INTERMETALLIC COMPOUND AND RELIABILITY STUDY OF SAC AND SNBI LEAD FREE SOLDERS

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INTERMETALLIC COMPOUND AND RELIABILITY STUDY OF SAC AND SNBI LEAD FREE SOLDERS

By

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACRONYMS AND ABBREVIATION

WEEE	Waste Electrical and Electronic Equipment
RoHS	Restriction of Hazardous Substances
EU	European Union
JEIDA	Japanese Electronic Industry Development Institute Association
NEMI	National Electronic Manufacturing Initiation
IMC	Inter-metallic Compound
PCB	Printed Circuit Board
BGA	Ball Grid Array
Sn	Tin
Pb	Lead
Bi	Bismuth
Ag	Silver
Cu	Copper
In	Indium
Zn	Zinc
Ni-P	Nickel phosphorus
RA	Rosin Activated
RMA	Rosin Mild Activated
SEM	Scanning Electron Microscope
CTE	Coefficient of Thermal Expansion
EDX	Energy Dispersive X-ray
OM	Optical Microscope

SMT	Surface Mount Technology
BSD	Backscattered Electron
XRD	X-ray Diffraction
SROs	Short Range Orders - solid crystal still remain in liquid within certain temperature range.
SAC	Tin-Silver-Copper
Metallurgical Bond	The bond between two metals whose interface is free of voids, oxide films, or discontinuities.
Critical thickness	The value of thickness at maximum shear strength of solder joint.

LIST OF APPENDICES

LIST OF PUBLICATIONS AND CONFERENCES

1.1 **Abdul K. A. W. and Nurulakmal M. S.** (2009). *Characterization of Sn-Ag and Sn-Bi Lead free solder Alloy*. Paper of 4th International Conference on Recent Advances in Materials, Minerals and Environment and 2nd Asian Symposium on Material Processing (RAMM and ASMP 09). 1st and 3rd June Bayview Beach Resort Penang.

1.2 **Abdul K. A. W. and Nurulakmal M. S.** (2010).*Wetting behavior and shear strength of* $Sn_{77.5}Bi_{20}Ag_{0.5}Cu_{2.0}$ *and* $Sn_{96}Ag_{3.5}Cu_{0.5}$ *(SAC) lead free solders on copper substrates.* Paper of 4th Colloquium on Post Graduate Research National Postgraduate Colloquium on Materials, Minerals and Polymers (MAMIP 10). 27th and 28th January Vistana Hotel Penang.

1.3 **Abdul K. A. W. and Nurulakmal M. S.** (2010). *The Effect of Indium and Bismuth Addition on IMC formation of* $Sn_{96}Ag_{3.5}Cu_{0.5}$ *Solder*. Paper of 19th Scientific Conference of the Electron Microscopy Society of Malaysia and 20th Annual General Meeting (EMSM 10). 14th - 16th December Bayview Hotel, Langkawi.

KAJIAN KE ATAS SEBATIAN ANTARA LOGAM YANG TERBENTUK PADA ANTARA MUKA DAN KEBOLEHPERCAYAAN PATERI BERASASKAN PATERI TANPA PLUMBUM SAC DAN SNBI

ABSTRAK

Disebabkan pertimbangan ke atas isu persekitaran, maka penggunaan pateri tanpa plumbum telah digunakan secara meluas dalam industri pembungkusan elektronik. Untuk mengantikan pateri dengan plumbum, pateri tanpa plumbum harus mempunyai takat lebur menghampiri takat lebur pateri dengan plumbum (183^0C) serta harus mempunyai kebolehbasahan, sifat fizikal dan mekanikal yang baik. Kajian ini ditumpukan ke atas pembangunan pateri berasaskan Sn-Bi dan SAC untuk aplikasi pembungkusan mikroelektronik. Satu kajian sistematik telah dijalankan ke atas ciri-ciri pateri, sifat kebolehbasahan, sifat-sifat mekanikal dan sebatian antara logam yang terbentuk pada antara muka pateri dan pertumbuhan di atas substrat kuprum dan Ni-P. Sebatian antara antara logam yang terbentuk pada antara muka pateri pada kuprum telah dikenalpasti sebagai Cu_6Sn_5, Cu_3Sn, AgZn dan Cu_5Zn_8, manakala pada substrat Ni-P adalah Ni_3Sn_4 dan $(Ni,Cu)_6Sn_5$. Ketebalan sebatian antara logam yang terbentuk pada antara muka pateri meningkat dengan rawatan haba. Penambahan 0.5% Ag dan 0.5% Cu meningkatkan kebolehbasahan pateri pada kedua-dua permukaan kuprum dan Ni-P disebabkan penurunan tegangan permukaan pateri serta meningkatkan kekonduksian elektrik. Manakala penambahan In, Zn dan Bi ke dalam pateri berasakan SAC menurunkan takat lebur dan juga memberikan kebolehbasahan yang lebih baik. Penambahan samada 4% Bi atau 9% In ke dalam pateri SAC, kedua-duanya mengurangkan kadar pertumbuhan sebatian antara logam yang terbentuk pada antara muka pateri serta meningkatkan

kebolehpercayaan sambungan pateri. Walaupun mempunyai pekali pengembangan haba yang relatifnya lebih tinggi, didapati bahawa pateri $Sn_{79}Bi_{20}Ag_{0.5}Cu_{0.5}$, $Sn_{77.5}Bi_{20}Ag_{0.5}Cu_{2.0}$, $Sn_{87}Ag_{3.5}Cu_{0.5}In_{9}$ dan $Sn_{87}Ag_{3.5}Cu_{0.5}In_{5}Zn_{4}$ mungkin merupakan calon terbaik untuk menggantikan pateri berplumbum kerana kebolehbasahan sangat baik, sudut yang lebih rendah dan takat lebur serta kekuatan yang lebih tinggi jika dibanding dengan pateri SAC (355).

