SCHOOL OF MATERIALS AND MINERAL RESOUURCES ENGINEERING

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SOLDERING CHARACTERISTICS AND CORROSION BEHAVIOUR OF INDIUM ADDED TO SAC305 SOLDER ALLOY

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Soldering characteristics and corrosion behaviour of indium added to SAC305 solder alloy**". I also declare that it has not been submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF SYMBOLS

α	Alpha
β	Beta
θ	Theta
γ	Gamma
d_0	Initial thickness of IMC layer
D	Thickness of IMC layer
λ	Wavelength

LIST OF ABBREVIATIONS

Ag	Silver
Al	Aluminium
As	Arsenic
Bi	Bismuth
Cd	Cadmium
Cl	Chloride
Cr	Chromium
Cu	Copper
DSC	Differential Scanning Calorimetry
EPA	Environmental Protection Agency
EC	European Commission
EU	European Union
EDX	Energy dispersive X-ray
Fe	Iron
ICDD	International Centre for Diffraction Data
In	Indium
IMCs	Intermetallic compounds
Na	Sodium

Ni	Nickel
Pb	Lead
PTH	Pin through hole
PCB	Printed circuit board
RoHS	European Reduction of Hazardous Substances Directive
SCE	Standard Calomel Electrode
Si	Silica
SiC	Silicon carbide
Sn	Tin
Sb	Antimony
SEM	Scanning Electron Microscope
SMT	Surface mount technology
WEE	Waste Electrical and Electronic Equipment Directive
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
Zn	Zinc

SIFAT PEMATERIAN DAN KELAKUAN KAKISAN DENGAN PENAMBAHAN INDIUM KEPADA ALOI PATERI SAC305

ABSTRAK

Unsur aloi elemen dipilih untuk mengkaji kesan indium kepada rintangan kakisan Sn-Ag-Cu aloi pateri. Dalam projek ini, komposisi indium berbeza-beza antara 1-4 wt. % dan dimasukkan ke dalam solder Sn-3.0Ag-0.5Cu. Kesan penambahan indium pada sifat leleh, struktur mikro, rintangan kakisan, kebolehbaikkan aloi pateri telah dikaji. Untuk sifat terma, dapat ditentukan bahawa penambahan indium menurunkan titik lebur SAC305 aloi solder sebagai suhu lebur berkurang dari 229.55°C menjadi 219.91°C. Untuk analisis morfologi sampel aloi pateri, boleh ditentukan bahawa penambahan 1 wt. % telah menghasilkan saiz mikrostruktur yang lebih kecil dan seragam.Selain daripada saiz mikrostruktur yang kecil, penambahan 1 wt. % indium juga telah menghasilkan kawasan penyebaran yang lebih besar bagi aloi pateri dengan 6.18 mm dan sudut pembasahan yang lebih rendah dengan 14.59° yang menunjukkan kelembapan aloi pateri yang baik. Di samping itu, berdasarkan data yang diambil dari analisa kadar polarisasi hakisan yang diplot, dapat dilihat bahawa penambahan 1 wt% indium kepada aloi pateri memberi kadar kakisan terendah dan ketahanan kakisan yang tinggi berbanding dengan aloi solder yang lain. Oleh itu, dapat disimpulkan bahawa penambahan 1 wt. % indium sudah mencukupi untuk mencapai sifat yang diingini seperti mikros dan mikrostruktur yang diedarkan secara seragam, kebolehkerjaan yang baik, sifat termal yang rendah dan kakisan yang baik untuk aloi solder SAC305.

SOLDERING CHARACTERISTICS AND CORROSION BEHAVIOUR WITH INDIUM ADDITION TO SAC305 SOLDER ALLOY

ABSTRACT

Alloying element indium is chosen in order to study the effects of indium to corrosion resistance of Sn-Ag-Cu solder alloy. In this project, the composition of indium was varied ranging from 1-4 wt. % and were added into Sn–3.0Ag-0.5Cu solder. The effects of indium addition on melting property, microstructure, corrosion resistance, wettability of the solder alloys were studied. For thermal properties, it can be determined that more addition of indium lowered the melting point of SAC305 solder alloy as the melting temperature is reduced from 229.55 °C to 219.91 °C. For morphological analysis of bulk sample of solder alloy, it can be determined that 1 wt. % of In addition to the solder alloy composition is already adequate as fine grain and uniformly distributed microstructure can be obtained. Fine grain size acquired due to 1 wt. % of In addition to solder alloy lead to greater spreading area with 6.18 mm and lower wetting angle with 14.59° which resulted in good wettability of solder alloy. In addition, based on the data acquired from plotted polarization curve corrosion rate analysis, it can be determined that the addition of 1 wt.% of In gives the lowest corrosion rate and high corrosion resistance compared to other prepared of solder alloys. Thus, it can be concluded that a mere amount of 1 wt. % of In addition to the solder alloy composition is already adequate in order to achieve desired properties like fine grain and uniformly distributed microstructure, good wettability, low thermal properties and good corrosion for SAC305 solder alloy.

CHAPTER 1

INTRODUCTION

1.1 Research background

In 1992, the world witnessed the ground breaking transition of lead-free technology being introduced into the electronics industry. The person who was responsible of setting up the basis of this foundation is none other than Albert Arnold Gore, an American senator who submitted an administration bill, of which is also known as The Reid Bill for consideration by the USA congress. Attached to the bill is a huge list, of which hosted the list of lead-containing material as well as the products formed by the materials, including the materials that are used during the production of electronics products. The Bill was further strengthened by the following lead tax implementation that found its way in 1993, of which every pound of lead is subjected to tax charging, given that it is found in either imported or domestic goods that were produced within the vicinity of the nation. On July, 1st 2006, the use of lead in producing electronic products was officially banned in European countries. To back up the decision of restraining the use of lead in electronic products which leads to the transition of lead-free technology in electronics industry, few main reasons were given, one of which includes the hazardous impacts that were being imposed on humans' health and environment.

