STUDY OF WETTABILITY AND CORROSION BEHAVIOR OF Sn-37Pb, Sn-8Zn-3Bi AND Sn-3Ag-0.5Cu SOLDERS

by

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **“STUDY OF WETTABILITY AND CORROSION BEHAVIOR OF Sn-37Pb, Sn-8Zn-3Bi AND Sn-3Ag-0.5Cu SOLDERS”**. I also declare that it has not been previously 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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KAJIAN KEBOLEHBASAHAN DAN KELAKUAN KAKISAN PATERI Sn-37Pb, Sn-8Zn-3Bi DAN Sn-3Ag-0.5Cu

ABSTRAK

Pateri berdasarkan-plumbum telah dignnakan dengan meluas untuk sangkutan-cip dan proses cagak-permukaan di dalam industri elektronik dan aplikasi marin. Walau bagaimana pun, wsebabkan oleh isu-isu toksik yang berkaitan dengan plumbum, maka usaha untuk membangunkan penggantian keberkesanan-kos bahan bebas-Plumbum sedang berjalan. Kerja ini menyiasat kelakuan dan kerintangan kakisan untuk dua pateri bebas-plumbum, iaitu Sn-8Zn-3Bi dan Sn-8Ag-0.5Cu, dan membandingkan perstasi berdasarkan-plumbum Sn-37Pb pada suhu ambien. Perebakan, sudut pembasahan, ricikan, dan kekerasan telah diukur secara eksperimen menggunkan kaedah piawai dan peralatan. Keputusan eksperimen menunjukan bahawa Sn-8Zn-3Bi. Mempunyai sudut pembasahan tertinggi, mankalu Sn-37Pb mempaerkan perebakan tertinggi sebatian intermetalik $Cu_6 Sn_5$ kebiasaanya didapati dalam Sn-37Pb dan Sn-3Ag-0.5Cu, mankalu, Cu_6Sn_8 pula dikesan untuk Sn-8Zn-3Bi. Kekuatan sambungan diperolehi oleh Sn-37Pb iaitu 0.09MPa, ia itu melebihi sebanyak 66% dan 33% berbanding dengan Sn-8Zn-3Bi dan Sn-3Ag-0.5Cu, setiap satu. Walau bagaimana pun, kakisan selepas di dalam air latu tidak membri kesan keatas magnitud Kekuatan ricik dengan ketara. Keputusan ini mungkin disebabkan oleh sela masa pendedahan yang agak singkat.Sn-8Zn-3Bi Mempunyai kekerasan tertinggi diantara kesemua pateri. Kakisan memyebabkan peningkatan dalam kekerasan untuk kesemua pateri dengan 3.1, 6.74 dan 2.49% untuk Sn-37Pb, Sn-8Zn-3Bi dan Sn-3Ag-0.5Cu setiap sutu .Peningkatan dalam kekersan Sn -8Zn-3Bi diseimbangkan oleh pembentukan lapisan oksida. Ujian pengutuban

memunjukan bahawa Sn-37Pb Mempunyai kadar kakisah tertinggi berbanding dengan pateri. Bebas-plumbum yang lain mankakala, kakisan berasaskan kehilangan berat, Sn-37Pb dan Sn-3Ag-0.5Cu mempunyai kerintangan kakisan baik selepas pendedahan selama 360 jam, maka dapat dirumuskan bahawa sungguh pun kelakuan yang agak hampir untuk kesemua pateri ini, dan beberapa keadaan, pateri bebas–plumbum yang dikaji dalam Kerja ini mempamerkan sebagai calon. Berpotensi pengganti Sn-37Pb dalam penggunaan apabila melibatkan perihal kakisan.

STUDY OF WETTABILITY AND CORROSION BEHAVIOR OF Sn-37Pb, Sn-8Zn-3Bi AND Sn-3Ag-0.5Cu SOLDERS

ABSTRACT

Lead-based solders have been used extensively for chip-attach and surface-mount processes in the electronic industry, and in marine applications. However, because of toxicity issues related to lead, efforts to develop a cost-effective lead-free replacement have been ongoing. This work investigates the corrosion behavior and resistance of two lead-free solders, namely Sn-8Zn-3Bi and Sn-3Ag-0.5Cu, and compares their performances with a common lead-based solder of Sn-37Pb at ambient temperature. Spreading, wetting angle, shear, and hardness were measured experimentally using standard methods and instrumentations. Experimental results showed that Sn-8Zn-3Bi has the highest wetting angle, while Sn-37Pb demonstrated the highest spreading. Intermetallic compounds Cu_6Sn_5 were found to be common in Sn-37Pb and Sn-3Ag-0.5Cu, on the other hand, Cu_6Sn_8 was detected for Sn-8Zn-3Bi. The highest joint strength was given by Sn-37Pb represented by 0.09 MPa, which is higher by 66% and 33% than those of Sn-8Zn-3Bi and Sn-3Ag-0.5Cu, respectively. However, corrosion after 240 hr in seawater did not affect the magnitudes of shear strength substantially. This outcome was attributed mainly to the short time duration of exposure. Sn-8Zn-3Bi has the highest hardness among all solders. Corrosion caused an increase in hardness of all solders by 3.1, 6.74 and 2.49% for Sn-37Pb, Sn-8Zn-3Bi and Sn-3Ag-0.5Cu respectively. The high increase in hardness of Sn-8Zn-3Bi was attributed to the formation of oxide layer. Polarization test revealed that Sn-37Pb has the highest corrosion rate compared to the other lead-free solders. While, on weight-loss basis corrosion, Sn-37Pb and Sn-3Ag-0.5Cu has good corrosion resistance after 360 hr of exposure. It was concluded that in spite of the close behavior of these solders in some instances, lead-free solders studied in this work demonstrated a promising candidate as replacement of Sn-37Pb in applications where corrosion is of concern.

