DETERMINATION AND CHARACTERIZATION OF LEAD FREE SOLDER ALLOYS

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Technology
In
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SUBMITTED
BY

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This is to certify that the thesis entitled, "**DETERMINATION AND CHARACTERIZATION OF LEAD FREE SOLDER ALLOYS**" submitted by **Prerna Mishra** in partial fulfillment of the requirement for the award of **Master of Technology** degree in **Metallurgical and Materials Engineering** with specialization in **Metallurgical and Materials Engineering** at the National Institute of Technology Rourkela is an authentic work carried out by her under our supervision and guidance. To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Research Guide

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ABSTRACT

In recent years the development of lead free solders has emerged as one of the key issues in the electronic industries .So far eutectic or near eutectic Sn – Pb alloys have been widely used due to their low melting temperature and good wettability. Sn – Zn solder alloys have been considered as one of the most attractive lead free system that can replace toxic Sn – Pb solder without increasing the soldering temperature. However there are some drawbacks in Sn – Zn lead free system such as poor oxidation resistance, wettability and embrittlement behavior. In order to overcome these drawbacks and to further enhance the properties of Sn- Zn solder a small amount of alloying elements like Bi (Bismuth), Ag (Silver), Al (Aluminium), Cu (Copper), In (Indium), Chromium (Cr), Antimony (Sb), Nickel (Ni), Ge (Germanium) were added.

This work aims to investigate the effect of Bi (Bismuth) addition on the microstructure, thermal and mechanical properties of Sn – Zn lead free system. The microstructure of all the solder alloys was investigated using a Scanning electron microscope (SEM). The composition of the solder alloys was determined using Energy dispersive X- ray spectroscopy (EDX). Differential scanning calorimetry (DSC) was done to find out the melting temperature of the alloys. Phase analysis for the alloys was done using X- ray diffraction. Tensile test was performed to find out the mechanical properties of the alloys.

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LIST OF ABBREVATIONS

Al	Aluminum
Pb	Lead
Cd	Cadmium
Bi	Bismuth
Sb	Antimony
Sn	Tin
Cr6+	Hexavalent chromium
Hg	Mercury
Zn	Zinc
Ag	Silver
Cu	Copper
Ni	Nickel
α	Alpha
β	Beta
IMC	Intermetallic Compound
SEM	Scanning Electron Microscope
XRD	X – Ray Diffraction
DSC	Differential Scanning Calorimetry
EDX	Electron Dispersive X- Ray Spectroscopy
EPA	Environmental Protection Agency
EC	European Commission
WEEE	Waste Electrical and Electronic Equipment
RoHS	Restriction of Certain Hazardous Substance
WHO	World Health Organization
PCB	Printed Circuit Board
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl
dl	Decilitre
µg	Microgram

mg	Milligram
l	Litre
wt.%	Weight percentage
TV	Television
CD	Compact Disk
NC	Numeric Control
LAN	Local Area Network
ECG	Electro Cardiogram
$PbCO_3$	Lead Carbonate
ZnO	Zinc Oxide
kN	Kilo Newton

CHAPTER 1

INTRODUCTION

1. INTRODUTION

Solder alloys have been widely used as the interconnecting material in electronic packaging and assemblies because they provide both electrical interconnection as well as mechanical support. Sn-Pb solders were first used about 2000 years ago for metal inter connections. Pb containing solders especially the eutectic or near eutectic Sn-Pb alloys has long been the predominant choice of the electronics industry due to its low melting temperature (around 183°C),better wetting behavior and mechanical properties [1] [2] [3]. Despite of all these advantages the toxicity of heavy metallic element Pb has led in recent decades to increasing efforts to restrict its use. Following the banning of Pb in paints, fuels and plumbing application throughout the majority of the world, otherwise it could be demonstrated to present a direct risk to human health and environment [4].

Science and engineering of soldering has taken a major change in direction ever since the legislation that mandates restriction of certain hazardous substances (RoHS) [5] and the waste electrical and electronic equipment (WEEE) [6] had been introduced by many countries. The first administrative region of the world to actively legislate against Pb use in electronics has been the European Union, which has introduced RoHS and WEEE directives. These directives target the electrical and electronic equipment and are designed respectively to outlaw many harmful substances from use and make the producers of electrical and electronic goods responsible for their safe disposal or recycling at the end of their lives.