INTERMETALLIC COMPOUND AND RELIABILITY STUDY OF SAC AND SNBI LEAD FREE SOLDERS

ABSTRACT

Due to the environmental concern for lead toxicity, the use of lead-free solder has been widespread in electronic packaging industries. In order for lead-free solder to replace the current lead solder, lead-free solder should have as close melting point as lead solder (183^0C) and also has good wettability, excellent physical and mechanical properties. This thesis is devoted to the research and development of lead-free Sn-Bi and SAC based solder alloy for microelectronic packaging applications. A systematic study was conducted on the solders characteristics, wetting behavior, the interfacial reaction, mechanical properties and growth kinetics of solders on Cu and Ni-P substrate. The IMCs formed at the interface between the solder and Cu substrate were identified as Cu_6Sn_5, Cu_3Sn, AgZn and Cu_5Zn_8, and for Ni-P substrate were Ni_3Sn_4 and $(Ni,Cu)_6Sn_5$ and the thickness of IMCs increased with thermal aging. Addition of 0.5% Cu and 0.5% Ag improved the wettability on both Cu and Ni-P substrate by reducing the surface tension of molten solders and also increased conductivity of solder alloys. Whereas, addition of In, Zn and Bi in SAC based solder reduced the melting point and gave better wettability to the solder**.** Either additions of 4% Bi or 9%In in SAC solder reduce the rate of IMC growth during aging process on both Cu and Ni-P substrate, and therefore improved the reliability of solder joint. Despite the relatively higher coefficient thermal expansion result, it was found that $Sn_{79}Bi_{20}Ag_{0.5}Cu_{0.5}$, $Sn_{77.5}Bi_{20}Ag_{0.5}Cu_{2.0}$, $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ and $Sn_{87}Ag_{3.5}Cu_{0.5}In_5Zn_4$ may be the best candidates to replace tin-lead solder due

to excellent wettability, lower wetting angle, lower melting point and higher strength compared to SAC (355) solder.

CHAPTER 1

INTRODUCTION

2.1 Overview

Solder is a fusible metal alloy with a melting range of 90 to 450^{0}C (Althouse et. al., 2003). Solder used in a process called soldering where it is melted to joint metallic surfaces. For more than 50 years, lead containing solders have been used throughout the electronic industry for attaching components to PCBs. These solders have been extensively used because they are inexpensive; perform reliability under a variety of operating conditions, and posse's unique characteristics such as low melting point, high strength ductility and fatigue resistant, good wettability, high thermal cycling and joint integrity (Richards, 2001). Today's society is moving away from lead-based materials due to their toxicity. Lead has been found to cause kidney, brain and central nervous system damage in humans. Danger from lead not only affects human, but also environment. The European Union through a proposal known as the Waste for Electronic and Electrical Equipment (WEEE) has set January 2008 as the date for electronics to become lead free. The European Union also approved proposal knows as the Reduction on Hazardous Substance (RoHS), which sets July 1, 2006 as the date that targeted hazardous material may no longer be used. The Japanese Ministry of International Trade and industry has set 2005 as the date for use of lead to be reduced by two-thirds. The Japan Institute for Electronic Packaging calls for the total elimination of lead based solders between 2010 and 2015.

1.1 Problem Statement

Fabricating lead-free solder that have properties and melting point close to eutectic tin-lead and cost effectiveness has been a great challenge to researchers. A various number of compositions have been studies to replace tin lead solder such as Sn-Ag, Sn-Bi, Sn-Zn, Sn-In and SAC based solder. Among those candidates SAC solder becomes widely used in most electronic applications. The benefit of using SAC is better shock resistance, improved functionality, higher reliability, environmental friendliness, ease of implementation and cost effectiveness. However, the main problem of SAC solder is higher melting point and has higher wetting angle compared to tin-lead. The higher melting point caused higher soldering temperature. Most of the sensitive components and substrates cannot withstand this temperature and pose a risk to the polymer substrate and under fill material. Sn-Bi solder come closer to meet existing parameter of tin-lead solder. However, Sn-Bi existing solders are not acceptable for all applications because of wide liquidus temperature range and the presences of a small DSC peak near 139^0C contributed to segregation of bismuth in solder that will worsen the mechanical properties.

1.2 Objective

The objective of this project can be simplified as:

- ❖ To fabricate lead-free solders with melting point close to eutectic tin-lead 183^0C
- ❖ To study the effect of adding alloying elements on melting point, wettability and reliability of Sn-Bi and SAC based solder alloys.
- ❖ To evaluate IMC formation of the solder joint on Ni-P and Cu substrate.

- ❖ To study the effect of aging to the solder joint at temperature of 160^0C for 100 hour.

1.4 Scope of Research

The focus of this study was to fabricate tin-silver and tin-bismuth solder alloy that is closer to meet the existing properties of tin-lead. Thermal analysis was done using Differential Scanning Calorimetry (DSC) to determine the melting point of each solder fabricated. The solders with acceptable melting points were then proceed to the next level. Solder was re-flowed on copper or Ni-P substrate to evaluate the wetting angle and the IMC formation. Rhesca Solder Checker Instrument model SAT-5100 was used to determine the wettability of the solder. The microstructure and elemental analysis were carried out by using SEM and EDX on solder alloy and solder joint. The phase that formed in solder alloys was determined using XRD. The evaluation of mechanical properties of solder joints were done using Universal Testing Machine (UTM) via lap joint shear test, and ball pull and shear test. Dilatometer is used to measure the Coefficient of Thermal Expansion (CTE) of solders. In addition density, hardness and electrical conductivity of the solder alloys were also evaluated. Aging process was done to understand the IMC growth at solder joint during service temperature over a period of times.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Soldering is a metallurgical process used since the ancient times. Diffusion soldering is an attractive joining method for the formation of thermally and mechanically stable lead-free bond in electrical and electronic at relatively low process temperatures, which involves inter-diffusion, reaction diffusion, and isothermal solidification. The fundamental requirement for the diffusion soldering process is the existence of at least one inter-metallic compound between the components to be joints. In electronic packaging, lead has been banned due to environmental issues and healthy concern. It is widely known that lead is related to certain health risks. If lead particles are inhaled or ingested, its can accumulate in the human body causing damage to the blood and central nervous systems. Solder alloys have been manufactured with liquidus temperatures as low as 10.7^0C, as exemplified by the ternary eutectic $Ga_{62.5}In_{21.5}Sn_{16}$ alloys and as high as 424^0C as in case of the $Ge_{55}Al_{45}$ binary eutectic composition (Vianco, 1999). Solder can be categorized in three group's base on melting point of the solder as shows in Table 2.1.

Table 2.1: Classification of solders based on melting point of solder alloys.

Solder	Temperature (^{0}C)
Low temperature solder	≤ 138
Mid-range temperature solder	$138 < t \leq 235$
High Temperature solder	$235 < t \leq 450$

Most of electronic assemblies currently use solder in order to create connection between components and the printed circuit board. Although conductive adhesive can be pressed into service for this application, solder remains far and away the most widespread joining medium. Familiarity, low cost, high reliability and ease of use means that solder will continue to be an important joining material. Solder interconnects perform three functions as mechanical, electrical and thermal. Solder provides an electrical connection path from the silicon chip to the circuitry on the substrate within the package (first level interconnection), between the different packages and between the package and the Cu traces on the printed wiring board or PWB (second level interconnection) (Shangguan, 2005). It also serves as a path for dissipation of heat generated by the semiconductor (Abtew and Selvaduray, 2002). Solder provides a mechanical and electrical joint that is essential to keep components in place once a circuit has been assembled. While the mechanical strength is important, it is also necessary to ensure that the soldered joint provide a good electrical connection is made between the two connections which require joining. This can only be achieved satisfactorily if the medium can achieves a good electrical connection.

