (ii)komposisi intermetalik adalah $Cu_{10}Sn_3$ and Ag_4Sn. $Cu_{10}Sn_3$ berwarna gelap dan; (iii) Ag_4Sn berwarna kelabu. Fasa-fasa ini telah di tentukan melalui ujian XRD dan analisis unsur menggunakan EDX. Penambahan gallium sehingga 1.0%, didapati semakin banyak kehilangan berat berlaku yang di kesan melalui ujian TGA dan juga ketumpatan sampel berkurang apabila kandungan gallium meningkat. Nilai CTE bagi kesemua sampel berkurang apabila kandungan gallium meningkat. Kekuatan tegangan dan ricih menunjukkan peningkatan apabila kandungan Ga meningkat di dalam Sn3.0Ag0.5Cu. Dapat disimpulkan bahawa penambahan Gallium dapat mengubah beberapa sifat pateri Sn3.0Ag0.5Cu.

THE INFLUENCE OF GALLIUM ADDITION ON THE PROPERTIES OF Sn3.0Ag0.5Cu LEAD FREE SOLDER

ABSTRACT

The work focused on the effect of Gallium (Ga) additions on the physical, mechanical and metallurgical properties of Sn3.0Ag0.5Cu lead free solder (by the weight percentage). Ten different samples were produced with different percentage of Ga ranging from 0.1% to 1.0%. It was found that addition up to 1.0%Ga reduces the electrical resistivity. No significant effect of Ga on SAC wettability compared to other lead free solder materials where; the wetting force, F_{max} are ranging from 4.00mN to 5.9mN. On average, the trend of wetting angle increased from 40^{O} up to 60^{O} while the spreading area of the solder alloy decreased when the percentage of Ga increased. No significant effect on melting temperature. All samples doped with 0.1% - 1.0%Ga have a melting temperature between 216-217^{O}C. Based on the microstructure study; there are three major phases that exist which are; Sn rich phase appears as white phase, (ii) Intermetallic compound are mainly $Cu_{10}Sn_3$ and Ag_4Sn. $Cu_{10}Sn_3$ is a dark phases, (iii) Ag_4Sn which is in grey phases. These phases have been confirmed using XRD analysis and also found comply by elemental analysis via Electron Diffraction X-ray (EDX). The addition of gallium up to 1.0%, more weight loss occurs to the samples during Thermal Gravimetry Analysis (TGA) and also the density of the samples decrease when the addition of Gallium increases. The Coefficient of Thermal Expansion (CTE) value is slightly decreased as the Gallium content increases. The tensile and the shear strength of the samples show the increasing trend as the Ga content increase in the Sn3.0Ag0.5Cu. It can be concluded that Gallium can alter several properties of the Sn3.0Ag0.5Cu.

CHAPTER 1

INTRODUCTION

1.0 Introduction

The European Union directive on waste electronic and electrical equipment (WEEE) and the restriction of hazardous substances (ROHS) stated that electronic product in the market on Europe should be free from lead as of 1 July 2006. In Japan, Pb containing device should be recycled under the law of recycling and the recycling fees were increased. The environmental protection agency’s (EPA) at United State, the electronic company must report the toxic release from their factory annually and the reporting for Pb was reduced to 100 pounds. The increasing environmental awareness on the global, government, organizations and companies turn to get a pressure to find a replacement of SnPb solder and they recommended to use non-toxic solder in the product of electrical and electronic (Nurmi et al., 2004).

Consequently, many companies tried to eliminate Pb in the product that they produce. To ensure that this task can be achieved, many researches have been developed to find and test new materials that have the same properties as SnPb and at the same time replace it. These new alloys should fulfills the needs of application and have an excellent properties. Two factors that should be considered to produce and developed this alloys are solderability and reliability.

There are many types of solder compositions that are suitable to replace SnPb solder, for example SnAg, SnAgBi, SnAgCu, SnZn, SnCuIn and SnAgBiCuGe (Nurmi et al., 2004). Among Pb free solder alloys, SnAgCu (SAC) is the most widely used and the most suitable to replace SnPb. This research included investigation on mechanical, physical and metallurgical properties of the alloys. SAC is tin-rich alloys with the composition of 3.0% to 4.0% silver (Ag) and 0.5% to 0.6% copper (Cu). For this alloys, the composition of the specific alloys can be determined by weight percentage. For the main solder materials in this project, Sn3.0Ag0.5Cu, the specified composition contains 96.5% Sn, 3.0% Ag and 0.5% Cu is selected. When the result was analyzed in a point, it shows that the ternary alloys Sn3.0Ag0.5Cu and Sn3.9Ag0.6Cu are same, this alloys have over 99% liquid at 220^{O}C (Handwerker, 2005). Most of them used Sn as the basic element to produce new Pb-free solder.

Variation of the composition can significantly affect the reliability and the mechanical properties of these alloys. This is because when the amount of Ag and Cu are varied, the concentration of this element in a solder matrix is relatively very small. Comparing to the SnPb, variation of Pb in the solder are not critical because of the amount of Pb are high (Nurmi et al., 2004). The following is encapsulation of some interesting findings within practical dosage range (all dosage are expressed in weight percentage) where the increasing of Cu in SnAg solder alloy can decrease the solution of the substrate, lowering the melting temperature and improve the wettability, creep resistance and fatique characteristic. SAC solder alloy also not sensitive to the contamination compared to Bi containing solder (Chen et al., 2003).