CHAPTER 1

INTRODUCTION

1.1 Background

As with the rest of western civilization during the middle ages, soldering exprienced little progress, being limited to the making of jewelry and common household implements. The industrial revolution quickly expanded the use of soldering technology, particularly with the availability of portable heat sources, i.e., compressed gas for torches and electricity for the resistive heaters in soldering irons. Plumbing, including conduit and radiators, food and water containers, as well as lightduty tools and sheet-metal construction for automobile fenders and panels were some of the many uses to which soldering was applied (Norrish, 2009). However, it was the advent of electronics in the early 20th century, and its continuing evolution to the present day, which has quickly become the hallmark application of soldering technology. Today, soldering technology can be categorized into two general fields based upon application (Weman, 2009):

(1) Electronics soldering, which describes the assembly of silicon microchip devices, printed circuit boards, motherboards, and connectors for the purpose of electrical signal transmission, and

(2) Structural soldering, which pertains to the role that is primarily that of mechanical fastening, i.e., nonelectronic applications.

Clearly, many of the advances in soldering technology over the past half-century, both in the development of materials as well as new processes, have taken place in the electronics arena. However, these new materials and processes as well as an enhanced understanding of electronic solder joint properties can be applied equally to structural soldering application (Lau, 2000; Yunus et al., 2003).

Over long years of using welding solders in industry, a wide range of solder alloys have been introduced. Among theses solders, lead (Pb)-based solders have been the most extensively used solders for electronic industry, particularly in chip-attach and surface-mount processes (Maveety et al., 2004). The Pb solder alloys are widely used because they are cheap and has good material properties, i.e. physical and mechanical properties (Mayappan et al., 2006). However, increasing environmental and health concerns over the toxicity of Pb combined with the strict legislation on banning the use of Pb-based solders (Abtew et al., 2000; Zhou et al., 2005; Li and Basaran, 2009).

The research effort for alternative solder alloys has been successful in identifying several candidates, A relatively large number, approximately 70, of Pb-free solder have been proposed, among them Sn-Bi, Sn-In, Sn-Zn, Sn-Ag, Sn-Ag-Cu and Sn-Cu) as a replacement for conventional Sn-Pb solders in ball-grid array (BGA) and flip-chip technology (Abtew and Selvadoray, 2000; Ghosh, 2001; Zeng and Tu, 2002; Li et al., 2002; Yoon et al., 2003; Arra et al., 2004; Yoon et al., 2004; Chen et al., 2006; Li and Basaran, 2009). During the transition period from Sn–Pb to Pb-free solders, existing high reliability products with Sn–Pb joints that remain in the field likely have to be repaired with Pb-free alloys. Nowadays, the Pb-free solder alloy has been widely used as a replacement for traditional Sn–37Pb eutectic alloy (Maveety et al., 2004; Mayappan et al., 2006). The Sn-Ag-Cu ternary alloy is the most general

Pb-free solder, which has the advantages of good wetting property, superior interfacial properties, high creep resistance and low coarsening rate (Zeg et al., 2002; Bai and Chen, 2009; Gao et al., 2009).

Among the important issues for the development of Pb-free packaging systems, the development of an appropriate Pb-free surface finish on a printed circuit board (PCB) is important. In soldering electronics devices on PCBs, the manufactures use many types of surface finishes (e.g. plating). These finishes can strongly influence the interfacial reaction and wetting properties. The thickness of the intermetallic compound (IMC), composition, microstructure, mechanical properties and reliability of solder joints are strongly dependent on the surface finish layers (Hung et al., 2001; Chong et al., 2006; Nurmi et al., 2008; Xia and Xie, 2008). Furthermore, joint reliability is one of the most critical criteria in the development of alternative solders (Yoon et al., 2004; Chen et al., 2006). Since the joining process is a direct consequence of an interfacial reaction between the solder and substrate, understanding the interactions between these materials is integral to the development of a reliable joining system. The solder joint reliability is a result of many factors including various design and process parameters. In particular, voids, which arise as a result of the process parameters, have been observed to be a critical factor that affects the solder joint reliability in the candidate solders (Yunus et al., 2003; Nurmi et al., 2005; Yu et al., 2008; Kim and Jung, 2006). Voids can degrade the mechanical robustness of the board level interconnections and affect the reliability and conducting performance of the solder joint.

The wetting of the new solders is of critical importance in order to be approved as an alternative to Pb solders. The wetting of liquid on solid surface is a topic of fundamental interest for widespread technological applications. Surface characteristics, for instance the surface roughness, influence the wetting behavior. The substrate surface roughness will influence the surface energy and the wetting behavior of the reacting or non-reacting liquid/solid interface (Lin and Lin, 2003). The wettability between solder and substrate is a very important issue in reliability of electronic packaging (Abtew and Slvaduray, 2000). The driving force for wetting between liquid solders and substrates are mainly the surface energies and the interfacial reaction.