2.2 Soldering Materials

2.2.1 Tin-Lead Solder

From the very beginning of the electronics industry, solder joints have been made primarily by tin and lead alloy. In particular, the eutectic tin-lead alloy has been used almost exclusively in electronic due to its unique characteristic (cost, availability, ease of use, low melting point, excellent wetting on Cu and it alloys and electrical/thermal/mechanical/chemical characteristic) (Shangguan, 2005; Zhang et. al., 2007; Hui et. al., 2000; Chen et. al., 2007). The eutectic tin -lead solder provides an excellent electrical conductivity and suitable mechanical strength for joining (Shangguan, 2005). It is also a critical material in virtually all electronics because it is uniquely capable of meeting high technology performance in cost efficient manner.

2.2.2 Lead-Free Solder Requirement

When trying to identify an alternative to lead solder, it is important to ensure the properties of lead-free solder are comparable or superior. According to recent report (Shangguan, 2005; Ramani, 2007; Nurfazlin, 2009), lead in solders contributes outstanding properties to overall reliability of tin-lead solder such as;

- ❖ Reduces the surface tension of pure tin to improve the wettability.
- ❖ Reduces the rate at which substrates are dissolved by tin.
- ❖ Enable tin and copper to rapidly form inter-metallic compounds by diffusion
- ❖ Provide ductility to tin-lead solders.
- ❖ Addition of lead prevents the transformation of β-tin to α-tin. If the transformation occurs, it will cause increasing in solder volume and loss of structural integrity.
- ❖ Tin-lead solder have low melting point of 183^0C for eutectic solder, which allows the use of low re-flow temperature in the electronic packaging process and ensures reliability of the package.
- ❖ Low cost.

However, the new lead-free solders needs to have closer melting temperature to existing tin-lead solder, particularly eutectic and near eutectic solder in order to have similar re-flow profile during the manufacturing process. The other requirements need to be fulfilled by lead-free solder are:

- Non-toxic or less toxicity compare with lead solder. Any elements choosen to replace lead in solder must not be harmful to people and environment.
- Acceptable processing temperature. Any design of alloy must be able to perform a good wettability under the current processing temperature or close.
- Narrow plastic range. This will minimize any reliability or formation of weak phase that may have resulted by the large plastic range.
- Good wettability on substrates. Compatible with a standard surface finish.
- Form reliable joint. Reliability of solder alloy depending on the coefficient of thermal expansion, elastic modulus, yield strength, shear strength, tensile strength fatigue and creep behavior of the alloy.
- Available and affordable. All elements chosen as the candidate for the lead free alloy must be available at a reasonable price.

2.2.3 The Development of Lead-Free Solder

A relatively large number of lead-free solder alloys has been developed from binary, ternary, quaternary and even more systems. It can be noticed that, a very large number of these solder alloys is based on Sn as the primary material or major constituent. Table 2.2 shows the lead-free solder that has been developed.

Table 2.2: Proposed lead-free solder alloys with their melting temperature (T_m = melting temperature, T_s= solidus temperature, T_l = liquidus temperature, T_e = eutectic temperature.

Alloys Composition (wt.%)	Ts (^{0}C)	Ti (^{0}C)	Tm (^{0}C)	Te (^{0}C)	References
$Sn_{98}Ag_2$	221	225			Abtew and Selvaduray, 2002
$Sn_{50}In_{50}$	117	125			Cheng and Lin, 2000
$Sn_{97}Cu_3$	227	275			Abtew and Selvaduray, 2002
$Sn_{96}Ag_4$	221	225			Abtew and Selvaduray, 2002
$Sn_{58}Bi_{42}$			170	139	Abtew and Selvaduray, 2002
$Sn_{58}In_{42}$	117	140			Abtew and Selvaduray, 2002
$Sn_{64}In_{36}$	117	165			Abtew and Selvaduray, 2002
$Sn_{99.3}Cu_{0.7}$				227	Wu et al., 2004
$Sn_{96.5}Ag_{3.5}$				221	Wu et al., 2004
$Sn_{43}Bi_{57}$				139	Cheng and Lin, 2000
$Sn_{95.5}Ag_{3.5}In$			217		Abtew and Selvaduray, 2002
$Sn_{94.9}Ag_{3.6}Cu_{1.5}$			225		Abtew and Selvaduray, 2002
$Sn_{89}Ag_4Sb_7$		230			Abtew and Selvaduray, 2002
$Sn_{95.5}Ag_{4.0}Cu_{0.5}$			218		Anonymous, 2000
$Sn_{91.7}Ag_{3.5}Bi_{4.8}$	208	215			Anonymous, 2000
$Sn_{93.5}Ag_{3.5}Bi_3$	216	220			Anonymous, 2000
$Sn_{77.2}Ag_{2.8}In_{20}$	179	189			Anonymous, 2000
$Sn_{88}Sb_4Zn_8$	198	204			Abtew and Selvaduray, 2002
$Sn_{81}Zn_9In_{10}$			178		Abtew and Selvaduray, 2002
$Sn_{88}Zn_6Bi_6$			127		Abtew and Selvaduray, 2002
$Sn_{93.6}Ag_{4.7}Cu_{1.7}$				217	Abtew and Selvaduray, 2002
$Sn_{95.5.}Ag_4Cu_{0.5}$	216	222			Abtew and Selvaduray, 2002
$Sn_{91.2}Ag_2Zn_6Cu_{0.8}$	217	217			Abtew and Selvaduray, 2002
$Sn_{81}Zn_9In_{10}Cu$					Abtew and Selvaduray, 2002
$Sn_{80}Zn_8In_{10}Bi_2$				175	Abtew and Selvaduray, 2002
$Sn_{96.2}Ag_{2.5}Cu_{0.8}Sb_{0.5}$	213	219			Anonymous, 2000
$Sn_{89.2}Ag_2Cu_{0.8}Zn_8$	215	215			Abtew and Selvaduray, 2002
$Sn_{96.7.}Ag_{2.8}Cu_{0.5}$			218		Rizvi et. al.,2006
$Sn_{95.7.}Ag_{2.8}Cu_{0.5}Bi$			214		Rizvi et. al.,2006
$Sn_{89}Zn_9Ag_{1.5}Bi_{0.5}$	215	215			Liu et. al., 2006
$Sn_{90.5}Zn_9Ag_{0.5}$			199		Chen et. al., 2007
$Sn_{90.5}Zn_9Ga_{0.5}$			196		Chen et. al., 2007

According to Table 2.2, majority of lead free solder alloys have melting point around 200^{0}C-220^{0}C. Sn-Cu, Sn-Ag and Sn-Ag-Cu system has liquidus temperature that significantly higher than eutectic tin lead solder. Increasing in melting point will cause the higher processing temperature.