Due to the inconveniences caused by the usage of lead in electronics, the manufacturing of lead free electronics has successfully climb its way to be made globally famous. Whilst new materials are currently being proposed as potential substitutes to replace the usage of the conventional lead-based alloys for solder manufacturing, the usage of the said alloy is no longer considered relevant. In order to further understand their micro structure, in terms of its stability as well as their reliability an extensive investigation has been conducted to study the said property.

Consortia, industry alliances as well as individual companies have taken it upon themselves to conduct huge amount of investigations, of which eventually open the path for the industry to view the prospects of the ternary eutectic Sn-Ag-Cu (SAC) solder alloys to be considered as the main replacement for the lead-bearing solder in terms of the reflow application.

In choosing a lead-free solder as replacement for Sn-Pb eutectic, the first things to start at is the melting behaviour, the lead free solder candidates must have solidus or liquidus temperature that is equivalent or close to that of tin–lead eutectic solders which is 183^{O}C. For mechanical properties wise, candidates must either have equal or better mechanical properties in terms of shear and tensile strength compared to tin-lead eutectic solder. Lead free solder must also have equal or better physical properties in terms of electrical and thermal conductivity, thermal expansion coefficient and wettability. Besides that, lead free solder candidates must also have equal or better corrosion resistance, ductility, and candidates must have good solderability (Schlesinger and Paunovic, 2010).

In all ternary solder alloys, eutectic and near-eutectic Sn-Ag-Cu (SAC) alloys seem to be the most promising alloy systems to replace traditional Sn-Pb alloys. Their thermo-mechanical properties are better than traditional Sn-Pb solders. The eutectic temperature of SAC alloy is 34°C higher than that of the eutectic Sn-Pb solders which answers why SAC alloys has better thermo-mechanical properties and how they can function at higher temperatures. SAC solders were reported to have fine and stable microstructures and higher shear strength compared to Sn-Pb alloys (Ye.et.al, 2000) during solidification, depending on the cooling rate, various phases may form. Reaching fully eutectic microstructure is usually not possible since the eutectic point will deviate due to faster cooling rates applied during solidification. Because of these deviations; β-Sn, Ag_3Sn and Cu_6Sn_5 may form at various amounts in both eutectic and near-eutectic SAC solders.

According to Manko (2001) both the wetting ability as well as the formation of intermetallic compound of base metal of solders are deemed as the most essential property in order to ensure that the establishment of good bonding property is to be proven a success. Solders are known to perform three functions, mainly comprising the electrical, mechanical and thermal connection.

Soldering material or soldering interconnections acts as the bridge or advocate between the connection between the electrical connection in ships and printed circuit boards which are made used by a range of solder alloys. It generically lists alloys of tin (Sn) and one or more of the following elements: Lead (Pb), Silver (Ag), Bismuth (Bi), Indium (In), Antimony (Sb), Cadmium (Cd), Zinc (Zn), Copper (Cu) and Nickel (Ni). In interconnected paths, the mechanical supports are being provided by the said material which is the solder. Instantaneously, solders must also be able to have the ability to disperse the heat produced when the component is of use. According to Shangguan (2005), it is crucial for the heat to dissipate in order to ensure the efficiency as well to maximize the performance of the electrical device.

Different alloying elements that are added serves different roles in solder alloy. Silver functions as the provider for mechanical strength, when compared to lead its performance is worse in terms of ductility. Resistance to thermal cycles fatigue is improved and made better when there is an absence in the existence of lead. As for copper, the melting point is increased, resistance to thermal cycle fatigue is enhanced, and the wetting properties of the molten solder is improved. The rate of dissolution of copper from the board and part leads in the liquid solder is also slowed down. The presence of bismuth within the solder alloy helps to lower the melting point as well improves the wettability properties drastically. If there is an adequate presence of lead and tin in the solder alloy, bismuth will start to form crystals of $Sn_16Pb_{32}Bi_{52}$ at melting point of mere 95°C. $Sn_16Pb_{32}Bi_{52}$ will diffuse along the grain boundaries and may cause a joint failure at relatively low temperatures. A high-power part pre-tinned with an alloy of lead can therefore desolder under load when soldered with a bismuth-containing solder.

On the other hand, indium lowers the melting point as well as improving the ductility. A ternary compound that undergoes phase change at 114°C will be formed when lead is present. Zinc also lowers the melting point and is considered to be low-cost. However, it is highly susceptible to corrosion and oxidation in air, therefore zinc-containing alloys are unsuitable for the use to achieve several purposes, i.e. wave soldering, and zinc-containing solder pastes have shorter shelf life than zinc-free. The addition of antimony is done in order to increase the strength without affecting the wettability.

1.2 Problem statement

Pb-Sn solders were commonly used in electronic packaging due to their excellent performances based on their good electrical, mechanical, and thermal properties. However, with the rising concerns about lead pollution of the environment and its toxic effects, the use of lead has been banned in many parts of the world. For the substitution of Pb from the electronics industry, many types of solder alloy have been suggested as alternatives. Sn-based solder alloys with some alloying elements such as Cu, Ag, In, Bi, and Zn have been tried by several researchers. Among them, eutectic Sn-Ag alloy for its good mechanical properties, high reliability, and lack of patent coverage has been most widely recommended. Recent investigation suggested that the presence of alloying elements in the solder alloy has a marked effect on the properties and performance of Sn-Ag-Cu solder joints.

The addition of a fourth alloying element, such as Mn, Ce, Ni, Ti, or Bi, to low-Ag content Sn-Ag-Cu alloys provides a marked improvement in microstructural modifications and mechanical properties, and for this reason, these alloys have attracted considerable attention. The net result of these minor alloying additions includes the following: (1) alteration of the bulk alloy microstructure and mechanical properties and (2) control of the interfacial intermetallic layer(s) (Shnawah et. al, 2012). However, only a few information available on the corrosion behaviour on SAC eutectic alloy.