Considering the crucial role of Pb-free solders in industrial applications nowadays, it is important to understand the entire aspects involved in the development and characterization of these solders in order to assign their properties and performance. This work focuses on studying the corrosion behavior, physical and mechanical properties of Pb-free ternary solders, namely, Sn-3Ag-0.5Cu and Sn-8Zn-3Bi on Cu substrate. Polarizability, wetting angle, spreading phenomenon, and shear stress are among the important variables to be studied. It is also worthwhile comparing the result with the conventional 63Sn–37Pb solder in order to assess the properties of the Pb-free solders.

1.2 Problem Statement

The adoption of a Pb-free solder poses a major challenge for a number of reasons. The range of information required before an informed decision can be made is indeed enormous. The number of research papers published on Pb-free solders has tended to focus on a few alloy systems, notably the Sn-Bi, In-Sn and Sn-Ag systems. However, information available in literature on ternary solders, such as Sn-3Ag-0.5Cu and Sn-8Zn-3Bi solders are limited. A more investigation, which will include mechanical properties of shear strength, wettability and spreading phenomenon, which are the basic and most important properties of solder alloy, under realistic service conditions, are necessary.

With increasing demands for high performance electronic devices, such as high-speed, high power transistors in elctronic controling devices for wet environment and under seawater, the application is consider harsh and higly corrosive environment. A fast survey on literature shows clearly a gap in information on corrosion behavior of solders. More limited information regarding corrosion are noticale on Sn-3Ag-0.5Cu and Sn-8Zn-3Bi solders. The properties of these lead free alloys in corrosive environments have not been widely reported, though it is of importance in many automotive, aerospace maritime and defense applications. Therefore, investigation on the corrosion mechanism of these solders and their joints will lead to further insight into the interfacial reaction that occur between dissimilar metals and these alloys during and after solder joining process under harsh environment. The increase in the requirement to produce the joints with high strength and reliability it is really needed to understand the corrosion mechanism of Sn-3Ag-0.5Cu and Sn-8Zn-3Bi joints since little information on corrosion attack for solder joint are published especially newly develop lead free solder.

1.3 Research Objective and Scope

The search and characterization of Pb-free solders are currently an attractive area of research that needs to be further investigated and explored. This field of science started to gain a great attention due to the building up of the international environmental concerns against Pb solders for their harmful effects. Many industrial sectors may benefit from any progress can be made in the field of alternative Pb-free solders. Therefore, it comes quite attractive and as a matter of importance as well to choose the general objective of this research which is to study the corrosion resistance, physical and mechanical properties of two ternary Pb-free solder alloys, namely Sn-3Ag-0.5Cu and Sn-8Zn-3Bi on Cu substrate and compare the results to the binary conventional 63Sn–37Pb solder. In order to achieve this objective, the following scopes have been adopted:

1. To investigate the wetting angle and spreading phenomenon of Sn-37Pb, Sn-8Zn-3Bi and Sn-3Ag-0.5Cu solders and characterize the formation and composition of the intermettalic compounds (IMC) formed during soldering.
2. To evalute shear strength and hardness of solder joints using Sn-37Pb, Sn-8Zn-3Bi and Sn-3Ag-0.5Cu solders under similar environment to wet and marine conditions.
3. To investigate the corrosion rate of Sn-37Pb, Sn-8Zn-3Bi and Sn-3Ag-0.5Cu solders through the conduct of a potentiodynamic polarization test at ambient temperature. Also, to study the mechanisim of corrosion of these solders under real corrosive environments using seawater at ambient temperature over different time durations.

1.4 Thesis Outline

As has been discussed in the previous sections, this work focuses on Pb-free solders as alternative welding solders to the conventional Pb solders. Theoretical and experimental works that have been undertaken were specified in this thesis. This thesis is organized as follows: an introduction of the process along with the problem statement and the objectives are presented in chapter 1. Chapter 2 reviews the previous studies on Pb-free solders including their development, characterization and testing results, with all related aspects. The experimental work including chemicals used, equipment description, experimental procedure and measurements are presented in chapter 3. The results and discussion of this thesis are concentrated in chapter 4. Finally, the conclusion from the current work and recommendations for further researches are gathered in chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Solder materials play a crucial role in the reliability of joint assemblies in electrical industry in different levels of the electronic assembly sequence. As a joining material, solder provides electrical, thermal and mechanical continuity in electronics assemblies. Solder alloys melt during the soldering process, and then the molten solder wet the substrates to be joined. Apparently, this process requires high performance and quality of the solder, which are important to the integrity of a solder join, which in turn is vital to the overall functioning of assembly. Therefore, physical, chemical and mechanical properties along with performance evaluation of solders have been the subject of a large number of studies. It is a matter of great importance to go through these recent studies for gaining useful information on solder alloys and to address the relevant fundamental aspects. A review of some of these studies is presented below.