2.2.3.1 $Sn_{42}Bi_{58}$ Solder Alloys (138^{0}C)

The low melting point of this alloy makes it suitable for soldering temperature-sensitive components and substrates. $Sn_{42}Bi_{58}$ solder has reasonable shear strength and fatigue properties, low-temperature eutectic solder with high strength, particularly strong but very brittle (Anton and Angela, 1998). It used extensively in through-hole technology assemblies in IBM mainframe computers, where a lower soldering temperature was required. This solder was good for electronics application and used in thermoelectric applications due to excellent thermal fatigue performance.

2.2.3.2 $Sn_{91.8}Ag_{3.4}Bi_{4.8}$ Solder Alloys (200-216^{0}C)

Generally, bismuth is added to Sn-Bi-X solder alloys in order to depress the melting point. Another benefit of adding Bi is greater joint strength. This particular alloy was developed by Sandia National Labs (Anton and Angela, 1998). The result showed that there were no electrical failures on the surface mount devices after 10000 thermal cycles at temperature of 75^{0}C compared to tin lead solder.

2.2.3.3 $Sn_{90}Bi_{7.5}Ag_{2.0}Cu_{0.5}$ Solder Alloys 138^{0}C (198-212^{0}C)

Although the addition of bismuth to the Sn-Ag-X system imparts greater strength and improves wetting, too much bismuth (more than 5%) will cause segregation of bismuth rich leading to the presence of a small DSC peak around 138^{0}C corresponding to the binary Sn-Bi eutectic or ternary Sn-Ag-Bi eutectic at 136.5^{0}C (Anton and Angela, 1998). This eutectic peak has an uncertain effect on joint reliability of the solder as temperature approach 138^{0}C.

2.2.3.4 $Sn_{96}Ag_{3.5}$ Solder Alloys (231^0C)

This alloy exhibits adequate wetting behavior and strength and is used in electronic industries as well as soldering waterfall system. According to Anton and Angela (1998), several sources have also reported good thermal fatigue properties compared to lead solder. In a tin-lead system, the relatively high solid solubility's of lead in tin and vice versa, especially at elevated temperatures, lead to microstructural instability due to coarsening mechanism. These regions of inhomogeneous microstructural coarsening are known as crack initiation sites. It is well documented that these types of microstructure in tin-lead alloys fail by the formation of a coarsened band in which fatigue crack grows. By comparison, the tin-silver system has limited solid solubility of Ag in Sn, making it more resistant to coarsening. As a result, $Sn_{96}Ag_{3.5}$ solder forms a more stable and uniform microstructure that is more reliable. Although the $Sn_{96}Ag_{3.5}$ solder alloys itself exhibit good microstructural stability, when solder on substrate. The combination of higher tin content compared tin-lead solder and higher re-flow temperature environments accelerates the diffusion rate of copper substrate in tin. As its corresponding composition is reached, the brittle Cu_6Sn_5 IMCs is nucleated and begin to grow lower its mechanical properties of the joint.

2.2.3.5 SAC Solders Alloys

SAC solder alloys become the most promising solder and the best alternative for tin-lead solders replacement (Handwerker, 2005; Nurmi et. al., 2005). The alloy has been recommended by several industry consortiums, including Inter-National Electronics Manufacturing Initiative (iNEMI), EU consortium known as IDEALS (Improved Design Life and Environmentally Aware Manufacturing of Electronic

Assemblies by Lead-Free Soldering), and the Japan Electronics and Information Technology Industries Association (JEITA). The melting temperatures of SAC solder range from 216^0C-220^0C according to the composition of the alloys. Because the mechanical stability of the joint degraded when the melting point is approached, elevated temperature cycling produces more damage for tin-lead solder (melting temperature 183^0C) as compared to higher melting point of the solders. The higher melting points of SAC solders make SAC solders an ideal solder in high operating temperature application up to 175^0C. However, there is a fear of bad effect on reliability of solders caused by over-heating part at the time of melting the solder because of higher re-flow temperature. As for wettability, SAC solder does not wet the substrates as well as tin-lead solder.

2.2.3.6 $In_{52}Sn_{48}$ Solder Alloys (118^0C)

The melting temperature of $In_{52}Sn_{48}$ solder alloys makes it suitable to low temperature application. With regard to properties of Indium in $In_{52}Sn_{48}$ solder, it displays good oxidation resistance, but is susceptible to corrosion in a humid environment. $In_{52}Sn_{48}$ solder is very soft metal that has a tendency to cold weld. This solder displayed a poor high temperature fatigue behavior due to its low melting temperature. The high Indium solder usage is limited due to cost and availability constraints.

2.2.4 Material Selection Regarding Health Risk

When choosing alternative metals, consideration must also be given regarding environmental issues and health risk. Previous studies in USA and Europe came to following conclusions concerning toxicology of some alternative metal.

- Cadmium is extremely toxic and should not be used (high risk)
- Antimony is very toxic and should not be considered as a major alloying element (medium risk in Europe-this material considered as a potentially carcinogenic)
- Ag and Cu are used in the lead free alloys in small concentration- in Europe these materials are seen as low risk.
- Sn and Zn are essential elements in a human diet, yet may be toxic if exposures are sufficiently high (low risk).
- Bi is a relatively benign metal with a history of medicinal uses (low risk)

Basically, the main alloying elements like Zn, Bi, Ag and Cu are considered to be a green material except for In that has lower toxicity compared to lead. Table 2.3 shows toxicity effect on human of the alloying elements choosen in making the solder alloys.

Table 2.3: Toxicity effect of alloying element used in making the solder in this research.