Although SAC have many merits, it has higher eutectic temperature, i.e., 216 – 217^{O}C, compared to SnPb solder, which is 34^{O}C lower than SAC system (Handwerker, 2005). However soldering at these temperature may cause some damage to electronic components in one hand and encourage the migration of elemental species from substrate and solder materials leading to dramatic changes in microstructure, void generation, physical and mechanical properties. There is some way to improve the high temperature performance by adding a surface active element to the solder, i.e. rare earth (RE) and transition element (TE) (Chen et al., 2003). The addition of rare earth also can alter the mechanical, physical and metallurgical properties of SAC.

To improve the next generation of solder alloys, there are saveral factors that must be considered:

I. High reliability over a wide application and product design range
II. High process yields with existing processing equipment
III. Compatibility with the fabrication needs for various solder forms
IV. Low toxicity
V. Low cost

1.1 SAC Adding With Rare Earth (RE)

The formation of intermetallic compound (IMC) between the metal substrate and the solder alloy can affect the most suitable Pb-free solder alloys. This is because, if the IMC layer that are formed are too thick at the interface, it can be brittle. This situation will lead to the failure of the connection of the solder and substrate. The thickness of the IMC formed as well as its microstructure greatly influences the growth mechanism of IMC layer at the solder interface. The solder joint that are being formed must be able to provide a good mechanical and wetting properties when they are subjected to isothermal aging. Therefore the metallurgical reactions that occur at the solder joint must be considered, this is because to make sure that a thin IMC layer is formed at the solder joint.

In order to improve the properties of SAC solder such as reducing intermetallic compound (IMC) growth, void generation and reliability, traces of rare earth (RE) and transition element (TE) (Ce, Ca, P, Ge, etc.) need to be added and tested to improve it's properties. Therefore, these works are focuses on the influence of the gallium (Ga) addition to the Sn3.0Ag0.5Cu lead free solder. Ga is classified as low melting temperature rare earth element. The investigated sample is with addition of 0.1-1.0wt%Ga.

The previous research related to this topic was done by Chen et al. (2003), they found that adding the rare earth of Ce-based to the SAC solder affected several properties of this alloy. They stated that increasing of Ce-based content up to 1.0% improved room temperature creep rupture life of SAC solder joint increased 7 times greater than SAC solder. Ce-based addition may alter the electrical properties of the solder alloy and melting temperature. Electrical conductivity of dopped sample was decreased slightly but it still mechanically superior compared to SnPb solder. The result of coefficient of thermal expansion (CTE) showed that SnAgCu(Ce-based) is closer to Cu compared to SnPb. Ce-based alloy did not give an apparent effect to the spreading properties, but when Ce was added up to 1.0%, the spreading area of the solder were decrease due to the mass oxide that was formed on the substrate. While, for the mechanical properties, when addition of Ce added to the solder, it can improve the ultimate tensile strength of the solder and also increased the elongation of the solder up to 30%. SnAgCu0.1Ce showed a superior ductility comparing to the

SAC bulk solder. However, when the Ce contents increased to 1.0%, the ductility of the solder became low. Ce addition alters the microstructure of the solder, when percentage of Ce increased up to 1.0%, the microstructure of the sample led to a refining trend.

Most of the result showed that when the Ce content increased up to 1.0%, the effect of the Ce was obvious. However, not all properties can be improved with the addition of RE element. The optimum content of RE elements in the solder is within 0.05 – 0.5% and it is not advice to add RE elements beyond 1.0% (Chen et al., 2003).

The previous work did not state the specified RE that they used (Chen et al., 2003). They used Sn3.8Ag0.7Cu as the main solder. However, this present work used Ga as an additive to Sn3.0Ag0.5Cu. Figure 1.0 shows the SnAgCu ternary phase diagram, it is labeled with blue and purple rectangles, blue one means this alloys is correspond to iNEMI which this ranges of alloys in their product. The composition of the solder that are used by iNEMI is Sn3.8Ag0.6Cu. Though, the purple represent the solder that are used by JEITA (Handwerker, 2005). The composition of this solder is Sn3.0Ag0.5Cu same as the main solder that was used in this project. The red and green lines are characterizing the region that contains a solid phase of the solder. The red bounded region contains less than 1% solid and green one less than 0.5% solid.