2.2 Solderability

Solderability is only one of the five soldering parameters that is not controlled during the process of welding (Humpston and Jacobson, 2004). Figure 2.1 shows the reliability balance with respect to the five parameters that normally affect a soldering operation (Time, Temperature, Solder alloy, Flux activity, and Solderability). The more constant of these parameters being the time, temperature, and solder alloy (provided the solder is not contaminated). These three parameters can be controlled by the user during production. The manufacturing organization can also exercise control over the flux type (activity) by selection and monitoring. The quality of the surfaces in terms of solderability, however, depends on the supplier and in house storage and handling. From the reliability balance shown in Figure 2.1, it can be seen that a minimum level of solderability is required for every type of flux to be used. If the solderability level falls below the minimum acceptable flux activity, bad results can be guaranteed. The flux activity must be equal to or better than the matching solderability level (Manko, 2001).

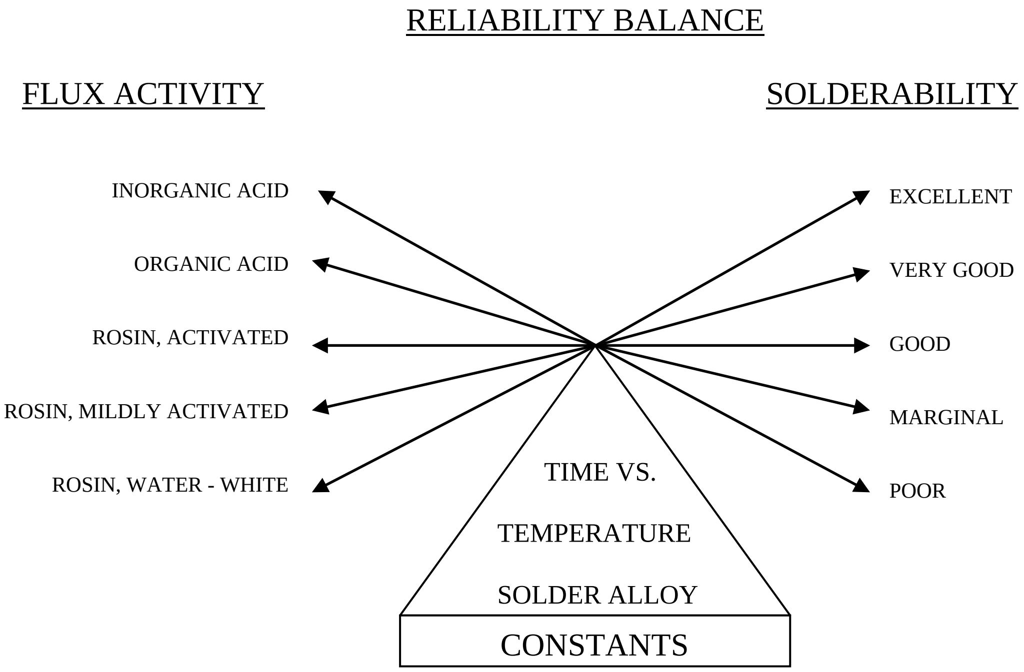

Figure 2.1: The reliability balance shows the interaction between soldering parameters (Manko, 2001)

During reflow soldering the liquid solder alloy wets the surface of both metals to be joined and upon solidification forms the solder joint. This solder joint is significantly dependent on the solderability (Vianco, 1999). For soldering process, few conditions must be met for effective process (Blackwell, 2000) such as:

- Wettability. The nature of component terminations and board metallisations must be such that the surface is wetted with molten solder within the specified time available for soldering, without subsequent dewetting.

- Metallization dissolution. The component and board metallisations must be able to withstand soldering times and temperatures without dissolving or leaching.

- Thermal demand. The mass of the traces, leads and thermal aspects of packages must allow the joint areas to heat to the necessary soldering temperature without adversely affecting the component or board materials.

Wettability is closely related to solderability in welding process, which is defined as the ability of a metal surface to promote the formation of an alloy at the interface of the base material with the solder to ensure a strong, low resistance joint. Moreover, surface tension is always correlated with wettability or solderability of a component (Shen and Chan, 2008). Surface tension is defined as the attraction that molecules at the surface of a drop of liquid have for each other. If that attraction is greater than the attraction for the material which the liquid touches, the liquid will not spread, but will remain in drop form. In addition to the importance of these two parameters in solderability, the base metal is highly correlated with solderability. In the case of soldering printed circuit board, the component’s leads or pins and board’s metallic circuitry are the base metals that will contact the solder. Metals, such as aluminum, high alloy steels, cast iron and titanium have very low solderability. These materials are important because they provide choices of material in the construction of soldering machine, and also as temporary covers for components that are not to be soldered (Tai, 2003). Table 2.1 describes the general solderability of different base materials.

Table 2.1: Solderability of different base metal (Li, 2006)

Solderability	**Base Metal**	**Remarks**
Excellent	Tin Cadmium Gold Silver Palladium Rhodium	Noble metals dissolve easily in solders, resulting in brittle joints.
Good	Copper Bronze Brass Lead Nickel-Silver Beryllium-Copper	High thermal conductivity of these metals requires high heat input during soldering. Oxidizes quickly so proper flux must be used.
Fair	Carbon Steels Low-Alloy Steels Zinc Nickel	Solder joint become brittle in sulfur-rich environments. Avoid higher temperatures in the presence of lubricants (which contain sulfur).
Poor	High-Alloy Steels Stainless Steels	Too much chromium oxide the surface needs to be cleaned with an aggressive flux.
	High temperature applications	Good high temperature properties, Good fatigue strength. Medium or low flow properties.
Very difficult	Cast Iron Chromium Titanium Tantalum Magnesium	Require pre-plating with a solderable metal.