Corrosion could be a serious problem causing the failure of electronic devices. Many times the components get exposed to different corrosive chemical and physical environments that consist of different species such as chlorides, sulfates, sodium, ammonium, potassium, magnesium, and calcium ions. In order to increase the mechanical properties and reliability of flip chip package, underfill materials are used to fill the gap between the chip and printed circuit board. Furthermore, the solder joints are protected from working environments. However, they continue to be corroded due to the absorbed moisture and corrosive particles. Some electronic packages, such as in wire bonding, solders are exposed directly to corrosion media like air, moisture, and oceanic environments. To increase the reliability, solder materials must be resistant to such corrosive environment. In addition, during assembly, halide-containing fluxes also degrade the corrosion resistance of the interconnects; hence these fluxes should be avoided. Solder provides electrical, thermal, and mechanical continuity in assemblies (Abtew and Selvaduray, 2000). To achieve these functions, the best solder alloys are to be carefully chosen to deal with surface finishing materials and fluxes.

Rosalbino et al. (2009) investigated the corrosion behaviour of Sn-Pb, Sn-Ag-In and Sn-Ag-Bi alloys and reported poor corrosion behaviour of Sn-Ag-In and Sn-Ag-Bi alloys as compared to that of Sn-Pb. Although additions of Bi and In depressed the melting temperature of Sn-Ag-based lead-free solder alloys (Yeh, 2003) and Bi into Sn-Ag system solder improves the wetting/spreading behaviour of the solder (Wu et al.,2000), they cannot be a good choice of solder alloy to be used in corrosive environment. Again, corrosion resistance of the solder strongly depends on its microstructural characteristics. Osorio et al. (2011) reported the results of an electrochemical corrosion study of Sn-Ag solder alloy in 0.5 M NaCl solution. In this study, better corrosion resistance was exhibited for fine dendritic arrays and a mixture of spheroids and fiber-like Ag3Sn particles. According to Wang et al. (2012), poor corrosion resistance was exhibited by slowly (furnace cooled) cooled SAC 305 solder due to large Ag3Sn particles. Therefore, concentration of different alloying element can also play an important role in improving both corrosion resistance properties. Studies on the effect of Cu and Ag on the corrosion behaviour of Sn-Ag based solder alloy are scarce. Rosalbino et al. (2009) investigated corrosion behaviour of Sn-3Ag-*x*Cu alloys in 0.1M NaCl solution and compared to that of Sn-Pb solder. The results showed enhanced corrosion resistance with the increase of Cu content.

In this study, alloying element indium is chosen to study the effects of indium on corrosion resistance to Sn-Ag-Cu solder alloy. Indium is well known as a beneficial element to solders, which can effectively reduce melting temperature and improve the wettability of solder. Therefore, indium with varies composition ranging from 1-4 wt.% were added into Sn–3.0Ag-0.5Cu solder, and the effects of indium addition on melting property, microstructure, corrosion resistance, wettability of the solder alloys were investigated.

1.3 Objectives

The objectives of this research are as follow:

i) To prepare different types of Sn-3.0Ag-0.5Cu lead free solder alloys with indium addition ranging from 1-4 wt. %.

ii) To study the effect of alloying element indium on melting point, wettability and microstructure of prepared solder alloy.

iii) To determine the corrosion behaviour of prepared solder alloys

1.4 Project overview

This thesis is further divided into five chapters which comprises the introduction part, literature review, experiment procedures, results and discussions and conclusion and recommendations part. In Chapter 1, readers will be exposed to the introduction, the background information, as well as the aim and scope of this thesis. Next, in the literature review, the findings of the general research that was done on this topic will be presented, focusing the details on the past and current studies that was done by other researchers; as well as insights on the solder and soldering technologies. Chapter 3 will further discuss and provide brief information regarding to the microstructural arrangement of the alloy system in interest, which is the Sn–Ag-Cu solder alloy as well as its performance tests that was conducted, being presented in detail.

CHAPTER 2

LITERATURE REVIEW

2.1 Solder and soldering technologies

Solder, is derived from an Old French word, *soudure* which originate from a Latin word *solidare*. This term bears the meaning of being fastened together or coalesced. According to Humpston and Jacobson (2004) a solder can be defined as a fusible metal alloy possessing a melting point within the range of below 450°C. Melted, solder acts as a filler material that is being used to join metallic surfaces. Being extensively used in the electronics and plumbing fields, this process is often referred to as soldering. Not only does it serve as an electrical connection, it also provides a physical connection between both the component as well as the printed circuit board (Shangguan, 2005).

Due to its joining properties, solder alloy also primarily serves for electronic circuits in terms of electrical, thermal and mechanical support. In order to be deemed as reliable and applicable for electronic assembles, solder is ought to meet up to a number of requirements. One of which conforms the most basic requirements of solder alloys can be generally defined by its wettability and ability to form intermetallic compounds at the interface of both nickel, copper as well as other metallic substrates. In which, in Table 2.1 are the listed of the basic properties of solder alloys.

Table 2.1: Important properties of solder alloys (Abtew and Selvaduray, 2000)

Manufacturing Related Properties	**Reliability and Performance Related Properties**
Melting/liquidus temperature	Electrical conductivity
Wettability (of copper)	Thermal conductivity
Cost	Coefficient of thermal expansion
Environmental friendliness	Shear properties
Availability and number of suppliers	Tensile properties

Manufacturing using current processes	Creep properties
Ability to be fabricated as balls	Fatigue properties
Copper pick up	Corrosion and oxidation resistance
Recyclability	Intermetallic compound formation
Ability to be made into paste	

It is known that electronic devices are being used at a huge range of varying temperatures. Ranges of common temperatures for specific products are given in Table 2.2. In Table 2.1, the validity of the properties of reliability and performance at random temperatures is compulsory. Hence, the existing solder alloys that are generally used in the production of these electronic devices are ought to be able to meet all the required reliability demands.