Element	Toxicity	References
Sn	- Relatively harmless to human - Large amount of tin can cause stomachs aches, anemia, liver in case of ingest or inhalation - Long term inhalation of tin (15-20 years) may cause a benign pneumoconiosis	ASTDR, 2010
Bi	- Relatively less toxicity to human compare with lead - Large amount of bismuth can cause renal failure with degeneration and necrosis of	TOXNET, 2002

	the epithelium of the renal proximal tubules, fatty changes and necrosis of the liver, reversible dysfunction of the nervous system, skin eruptions and pigmentation of the gums and intestine.	
Ag	- Highly inert and is generally considered to be lower toxicity to human. - Long term exposure may cause argyria, which is a silver poisoning that leads to permanent blue-gray discoloration of the skin, eye and mucous membranes.	Smith and Edwin, 2002
Cu	- Relatively harmless to human - However copper and copper compounds can cause respiratory irritation, abnormal pain, nausea, vomiting, and diarrhea as documented when factory workers are exposed to copper dust.	TOXNET, 2002
In	- Relatively less toxicity to human compare with lead - A small dose of Indium can stimulate the metabolism. Indium compounds can damage the heart, kidney and liver	Lanntech, 2010
Zn	- Relatively harmless to human - Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experiences a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Despite a good effect of zinc, very high level of zinc can damage the pancreas and disturb the protein metabolism and cause arteriosclerosis.	Lanntech, 2010

2.2.5 Material Selection Regarding Cost of Material

Manufacturers of electronic industries were not likely to change to alternative solder with an increase cost but due to legislative pressure, they need to find alternative solder that demonstrated better properties at lower cost. Eutectic SAC solder becomes widely used in electronic industries because of superior mechanical properties but in term of cost, SAC solder was far more expensive than tin-lead solder.

Table 2.4: Prices per kg solder alloys in Ringgit Malaysia element used in making solder alloys according to alloys prices August 2011(Index Mundi, 2011).

Metal	Prices (per metric ton) August 2011	Prices (per kg) August 2011	Solder	Prices (per kg)
Sn	RM 71, 640.00	RM 71.64	Sn-Pb (eutectic)	RM 47.78
Bi	RM 82, 500.00	RM 82.50	$Sn_{80}Bi_{20}$	RM 73.81
Ag	RM 3, 290, 970.00	RM 3290.97	$Sn_{80}Bi_{20}Ag_{0.5}$	RM 89.85
Cu	RM 26, 730.00	RM 26.73	$Sn_{79.5}Bi_{20}Ag_{0.5}Cu_{0.5}$	RM 89.63
In	RM 2, 250 000.00	RM 2250.00	$Sn_{79.5}Bi_{20}Ag_{0.5}Cu_{2.0}$	RM 88.96
Zn	RM 6, 530.00	RM 6.53	SAC (eutectic)	RM 183.91
Pb	RM 7, 150.00	RM 7.15	$Sn_{96}Ag_{3.5}Cu_{0.5}$	RM 184.08
			$Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$	RM 184.54
			$Sn_{87}Ag_{3.5}Cu_{0.5}In_9$	RM 380.14
			$Sn_{87}Ag_{3.5}Cu_{0.5}In_5Zn_4$	RM 290.40

In Table 2.4, the cost of solder alloys that has been selected in this research were calculated and compared with the prices of eutectic tin lead and eutectic SAC. On an elemental basis, lead and zinc are the cheapest metals and silver and indium falls in the expensive category. In term of cost it is highly likely that electronic industries would adopt $Sn_{79.5}Bi_{20}Ag_{0.5}Cu_{2.0}$ solder as replacement compared to SAC solder. Due to importing issues of bismuth, particularly outside Europe will limit the usage of Sn-Bi based solder in electronics industries. Due to that factor, this research also concentrates on possible material that will reduce melting point of the SAC with far greater mechanical properties regardless of cost issues.

2.3 The Usage of Lead-Free Solder in Electronic Packaging

Solder material serves two primary functions as the interconnect material and a surface coating for component. Soldering technology plays a key role in various levels of electronic packaging, such as flip chip connection (C4), solder ball grid array (BGA) or IC package assembly to print circuit board (PCB) (Jeffrey et. al., 2001 and Weng, 2005). Solder joints serve critically as electrical connections as well as mechanical and physical connection. When either of the functions is out of service, the solder joints are considered as failure, which can often threaten a shutdown of the whole electronic system.

2.3.1 Overview of Flip-Chip Product

The term flip describes the method of electrically connecting the die to the package substrate. Flip-chip is an alternative way to connect a chip/die to an electronic package. Flip-chip technology provides the shortest possible leads, lowest inductance, highest frequency, best noise control, highest density, greater number of inputs/outputs (I/O), smallest device footprints and lowest profile when compared with other popular interconnect method such as wire-bonding and tape automated bonding (Ding, 2006; Weng, 2005). Figure 2.1 and Figure 2.2 shows schematic of a flip-chip package. In contrast to wire-bonding technology, the interconnection between the dies and carrier in flip chip packaging occurs when using a conductive bump placed directly on the die surface. The bumped die is then flipped and placed to face down so that the bumps connect directly to the carrier. A complete flip-chip package assembly is the direct electrical connection of a flipped integrated circuit (IC) onto a silicon die, circuit board, substrates or carriers using solder bumps and under fill. Flip-chip has been utilized as a Controlled Collapse Chip Connection (C4) dies bumping technology for die-to-substrates interconnection. This interconnection technology mount onto the substrate using a matrix of solder bumps on the surface, matching array of solder bumps or land on a substrate (Weng, 2005). The die connects to the substrate using a re-flow process consists of heating the package to the re-flow temperature and cools down to room temperature using controlled re-flow profile. The solder bumps will be protected by a layer of underfill epoxy. The substrates are a multilayered structure carrying an electrical circuit and provide a mechanical and electrical path between the die and the application board. The various layers are connected by a channel that runs perpendicular to the layers. The center layer of the substrate is a fiber reinforcement resin core which divides the substrate into upper and bottom layers and these two layers are connected using the plated through hole (Weng, 2005).