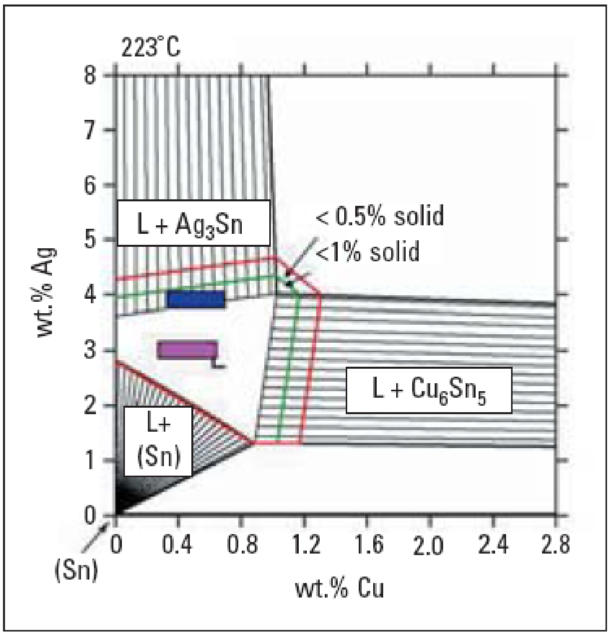

Figure 1.1: SnAgCu ternary system phase diagram (Handwerker, 2005)

1.2 Significant of Study

Investigation of SnAgCu-Ga solder system helps understanding the mechanism of the IMC formation as well as the physical properties. The formations of IMCs affect the strength of the solder thicker lead to brittle connection between solder and substrate. Therefore, the IMC growth should be controlled to a sufficient thickness to avoid the brittle failure.

This work is also devoted to understand the evolution of the IMC morphology during the solid state reaction for the hypoeutectic SnAgCu-Ga solder alloy composition with the time and temperature variable.

1.3 Objectives

I. The aims of these research projects is to investigate effect on addition of trace amount of RE (Ga) addition on SnAgCu system.
II. To evaluate the microstructure evolution of IMC formed at the solder interface and SnAgCu-Ga solder system.
III. To evaluate the wettability of solder alloy and mechanical strength of solder joint.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Nowadays, the international microelectronics industry was trying to produce a new product that is free from Pb usage. This is because, Pb are known as a toxic material and can affect global health and environmental. To ensure that these Pb solders can be replaced, all aspects such as melting point, toxicology, cost, availability, chemical resistance, solderability and also reliability must be considered (Hendwerker, 2005).

To achieve this objective, many research projects were carried out, but recently a lot of interest in SnAgCu based solder is shown, and this type or composition of solder seem to become the most popular. The main reason for choosing SAC solders is because the competitive prices to that of Sn-Pb or other Pb free solder alloys, its mechanical properties are good compared to Pb solder and also its melting temperature (Nurmi et al., 2003).

SAC solder is the most suitable alloy to replacing Pb solder compared to other types of Pb free solder. The fact shows that bismuth (Bi) containing alloys have a good reliability and can be used in surface mount joint, but when the Pb exist in the joint, the reliability of the joint will decreased slightly. Other example for the weakness when using other materials is, indium (In) may tends to lead crack in the solder joint and also zinc (Zn) containing alloys are hard to use in most application because of the oxides, formation of Zn can oxidize very fast in the processing process. When it comes to cost consideration, Bi and In are limited and the supplies are very less, it makes the price very high so it makes it very costly (Hendwerker, 2005; Chen et al., 2003).

To make sure a new development of Pb free solder can be achieved, it is important to access the quality and reliability of the new solder alloys. Not only that, the solder should have suitability for joining and mounting with the electronic component and also it suitable for terminal surface finishing of electronic component.

Thus, Pb free soldering must using some calibration to protect the component from damage because of higher soldering temperature. To make sure that the quality and reliability of Pb free solder joints and the materials and also the solder must suitable for the application (Yamamoto and Tsubone, 2007).

2.2 Solder

The word solder comes from the Middle English word which called *soudur*, in the Old French, it is called *soldure* and *soulder* and from the Latin word, *solidare*, all the words means "to make solid". A solder is referred to a fusible metal alloy that are produced as a product with a melting point or melting range below 450°C (840 °F). In the application it can be melted to join metallic surfaces, especially in the fields of electronics and plumbing, the process is called soldering. Solder purposes not only does to make an electrical connection, but it’s also used to afford a physical connection between the component and it’s supporting printed circuit board (http://en.wikipedia.org/wiki/Solder, 2007).

There is various type of solder that have been used in the electronic industry lately such as Pb solder, hard solder, flux core solder and also Pb free solder. Previously, Pb solder is the most widely used in the electronic industry but when the global aware that Pb can give a bad impact to the health and environmental, Pb free solder has been produced to replace the usage of Pb solder. Nowadays most of the companies use this type of solder to make a connection in the electronic product (http://en.wikipedia.org/wiki/Solder, 2007).

2.2.1 Lead (Pb) Solder

In electronics industries and products, solders are usually using Sn base as a main composition. It normally consists of 60% tin (Sn) and 40% lead (Pb) and is described by a percentage of weight as their main composition of Pb solder alloy. Pb solder are usually produced near the eutectic mixture and it has a lower melting point which is below 190°C [374 °F]. These compositions are commonly designated as Sn60/Pb40 and widely used in the industry. The eutectic ratio of 63/37 corresponds closely to a formation of α and β eutectic compound.

Pb solder was used until 1980s, assuming that the amount of Pb that could leach into water from the solder was negligible. Since even small amounts of Pb have been found to be detrimental to health, Pb in solder was replaced by Cu or Sb, with

Ag often added, and the proportion of Sn also increased (http://en.wikipedia.org/wiki/Solder, 2007).

