PROPERTIES OF LOW TEMPERATURE INDIUM-BASED TERNARY LEAD FREE SOLDERS SYSTEM

MOHAMAD SALIMIN BIN JAHARI

Universiti Sains Malaysia

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by

MOHAMAD SALIMIN BIN JAHARI

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LIST OF ABBREVIATION

Bi-In-Sn	:	Bismuth-Indium-Tin
Bi-Sn-Zn	:	Bismuth-Tin-Zinc
CTE	:	Coefficient of Thermal Expansion
DSC	:	Differential Scanning Calorimetry
DTA	:	Differential Thermal Analysis
LCD	:	liquid crystal diode
SEM	:	Scanning Electron Microscopy
SMT	:	Surface Mount Technology
Sn-In-Zn	:	Tin-Indium-Zinc
Sn-Pb	:	Tin-Lead
SWG	:	Standard wire gauge
TE	:	Thermal Expansion
TGA	:	Thermogravimetric Analysis
XRD	:	X-ray diffraction

PENCIRIAN SISTEM PATERI BEBAS PLUMBUM TERNARI SUHU RENDAH BERASASKAN INDIUM.

ABSTRAK

Pendekatan sistem pateri ternari digunakan untuk membangunkan pateri bebas plumbum bersuhu lebur rendah. Sistem pateri bebas plumbum Bi-24.8In-18.6Tin, Bi-39.3In-17.5Sn dan In-36.1Bi-15.6Sn disediakan. Sebagai tambahan, Sn-10.11In-6.2Zn and Bi-44Sn-2.1Zn juga dihasilkan untuk perbandingan kekuatan. Diketahui bahawa takat lebur sistem ternari Bi-In-Sn adalah dalam julat 60^{o}C hingga 80^{o}C bergantung kepada peratusan komposisi. Pencirian mikrostruktur dilakukan untuk semua aloi pateri menggunakan Mikroskop Imbasan Elektron(SEM). Pelbagai ujian seperti ujian pembasahan, ujian serakan, ujian kekuatan dan analisis ujian terma dilakukan sebagaimana yang dibincangkan. Kebolehbasahan bagi Bi-24.8In-18.6Sn, Bi-39.3In-17.5Sn, In-36.1Bi-15.6Sn, Bi-44.2Sn-2.1Zn dan Sn-10.1In-6.2Zn adalah didapati memuaskan dari segi daya pembasahan serta masa pembasahan yang diperolehi adalah masing-masing (3.67mN, 0.434sec), (4.34mN, 0.277sec), (4.71mN, 0.169sec), (2.76mN, 0.440sec) and (5.43mN, 0.448sec). Sudut sentuh bagi aloi pateri Bismuth-Indium-Timah adalah kurang daripada 30^{o} yang menunjukkan kebolehbasahan yang baik di atas substrat kuprum. Dalam perbandingan kekuatan Bi-24.8In-18.6Sn menunjukkan nilai tegangan yang paling tinggi manakala Bi-48.3In-15.6Sn mempunyai nilai ricih yang paling tinggi. Aloi pateri Bi-In-Sn mempunyai nilai pekali pengembangan terma yang lebih kecil berbanding aloi Sn-10.11In-6.2Zn, Bi-44Sn-2.1Zn dan Sn-37Pb eutektik.

PROPERTIES OF LOW TEMPERATURE INDIUM-BASED TERNARY LEAD FREE SOLDERS SYSTEM

ABSTRACT

The ternary solder system approach is used to develop low melting lead free solders. Bi-24.8In-18.6Sn, Bi-39.3In-17.5Sn and In-36.1Bi-15.6Sn lead free solder systems were prepared. In additions, Sn-10.11In-6.2Zn and Bi-44Sn-2.1Zn were also made for strength comparison. It was found that melting point of Bi-In-Sn ternary systems range from 60^{o}C to 80^{o}C depending on the percentage of the composition. Microstructure characterization was carried out for all solder alloys using Scanning Electron Microscope (SEM). Various tests such as wetting test, spreading test, strength test and thermal test analysis were applied and discussed. Wettability of Bi-24.8In-18.6Sn, Bi-39.3In-17.5Sn, In-36.1Bi-15.6Sn, Bi-44.2Sn-2.1Zn and Sn-10.1In-6.2Zn was found to be satisfactory with good wetting force and wetting time (3.67mN, 0.434sec), (4.34mN, 0.277sec), (4.71mN, 0.169sec), (2.76mN, 0.440sec) and (5.43mN, 0.448sec) respectively. Contact angle for Bismuth-Indium-Tin solder alloys is less than 30^{o} which showed good wettability on copper substrate. In strength comparison Bi-24.8In-18.6Sn showed the highest in tension while Bi-48.3In-15.6Sn in shear. Bi-In-Sn solder alloys have smaller coefficient of thermal expansion than Sn-10.11In-6.2Zn, Bi-44Sn-2.1Zn and eutectic Sn-37Pb alloy.

CHAPTER 1
INTRODUCTION

1.1 Overview

Nowadays, there is rapid development of technology in many industrial fields. Along with that, study and research is done to ensure that technology growth will not only make our daily routine easier but its application is safe. As far as our concern, we do not want human and environment become the victim of the unsafe technology. Simply said, we want the kind of technology which is secure for both human and environment.