As cited by Environmental Protection Agency (EPA) of US, Pb and Pb containing compounds is one of the top 17 chemicals causing greatest threat to human life and environment.1st July 2006 has been officially designated by European Union as the date when the “Directive on the Restriction of Hazardous substances in Electrical and Electronic equipment will require “the use of lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium ($Cr6^+$) and halogenated flame retardants" be phased out. This led to the development of lead free solders which has emerged as one of the key issues in electronic packaging and industries [7] [8] [9].

For developing a new solder one need to think of various properties such as melting temperature, mechanical properties, microstructure, wettability, and pasty range, solder ability, reliability and cost of solder joints [10] [11]. One major limiting factor in the selection of a Pb free alloy is that the entire electronics manufacturing industry is accustomed to the low melting point of the eutectic Sn- Pb alloy (183^{o}C) and components are designed to withstand soldering temperature associated with this. Any rise in the processing temperature of printed circuit boards (PCBs) will have adverse effects on component reliability. This narrow window of melting points restricts research to a handful of alternative alloys based on Sn with other elements added. Alongside the temperature requirements, there are number of metallurgical and mechanical properties of Sn-Pb which an alternative alloy has to rival in order for it to be a successful replacement.

Researchers have developed a large number of binary Pb free solder alloys such as Sn-Zn, Sn-Cu, Sn-Ag, Sn-Bi, Sn-Sb and Sn-In. Among these binary systems Sn-Zn solder alloys possess several fascinating features such as Sn-9Zn eutectic alloy has melting temperature (198^{o}C) very close to that of Sn-Pb eutectic alloy (183^{o}C) and also offers better mechanical properties as compared to conventional Sn-Pb solders. In addition to this it has low cost as well as low reflow temperature of 222^{o}C also nontoxic to human health and environment [12] [13] [14]. Sn-Zn solders are quite capable in terms of mechanical integrity but have poor oxidation and corrosion resistance [15] [16] [17] [18]. The wettability of Sn-Zn solder has been an important issue because during soldering the highly active Zn atoms get oxidized forming voids at the interface. Zinc oxide formed by the oxidation of Zn floats on the liquid surface and prevents the solder from wetting the substrate [19] [20]. Therefore the Sn-Zn eutectic solder is difficult to handle due to its poor wettability, reliability, strength, easy oxidation and microvoid formation. In order to overcome these drawbacks and to further enhance the properties of Sn-Zn lead free system small amount of alloying elements such as Bi, Cu, In, Ag, Al, Ga, Sb, Cr, Ni, Ge were added to develop ternary and even quaternary Pb free systems as suggested by many researchers [21] [22] [23] [24].

It has been found that the addition of Bi to the eutectic composition of Sn-Zn lead free system has improved various soldering properties. Addition of Bi decreases the melting point of the system and improves the wettability of Sn-Zn solder on Cu substrate. The wetting area increases by 2 -10 wt% approximately on addition of Bi content. On addition of Bi the surface tension of the solder has been decreased which has enhanced its wettability. Similarly the mechanical properties of the Sn-Zn solder have been improved on Bi addition but up to a certain extent [25] [26].

1.1OBJECTIVE

Objective of this work is to prepare the different types of lead free solder alloys and to investigate the effects of Bi addition on the microstructure, melting behavior, mechanical properties, wettability and X- ray diffraction pattern of solidified Sn – Zn solder alloy. Objective of this work are –

1. Determination of microstructure and compositional analysis of lead free solder alloys by Scanning electron microscope (SEM) and Energy Dispersive X – ray spectroscopy (EDS or EDX).
2. Phase Analysis by X – ray diffraction technique (XRD).
3. Determination of Melting point of the alloys by Differential Scanning Calorimetry (DSC).
4. Determination of Ultimate Tensile Strength by Universal Testing Machine (UTM).