2.3 Solder Techniques

There are three types of soldering methods; hand soldering, reflow soldering and wave soldering. However, soldering techniques for circuit board fall into two main categories: wave and reflow soldering, wave soldering is more commonly used with through-hole mounted components. Reflow soldering is used with surface mounted devices (SMD) in which the component leads rest on a metallised connection pads.

2.3.1 Wave Soldering

Wave soldering is a very effective technique for joining components to printed circuit boards (PCBs) in large quantities. A printed circuit assembly (PCA) consists of the printed circuit board, connectors, and all components. As in all metallic joining applications, there are three basic steps to the soldering process. The first step prepares the surface for soldering. The next step applies molten solder to the bottom side of the assembly. The final step consists of allowing the joint to solidify by cooling. Defects that result in joint reliability issues can result from all of these stages. Several studies focused on the optimization of wave soldering process in order to reduce joint defects. The process parameters should also be optimized to truly capitalize on the machine investment. Some examples of process parameters are solder temperature, solder wave height, conveyor speed, and preheat temperature setpoints. The optimal wave soldering machine and wave soldering process depend on the PCA design intended for production. Both wave soldering process parameter identification and process hardware selection must be examined to optimize the total process and reduce solder joint defects (John, 1991).

A typical wave soldering system includes station that first apply flux to the bottom surface of the assembly and up to the plated through-holes, a second station that preheats the assembly by radiation, and a third station that applies the solder in the form of a wave, which also supplies the bulk of heat to the joints by conduction (Strauss, 1994), as shown in Figure 2.2. The preheat process in the system is to allow faster conveyor speeds resulting in less heat stress on the components. The soldering temperature is maintained at the lower end of its temperature range to avoid leaking. Mostly, the wave is split into two sections. One is a narrow, turbulent wave to wet all the components and two is a smooth wave which removes excess solder. For best results, the solid contents of the solder flux should be minimized (Skipp, 1988).

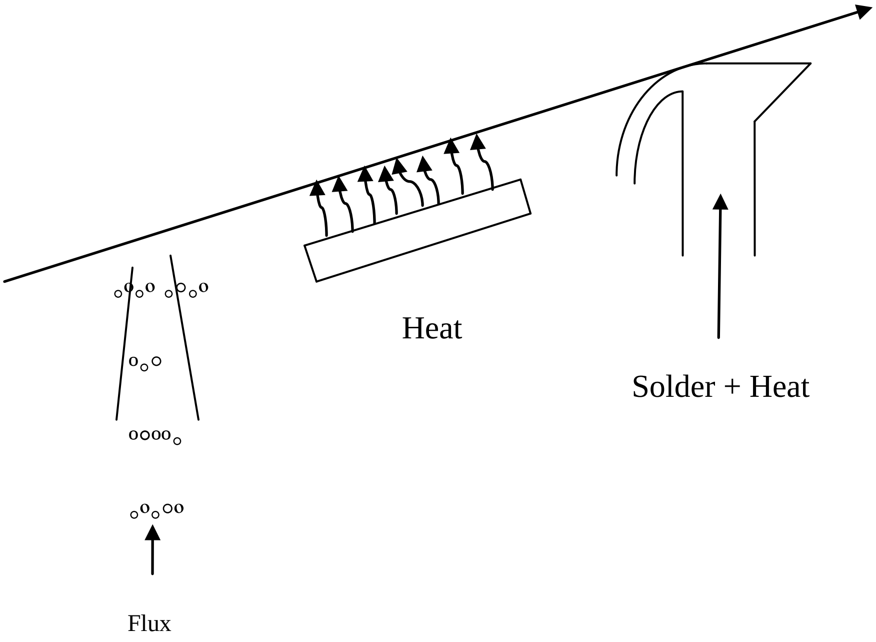

Figure 2.2: The principle of wave soldering (Li, 2006)

2.3.2 Reflow Processing

The solder reflow process can be achieved by using almost any available practical heat source. Hot air guns, hot plates, small soldering irons, have been used to build small experimental or prototype surface mount assemblies. The maximum temperature and time are controlled manually. While this is useful to get an initial familiarization, it will not provide the quality and reliability needed for a high volume commercial product. To do this will require a repeatable, controllable, and cost effective heat source (John, 1991).

The soldering process involves four basic elements: the base metal, soldering flux, solder alloy and heat (temperature). To begin with, solder and flux are placed on one or both joint surfaces, either together in the form of a solder paste or separately, first the solder in the form of a metallic coating and then the flux at a later stage. Subsequently the joints are put together. The important point is that all this happens at room temperature though with some procedures, the solder may have been pre-deposited on one or both joint surfaces by a hot-tinning method. With all reflow strategies, the assembled joints are finally heated to a temperature high enough to melt the solder, and for long enough to let it tin the joint surfaces and fill all the joint gaps. As soon as this has been achieved, heating is discontinued and the solder is allowed to solidify, the faster the better (Strauss, 1994). Table 2.2 shows a summary list of the profile.