Table 2.2: Temperature ranges of electronic products (Abtew and Selvaduray, 2000)

Temperature Range (°C)	**Devices**
-40 to 100	Most consumer electronics (TV,PC,freezer,washing machine,etc)
-40 to 125	Reliable consumer electronics (mobile phone,notebook,etc)
-40 to 150	Vehicles (especially in engine room and factory equipment)

2.2 Soldering materials

The soldering interconnections are made used by a range of solder alloys. It generically lists alloys of tin (Sn) and one or more of the following elements: Lead (Pb), Silver (Ag), Bismuth (Bi), Indium (In), Antimony (Sb), Cadmium (Cd), Zinc (Zn), Copper (Cu) and Nickel (Ni). Different elements serve different roles in the solder alloy.

While silver functions as the provider for mechanical strength, when compared to lead its performance is worse in terms of ductility. Resistance to thermal cycles fatigue is improved and made better when there is an absence in the existence of lead. As for copper, the melting point is increased, resistance to thermal cycle fatigue is enhanced, and the wetting properties of the molten solder is improved. The rate of dissolution of copper from the board and part leads in the liquid solder is also slowed down. The presence of bismuth within the solder alloy helps to lower the melting point as well improves the wettability properties drastically. If there is an adequate presence of lead and tin in the solder alloy, bismuth will start to form crystals of $Sn_{1}6Pb_{32}Bi_{52}$ at melting point of mere 95°C. $Sn_{1}6Pb_{32}Bi_{52}$ will diffuse along the grain boundaries and may cause a joint failure at relatively low temperatures. A high-power part pre-tinned with an alloy of lead can therefore desolder under load when soldered with a bismuth-containing solder.

On the other hand, indium lowers the melting point as well as improving the ductility. A ternary compound that undergoes phase change at 114°C will be formed when lead is present. Zinc also lowers the melting point and is considered to be low-cost. However, it is highly susceptible to corrosion and oxidation in air, therefore zinc-containing alloys are unsuitable for the use to achieve several purposes, i.e. wave soldering, and zinc-containing solder pastes have shorter shelf life than zinc-free. The addition of antimony is done in order to increase the strength without affecting the wettability.

In the event of identical solidus and liquidus temperature of a solder alloy, it is referred to as eutectic solder alloy while the opposite situation calls for a term of non-eutectic solder alloy. There are three main forms of which solder alloys existed commercially, which includes the solid, paste and powder forms.

2.2.1 Lead solder and related issues

Lead and its contents are deemed as one of the top most hazardous chemicals that can impose serious dangers towards human lives. This is according to the Environmental Protection Agency (EPA) that has listed lead as one of the elements that resides within the list of world’s 17 top most dangerous chemicals. Lead or Pb, forms a bond chemically with the essential protein that can be found inside the humans’ bodies and thus altering its biological functions. As the level of lead inside the mainstream elevated and exceeds the permitted levels or the normal concentration allowed for it to be in our bodies, it would eventually lead to a serious case of lead poisoning.

Among the effects of lead poisoning that were recorded includes vomiting, diarrhoea, convulsions, loss of appetite, abdominal pain and constipation. While the more serious effects ranges from the damage of vital organs such as kidney, liver and the brain. The build-up of lead inside the body is also a cause of concern of osteoporosis, which is a condition that causes the bones to be brittle. However, the most disconcerting part of excessive exposure to Pb is the fact that it has the ability to cause mental retardation, behavioural disorders, anaemia, high blood pressure as well as being recorded as one of the culprits behind stillborn occurrences.

Among the accidental cases involving lead poisoning that can be used to illustrate how deadly this occurrence is towards the humans’ health happened on October 5 in 2010. Around 400 children died in Nigeria due to lead poisoning, Zamafara describes lead poisoning as epidemic. While in China, more than 1000 children from 10 different villages were discovered to have excessive lead content inside their bloodstream. This may be caused by the fact that their residence is near the Yuguang Gold and Lead smelter plant. After the incident, a number of 15000 people shifted from that area and the Government eventually stopped the production of lead from 32 plants.

The long term effects of poisonous elements used in electronic products has managed to capture the attention of European Commission (EC) which resulted in the establishment of a directive regarding Restriction of Certain Hazardous Substances (RoHS). This directive which has been implemented in all the 25 European Union member states since 1st July 2006 listed a number of hazardous substances that is to be banned of use in the production of electronic products in European countries. This includes Lead (Pb), Cadmium (Cd), Mercury (Hg), Hexavalent Chromium (Cr6+), polybrominated biphenyl (PBB) and polybrominated biphenyl ether (PBDE) flame retardants. While in Japan, though there is no official law that prohibits the usage of lead in consumer products, there is a law which involves the prohibited disposal of lead in landfills and other waste disposal yards.

2.2.2 General criteria to select solder alloy

There are some strict performance requirements for solder alloys used in microelectronics. Generally, solder alloy must meet the expected levels of electrical and mechanical performance, and must also have the desired melting temperature. It must adequately wet common PCB surface, so that it forms inspectable solder joints (Abtew and Selvaduray, 2000). When trying to identify an alternative to Sn-Pb eutectic solders, it is important to ensure that the properties of the replacement solder are comparable to or superior than Sn-Pb solders (Manko, 2001).

Some considerations that are needed when replacing Sn-Pb solder with lead-free solder are the properties of lead-free solder. In choosing a lead-free solder as replacement for Sn-Pb eutectic, the first things to start at is the melting behaviour, the lead free solder candidates must have solidus or liquidus temperature that is equivalent or close to that of tin–lead eutectic solders which is 183°C. For mechanical properties wise, candidates must either have equal or better mechanical properties in terms of shear and tensile strength compared to tin-lead eutectic solder. Lead free solder must also have equal or better physical properties in terms of electrical and thermal conductivity, thermal expansion coefficient and wettability. Besides that, lead free solder candidates must also have equal or better corrosion resistance, ductility, and candidates must have good solderability (Schlesinger and Paunovic, 2010).