CHAPTER 2

LITERATURE

REVIEW

2.1 ELECTRONIC PACKAGING

Electronic packaging refers to the method of enclosing, protecting and providing physical structure to electronic devices, components and assemblies. In recent years, electronic devices require more resistors, transistors or diodes on a single semiconductor chip. All these discrete circuit components are embedded in or on the chip and are connected to the printed circuit board (PCB). Through various technologies establishment of interconnections for all these tiny components can be achieved. Large amount of heat is generated when the device is in operation and this heat has to be removed so that the device can perform its functions properly. Semiconductor chips are fragile and require 'armour' coating to protect them from chemical, mechanical and environmental damage. Hence, the concept of "electronic packaging" has been introduced to describe manufacturing process or the hardware that provide the electrical connections, the removal of excessive heat and the protection from environmental damage [27] [28].

2.2 THE APPLICATIONS

The electronic packaging assemblies are used in following areas: [29]

- **Computers and Business Equipment:** Calculators, printers, desktop computers, photocopiers, workstations, personal digital assistants, high performance computers etc.
- **Communications:** Cellular phones, handsets, line cards, LAN cards and switches, modems, fax machines, routers, pagers, main switches etc.
- **Automotive Electronics:** Engine control and management systems, transmission controllers, braking controllers, traction controllers, suspension, wipers, lighting, air conditioning and heating, safety, electronic dashboard, convenience and entertainment systems etc.

- **Consumer Electronics:** VCR, CD players, watches, compact audio systems, portable audio players, smart cards, microwave, ovens, TV sets, game systems and cartridges etc.
- **Industrial and medical systems:** Test and measuring devices and instruments, process control systems, motor controls, calibrators, uninterruptible power systems, NC controls, robotics, ECGs, implants medical imaging systems etc.
- **Military Electronics:** Mobile Communications, missiles, avionics radar, satellite links land – based radar and communication systems.

2.3 SOLDERING AND ITS REVIEW

Soldering is a process in which two or more metals are joined together by melting and flowing a filler metal (solder) into the joints with a melting temperature well below those of the substrates and typically less than 450^{o} C.The term “solder” refers to a group of metal alloys which melt at relatively low temperatures and whose purpose is to form a joint between two others, possibly dissimilar materials.The distinction between soldering and brazing is only the temperature at which the joining operation takes place; around 450^{o}C in the case of soldering.Both these techniques involve a filler metal which in the molten state adheres to the two substrates by capillary action to be joined, then freezes to form a permanent joint, as opposed to welding where the substrates themselves are melted to fuse together. The most common alloy system in soldering is that of Sn and Pb. Their relative proportions in a binary alloy can be varied to give melting points up to that of pure Pb (327.5^{o}C) but the most important ratio is 63 Sn/37Pb (wt.%), which is the eutectic point.This eutectic mixture melts sharply at 183^{o}C and is used universally to join wires and components in electronic circuits and assemblies, manually or by automated processes [30].

2.4 SOLDERING MATERIALS

There are a range of solder alloys that are used for soldering interconnections. These solders are basically alloys of tin (Sn) and one or more of the following elements: Lead(Pb), Silver(Ag), Bismuth(Bi), Indium(In), Antimony(Sb), Cadmium(Cd), Zinc(Zn), Copper(Cu), Nickel(Ni) etc. If a solder alloys solidus and liquidus temperatures are identical it is called eutectic solder alloy, otherwise it is a non-eutectic solder alloy. Solder alloys available commercially are in solid form, paste form or powder form [31].

2.5 SOLDERING METHODS

2.5.1 REFLOW SOLDERING

Reflow soldering is the joining of mating surfaces that have solder between them, placing them together, heating them until the solder fuses, and allowing them to cool in the joined position. Reflow soldering requires a few steps. The first step is placement of the flux and the solder alloy on the surfaces to be soldered.

The second step is placement of components on the placed solder. The third step is heating and then the cooling of the assembly. During the heating stage, the solder melts and spreads over the surfaces. During cooling, molten solder solidifies and solder joints form. The last step is cleaning the residues of the flux. If solder pastes are used, instead of solder bars etc., the soldering steps become different. Solder pastes can be placed directly on the metallization on the circuit boards using stencil printing method. After that, the components are placed on the printed solder paste pattern and the assembled boards are then passed through the reflow oven to form solder joints. In the reflow soldering process, there are different heating methods that can be used and these include conduction, infrared, vapour phase, hot gas convection induction, laser, focused infrared, white beam and vertical reflow methods [32].