1.2 Statement of Problems

The solder alloy normally used in microelectronic industry is eutectic 63Sn-37Pb alloy with melting point 183^{o}C. However the use of lead in microelectronics has been restricted by legislation because of health and environmental concern. According to the European Union Waste Electrical and Electronic Equipment Directive (WEEE) and Restriction of Hazardous Substances Directive (RoHS), lead has to be eliminated from electronic systems by July 1, 2006 (Wikipedia, 2006).

Government regulations are becoming stricter, and managing of waste materials is becoming more regulated. Now is the time to take a solemn look at alternative materials for making electrical interconnection due to extinction of lead usage in solder. Generally, electronic manufacturing environment is a clean and safe place to work in; however, governments are still targeting the removal of lead from solder, due to lead pollutants generated in other industries (Karl, 1995). Furthermore, new lead-free solders offer better properties and enlarge the current range of application of soldering technology (Moelans et al., 2003). The growth of various industrial sectors increased the usage of solder alloys especially in electronic industry. Manufacturing of electronic products need solder joint for mounting process of electronic components.

Health and environmental problem due to the usage of toxic lead has attracted researchers to find alternative materials as a replacement of lead in solder alloys. The focus is not just the termination of lead in solder but also producing low temperature lead free solder. Alloys which are considered as low melting are alloys with melting temperature between $50^{o}C$ to $180^{o}C$ (Mei et al., 1996).

The development of low melting solder which is similar or lower melting point compared to eutectic Sn-Pb is becoming more famous among researchers especially for those who are involved in microelectronic industries. This is encouraged by higher demand for low temperature lead free solder to prevent the damage of electronic devices due to high operating temperature. At the same time by using low temperature lead free solder, it can terminate the use of lead for the safety of workers.

Surface mount technology (SMT) is demanding the use of low temperature solder alloy to prevent damages due to heat influence. Electronic devices used for SMT is sensitive to high temperature. Moreover, excessive heat can lead to damage of electronic components such as liquid crystal display (LCD) and circuit board.

Alloys which are suitable for lead-free solders must fulfil many requirements (Moelans et al., 2003):

i. good wettability to the substrate,
ii. ability to form a strong chemical bond with the substrate,
iii. suitable melting temperature and solidification behaviour,
iv. good mechanical properties like high strength and good resistance to mechanical and thermal fatigue, corrosion resistance;
v. good electrical conductivity,
vi. safe for health and environment,
vii. possibility for easy assembly and,
viii. low material cost.

Yoon et al. (1999) reported that in the electronic devices assembly, solder joints are an important part of packaging integration because solder joint serves both as electrical contacts and as the mechanical support.

The development of lead free solders is widely done all around the world. Lead free solder offers many benefits to the electronic industries. Several lead free solders having low melting temperature which is really good for electronic devices assembly in term of low temperature processing. Many devices and components used in electronic industries are sensitive to high temperature and might be damaged. Using low melting temperature lead free solders in electronic devices assembly can prevent the damages during assembly process. However, there are many other factors that should be considered before the low temperature solders can be fully applied in the electronic devices assembly.

The solder properties should be as good as the eutectic and near eutectic lead solder which have been used for a very long time in electronic industries. That is a great challenge to the researchers and electronic manufacturers in developing this new low temperature solder. The solderability and reliability of the new low temperature solder should be as good as conventional lead solder or even better. Beside that the materials or elements used to produce low temperature solders must be available for a long period and considerable in term of cost. This is to ensure that low temperature solders not only offer great properties but will not affect productivity in the electronic industries especially the processing cost. Consequently the electronic products can be offered at a competitive price in the market.

1.3 Objective of the research

Research on lead free solder is expanded everyday. In this study the focus is on the development of low melting solder alloys which is expected to have good solderability properties and considerable manufacturing cost.

The main objectives of this research are:

1. To investigate the formation of low temperature Sn-Bi-In solder system
2. To evaluate the mechanical properties of produced solder alloys
3. To study the interfacial reactions between solders and the contacted surface

1.4 Research Approach

In this research, solder alloys were produced by melting raw materials (weight percent - wt %) mixture based on certain composition. The selection of composition is based on previous research by Moelans et al. (2003). Raw materials used in this research are tin, indium, bismuth and zinc having 99.99% purity.