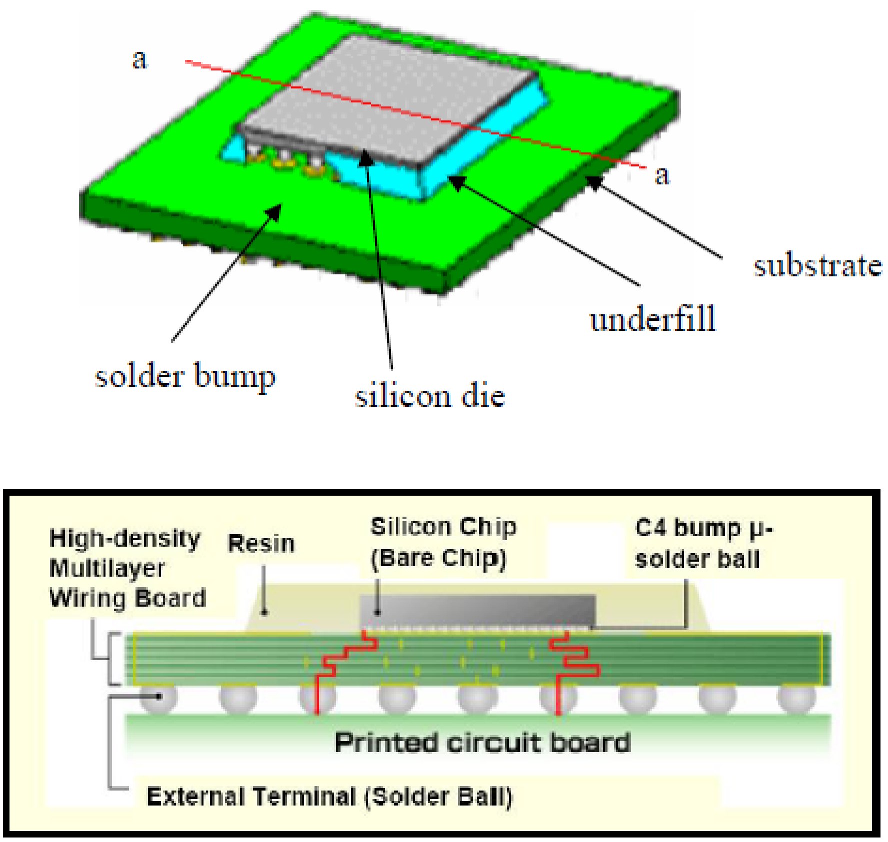

Figure 2.1: Cross section of the package: a) 1_{st} and 2_{nd} levels interconnection of flip-chip product (Sharif and Chan, 2005).

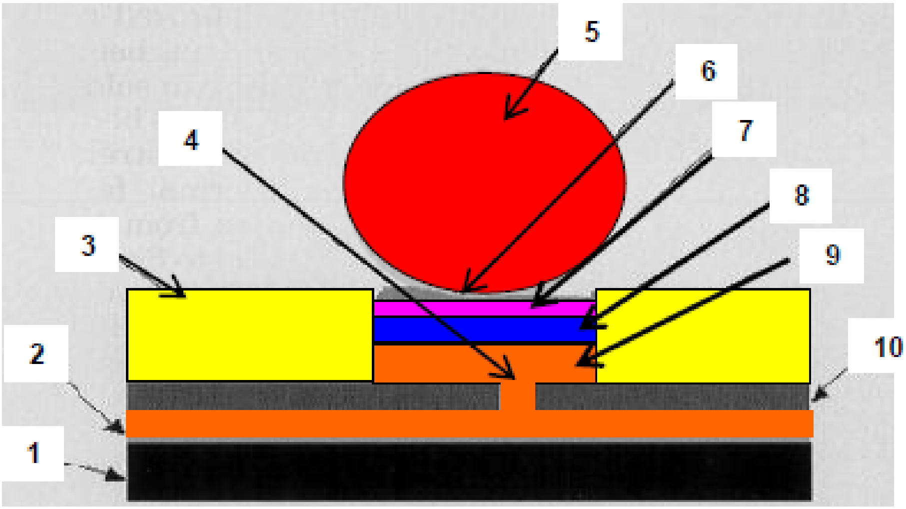

Figure 2.2: A schematic illustration of Cu position in interconnection of flip-chip product (Sharif and Chan, 2005).

2.4 Soldering Technique

Soldering operations can be performed using wave soldering, re-flow soldering and hand soldering depending on soldering packages. Currently, mass-production printed circuit boards (PCBs) are mostly wave soldered or reflow soldered, though hand soldering of production electronics is also still standard practice for many tasks.

2.4.1 Wave Soldering

Wave soldering was developed in England in 1956 and became the most important soldering process (Denis and Paul, 2006; Theriault et. al., 1999; Peter and Des, 2005). As shown in Figure 2.3, the wave solder process consists of three steps that are an application of flux, pre-heating and true wave soldering step. In the first step, the PCB is transported through a flux application station where the flux is applied. The purposed of the flux is to improve the wettability of the solder to connection pad and to remove any oxide layers between the solder and the metals on the board, to ensure optimal surface contact. In the next step, the board is transported to pre-heat section where the flux is activated and solvent used to dilute the flux are dried. This process step also serves to reduce the thermal stress placed on the PCB in the last waste-soldering step. In final step, the bottom of the board passes over a wave of the solder and solder joint are subsequently formed.

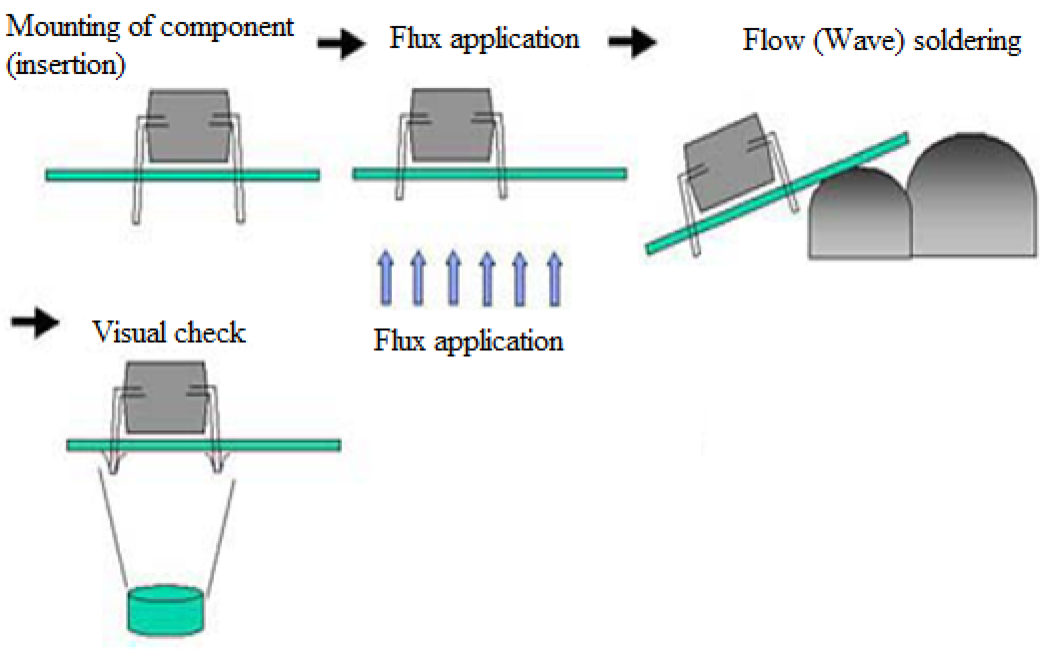

Figure 2.3: Process description of wave soldering with through-hole component. After the leads of the components are inserted to the holes on the board and flux has been applied, a molten wave of solder is applied to form solder joints (NEC, 2000).