2.2.2 Hard Solder

For brazing application, the alloys that are generally been used including Cu/Zn or Cu/Ag alloys, these materials have high melting point. The eutectic solder has the lowest melting point amongst solders, which is 360 °C. In the silversmithing or jewelry making industry, there special hard solders are used. It contains a high amount of metal and no Pb is used as a material of solder alloys. These solders have a different level of hardness, known as enameling, and they were categorized as hard, medium and easy. Enamelling solder has a high melting point, this is due to prevent the joint desoldering during heating in the enameling process. The other type of solder are used in decreasing order of hardness during the process of making an item, it also been used to prevent a previously soldered seam or joint desoldering while soldering a new joint. Easy solder often used to repair work piece (http://en.wikipedia.org/wiki/Solder, 2007).

2.2.3 Flux Core Solder

Solder often produced in pre-mixed or used with flux. The purpose of this flux is to remove impurities called oxidized metals at the contact points of the joint. When the oxidized metals are not at the contact point, it can improve the electrical connection. Practicality, solder is often produced in a hollow tube shape like a cylinder and filled with flux in the hollow part. Mainly, cold solder is soft, it can be rolled and packed in a coil shape to make it convenient and compact. There are two types of flux that have been used in the solder coil, first is acid flux. It has been used for metal mending, and the second is rosin flux, that has been used for electronic applications. Due to concerns over environmental and hazardous waste disposal, the electronics industry replaced rosin flux to water-soluble flux, which in return can be removed using deionised water and detergent, as an alternative of hydrocarbon solvents (http://en.wikipedia.org/wiki/Solder, 2007).

2.2.4 Lead-free Solder Alloys

According to the European Union Waste Electrical and Electronic Equipment Directive (WEEE) and Restriction of Hazardous Substances Directive (RoHS), lead had to be eliminated from electronic systems by July 1, 2006 (Gao and takemoto 2006). These actions lead too much interest in Pb-free solders. This new type of solder contains Sn, Cu, Ag, and sometimes Bi, In, Zn, Sb, and other metals in varying amounts in their compositions. The Pb free replacements for conventional Sn60/Pb40 solder have higher melting points than Sn-Pb, thus it required being re-engineering of most components and materials that have been used in the electronic assemblies. SAC solders are used by 2/3 of Japanese manufacturers for reflow and wave soldering process, and by about ¾ companies for hand soldering.

Below are the facts about Pb free solder that have been used in the industry (http://en.wikipedia.org/wiki/Solder, 2007)..

I. SnAg3.0Cu0.5, tin with 3% silver and 0.5% copper, has a melting point of 217-220°C and is predominantly used in Japan. It is the JEITA recommended alloy for wave and reflow soldering, with alternatives SnCu for wave and SnAg and SnZnBi for reflow soldering.

II. SnAg3.5Cu0.7 is another commonly used alloy, with melting point of 217-218°C.

III. SnAg3.5Cu0.9, its melting point is 217°C, determined by NIST to be truly eutectic.

IV. SnAg3.8Cu0.7, its melting point is 217-218°C, preferred by the European IDEALS consortium for reflow soldering process.

V. SnAg3.8Cu0.7Sb0.25 is preferred by the European IDEALS consortium for wave soldering process.

VI. SnAg3.9Cu0.6, its melting point is 217-223°C, is recommended by the US NEMI consortium for reflow soldering.

VII. SnCu0.7, with melting point of 227°C, is a cheap alternative for wave soldering, recommended by the US NEMI consortium.

VIII. SnZn9, with melting point of 199°C, is a cheaper alloy but is prone to corrosion and oxidation.

IX. SnZn8Bi3, with melting point of 191-198°C, it has a good resistance to corrosion and oxidation due to its zinc content.

X. SnSb5, tin with 5% of antimony, is the US plumbing industry standard. Its melting point is 232-240°C. It has a good resistance to thermal fatigue and good shear strength.

XI. SnAg2.5Cu0.8Sb0.5 melts at 217-225°C and is patented by AIM alliance.

XII. SnIn8.0Ag3.5Bi0.5 melts at 197-208°C and is patented by Matsushita/Panasonic.

XIII. SnBi57Ag1 melts at 137-139°C and is patented by Motorola.

XIV. SnBi58 melts at 138°C.

XV. SnIn52 melts at 118°C and is suitable for the cases where low-temperature soldering is needed.

Different elements serve different roles in the solder alloy:

I. Silver provides mechanical strength, but has worse ductility than lead. In absence of lead, it improves resistance to fatigue from thermal cycles.

II. Copper lowers the melting point, improves the resistance to thermal cycle fatigue, and improves wetting properties of the molten solder. It also slows down the rate of dissolution of copper from the board and part leads in the liquid solder.

III. Bismuth significantly lowers the melting point and improves wettability characteristic. In presence of lead and tin, bismuth forms a crystal of Sn16Pb32Bi52 with melting point 95°C, which is diffuses along the grain boundaries and may cause a joint failure at relatively low temperatures. A lead-contaminated high-power part can therefore desolder under load when soldered with a bismuth-containing solder.

IV. Indium can lower the melting point of the alloys and improves its ductility. In presence of lead it forms a ternary compound that undergoes phase change at 114°C.

V. Zinc can lowers the melting point and it can save cost. However it is highly subject to corrosion and oxidation in air, therefore zinc-containing alloys are incompatible for eg. Wave soldering, and zinc-containing solder paste have shorter shelf life than zinc-free.