2.5.2 WAVE SOLDERING

Wave soldering is completely different from reflow soldering. In this method, printed circuit board (PCB) assembly passes over a continuous wave of solders. The crest of the liquid solder wave touches and wet the exposed metallization of the assembly and solder joints form upon cooling.

The steps of wave soldering are as follows

1. Automatic insertion of leads of through hole components into the holes in the printed circuit board (PCB).
2. Dispensing of adhesives at locations of surface mount components to be placed throughout the PCB.
3. Placements of surface mount components over the dispensed adhesive.
4. Curing of adhesive to make a temporary bond so that components can be hung beneath the circuit board. The success and the reliability of the wave soldered joint depend on the wettability of the solder, the type of flux, the solder bath temperature and the dwell time of soldering [33].

2.6 GENERAL CRITERIA TO SELECT A SOLDER ALLOY

To select a solder alloy, the following criterion should be checked out [34]

- It should have a melting range that is suitable for service temperature range.
- It should have mechanical properties that are compatible with service conditions.
- It should be metallurgically compatible with surrounding metallization.
- It should have a reasonably low rate of intermetallic compounds (IMCs) formation at the service temperature.
- It should have an acceptable wettability on surrounding metallization.

- It should be stable in the ambient environment.

2.7 USEFUL PROPERTIES OF Sn-Pb

One of the primary qualities of Sn-Pb is its low melting temperature, which allows soldering to be carried out with minimum operating risks and without expensive equipment. Perhaps even more importantly, this low melting point allows small and sensitive electronic components to be joined together by the soldering process without heat damage. Apart from this fundamental quality is the ductility of Sn-Pb, which displays an elongation commonly reaching 100% and in some cases super plasticity after deformation at high temperatures [35]. This ductility allows Sn-Pb solder joints to accommodate thermal and mechanical strains; especially important when joining fragile and brittle electronic components.

2.8 ROLE OF Pb IN Sn-Pb SOLDER

Pb contributes outstanding properties and reliability in Sn-Pb solder and is stated as following:

[1] Pb reduces surface tension of pure Sn which enhances the wetting ability.

[2] Pb provides ductility to Sn-Pb solders.

[3] Pb enables Sn and Cu to form intermetallic compounds by diffusion.

[4] Addition of Pb prevents transformation of β – Sn to α- Sn and if this transformation occurs there is volume increase and loss of structural integrity hence loss of reliability. Transformation of β – Sn to α – Sn is called “Sn – pest” or “Sn – disease”.

[5] Sn – Pb solders have low melting temperature of 183^{o}C for eutectic solder, which allows use of low reflow temperature in packaging process thus ensures reliability of the packages.

[6] Apart from all these benefits of Pb, cost of Pb is low and is very abundant [36] [37].

2.9. ROLE OF SN

2.9.1. CRYSTALLOGRAPHIC PROPERTIES

Sn comprises the matrix of all of the Pb-free alloys. Sn has two allotropes, referred to as 'white tin' (beta (β) phase, metallic) and 'grey tin' (alpha (α) phase, semiconductor). The overwhelmingly common form of Sn is the beta phase, which is stable at temperatures from 13 ºC to 231.9 ºC liquidus. Below 13 ºC the alpha phase is the one which is thermodynamically stable but it is rarely encountered in real life. Transformation temperature between the two phases is 13°C and in this transformation, a metal (white Sn) changes to (gray Sn) which has unique electrical and optical properties. The structure of β-Sn is body centered tetragonal with lattice parameters a= b= 0.5820 nm and c = 0.3175 nm [38]. The c/a ratio of 0.546 gives rise to highly anisotropic behavior in Sn.

Sn easily wets the substrate and spreads on it. This makes Sn a major component in most of the solder alloys. Whisker growth in Sn takes place at about 51°C but these whiskers are nothing but tetragonal white Sn that grows due to internal stresses and strains. Longer whisker may cause short circuits in printed circuit assemblies which get suppressed with addition of Pb [39] [40].