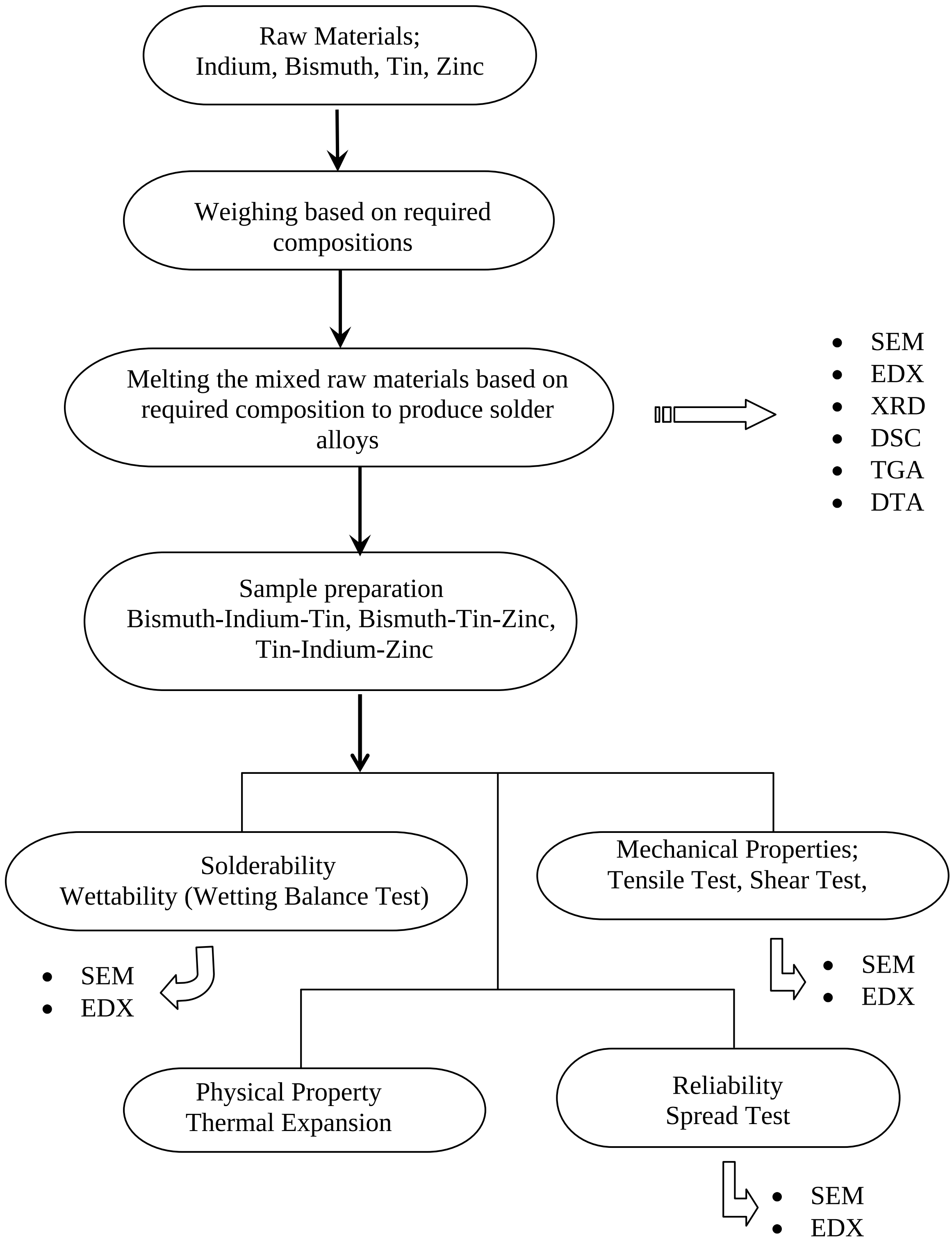
Solder preparation was started with weighing the raw materials based on weight percent (wt %) of selected composition. Then, elements are mixed and melted in the alumina crucible. Molten solder is stirred and hold for a few minutes at highest temperature (400^{o}C) of the Solder Checker machine to ensure all the elements are well mixed and the molten alloy is homogenous. Molten solder is cooled at room temperature and a bulk of solder alloy is obtained.

Mixture of raw materials is melted and poured into a special mould to produce a disc shape solder pellet with dimension 2 mm in thickness and 5 mm diameter that is required for spreading test. The solder piece was removed from the mould and punched with 5 mm puncher.

Several testing was carried out to determine the properties of the solder alloys. Thermal analysis was done to determine the melting point of solder alloys. Phases exist in the solder alloy is observed through microstructural analysis.

Solderability and physical properties of the solder was determined by wetting test and spreading test. For wetting test and spreading test, flux was used. Flux is very important because the wetting of solder alloy on the substrate will only occurred with the existence of flux. Zinc chloride paste was used as a flux in this research. Mechanical properties of solder alloy are tested on the solder joint by doing tensile test and shear test.

1.5 Research Schematic Diagram



CHAPTER 2
LITERATURE REVIEW

2.1 BACKGROUND

Sn-Pb solders have been widely used to make electronic interconnections. The components of the Sn-Pb system are completely soluble in the liquid state but only partially soluble in the solid state. This is the most ordinary type of binary system and is the same as for numerous systems of copper-silver, copper-tin, copper-zinc, aluminium-copper and aluminium-magnesium (Manko, 2001).

The solderability of component is a measure of their total suitability for industrial soldering. Wassink (1989) stated that sufficient solderability of the parts used in the soldering process is a major qualification for the success of the process.

Surface mount technology (SMT) has been widely adopted in recent years. Unfortunately, SMT has also introduced new failure mechanisms. Solder joints are important for both electrical and mechanical connections. Solder does not have enough ductility to absorb repeated relative displacements (Lau, 1991).