Table 2.2: Summary of reflow profiling (Wood and Rupprecht, 2004)

STAGE	DISCREPTION
Preheat	To get heat into the assembly and bring it up to flux activation temperature. A typical target would be to reach 120°C within 30 to 90s, depending on the type of board.
Soak	To allow solvents evaporate from the solder paste and fluxes to activate at an elevated temperature, removing oxides and contaminants prior to soldering. Time is important because an overly extended soak time may "dry" out the solder paste, causing reoxidation. A typical soak would range from 120 to 170 °C and would last between 30 and 90s.
Reflow	To bring the component exceeds the liquidus points, to a temperature between 200 and 210 °C to allow soldering (63Sn-37Pb melts at 183°C). This will wet both the component leads and the board pads. The surface tension effects occur, minimizing wetted volume. This time generally would be between 30 and 60s.
Cool Down	Having a cooling stage is important because overly extended reflow times will cause changes in the solder joint structure that could affect reliability. There is also a practical side to ensuring that the board is back below reflow temperature before operator handling. The rework system should direct cold air through a separate air chamber because continuation through the heaters, even after they have been switched off, will promote extended reflow.

2.4 The Solder-Flux-Base-Metal System

Fluxes are the third material category for soldering processes; the solder alloy and the base material being the other two materials categories. While solder and base material compositions and properties are generally known, or at the very least, are nominally characterized, such is typically not the case for solder fluxes. The reason for this discrepancy is twofold. First, many mechanical design and solder process engineers are not familiar with the surface and reaction chemistry principles that are required to fully understand flux behavior. Even some flux engineers will admit that they do not fully understand how certain chemicals produce the so-called "fluxing action" that supports solder wetting and spreading. Secondly, flux chemistries are usually considered highly proprietary by their manufacturers and rarely disclosed (Vianco, 1999).

Flux is needed for most soldering process. Flux provides tarnish cleaning surface, heat transfer, wetting enhancement function, protect molten solder and substrate from oxidation, and promote solder spreading (Lin and Chen, 1999; Vaynman and Fine, 2000). The function of a flux is to clean the substrate, protect the solder melt and substrate from re-oxidation and improve the wettability between the solder and the substrate. Usually, fluxes contain activators that clean the substrate, vehicles that protect the surfaces of the substrate and molten solder from re-oxidation during soldering and also improve heat-transfer (Vaynman and Fine, 1999). The flux has the following three functions during the fabrication of a solder joint. First, the most widely considered role of the flux is its removal of the nascent oxide layer from the base metal surface. The second role of the flux is to reduce the surface tension of the molten solder. This is achieved by modifying the actual surface chemistry of the molten solder as well as by eliminating the oxide skin which forms on the molten solder. And the third function of the flux is to establish a barrier between the pristine base metal surface and the atmosphere during the soldering process (Shen and Chan, 2008).

Although the components of a flux (corrosive agent, vehicle, and wetting agents) and the functional principles of a flux (oxide removal, surface protection, and reduced solder surface tension) may be understood, the steps required to use a flux in an actual soldering process may not always be clear. This concern is of particularly importance in manual soldering processes, because the amount and timing of flux application is determined by the operator. Also, the heat source is typically concentrated, thus increasing the likelihood of thermal damage to the flux coating.

2.5 Lead Solder

The primary concern with the soldering of lead (Pb) is its low melting point 327 ºC. Care must be taken in the soldering process that the Pb structure is not melted. A second concern is that of the oxide which forms on the surface of Pb. Lead oxide tends to very tenacious and thick, making its removal somewhat difficult. Its reformation on pristine Pb metal surface is rapid. However, care should be exercised when fitting Pb structures in fixturing that the structure is not detrimentally deformed by clamps and braces (Blaskett and Boxall, 1990).

The Sn-bearing solders comprise the foremost group of alloys that can be successfully used to join Pb and its alloys. The 50Sn-50Pb solder, along with the other compositions of Sn and Pb, provide a variety of melting points and pasty ranges to suit many applications (Blaskett and Boxall, 1990). Pb has a finite solubility for Sn so that at an interface, Sn-Pb solubility zone comprises the solder-substrate metallurgical interaction. The 80Au-20Sn solder may also be use with Pb; the melting temperatures of the other Au-based solders are too high for use with Pb substrates. Also, In-bearing solders can be used successfully on Pb or Pb-alloy base metals. Mutual solubility between Pb and Sn comprises the interfacial reaction metallurgy in such joints. Bismuth (Bi)-containing solders may also wet to Pb, due to the limited solubility of Bi in Pb (56Bi-44Pb eutectic, T=125 ºC). Previous studies reported that a ternary Sn-Pb-Bi eutectic composition can form between the three constituents with a eutectic temperature of 95 ºC (El-Daly et al., 2009a; Zhou et al., 2009). Finally, the successful joining of Pb-based structures using corrosion-resistant Zn-based solders is more difficult to realize since the binary alloy phase diagrams exhibit no appreciable affinity between Zn and Pb; they appear to be mutually insoluble (Vianco, 1999). Mainly because of their use as solders Pb-Sn alloys form the second most important group of Pb alloys after Pb-antimony. Sn is also a major constituent in many bearing alloys, in some Pb alloys for cables and pipes manufacture.