2.9.2. MECHANICAL PROPERTIES

Pure Sn also has very poor mechanical properties at room temperature for example a tensile strength of only 11 MPa [41] and a hardness of 3.9 HB [42] but this is largely due to its low melting point as compared to other common engineering metals. Ductility is the exception, with tensile elongations of 53 % possible at room temperature [43]. The creep, hardness and tensile properties of Sn are very sensitive to alloying additions.

2.9.3. CHEMICAL PROPERTIES

Chemically, Sn is a relatively inert metal which does not react with air, water, nitrogen, hydrogen or weak electrolytes [41]. A stable oxide layer ($Sn0_2$) is slowly formed during ageing in air but this compound (known as ‘dross’ in the soldering industry) forms as a skin on Sn-based solders when molten. Chemical fluxes are used to counteract this and ensure good wetting of surfaces. Tin form intermetallic compounds rather than solid solutions. Neighboring elements to Sn in the periodic table such as In, Sb and Bi have appreciable solid solubility in [44], and form eutectic mixtures with it.

2.10 SOURCE OF EXPOSURE

There are many sources of Pb in environment. The most common ones are as follows:

a) DRINKING WATER: In drinking water the main source of Pb is: lead containing pipes, faucets and Pb containing solder which is used during repairing of pipes. Dissolution of Pb in water depends upon the acidic nature of water, amount of minerals in the water, temperature and time duration of water stay in the pipes. Around 14 – 20 % of Pb poisoning in USA occurs due to drinking water [45].

b) LEAD PAINT: Lead paint is the another common source of Pb .In order to improve durability, speed drying and to protect the surface from corrosion lead carbonate [$PbCO_3/Pb(OH)_2$] is added to the paint. Pb dust is collected due to peeling, chipping, and cracking thus children are mostly affected by lead paint [46].

c) LEAD AT WORK: Adults who work in the lead containing industry such as battery manufacturing, electronic components, pipe fitting, glass production and smelting operations are sources of lead and should take proper precautions to prevent contamination [47].

d) CONTAMINATED SOIL: Leaded gasoline and industrial operation like smelters are possible sources of contaminated soil.

Another common source of Pb is engine oil, jewelry, lunch boxes, dish washer.

2.11 Pb BASED MATERIALS - THE ISSUES

2.11.1 LEAD POISIONING

According to Environmental Protection Agency (EPA) lead and its compounds are one of the top 17 chemicals posing greatest threat to human life and environment. Pb forms bond when it comes in contact with proteins in human body and retards their normal functions. Lead poisoning occurs when the level of lead in blood cells exceeds more than normal concentration. Lead is a material with no biological advantages and it also interferes with metabolism of Calcium (Ca) and vitamin D [48-50]. Pb poisoning may also be termed as Plumbism. Pb paint is also harmful and therefore children are at a greater risk as compared to adults. World Health Organization (WHO) and the US centers for disease control and prevention stated that if the content of lead in blood is more than 10 µg/dl, it may retard tissue development [51-53].

2.11.2 ADVERSE EFFECTS OF Pb ON HUMAN LIFE

Lead toxicity affects variety of body functions and many organs. When a person is contaminated with Pb, it may cause the following effects: [54] [55]

IMMEDIATE EFFECTS

- Vomiting, diarrhea, convulsions etc.
- Appetite loss, abdominal pain, Constipation etc.
- Sleeplessness, irritability, and headache etc.

ULTIMATE EFFECTS

- Continuous exposure to Pb environment can damage the kidney, liver, brain

- Pb causes the osteoporosis (a disease that makes bone brittle)
- Excessive exposure to Pb can cause seizures, mental retardation, behavioral disorders, anemia, high blood pressure etc.
- In pregnancy Pb can cause the placenta and can affect the unborn child.
- Female workers who are in contact with high level Pb can suffer from miscarriages and stillbirths.
- A small amount of Pb can harm the intellectual development, behavior, size and hearing of infants.