Lastly, a lead-free alloy also needs to be environmentally friendly (Abtew and Selvaduray, 2000). Reliability of a solder alloy in packaging is mainly dependent to the coefficient of thermal expansion, elastic modulus, yield strength, shear strength, fatigue and creep behaviour of the alloy. Properties like yield strength, Young's modulus, creep, fatigue, coefficient of thermal expansion, electrical conductivity etc are defined as the mechanical and electrical properties (Manko, 2001). For solder materials, wettability plays an important role for the formation of solder to base metal contact. Wettability is defined as the tendency of a liquid to spread over a solid substrate. In general, if the wetting angle lies between 0° to 90° then proper wetting will take place over the substrate. But in soldering process this angle must be kept below 55°. According to theory of thermodynamics, proper wetting will only take place if there is a net decrease in total free energy at the interface. Wettability is generally affected by the viscosity of molten solder and also the chemical reaction at the interface. Wettability of solder also depend on the surface tension of the molten solder, which is defined as the amount of energy required to spread the liquid surface area over the solid substrate isothermally. Surface tension decides the degree of wetting, strength and reliability of solder joint (Manko, 2001).

2.2.3 Lead free solder

Leaded solders are used in electronic assembly industry for joining purpose, because of their advantages like low melting temperature, good wettability, strength, ductility, reliability, product performance and cost. But due to its hazardous effect towards human health and environment, material science community such as researchers and manufactures had developed new alternatives to replace the Sn-Pb solders. There are many solders that available in the market but does not full-fill the required properties, therefore projects are still running to get solution of this problem. Some of the projects for development of the lead-free solder are like TEIDA project in Japan, NCSM project in United States of America and IDEALS project in Europe (Puttlitz and Stalter, 2004). The alloying elements used are copper, zinc, indium, bismuth, nickel, antimony, silver and etc, instead of lead. Lead free solder can be categorized into three systems which are binary, ternary and quaternary. These are few binary lead free solder that are already developed such as Sn-Cu, Sn-Zn, Sn-Ag, Sn-Bi and Sn-Sb. For further improvement of properties, alloying elements may add into these binary alloy systems and thus producing ternary and quaternary system lead free solder (Zhang, 2010).

Compared to Sn-Pb solder, most of the lead-free solder are way more expensive but with inferior performance. Cost of these lead-free solders is about two to three times greater than the Sn-Pb solder due to the expensive alloying elements such as silver in Sn-Cu-Ag solder alloy. In contrast, the cost of Sn-Cu solder alloy is only 1.3 times higher than the traditional Sn-Pb solder, due to the absence of expensive metal, and this make it a more suitable candidate for practical production of consumer products (Zheng et al., 2011). Addition of rare earth elements like antimony and indium in lead free solder enhance the physical and mechanical properties (Zhang et al., 2009). Addition of silver in lead-free solder also increases these properties (El-Daly and Hammad, 2012).

However, silver and rare earth alloying elements are more expensive and not easily available.

2.3 Sn-Ag-Cu solder alloy

In all ternary solder alloys, eutectic and near-eutectic Sn-Ag-Cu (SAC) alloys seem to be the most promising alloy systems to replace traditional Sn-Pb alloys. They were first discovered in 1996 by a research group at Ames Laboratory in USA. SAC alloys have very high thermal shock resistance and mechanical vibration resistance and they can operate at temperatures up to 150°C. Their thermo-mechanical properties are better than traditional Sn-Pb solders. The calculated ternary eutectic composition is Sn-3.7Ag-0.9Cu (wt. %) as shown in Figure 2.1. The ternary eutectic composition was experimentally determined as Sn-3.5Ag-0.9Cu (wt. %) and the eutectic temperature is 217°C. Eutectic phases are Sn, Ag_3Sn and Cu_6Sn_5.

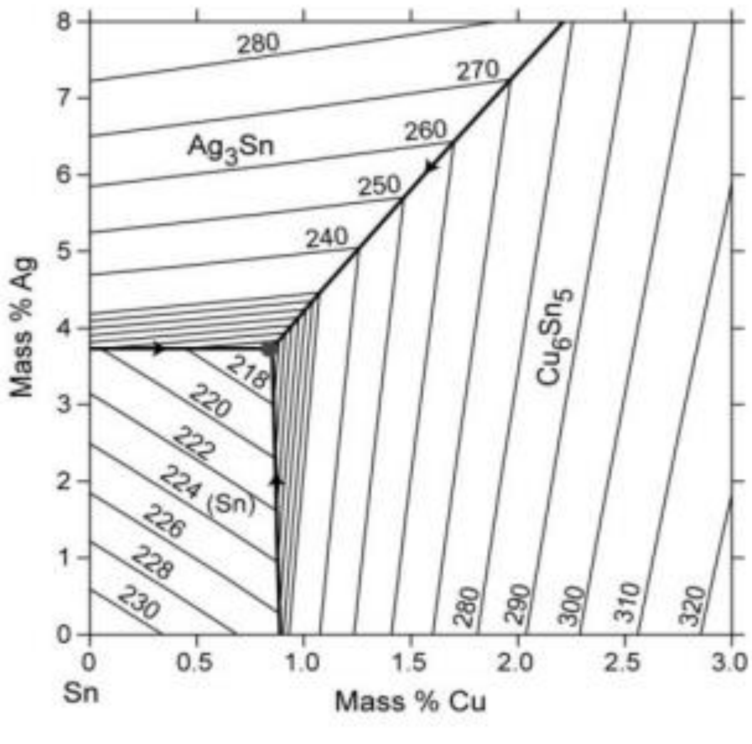

Figure 2.1: Sn-rich part of Sn-Ag-Cu ternary system (Moon et.al, 2000)