2.5.1 The Element Lead (Pb)

Pb has been commonly used for thousands of years because it is easy to extract and easy to work with. It is highly malleable and ductile as well as easy to smelt (Vianco, 1999). Pb is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Pb isotopes are the end products of each of the three series of naturally occurring radioactive elements. Pb occurs naturally in the environment. However, most Pb concentrations that are found in the environment are a result of human activities. Due to the application of Pb in gasoline an unnatural Pb-cycle has consisted. In car engines Pb is burned, so that Pb salts (chloride, bromide, and oxides) will originate. These Pb salts enter the environment through the exhausts of cars. The larger particles will drop to the ground immediately and pollute soils or surface waters, the smaller particles will travel long distances through air and remain in the atmosphere. Part of this lead will fall back on earth when it is raining. This Pb-cycle caused by human production is much more extended than the natural Pb-cycle. It has caused lead pollution to be a worldwide issue.

Pb has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. In addition to being soft, Pb is one of the heavier metallic elements, with a relatively low melting point and a high density. This high density is best utilized in shielding applications of radiation such as X-ray and nuclear energy. Unfortunately, this also makes nondestructive testing of solder more difficult (Manko, 2001).

Pb is a heavy metal with a high toxicity to humans and has no known beneficial effects in the body. It is toxic at very low exposure levels and has acute and chronic effects on health and the environment. Pb is not degradable in nature and will thus, once released to the environment, stay in circulation. New releases add to the already existing deposits of Pb in the environment. It can affect the nervous system, the reproductive system, and the heart and blood system. Even the lowest doses can impair the nervous system. Chronic low exposure is of concern. Pb accumulates in the bone structure in humans, and can be released under pregnancy from the bone structure to the blood. In the environment Pb is known to be toxic to plants, animals and microorganisms. Pb bioaccumulates in the skeleton and wet tissue in mammals and in aquatic algae and invertebrates.

2.5.2 The Element Tin (Sn)

Tin (Sn) is a soft, pliable, silvery-white metal with a melting temperature of 231 ^{o}C (Suganuma, 2004). Sn is not easily oxidized and resists corrosion because it is protected by an oxide film. Sn resists corrosion from distilled sea and soft tap water, and can be attacked by strong acids, alkalis and acid salts. Sn is used in for can coating: tin-plated steel containers are widely used for food preservation. Sn alloys are employed in many ways: as solder for joining pipes or electric circuits, pewter, bell metal, and dental amalgams. The niobium-Sn alloy is used for super conduction magnets, tin oxide is used for ceramics and in gas sensors (as it absorbs a gas its electrical conductivity increases and this can be monitored). Sn foil was once a common wrapping material for foods and drugs, now replaced by the use of aluminum foil (Callister, 2004). The ability of Sn to wet and spread on a wide range of substrates, using mild fluxes, has caused it to become the principal component of most solder alloys used for electronic applications.

Sn exists in two different forms with two different crystal structures in the solid state. White or β-tin has a body centered tetragonal crystal structures and is stable at room temperature. Gray Sn or α-tin, which has a diamond cubic crystal structure, is thermodynamically stable below 13 ºC. the transformation of β -Sn to α-tin, also referred as Sn pest, takes place when the temperature falls below 13 ºC, and results in a large increase in volume, which can induce cracking in the Sn structure. Due to its body centered tetragonal crystal structure that is anisotropic, the thermal expansion of Sn is also anisotropic. Therefore, when Sn is exposed to repeated thermal cycling, plastic deformation and eventual cracking at grain boundaries can occur. This effect has been observed in thermal cycling over a range as small as 30-75 ºC. Thus, thermal fatigue can be induced in Sn or Sn-rich phases of solder alloys even when no external mechanical strain is imposed (Abtew et al., 2000).

Sn resists oxidation well and maintains its luster on exposure to air. The metal is harder than lead but is soft enough to be cut with a knife. The ductility and/or malleability of Sn are great, and it can be rolled and extruded as well as drawn into wire. Tin has a relatively large crystal structure. When a bar of Sn is bent, it emits a unique sound called *tin cry*, assumed to be the result of friction of the crystal interfaces. Sn is not attacked by water and/or air, separately or combined. This makes it desirable for protective coatings. However, the presence of chlorides in marine water will facilitate the formation of stannous chloride (Manko, 2001).

2.5.3 Sn-Pb Solder Alloys

Eutectic and near eutectic Sn-Pb solder alloys are the most commonly used interconnect materials in microelectronic packaging (Wu et al., 2004). In the microelectronics industry it is widely accepted that reliability of a package is assessed by the integrity of solder joints in it. Computational mechanics is extensively used to simulate thermo mechanical reliability of these solder joints (Basaran and Jiang, 2002).

The material used as solder for the electronic packaging is near eutectic 60Sn-40Pb or eutectic 63Sn-37Pb solder alloy. Sn-Pb solder alloy is a highly rate sensitive heterogeneous material with a low melting point of 183 ^{o}C, hence during service it is operating at high homologous temperature. Sn/Pb solder alloy has good wetting characteristics and adheres well to copper and nickel. However, the structure of the alloy is non-homogeneous and deforms heterogeneously. Furthermore the size effect and microstructural evolution plays an important role in the deformation of this alloy (Bartels et al., 1994). The phase diagram of Sn-Pb binary system is shown in Figure 2.3. The phase diagram of this system is well established and a number of thermodynamic assessments are available for this system.