Making solder Pb-free has become an urgent task for the electronics assembly industry because more consumer products are moving towards environmentally friendly packaging. The elimination of Pb in the solder reduces not only toxicity but also the amount of radioactive elements, which are harmful and can cause malfunction of integrated circuits through alpha ray emission (Chan *et al.*, 2003; Zhong *et al.*, 2003). There is therefore a definite need to find a replacement for SnPb solder.

In recent years, a variety of lead free solders has been developed as replacements of Sn-Pb eutectic solder. Some lead-free solders have been practically used in precision electronic devices. Lead-free solders are required to have excellent properties such as suitable melting point and good solder joints. Beside it is enviable that the characteristics of lead-free solders are similar to the conventional Sn-Pb solder (Zhou et al., 2005) so that we can use the same processing equipment, conditions, and fluxes optimized for Sn-Pb solders (Kishan, 2005). One of the important requirements for electronics solders is processing temperature as low as Sn-Pb eutectic alloy.

Wider process windows in mass production environments would aid in achieving good manufacturing process yields with high productivity apart from allowing product circuit designers more flexibility in layout design and selection of components.

2.1.1 Solder

A solder is a fusible metal alloy, with a melting point between 90-450°C (Wikipedia, 2008). However, at this moment there is solder alloy with a melting point lower than 90^{o}C. Solder is melted to join metallic surfaces, especially in the fields of electronics and plumbing, in a process called soldering. Figure 2.1 show one of the solder available in the market in a wire shape.

The word solder comes from the Middle English word soudur, via Old French soldure and soulder, from the Latin solidare, meaning '"to make solid"'(Wikipedia, 2006). Elements which are commonly used as a solder alloys are tin (Sn), lead (Pb), argentums (Ag), bismuth (Bi), indium (In), antimony (Sb), and cadmium (Cd).

Figure 2.1: Reels of solder © Rapid Electronics (Wikipedia, 2007)

Solder for electronics use contains tiny cores of flux, like the wires inside a mains flex. The flux is corrosive, like an acid, and it cleans the metal surfaces as the solder melts. Without flux most joints would fail because metals quickly oxidize and the solder itself will not flow properly onto a dirty, oxidized, metal surface. The best size of solder for electronics in wire shape is 22swg. (Hewes, 2007)

2.1.2 Soldering Technology

American Welding Society (AWS) defined soldering as metal joining at temperature below 427^{o}C. Soldering depends on the wetting to form bonding through diffusion or formation of intermetallic compound on base metals. Soldering is a method of making a permanent electrical and mechanical connection between metals. Unlike glue, which forms a solely physical adhesive bond, solder chemically reacts with other metals to form a different alloy. While there are many different processes utilized in soldering, virtually all of them involve four basic elements: base metals, flux, solder, and heat (Hoban & Lunt, 1997).

Soldering is the process in which two metals are joined together by use of solder, a tin or lead alloy, which is melted at a relatively low temperature by a soldering iron and applied between the original components to bridge the gap while it is soft and malleable. Soldering is sometimes confused with welding, but is distinct in that welding causes the original metal pieces to melt together, while the addition of a third bridging material is optional. Soldering does not involve the melting of the metals to be joined, and always make use of the filler material.

Soldering is most commonly associated with electronic work, but the practice has a long history and is also utilized for plumbing, jewellery crafting, and a variety of other trades that require the ability to manipulate metal. Rahn (1993) assured that there is evidence to suggest that soldering was used even earlier, many different soldering techniques were widely used throughout the Greek and Roman Empires, as well as in Viking dominated Scandinavia. Archaeologists have found jewellery, weapons, tools, and cutlery that have been very skilfully soldered.

Throughout the years solder has been used in various applications, however it was the invention of electronic devices in the latter part of this century that guide to hasty advances in soldering technologies. The most frequent application of soldering is assembling electronic components to printed circuit boards (PCBs). Another common application is making permanent but reversible connections between copper pipes in plumbing systems.

Joints in sheet-metal objects such as food cans, roof flashing, rain gutters and automobile radiators have also historically been soldered, and occasionally still are.

Jewellery and small mechanical parts are still often assembled by soldering. Soldering is used to join lead came and copper foil in stained glass work. Soldering can also be used to make affect a semi-permanent patch for a leak in a container or cooking vessel.

Hoban and Lunt (1997) stated that there are two main classifications of soldering methods in use today: mechanical or non-electrical (using primarily acid flux), and electrical (using primarily rosin flux).

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 of use, they must be electrically connected to each other and to mechanical devices. The 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 almost always wave soldered or reflow soldered. In wave soldering, parts are temporarily adhered to the PCB with small dabs of adhesive, and then the assembly is passed over a small fountain in a bulk container 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 (more commonly) 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.

2.1.2(a) Wave Soldering

Wave soldering is a large-scale soldering process by which electronic components are soldered to a PCB to form an electronic assembly. The name is derived from the fact that the process uses a tank to hold a quantity of molten solder; the components are inserted into or placed on the PCB and the loaded PCB is passed across a pumped wave or cascade of solder. The solder wets to the exposed metallic areas of the board (those not protected with solder mask), creating a reliable mechanical and electrical connection. The process is much faster and can create a higher quality product than manual soldering of components. Wave soldering is used for both through-hole printed circuit assemblies, and surface mount. In the latter case, the components are glued onto the printed circuit board surface before being run through the molten solder wave.