2.11.3 ADVERSE EFFECTS OF Pb IN ENVIRONMENT AND OTHER SPECIES

The waste disposal which is disposed from electronic and electrical assemblies contain Pb and its compounds which are considered hazardous to the environment and these components are disposed in solid waste landfills and they come in contact with ground water. For the removal of Pb the normal purification method we use to purify water is not suitable. It is difficult to explain how lead forms bond with water [56]. Japan and USA are two major suppliers and the users of printed circuit board assemblies and in next 10 years this market will be doubled. Therefore proper disposal of Pb is not a small issue. Solution to the above problem is recycling of Pb but it has some limitations. It has been reported that the recycled Pb emits higher α – particle than pure Pb and it affects the performance of electronic circuits [57-59].

Due to the rapid industrialization Pb in our environment is increasing day by day. In India it has been found that water bodies have been contaminated with high level of Pb. Water containing Pb having content of 0.003 mg/l is said to be normal and non-hazardous to our ecosystem [60]. Lead is also present in soil in the form of soluble and insoluble organic salts and easily form bond with colloidal organic molecules. In plants Pb toxicity is mainly due to absorption, transport and intracellular localization. When Pb reacts with group of enzymes it retards their normal operation [61] [62]. Animals are also affected by Pb poisoning and symptoms are same as that of human like abdominal pain, peripheral neuropathy and behavioral changes. For hunting wild animals hunters generally use Pb bullets and if these hunted animals are eaten by predators they are at a risk. Therefore Pb shots have been banned in countries like USA and Canada [63] [64].

ACCIDENTAL CASES:

On October 5, 2010 around 400 children died in Nigeria due to Pb poisoning (Zamafara state Pb poisoning epidemic).In China more than 1000 children from 10 different villages were found to have excess Pb content in blood near Yuguang gold and Pb smelter plant. 15000 people shifted from that area after this incident and the Government stopped production of Pb from 32 plants [65] [66].

2.12 Pb BASED MATERIALS – THE LEGISLATIONS

European Commission (EC) concerning about the long term effects of poisonous elements used in electronic products has set up a directive regarding Restriction of Certain Hazardous Substances (RoHS) which has been implemented in all the 25 European Union member states since 1st July 2006. The hazardous substances include Lead (Pb), Cadmium (Cd), Mercury (Hg), Hexavalent Chromium ($Cr6^+$), polybrominated biphenyl (PBB) and polybrominated biphenyl ether (PBDE) flame retardants [67]. For Pb, Hg, Cr^{6+},PBB or PBDE maximum concentration value in materials should be less than 0.1 wt.% and for Cd it should be less than 0.01 wt.%. A broad range of electronic products are under RoHS directive but there are exemptions for certain products such as fluorescent lamps and tubes, cathode ray tubes, equipment's for switching, signaling, transmission and telecommunication. The RoHS directive has affected the entire world because of the globalization of the electronics manufacturing industry. In Japan, the use of Pb has not been banned yet but there are laws which prohibit Pb from being sent to the landfills and other waste disposal yards [68]. Similarly in India there is no such law which prohibits using Pb and its components. Despite of adverse effects caused by Pb, it is still widely used in consumer products. Due to harmful effects of Pb we may have only two options (a) 100% recycling of Pb (b) use of Pb free equipment. 100% recycling of Pb is very costly so therefore, it is a great challenge for the electronic industries to find suitable alternatives to Pb containing solders.

2.13 Pb FREE MATERIALS – THE PROBLEMS

Transition from Pb containing solder to Pb free solder may cause problems regarding (1) manufacturing, (2) cost and (3) reliability issues [69] [70]. Problems are as follows

- INCREASE IN PRODUCTION COSTS: The maximum content of Pb in Pb free solder is 0.1wt. % and is very difficult to control Pb contamination during manufacturing of Pb free materials. Alloy bath can be easily contaminated by the air, handling production floor or by the equipment. Therefore the production of Pb free materials requires special enclosed system which increases the production cost of Pb free materials.
- INCREASE IN PROCESS TEMPERATURE: Melting points of Sn – Pb are 231^{o}C and 327^{o}C respectively. The elements that can replace Pb are Ag, Al, Cu, Zn and all of them possess high melting temperature (961^{o}C for Ag, 660^{o}C for Al, 1083^{o}C for Cu, 420^{o}C for Zn) than that of Pb. Since Pb free solder alloys have higher melting points and this means that the furnace temperature has to be increased. Therefore assembly process of an electronic package with a PCB when a Pb free alloy is used is performed at relatively higher temperature. Improvements of all the components and the devices used in the assembly process are necessary to make them compatible with the increased processing temperature.