The eutectic temperature of SAC alloy is 34°C higher than that of the eutectic Sn-Pb solders. This explains why SAC alloys has better thermo-mechanical properties and how they can operate at higher temperatures. SAC solders were reported to have fine and stable microstructures and higher shear strength compared to Sn-Pb alloys (Ye.et.al, 2000) during solidification, depending on the cooling rate, various phases may form. Reaching fully eutectic microstructure is usually not possible since the eutectic point will deviate due to faster cooling rates applied during solidification. Because of these deviations; β-Sn, Ag_3Sn and Cu_6Sn_5 may form at various amounts in both eutectic and near-eutectic SAC solders. Currently, there are two SAC solder compositions that were indicated for the electronics manufacturers by two different organizations. National Electronics Manufacturing Initiative (NEMI) recommends Sn-3.9Ag-0.6Cu alloy and Japan Electronics and Information Technology Industries Association (JEITA) recommends Sn-3.0Ag-0.5Cu alloy. These alloys lie in the near-eutectic composition region, where, near-eutectic SAC alloy compositions fall into the composition range between Sn-3.8Ag-0.7Cu and Sn-4.0Ag-0.5 Cu. Although SAC compositions are widely used in electronics industry and recommended by NEMI and JEITA, several problems with these alloys exist. The performance and reliability related properties of SAC solders and the existing problems will be explained in the following chapters.

2.4 Soldering methods

There are two main classifications of soldering methods in use today, which are mechanical or non-electrical which use acidic flux primarily, and electrical which use rosin flux primarily (Hoban and Lunt, 1997). While advances in transistors, resistors, capacitors, diodes, and especially integrated circuits have revolutionized the world, these devices are of very little value as individual components. For these devices to be function, they must be electrically connected to each other and to mechanical devices. Majority of these electrical connections are made by soldering. Not only does solder make electrical connections, it is also used to provide a physical connection between the component and its supporting printed circuit board.

Currently, mass-production PCBs are mostly wave soldered or reflow soldered. In wave soldering, parts are temporarily adhered to the PCB with small dabs of adhesive, and then these PCBs will pass over a small fountain of molten solder. Reflow soldering is a somewhat newer process in which a solder paste, a sticky mixture of powdered solder and flux is used to stick the components to their attachment pads, after which the assembly is heated by an infrared lamp or by passing it through a carefully-controlled oven. Since different components can be best assembled by different techniques, it is common to use two or more processes for a given PCB; the surface mounted parts may be reflow soldered, followed by a wave soldering process for the through-hole mounted components, with some of the bulkier parts hand-soldered on last. In both Figure 2.2 and Figure 2.3, shown are the illustrations of the two basic types of connection in joining together the electronic components to PCBs which is mainly the pin through hole (PTH) as well as the Surface Mount Technology (SMT).

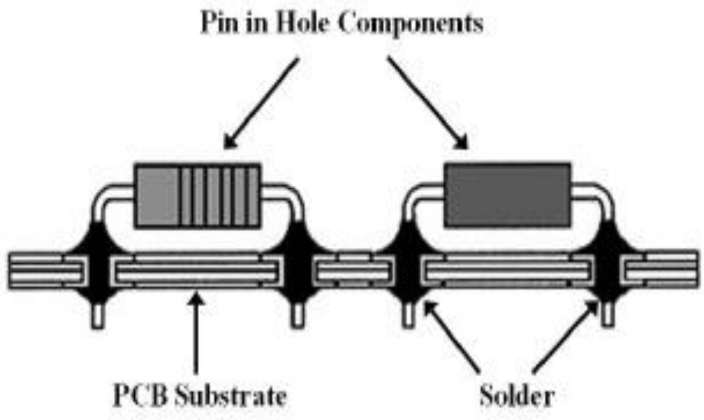

Figure 2.2: Cross-section of a pin through hole connection of a microelectronics component on a PCB (Abtew and Selvaduray, 2000)

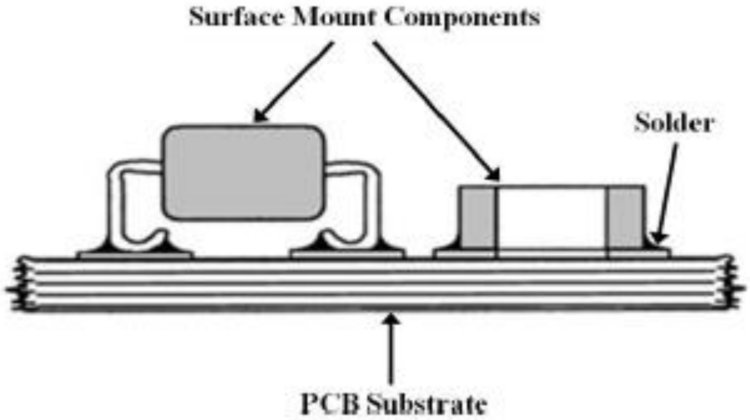

Figure 2.3: Cross-section of a surface mount connection of a microelectronics component on a PCB (Abtew and Selvaduray, 2000)

Establishment of the respective connections is based on different production approaches. Pin through holes connections are established by the wave soldering while surface mount types of connections are created by the reflow soldering.

2.4.1 Wave soldering

Assembled PCB is passed over a molten solder speed wave at a travel speed of approximately 5-10cm/s. Solidifying of both pin at electronic components as well as the surface of conductor substrates was achieved by the wetting process of solder alloys which then forms a solder joint. In Figure 2.4, a schematic representation of this method is shown including the steps of wave soldering:

i) Automatic insertion of leads into holed components of printed circuit board (PCB).

ii) Dispensing of adhesives at locations of surface mount components to be placed throughout the PCB.

iii) Placements of surface mount components over the dispensed adhesive.

iv) Curing of adhesive to make a temporary bond so that components can be hung beneath the circuit board. The success and the reliability of the wave soldered joint depend on the wettability of the solder, the type of flux, the solder bath temperature and the dwell time of soldering.