VI. Antimony is added to increase the strength of the solder without affecting wettability characteristic (http://en.wikipedia.org/wiki/Solder, 2007).

Many different solder compositions have been proposed as a replacement for tin-lead (Sn-Pb) solders, Abtew and Selvaduray have reported a relatively large number of lead-free solder alloys, and are summarized in Table 2.1, with their elemental compositions (Abtew et al., 2000). The solder alloys are binary, ternary and some are even quaternary alloys. It can be noticed that a very large number of these solder alloys are based on tin (Sn), the element tin being the primary or major constituent for these alloys. Two other elements that being major a constituent for the solder alloys are indium (In) and bismuth (Bi). Other alloying elements are zinc (Zn), silver (Ag), antimony (Sb), copper (Cu), magnesium (Mg) and in one case a minor amount of lead (Pb).

Table 2.1: Elemental Composition of Lead and Lead-Free Solder Alloys (Abtew et al., 2000)

Alloy	**Sn**	**In**	**Zn**	**Ag**	**Bi**	**Sb**	**Cu**	**Mg**	**Pb**
Sn-37Pb	63								37
Sn-40Pb	60								40
Bi-26In-17Sn	17	26			57				
Bi-32In		32			68				
Bi-41.7Sn-1.3Zn	41.7		1.3		57				
Bi-41Sn-1Ag	41			1	58				
Bi-41Sn-1Pb	41				58				1
Bi-42Sn	42				58				
Bi-43Sn (eutectic)	43				57				
Bi-45Sn-0.33Ag	45			0.33	54.7				
In-3Ag		97		3					
In-34Bi		66			34				
In-48Sn (eutectic)	48	52							
Sn-1Ag-1Sb	98			1		1			
Sn-1Ag-1Sb-1Zn	97		1	1		1			
Sn-2.5Ag-0.8Cu-0.5Sb	96.2			2.5		0.5	0.8		
Sn-2.8Ag-20In	77.2	20		2.8					
Sn-25Ag-10Sb	65			25		10			
Sn-2Ag	98			2					
Sn-2Ag-0.8Cu-0.6Sb	96.6			2		0.6	0.8		
Sn-2Ag-0.8Cu-6Zn	91.2		6	2			0.8		
Sn-2Ag-0.8Cu-8Zn	89.2		8	2			0.8		
Sn-3.5Ag	96.5			3.5					
Sn-3.5Ag-6Bi	90.5			3.5	6				
Sn-3.5Ag-1Zn	95.5		1	3.5					
Sn-3.5Ag-1Zn-0.5Cu	95		1	3.5			0.5		
Sn-3.6Ag-1.5Cu	94.9			3.6			1.5		
Sn-4.7Ag-1.7Cu	93.6			4.7			1.7		
Sn-4Ag	96			4					
Sn-4Ag-7Sb	89			4		7			
Sn-4Ag-7Sb-1Zn	88		1	4		7			
Sn-10Bi-0.8Cu	89.2				10		0.8		
Sn-10Bi-0.8Cu-1Zn	88.2		1		10		0.8		
Sn-10Bi-5Sb	85				10	5			
Sn-10Bi-5Sb-1Zn	84		1		10	5			
Sn-4.8Bi-3.4Ag	91.8			3.4	4.8				
Sn-42Bi	58				42				
Sn-45Bi-3Sb	52				45	3			
Sn-45Bi-3Sb-1Zn	51		1		45	3			
Sn-56Bi-1Ag	43			1	56				
Sn-57Bi-1.3Zn	41.7		1.3		57				
Sn-5Bi-3.5Ag	91.5			3.5	5				
Sn-7.5Bi-2Ag-0.5Cu	90			2	7.5		0.5		

*All compositions are in %wt.

2.3 Sn-Ag-Cu Solder Alloy

The ternary eutectic reaction for SnAgCu Pb free solder alloy is located at a composition of (3.2 – 4.7) mass % Ag and (0.5 – 1.7) mass % Cu at a temperature of (217.2 ± 0.2)ºC (Moon et al, 2000; Lin and Shih, 2007). However, the eutectic reaction point for SnAgCu is much higher comparer to SnPb etutectic point that is 183ºC. Furthermore, SnAgCu provides more good solderability and good mechanical properties (Lin and Shih, 2007). When using a thermodynamic calculation of the Sn-rich part of the diagram from the three elements in the binary systems and the available ternary data using the CALPHAD method (**CAL**culation of **PHA**se **D**iagrams), the result of the calculation is best fit to the experimental data 3.66 mass % Ag and 0.91 mass % Cu at a temperature of 216.3 ºC. Then when using the assessed ternary thermodynamics, solidification paths and freezing ranges will be presented for various solder compositions.

Fedorov et al., (1960), obtained three isopleths, where ternary eutectic reactions occur at 218 ºC is evident in the Sn-rich corner. But after that, Miller et al. (1994) conduct an experiment using differential thermal analysis, DTA and found that a ternary eutectic reactions occur at 217 ºC and placed its composition at 4.7 mass % Ag, 1.7 mass % Cu. In recent times, Loomans and Fine, (2000) presented the new ternary eutectic composition at 3.5 mass % Ag and 0.9 mass % Cu using thermal analysis data of the signal from the monovariant binary eutectics, L → (Sn) + Cu_6Sn_5 and L → (Sn) + Ag_3Sn.