As through-hole components have been largely replaced by surface mount components, wave soldering has been supplanted by reflow soldering methods in many large-scale electronics applications. However, there is still significant wave soldering where SMT is not suitable (e.g. large power devices and high pin count connectors), or where simple through-hole technology prevails (certain major appliances).

2.1.2(b) Reflow Soldering

The development and increased use of surface mount technology has led to the use of other soldering methods. While surface mount components can be wave soldered, they must first be attached to the circuit board with some type of adhesive or cement in order to keep them in place during soldering. This introduces another step in the assembly process. Since the whole surface-mount component is immersed in the wave, it must be constructed in such a manner to withstand the high temperature of the liquid solder. There is also a problem of gasses being trapped between the component and the board (Manko, 1995). Because of these difficulties with wave soldering; re-flow soldering is the preferred method of soldering surface mount components.

Reflow soldering is the most common means to attach a surface mounted component to a circuit board. In a re-flow process, solder paste is put on the component sites of the printed circuit board, and then the components are put on the board on top of the solder paste. The board and attached components are then heated to activate the flux, elevate the temperature of the base metals, and melt (or "re-flow") the solder (Hoban and Lunt 1997).

The goal of the reflow process is to melt the powder particles in the solder paste, with the surfaces being joined together, and solidify the solder to create a strong metallurgical bond. Often a separate adhesive is used to hold the device in place until soldering takes place. There are usually four process zones in conventional reflow process, consisting of preheat, thermal soak (often shortened to just soak), reflow and cooling.

2.2 Lead Solder

Solder used for electronics is a metal alloy, made by combining tin and lead in different proportions. With most Sn-Pb solder combinations, melting does not take place all at once. Fifty-fifty solder begins to melt at 183°C, but it's not fully melted until the temperature reaches 216°C (Circuit Technology Centre's Website, 2000). Between these two temperatures, the solder exists in a plastic or semi-liquid state. Figure 2.2 shows the eutectic diagram for tin-lead solder.

The plastic range of a solder varies, depending upon the ratio of tin to lead. With 60/40 solder, the range is much smaller than it is for 50/50 solder. The 63/37 solder, known as eutectic solder has practically no plastic range, and melts almost instantly at 183°C.

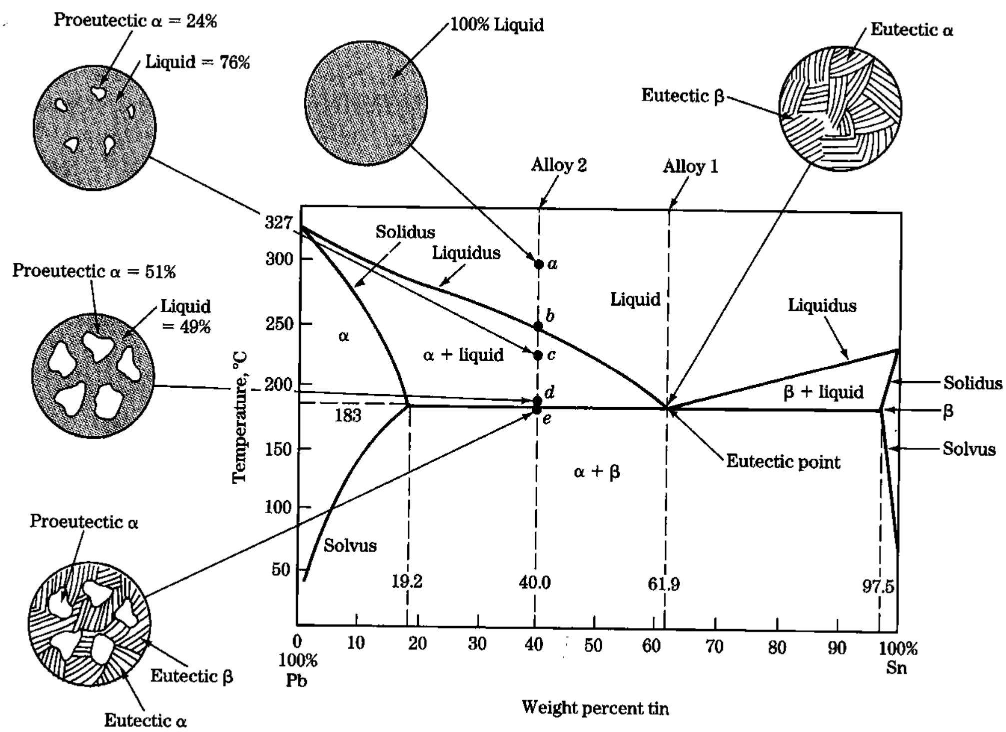


Figure 2.2: Sn-Pb eutectic diagram (Ben, 1990)

The solders most commonly used for hand soldering in electronics are the 60/40 type and the 63/37 type. Due to the plastic range of the 60/40 type, please be careful not to move any elements of the joint during the cool down period. Movement may cause disturbed joint. A disturbed joint has a rough, irregular appearance and looks dull instead of bright and shiny. A disturbed solder joint may be unreliable and may require rework. The extensive use of the Sn-Pb alloy is due the following reasons.