The Sn-Pb phase diagram is characterized by two solid phases each with substantial solid solubility and a liquid phase. Further, the system is characterized by a simple eutectic with a significant depression of the liquids temperature by almost 50ºC, from pure Sn at 232 ºC to the binary eutectic (Sn-37Pb) at 183 ºC (Suganuma, 2004). The eutectic Sn-Pb solder provides excellent electrical conductivity and suitable mechanical strength (Cheng and Lin, 2002). For Sn-Pb alloys, the eutectic point is 63 wt% Sn at a temperature 183 ^{o}C. The maximum solubility of Pb in Sn is 2.5 wt% and Sn in Pb is 19 wt% (Hwang, 1992).

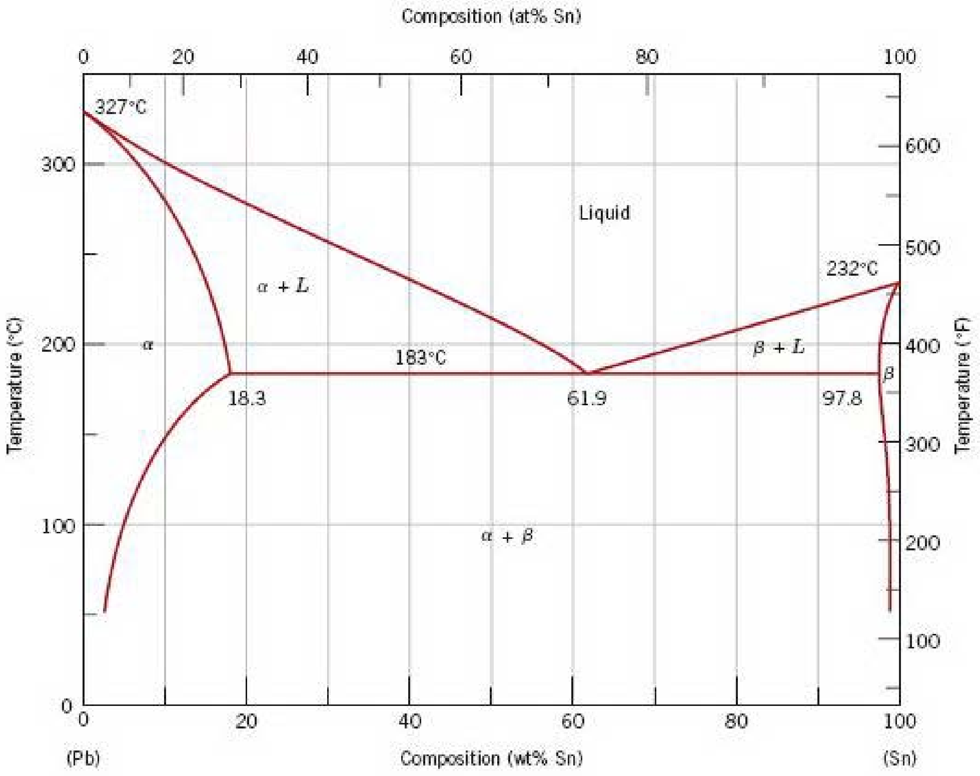

Figure 2.3: Sn-Pb binary phase diagram (Li, 2006)

2.6 Pb-Free Solders

Increasing environmental concerns and pending government regulations have pressured microelectronic manufacturers to find suitable alternatives to Pb-bearing solders traditionally used in electronics packaging (Zeng and Tu, 2002). When trying to identify an alternative to the Sn-Pb solders, it is important to ensure that the properties of the replacement solder are comparable to or superior than Sn-Pb solders. There are strict performance requirements for solder alloy used in microelectronics (Abtew and Selvaduray, 2000). In general, the 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 printed circuit board (PCB), form inspectable solder joints, allow high volume soldering and rework of defective joints, provide reliable solder joints under service conditions and must not significantly increase assembly cost.

Over recent years, Sn-rich solders have been developed as Pb-free solder candidates to replace the Pb-containing solders use in microelectronic applications. They have been receiving significant attention as suitable replacements for Pb bearing solders (Laurila et al., 2005; El-Daly et al., 2009b), but their introduction into electronics manufacturing requires major changes to current manufacturing processes, electronic components, and inspection requirements. Several Pb-free solder alloys generally require higher temperatures-upto 260 ºC as opposed to 215 ºC 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.

Understanding the behavior of intermetallics in Sn-rich solders is of particular concern as the microelectronics industry progresses towards Pb-free packaging (Tsukamoto et al., 2009). While the presence of intermetallic compounds (resulted from the reaction of the solder with the metallization on the substrate in the electronic package) is an indication of good wetting, excessive growth of the intermetallic can have a dramatically adverse effect on the toughness and reliability of the solder joint. Understanding their fracture behavior will lend insight to their reliability under mechanical and thermo mechanical strains (Hayes et al., 2008).

The development of Pb-free solders is become a critical subject for the new generations in electronic and automobile products. Many different solder compositions have been proposed as a substitute for Sn-Pb solders, Abtew and Selvaduray (Abtew et al., 2000) reported a relatively large number of Pb-free alloys, and are summarized in Table 2.3, with their elemental compositions. The solder alloys are binary, ternary and some are even quaternary alloys. It can be noticed that a very large number of these solder alloys are based on Sn, the element tin being the primary or major constituent. The two other elements that are major constituents are In (Indium) and Bi. Other alloying elements are Zn, Ag (Silver), Sb (Antimony), Cu, Mg, and in one case a minor amount of Pb.