Recently, from the experiment that are conducted by Moon et al., (2000). The phase diagram of the Sn-rich corner of the Sn-Ag-Cu system has been established using a thermal analysis during heating and cooling and from metallography. The location of the ternary eutectic composition is consistent with that obtained by Loomans and Fine, (2000) and not Miller et al. (1994) The present results indicate the eutectic composition to be (3.57 ± 0.5) mass % Ag and (0.95 ± 0.4) mass % at (217.2 ± 0.2)ºC (Figure 2.1) (Moon et al., 2000).

The microstructures of Sn-Ag-Cu alloys are in accordance with the prediction from the solidification paths. But, Sn-Ag-Cu alloys reveal supercooling prior to the formation of tin (Sn). This supercooling causes a rapidly grown dendritic pattern of the (Sn) phase and an additional growth of the primary intermetallic compounds. Therefore, it may consider that the microstructure between the large intermetallic particles is practically an independent solidification process, having the microstructure of an alloy with composition much more Sn-rich than the original alloy. There are three phases that are usually can be seen on the microstructure of SnAgCu that are Sn as a major phase, Ag_3Sn intermetallic in needle shape or rodlike shape intermetallic and Cu_6Sn_5 in a dot phase or rounded shape (Moon et al., 2000; Wiese and Wolter, 2004).

It has been reported that varying Cu content in the compositon of SnAgCu would lead to different IMC compositions when SnAgCu is soldered to Ni substrate. Figure 2.1 shows the SnAgCu solder alloy phase diagram. In SnAgCu solders, the composition of Cu_6Sn_5 IMC phase in solder matrix is same with the IMC that are formed at the interface of the wet Cu substrate. There is proven that the existence of the Cu_6Sn_5 phase in the morphology of these solder would have effect on the formation and growth behavior as well as roughness evolution of the IMC layer (Yu and Wang, 2007).

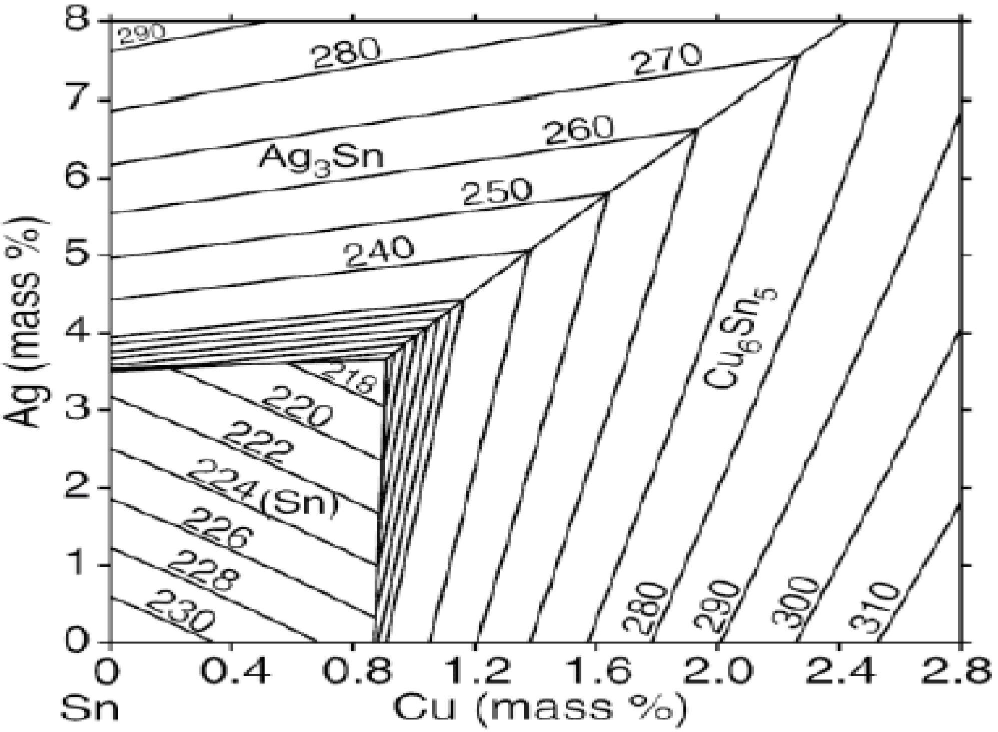

Figure 2.1: Sn-Ag-Cu solder Alloy ternary phase diagram (Moon et al., 2000)

2.3.1. Tin-Silver (Sn-Ag) Solder Alloys

The eutectic composition for the tin-silver (Sn-Ag) binary system occurs at Sn-3.5Ag and its eutectic temperature is 221°C (Figure 2.2). The microstructure consists of Sn and the intermetallic Ag_3Sn in the form of thin platelets (McCormack et al., 1993). McCormack et al. (1995) described the solidified microstructure of the binary eutectic Sn-3.5%Ag as consisting of a β-Sn phase with dendritic globules and inter-dendritic regions with a eutectic dispersion of Ag_3Sn precipitates within a β-Sn matrix. Addition of 1% Zn has been shown to improve the solidification microstructure of this alloy by eliminating the large β-Sn dendritic globules and introducing a finer and a more uniform two-phase distribution throughout the alloy (McCormack et al., 1995). The addition of Zn suppresses the formation of β-Sn dendrites and results in a uniform dispersion of Ag_3Sn. Similar to the Sn-0.07Cu alloy, this solder may be prone to whisker growth due to its high tin composition. However, there is no information available in the literature with regard to whisker growth in Sn-Ag (Abtew et al., 2000).