2.4.2 Re-flow Soldering

Re-flow soldering was introduced to improve the SMT. In this process, a solder paste, containing small solder sphere, flux and solvent are first applied to the board where the surfaces mount components are subsequently placed. The solder paste serves as temporary glue that holds the components in place prior to the soldering process. The PCB is then heated to above the melting point of the solder paste. At this temperature, the flux is activated. Oxides are removed and the solder subsequently form a solder joint as shown in Figure 2.4.

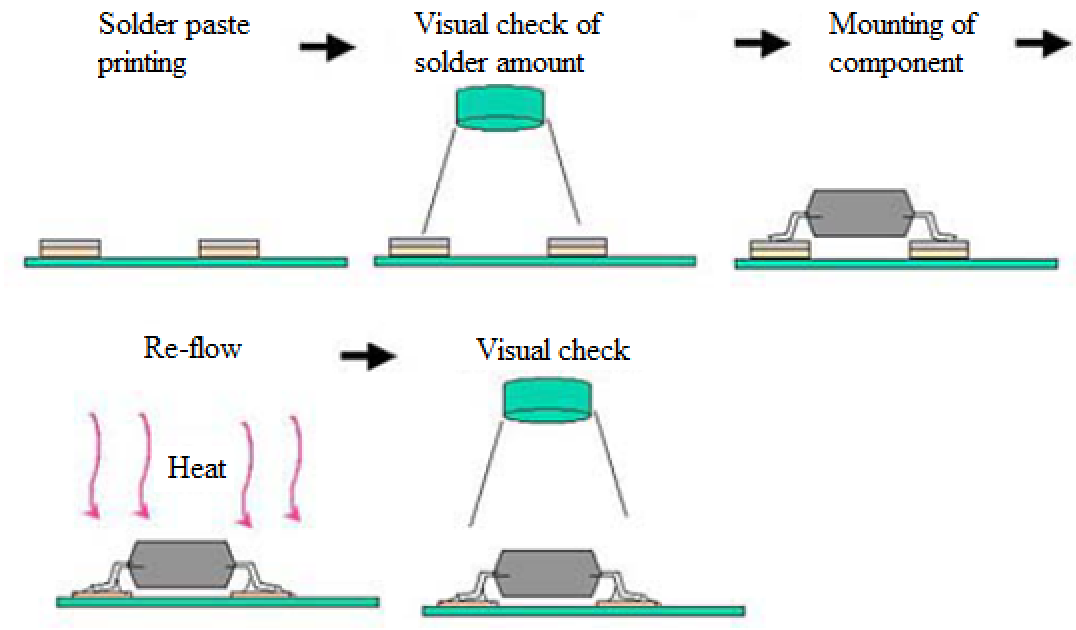

Figure 2.4: Process description of re-flow soldering with surface-mount components. Solder paste is applied to areas of the board where components are subsequently to be placed. Heat is applied to the board to melt the solder paste and form solders joints (NEC, 2000).

2.4.3 Hand Soldering

This process of soldering is the basic method involved applying heat the combination of solder and flux to produce desired joint formation. Hand soldering is typically performed with a soldering iron, soldering gun or a torch, or occasionally a hot-air pencil. Compared with the conventional method, the manual process requires a certain extent of skill and experience (Nurfazlin, 2009). This process is often associated with the aspect of quality assurance in which every joint is indirectly inspected for satisfactory interconnection before moving on the enst tip joint (Nurfazlin, 2009). Figure 2.5 shows the principle of hand soldering technique:

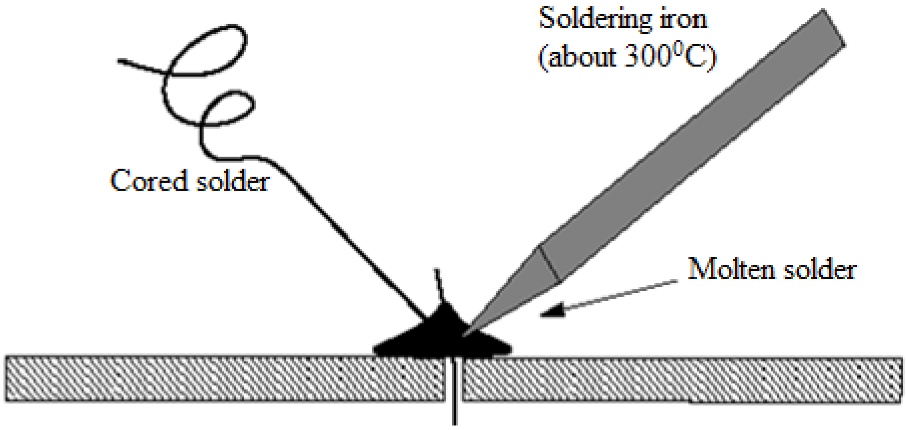

Figure 2.5: The principle of hand soldering technique. (Clear, 2011)

2.5 Re-flow Profile

For lead-free soldering, the characterization and optimization of the reflow process are most important factor that must be considered. There are many factors that affect the degree of IMC formation during the soldering process. Re-flow profile has a significant impact on solder joint performance because it influences wetting and the microstructure of a solder joint (Arra et. al., 2002; Salam et. al., 2004). Harris and Chaggar (1998) concluded that, the quantity of IMC is a direct function of the soldering time and temperature. During the reflow process, Cu substrate dissolves into the molten solder and forms the IMC layer at the interface. Fairly recently, reflow profile studies focused on shear strength performance and microstructural characterization (Jeon et. al., 2003; Bukhari et. al., 2005; Oliver et. al., 2000; Pan et. al., 2006; Webster et. al., 2007), with only very limited studies on the IMC layer thickness (Salam et. al., 2004). According to the studies, they come to an agreement that higher heating rate, dwell time and heating profile increased the IMCs thickness due to increasing rates of Cu dissolves into the molten solder. Although the roles of reflow profile on tin-lead solder joint performance has been well studied (Lee and Duh, 1998), its effect on lead-free soldered joints is not yet fully understood. It is still unknown which thickness of IMC layer could result in damage to the solder. Figure 2.6 shows the re-flow profile for conventional soldering. The graph illustrates the four basic stage re-flow oven for tin-lead solder.