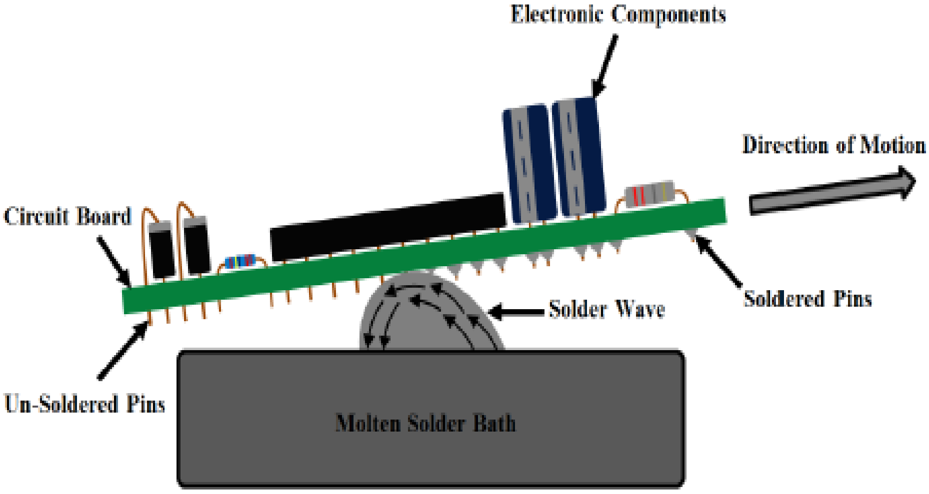

Figure 2.4: Wave soldering of PCB

The fact that during the soldering process, the temperature profile is off the limits from being a controlled parameter, causes the formation of undesirable microstructure and potential cracks, which is different from the reflow soldering of surface mount technique (SMT). Prior to the operation of soldering, the surfaces of the PCB which is desirably not come into contact with the solder, for instance the previously soldered SMT components, are masked. This process is also referred to as selective soldering.

2.4.2 Reflow soldering

The increased production of surface mount technology is as the result of expansion of development and frequency of usage of the solders, promoting to the creation of other soldering methods. Prior to SMT components being subjected to wave soldering, it is important to ensure that they, being the surface mount components are already being attached to the surface board by using adhesives or other binding materials such as cement (pozzolanic properties) in order to keep the structure in place throughout the soldering process. This brings forth another step into the situation of assembly process. Viewing the condition of the whole SMT components being immersed in the wave, it is vital for it to exhibit or possess high heat resistance qualities in order for it to be able to withstand the high temperatures of liquid solder. Manko (1995) mentioned of the issues with gasses being entrapped between the component and the board. Due to the issues that arises due to the wave soldering, it has somewhat widened the prospects for reflow soldering and eventually places it as the more viable and preferable method for the soldering of surface mount components.

In general, reflow soldering can be understood as the most common methods that is being used to glue or put together the surface mounted component to a circuit board. Solder paste is being used during the soldering process, and in order to make both of the components, namely the surface mounting component and the circuit board to be glued together, the solder paste is put onto its surface and the components are join together by placing the board onto the top of the already laid solder. Heat are then introduced to initiate flux, risen up the temperature of the base metals and then melt or reflow the solder (Lee, 2002b).

The aim of reflow process is to liquefy the powder particles existing within the solder upon cooling the solidified material in order to establish a strong metallurgical bond and further join both surfaces. In order to ensure that the device is being securely in place during the process of soldering, the use of separate adhesives is frequent and common. Listed are the four common process zones for conventional reflow soldering, which is initiated by the preheating, thermal soak, followed by the reflow and finally the cooling process.

This method requires a few steps of implementations. First off is the arrangement of the alignment of both flux and solder alloys surfaces prior to being subjected to soldering process. Next is the placement of components onto the already placed solder. Followed by the heating and cooling process of the assembled parts, the heating step itself involves the melting and distribution of the solders onto the surfaces. As for the cooling process, joints started to be in formation as the molten solder solidified. Lastly, the procedure involves the cleaning of the components from any residues of the flux.

Given that a different form of solders is being used, for instance, the replacement of solder bars by solder paste, the steps involved would be different and the already mentioned steps will not be applicable. Note that solder pastes can be directly used on the metallization of the circuit boards by using stencil printing method. The components are then placed on the printed solder paste pattern and the assembled boards are then passed through the reflow oven to form solder joints. There are various heating methods that is applicable for reflow process, of which includes conduction, infrared, vapour phase, hot gas convection induction, laser, focused infrared, white beam and vertical reflow methods. Figure 2.5 shows the schematic diagram of reflow soldering process.

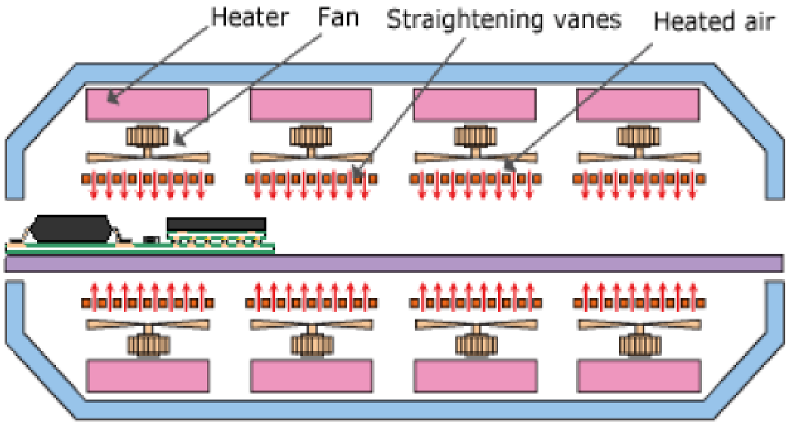

Figure 2.5: Schematic diagram of reflow soldering process (Renesas, 2014)

2.5 Effect of composition and alloying elements to microstructure of SAC solder

The microstructures of SAC solders are extremely sensitive to compositional changes. As such, take the comparison between the microstructures of both Sn-3.7Ag-0.9Cu and Sn-3.6Ag-1.0Cu, in Figure 2.6; one can clearly see the prominent changes that occurred in the microstructure, caused only by the substitution of 0.1 wt. % Ag with 0.1 wt. % Cu.