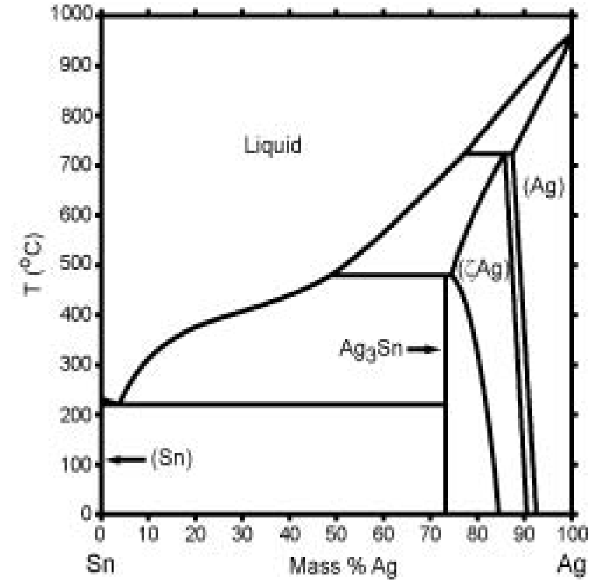

Figure 2.2: Sn-Ag phase diagram (http://www.metallurgy.nist.gov/phase/solder/agsn.html, 2007)

2.3.2 Copper-Tin (Cu-Sn) Solder Alloy

Cu–Sn is widely used in electric and electronic industry for microelectronic applications and as anode materials in specific electrochemical reactions (Correia et al., 2007). The Cu–Sn binary alloys represent a basic sub-system of ternary (Sn–Ag–

Cu, Sn–Bi–Cu) and quaternary (Sn–Ag–Cu–Sb, Sn–Ag–Cu–Zn, Sn–Bi–Cu–Zn) systems that are proposed as an alternative solder materials (Amore et al., 2007).

The eutectic point of the Cu-Sn solder alloys occur at 0.7Cu-sn at the temperature 400°C (Figure 2.3). The microstructural morphology of the Cu-Sn IMC layer at the solder/Cu substrate interface in solder joints is duplex and consists of ŋ-phase Cu_6Sn_5 and ε-phase Cu_3Sn IMC (So and Chan, 1996).

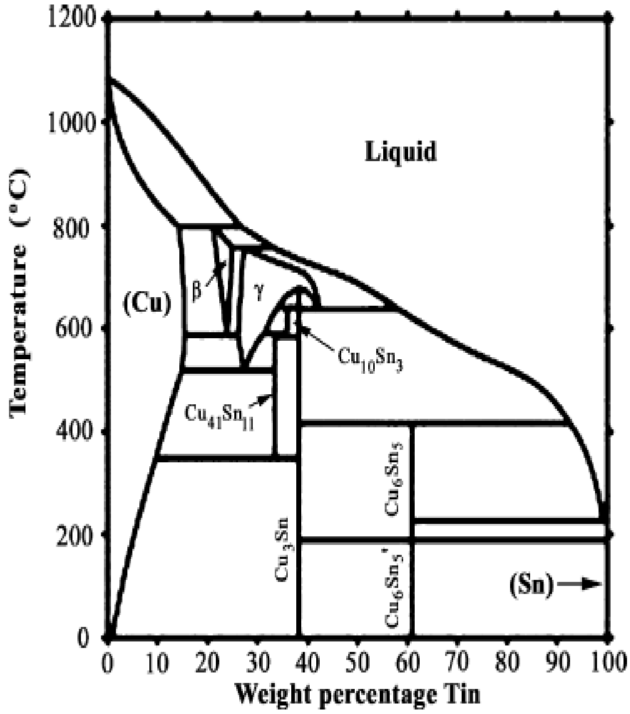

Figure 2.3: Copper-Tin Phase Diagram (Banovic, 2007)

2.3.3 Copper-Silver (Cu-Sn) Solder Alloy

Cu–Ag solder alloys have been found widespread applications in industries nowadays, especially in the electrical elements product, and the silver enriched alloys are usually used as the materials of coins (Zhao et al., 2007).

The eutectic reaction point of Cu-Ag solder alloy is a glass-forming binary alloy system with a positive heat of mixing in both solidus and liquidus states (the heat of mixing is 3 kJ mol^{-1} for the composition of Ag60Cu40). The remaining liquid has reached the composition of the eutectic alloy that is 28.1% Cu in 71.9% Ag at 779^{O}C (Figure 2.4). At this temperature the primary α crystal has grown as large as they can, no more crystals can form. The entire are remaining in liquid freeze condition through eutectic transformation. When the primary α crystals have grown dendritically, the eutectic solid or eutectic micro constituent will fill in the spaces between α dendrite arms to complete the solid grain.