1. The melting point (183^0 C - 189^0 C) is low enough to permit the design of components that can endure the high temperatures associated with the soldering process.
2. Though the solder oxidizes quite rapidly, the characteristics of the tin oxide films pose relatively few problems compared with the oxide films of some other low-melting metals.
3. Because of the affinity between tin and many other metals, good wetting can be achieved with the aid of only mildly active fluxes.
4. It provides reasonably good mechanical strength to the solder joint, which can be expected with soft-soldering.

By contrast, a mixture of lead and tin is eutectic because these metals are only partially soluble in each other when in the solid state. Lead and tin have different crystal structures (face-centred cubic (FCC) versus body-centred cubic (BCC)) and lead atoms are much larger. No more than 19.2% by weight of solid tin can dissolve in solid lead and no more than 2.5% of solid lead can dissolve in solid tin. The solid lead-tin alloy thus consists of a mixture of two solid phases, one consisting of a maximum of 19.2 wt% tin (the alpha phase) and one consisting of a maximum of 2.5 wt% lead (the beta phase).

For example, as a 40 wt% tin-lead liquid cools it will begin to have a liquid & solid phase coexisting. The solid (proeutectic) alpha phase has an increasing concentration of tin as cooling continues until the eutectic composition of 61.9 wt% tin is reached at 183ºC - when no more liquid phase exists. Solidification in the alpha proeutectic region consists of layered growth of solid nodules - with each layer containing a higher concentration of tin. This layering of increasing concentrations of tin is called coring. Faster cooling results in reduced coring.

The word eutectic is derived from Greek roots meaning "easily melted". A eutectic mixture has a eutectic composition for which complete liquefaction occurs at a lower temperature (the eutectic temperature) than for any other composition. For lead and tin the eutectic composition is 61.9 wt% tin and the eutectic temperature is 183ºC - which makes this mixture useful as solder. At 183ºC, compositions of greater than 61.9 wt% tin result in precipitation of a tin-rich solid in the liquid mixture, whereas compositions of less than 61.9 wt% tin result in precipitation of lead-rich solid.

2.2.1 Alternatives to lead

Sn-Pb solder alloys have been widely used in the electronic industries due to low melting point, good wettability, good corrosion resistance and good electrical conductivity. Due to restriction on the usage of lead, lead free solder is really needed.

Therefore, more efforts focusing on the design of solder alloys systems that can replace Sn-Pb solder is being done.

Alternative lead-free solder alloys are being developed, but their introduction into electronics manufacturing requires major changes to current manufacturing processes, electronic components, and inspection requirements. Several lead-free solder alloys generally require higher temperatures - up to 260°C as opposed to 215°C - to perform the soldering operation, which may affect the reliability of boards and components. Soldering equipment may not be capable of maintaining such high temperatures. The temperature profiles employed in reflow soldering may be longer, which will adversely affect productivity.

The issues of material compatibility are a major concern when employing lead-free soldering technologies on heritage lead-based assemblies. Certain alloys will form intermetallics when used on a component or board coated with lead-tin solder, which will reduce the resulting solder joint's mechanical integrity. There is no drop in "turnkey" of available lead-free solder alternatives due to the intermetallic formation. However, research is still carried out to fulfil the industries needed base on required specification and standard.

2.3 LEAD FREE SOLDER

2.3.1 Design for Environment

The original equipment manufacturer (OEM's) and semiconductor manufacturing companies have initiated the process of making their products lead-free. The activity is often called "Design for Environment" or "DfE." The "DfE" process in the electronics industry starts with the materials used in making the electronics equipment. (Kishan, 2005)

2.3.2 Solder Materials

A large number of lead-free solders have been developed and applications have been made for over 100 patents on various alloy compositions. The question of which lead-free solder is the "best" is often asked but is difficult to answer since there is no absolute drop-in replacement for tin-lead with identical melting temperature, cost, wetting and strength properties. Figure 2.3 shows a lead-free solder which is available in the market.

Figure 2.3: A coil of lead-free solder wire (Wikipedia, 2007).

The most convenient way to separate the available lead-free alloys is to first consider their melting temperature (Kishan, 2005). Most fit into one of the following categories: low melting temperature (below 180°C), melting temperature equivalent to the tin-lead eutectic (180-200°C), mid-range melting temperature (200-230°C), and the high-temperature alloys (230-350°C). By considering the service temperature that the alloy will experience, together with any maximum temperature limitations of the components or other items to be joined, an alloy of a suitable melting point can be found.

Lead-free alloys as a replacement for eutectic alloy 63Sn-37Pb (melting point, 183^{o}C) or near eutectic 60Sn-40Pb should have similar melting point or melting range. Certain Sn-based binary alloy is having a very low melting temperature or very high melting temperature.

Several lead free solders have been used in electronic devices, for example, personal computer and cellular hand phone by Japanese manufacturers. Lead-free solder should have good properties such as suitable melting point and good solder joint. In addition, lead-free solder need to have same characteristics as conventional Sn-Pb solder. This is to ensure the usage of available processing equipment and fulfil the processing characteristics and optimized fluxes for Sn-Pb solder.