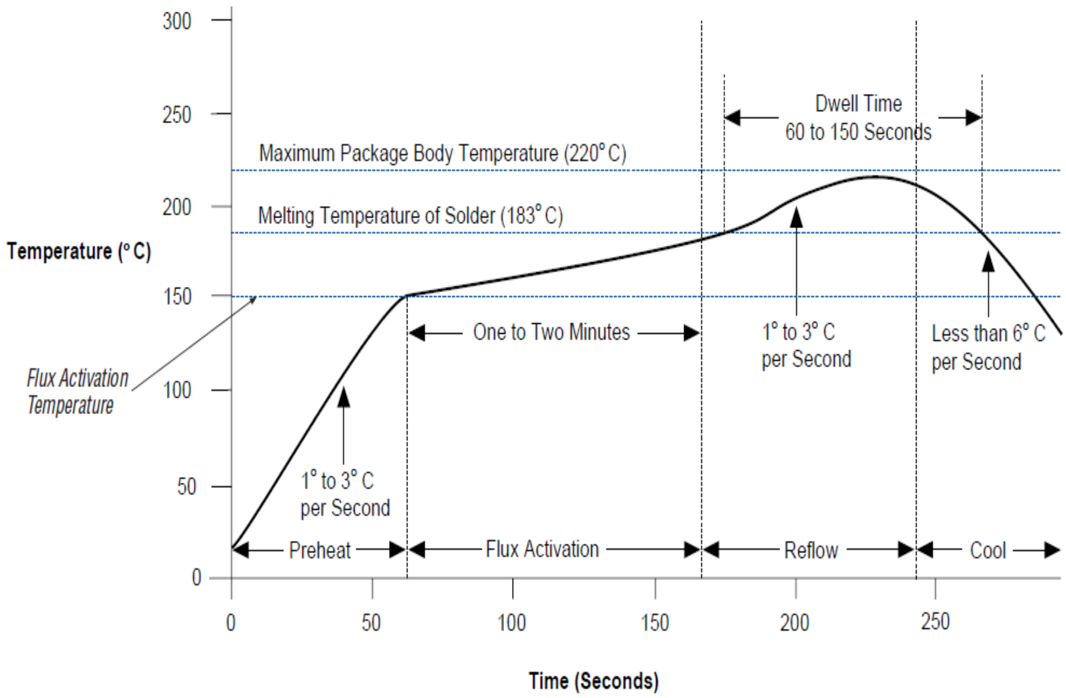

Figure 2.6: Temperature profile for conventional re-flow of tin-lead solder (Altera, 2002).

The 4 stages in the re-flow process are:

- ❖ Preheat stage- the solder paste dries and volatile ingredients evaporate.
- ❖ Flux activation- the paste should be kept for one to two minutes from 150^0C to near melting point temperature to make sure the flux in the paste can clean the surface properly and evaporates.

- Re-flow stage- the devices enter re-flow stage when the temperature increase at rate 1^0C to 3^0C per second at a temperature above the melting point. To prevent warping, bridging and cold solders joints, the temperature was maintained above melting point at least 60 to 150 seconds.
- Cool- cooling is the last stage in re-flow profile. The cooling rate normally uses are less than 6^0C.

The minimum re-flow temperature limit for eutectic tin-lead solder is usually 200^0C. The upper limit is approximately 235^0C, which is the maximum temperature to which most components can be exposed (Vaccaro, 2002). These high and low temperature limits provide a process window over 35^0C. A eutectic SAC solder has a melting point of 217^0C. This alloy required a minimum re-flow temperature of 235^0C to ensure good wetting. The maximum re-flow temperature for eutectic SAC solder around 245^0C to 260^0C range. Most of the standard PCB materials (glass/epoxy FR4) can be heated up between 260^0C and 280^0C. The glass transition for FR4 is around 130-145^0C, and at a temperature above 280^0C, the process of decomposition of the polymeric resin begins (Anton and Angela, 1998). Table 2.5 and 2.6 shows that re-flow temperature of solder depends on the package thickness and the volume of solder use for Actel industries.

Table 2.5: Tin-lead eutectic solder standard re-flow temperature (Actel, 2008).

Package Thickness	Volume (mm^3) <350	Volume (mm^3) ≥350
< 1.6 mm	235 + 0 ^{0}C/ - 5 ^{0}C	225 + 0 ^{0}C/ - 5 ^{0}C
≥ 2.5 mm	225 + 0 ^{0}C/ - 5 ^{0}C	225 + 0 ^{0}C/ - 5 ^{0}C

Table 2.6: Lead-free solder- standard reflow temperature (Actel, 2008).

Package Thickness	Volume (mm^3) <350	Volume (mm^3) 350-2000	Volume (mm^3) >2000
<1.6 mm	260 + 0 ^0C	260 + 0 ^0C	260 + 0 ^0C
1.6 mm -2.5 mm	260 + 0 ^0C	250 + 0 ^0C	245 + 0 ^0C
≥ 2.5 mm	250 + 0 ^0C	245 + 0 ^0C	245 + 0 ^0C

2.6 Flux

Reliability of a solder joint can only be accomplished with truly cleaned surface. Flux is a substance used to promote fusion between solder and substrate. Flux function as chemical to remove metallic oxides and preventing the reformation of new oxide during soldering, thermally enhancing the heat transfer from the molten solder to the joint during soldering operation and physically influence the surface tension equilibrium in the direction of solder spreading by decreasing dihedral angle (Manko, 2001; Lambert, 1988). Fluxes are mixtures of three primary components;

- The corrosive agent such as acid or alkaline material.
- A vehicle, typically water or alcohol, which puts the corrosive agent into solution or suspension as a mixture for ease of handling and application
- Wetting agents which are chemical additions to help the flux spread over the surface.

The type of fluxes has to be carefully chosen according to the melting point and solder itself (different solder alloying elements need a different kind of fluxes). A good flux should melt at a temperature around 20^0C to 50^0C lower than the melting point of solder.

2.6.1 Functions of Flux

The flux must serve several functions during the fabrication to promote good wettability of solder joint.

- The most widely considered the function of flux is to remove the nascent oxide layer from the substrate. Elimination of the oxide layer serves two purposes. First, it provides the molten solder with higher surface tension of a substrate (as opposed to lower surface tension of its oxide) which contributes to the driving force for solder spreading (Vianco, 1999). Secondly, the availability of pristine base metal permits a metallurgy reaction between solder and substrate.
- The second role of the flux is to reduce surface tension of the molten solder. This is archived by modifying the actual surface chemistry of the molten solder as well as by eliminating the oxides skin which forms on the molten solder (Vianco, 1999). Lowering the surface tension of the solder assist in its capability to spread horizontal and vertical surface.
- The third function of flux is to establish a barrier between substrate and atmosphere during the soldering process. As a barrier of coating, flux prevents re-oxidation of the substrate during preheating state of soldering.

Another function that must be served by flux are;

- The flux shall have uniform consistency on the substrate.
- Harmless to the component.
- Easily removed from component.