Ag and Cu have a large miscibility gap and relative atomic size difference is 12%. At steady state, some reaction occurs at which the solubility of the elements into the other element. The maximum solubility of Cu in Ag is 8.27 at.% Cu at the eutectic temperature of 779.1^{O}C, and Ag in Cu is 7.47 at.%. Solid solution, amorphous or nanocrystalline of Cu-Ag solder alloys can be produced using some different methods, including splat quenching, vacuum evaporation, ion beam mixing, solid-state reaction in metal multilayers and mechanical alloying (Chen and Zuo, 2007).

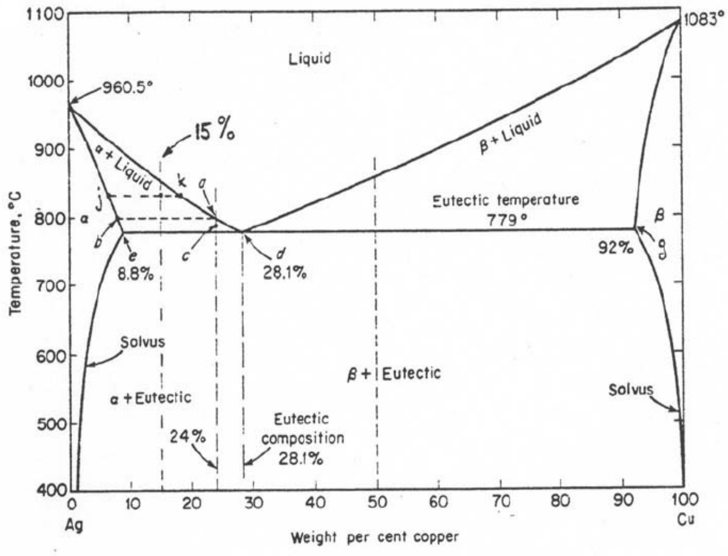

Figure 2.4: Copper-Silver phase diagram (SIMSMC, 2002)

2.3.4 Tin-Gallium (Sn-Ga) Solder Alloy

The phase diagram of the Ga–Sn system is represented in Figure 2.5. It shows that a eutectic reaction occur at 8.5 at.% Sn-Ga and at the temperature of 20.5^{O}C. As can be seen, above 232^{O}C the Ga–Sn alloys are in liquid state, which makes it easy to study their temperature-dependent properties in a wide temperature range (Jia et al., 2007).

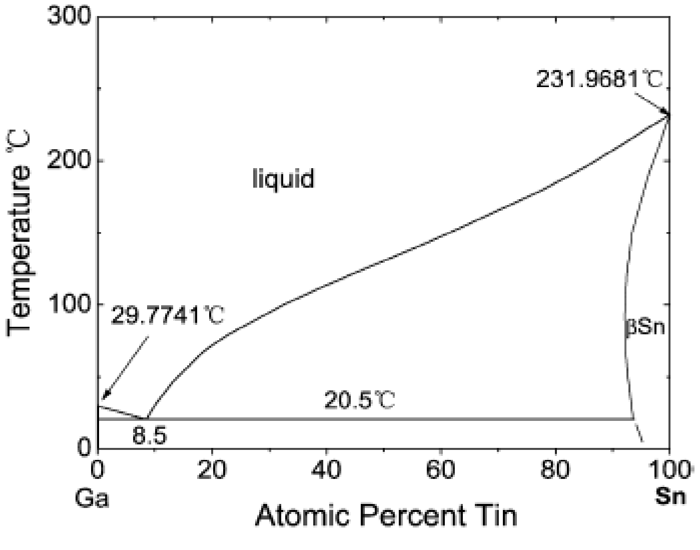

Figure 2.5: Tin-Gallium Phase Diagram (Jia et al., 2007)

2.3.5 Silver-Gallium (Ag-Cu) Solder Alloy

The crystal structures of the intermetallic phases in the Ag–Ga system have been studied since the 1930s. Ag–Ga phase of about 30 at.% Ga shows a high temperature polymorphism, and it is conventionally named the ζ phase below 440°C and the ζ phase above 440°C. The structure of the ζ phase was studied and the result is to be $P62m$ with lattice parameters of $a = 7.7710$ and $c = 2.8788$A°. These structure shows that Ag atoms are in the 3g and 3f sites and Ga atoms is the 1b and 2c sites in the unit cell of the ζ phase with a chemical formula of Ag_2Ga. However, the Ag_2Ga phase was identified to have a homogeneous range of compositions. The homogeneous range of compositions resulted from the partial substitution of Ag atoms in the Ga sites.

New intermetallic solid solution compound Ag_2Ga_3 was found and it is peritectic. It's melted at 326°C in the Ga-rich region (Zhang et al., 2007). There are two intermediate phases that exist in the Ag–Ga solder alloys system. The first one is called high temperature phase or Mg type that forms peritectically at 611°C and the second one is low temperature phase or Ag_2Ga type, it forms at 425°C. Compounds of the Ag_2Ga_3 composition occur at peritectic reaction at 611°C. There's also other reaction which is eutectoid reaction at 381°C (Figure 2.6) (Gumeniuk et al., 2005).