Most of lead free solders are Sn-based. Special solders category used are eutectic alloy and inert metal such as aurums (Au), argentums (Ag) and copper (Cu). These eutectic alloys are used as solders because of their low melting point. So, all solder bonds will melt or become solid at one single temperature. If not there might be a possibility of partial melting or partial solidification can occur. Other additional alloy elements such as bismuth (Bi), zinc (Zn), indium (In) and germanium (Ge) are considered as combined Sn eutectic alloys.

Different elements serve different roles in the solder alloy (Wikipedia, 2007):

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

- Copper lowers the melting point, improves 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 lead in the liquid solder.
- Bismuth significantly lowers the melting point and improves wettability. In presence of lead and tin, bismuth forms crystals of Sn16Pb32Bi52 with melting point of only 95 °C, which 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.
- Indium lowers the melting point and improves ductility. In presence of lead it forms a ternary compound that undergoes phase change at 114 °C.
- Zinc lowers the melting point and is low-cost. However it is highly susceptible to corrosion and oxidation in air, therefore zinc-containing alloys are unsuitable for some purposes, e.g. wave soldering, and zinc-containing solder pastes have shorter shelf life than zinc-free ones.
- Antimony is added to increase strength without affecting wettability.

Lead-free solder joints may produce mechanically weaker joints depending on service and manufacture conditions, which may lead to a decrease in reliability using such solders. "Tin Whiskers" are another problem with many lead-free solders, where slender crystals of tin slowly grow out of the solder joint. These whiskers can bridge a short circuit years after a device's manufacture.

- SnAgCu solders are used by two thirds of Japanese manufacturers for reflow and wave soldering, and by about ¾ companies for hand soldering.

- 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 Japan Electronics and Information Technology Industries Association (JEITA) recommended alloy for wave and reflow soldering, with alternatives SnCu for wave and SnAg and SnZnBi for reflow soldering.
- SnAg3.5Cu0.7 is another commonly used alloy, with melting point of 217-218 °C.
- SnAg3.5Cu0.9, with melting point of 217 °C, is determined by National Institute of Standards and Technology (NIST) to be truly eutectic.
- SnAg3.8Cu0.7, with melting point 217-218 °C, is preferred by the European IDEALS consortium for reflow soldering.
- SnAg3.8Cu0.7Sb0.25 is preferred by the European IDEALS consortium for wave soldering.
- SnAg3.9Cu0.6, with melting point 217-223 °C, is recommended by the US National Electronics Manufacturing Initiative (NEMI) consortium for reflow soldering.

- SnCu0.7, with melting point of 227 °C, is a cheap alternative for wave soldering, recommended by the US NEMI consortium.
- SnZn9, with melting point of 199 °C, is a cheaper alloy but is prone to corrosion and oxidation.
- SnZn8Bi3, with melting point of 191-198 °C, is also prone to corrosion and oxidation due to its zinc content.
- SnSb5, tin with 5% of antimony, is the US plumbing industry standard. Its melting point is 232-240 °C. It displays good resistance to thermal fatigue and good shear strength.

- SnAg2.5Cu0.8Sb0.5 melts at 217-225 °C and is patented by AIM alliance.
- SnIn8.0Ag3.5Bi0.5 melts at 197-208 °C and is patented by Matsushita/Panasonic.
- SnBi57Ag1 melts at 137-139 °C and is patented by Motorola.
- SnBi58 melts at 138 °C.
- SnIn52 melts at 118 °C and is suitable for the cases where low-temperature soldering is needed.

2.4 Binary Alloys

2.4.1 Tin-Bismuth Solder Alloy

Morris et al. (1993) reported the tin-bismuth (Sn-Bi) system has a eutectic composition of 42Sn-58Bi and a relatively low eutectic temperature of 139°C (Figure 2.4). The room temperature equilibrium phases are Bi and Sn with about 4 wt% Bi in solid solution. Since tin has very low solubility in Bi at the eutectic solidification temperature of 130°C, the Bi phase is essentially pure Bi. However, the maximum solubility of Bi in Sn is about 21 wt% (Kabassis *et al.*, 1986). As the alloy cools, Bi precipitates in the Sn phase. At moderate cooling rates, the eutectic Sn-Bi microstructure is lamellar, with degenerate material at the boundaries of the eutectic grains. This microstructure is similar to the one theoretically predicted by Croker *et al*. (1973) for relatively slow cooling rates.

Wild (1971) observed cracks on slowly cooled eutectic Sn-Bi solder joints. Slow cooling resulted in the formation of large grains. Tin precipitates from the solder matrix along the boundaries of these large grains through which cracking occur. Cracking was not observed during rapid cooling. Cooling rates, however, were not specified in the literature. It has also been reported by Glazer (1995) that recrystallization of the alloy produced an expansion of up to 0.0007 in. /in. Wild (1971) stated the expansion results in embrittlement, which may be due to strain hardening caused by deformation that occurs to accommodate the expansion.