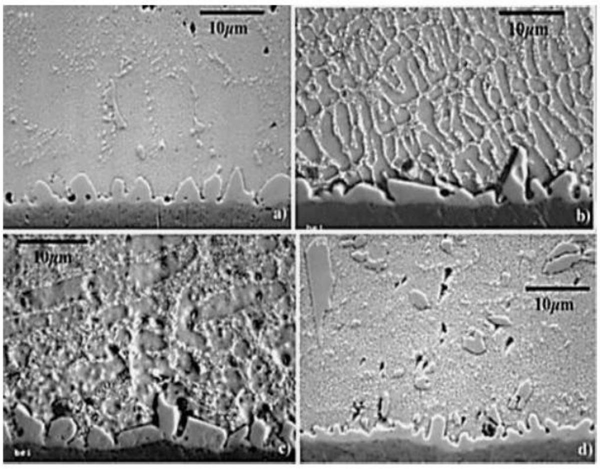

Figure 2.6: Back-scattered electron (BSE) images of solder joints made from: a) Sn-3.0Ag-0.5Cu, b) Sn-3.9Ag-0.5Cu, c) Sn-3.7Ag-0.9Cu d) Sn-3.6Ag-1.0Cu (Anderson I.E.et.al, 2002)

Note that the amount of eutectic phase faced an increment, while the amount of β-Sn decreased. However, a number of Cu_6Sn_5 intermetallic compounds (IMCs) were observed existing in the matrix. The properties of the intermetallic compounds are clearly different from its constituent elements. The amount, size and distribution of the intermetallic compounds must be controlled since almost all the intermetallic compounds are hard and brittle phases. Large or localized IMCs can cause the undesirable embrittlement of the solders joints. However, it is important to acknowledge that small amounts of intermetallic compounds can improve both mechanical and thermal properties of the solders. Homogenous distribution of small IMCs can also help to improve the hardness and fatigue resistance (Harris et.al, 1998).

Ag_3Sn is also another type of IMC that can be formed within the matrix of the SAC solders. It exists in the form of large plates which is also being referred to as blades. This form of Ag_3Sn is usually seen as the least desirable phase, since it degrades the mechanical properties of the solders and cause catastrophic failures of electronic components. It is discovered that the most effective parameters on both size and the dispersion of the Ag_3Sn particles are the composition and cooling rate. It is known that the particle size of pro-eutectic Ag_3Sn are larger than the eutectic Ag_3Sn particles. Of which the eutectic particles are usually small and is most common in rounded or needle like shaped (Sunagama, 2001). The huge size of Ag_3Sn plates has the ability to influence the mechanical properties of the solder alloys. This is done by local inhibition of plastic deformation and promoting the formation of stress concentrating at the interface between the Ag_3Sn plate and the surrounding β-Sn (Frear et. al, 2001).

Due to these reasons, the formation of large Ag_3Sn plates must be avoided should the integrity of the solder joint upon being forced by any existing mechanical or thermal loads during its service life is to be maintained. As mentioned in the earlier part of this chapter, the composition of the solder alloy and the cooling rate during solidification are identified to be the most effective parameters on the formation of large Ag_3Sn plates.

2.5.1 Effect of silver content

Given if the silver content that exists in the solders is less than 3wt. %, the formation of large Ag_3Sn particles will be effectively reduced, even if it is being subjected at very low cooling rates which is at or lesser than 0.02°C/s. Silver content that is recorded to be lower than 2.7 wt. % in composition, prohibits the nucleation as well as the growth of Ag_3Sn. However, the situation can be reversed, given there is an undercooling of 20°C (Kang et al., 2003). Note that Ag has a limited solubility in Sn. Therefore, for those insoluble or non-dissolved particles of Ag is considered to proceed with the formation of Ag_3Sn IMCs. It was found that an increase in the Ag content from 3.0 wt. % to 3.8 wt. % results an increase of 28 vol. % in the Ag_3Sn content. Similarly, formation of large Ag_3Sn blades were observed due to change in Ag content from 3.0 wt. % to 3.9 wt. % as shown in Figure 2.7. Table 2.3 shows the effect of Ag content on the number of large Ag_3Sn plates.

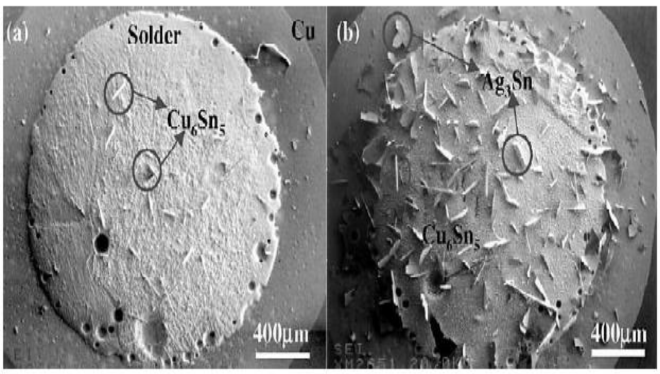

Figure 2.7: Results of microscopic examination of a) Sn-3.0Ag-0.5Cu and b) Sn-3.9Ag-0.5Cu (Kim et.al, 2003)