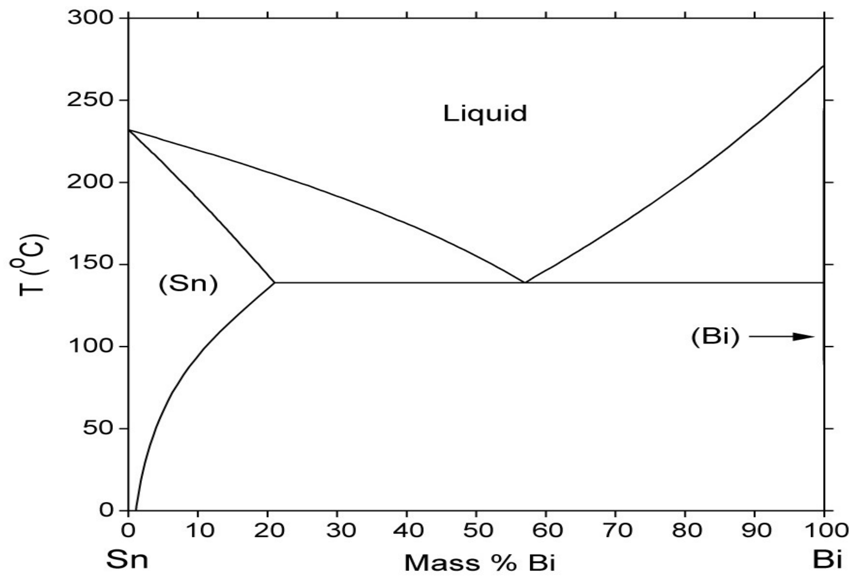


Figure 2.4: Tin-Bismuth Phase Diagram (Metallurgy Webmeister, 2003)

2.4.2 Tin-Indium Solder Alloy

The indium-based solder with the composition of In-48Sn is the one that is commonly used for SMT applications. The eutectic composition is In-48Sn, and the eutectic temperature is 117°C. The two phases that form are intermetallic phases - an Indium-rich, pseudo-body-centred tetragonal phase, β, which has 44.8 wt. % Sn, and a hexagonal Sn-rich phase,γ with 77.6 wt. % Sn (Glazer, 1995). Mei and Morris (1992) described the microstructure of In-48Sn solder on a Cu substrate as having lamellar features. The Sn-rich phase is composed of equiaxed grains. The Indium-rich phase contains Sn precipitates. A similar structure with less irregularity was observed by Freer and Morris (1992) on a Ni substrate and significant microstructural coarsening was observed by Seyyedi (1993), after prolonged aging of the solder joints made on a Cu substrate.

2.4.3 Tin-Zinc Solder Alloy

One of the important requirements for electronic solders is processing temperature as low as Sn-Pb eutectic alloy. As substitution candidate, the melting point of Sn-Zn eutectic alloy is closest to the Sn-Pb eutectic alloy. New research are done for Sn-Zn base solder alloy to improve other properties (Katsuki et al., 2000; Wu et al., 2000; Kim et al., 2003; Shiue et al., 2003; Song et al., 2003).The most crucial problems with Sn-Zn binary alloy is poor wettability. High surface tension of liquid phase and zinc oxide (ZnO) float on the liquid surface has restrained this solder from wetting copper (Katsuki et al., 1998; Lin et al., 1998, 2003; Yu et al., 2003). The Sn-9Zn eutectic solder alloy appears to be an attractive alternative, with a melting temperature of 198°C that is relatively close to eutectic tin-lead solder (Figure 2.5).

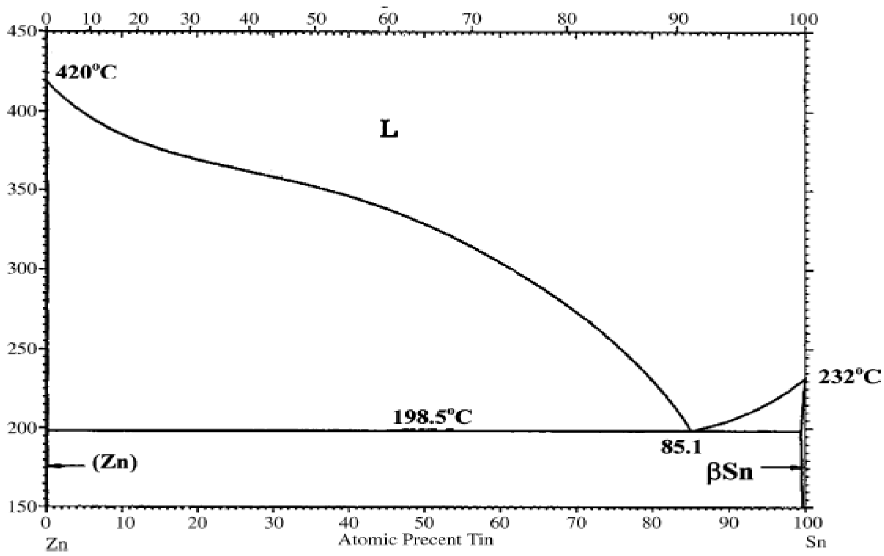


Figure 2.5: Tin-Zinc Phase Diagram (Islam et al., 2005)