- DEGRADATION OF JOINT RELIABILITY: Other than processing temperature, wetting difficulties, higher consumption of metallization and formation of thick intermetallic layer are the well-known problems for Pb free materials. When a Pb free alloy consumes all the metallization, there is formation of intermetallic layer and thus packaging interconnection fails. Due to these reasons the use of Pb free solders where high interconnection reliability is required is questionable.

Adhesives are also Pb free green materials and have been proved to be successful as interconnecting materials in electronic packaging. The process temperature of adhesives is far lower than Pb free alloys and even lower than the Pb based alloys. However, adhesives absorb moisture and properties are very sensitive to temperature changes. Therefore the use of adhesives is restricted and their performance can be erratic when exposed to high temperature and humidity.

2.14 Pb FREE INTERCONNECT MATERIALS FOR ELECTRONIC PACKAGE

Pb based materials have been used as interconnect materials from many decades to provide electrical path to the PCB in electronic packages. Electronic industries have to search for alternatives of Pb based materials due to the implementation of the RoHS directive. The interconnect materials that do not contain the hazardous "Pb" are generally referred to as Pb free material.

2.15 Pb FREE MARETIALS – THE REAL DEFINITIONS

Basically Pb free material means a material without Pb, but a material with a trace of Pb can also be considered as a Pb free material. According to RoHS directive if an interconnecting material contains less than 0.1 wt. % Pb it can be treated as "Green" or "Pb free". Furthermore, ISO 9453 standard allows less than 0.05-0.10 wt.% Pb but ASTM B32-96 standard accepts less than 0.1 wt.% Pb generally and 0.2 wt.% Pb for special case to define the material as Pb free [69].

2.16 ALLOYS AS GREEN SOLDERS

There are numerous choices of lead free solders in the market. At present the most widely used lead free solders are Sn-Zn, Sn-Cu and Sn-Zn-Bi, Sn-Ag-Cu alloys. The Sn-Zn alloy has a melting temperature of 198^{o}C which is close to that of the Sn-Pb solder. While there are benefits of using this solder as a lead free alternative because of its low melting point, there are also some serious problems with this solder. The most important shortcoming of this solder is that the Zn in the alloy causes excessive oxidation and this causes severe drossing in soldering pots. Moreover wettability of this solder is very inferior compared to the Sn-Pb solder and other lead free solders. Bi is often added to the Sn-Zn solder to reduce the liquidus temperature, to improve the wetting and corrosion behaviors.

Sn-Cu and Sn-Ag-Cu are very promising and commonly used lead free solders with melting temperatures 227^{o}C and 218^{o}C respectively. Lower cost is the most significant advantage of the Sn-Cu solder over the Sn-Ag-Cu solder and some other solders. Also, this solder consumes less copper in the coating process and produces comparatively stable IMC layer along the bond line and shows almost similar reliability performances to the Sn-Pb solders. However, the high melting temperature of this solder prevents it from being used in some soldering processes . Addition Ag into the Sn-Cu solder results in a decrease of about 5-10^{o}C in the melting temperature and an increase in the cost by about 2.18 times compared to the Sn-Cu solder. Although the solderability of Sn-Ag-Cu solder is better than Sn-Cu solder, it is still not as good as the Sn-Pb solder [71][72].

2.17 IMPORTANT LEAD FREE SOLDERS

2.17.1 SN-ZN BASED SOLDERS

Sn-Zn based alloy is one of the best alternatives for Sn-Pb solder because its melting temperature is very close to Sn-Pb eutectic. Eutectic composition of binary Sn-Zn solder is Sn-9 wt. % Zn and has a eutectic temperature of 198^{o}C. Microstructure of Sn-Zn consists of two phases i.e. a body centered tetragonal Sn matrix and secondary hexagonal zinc phase. Sn-Zn solder is expensive, non-hazardous, and possess better mechanical property [73]. Apart from these advantages Sn-Zn binary system has some limitation like poor oxidation and corrosion resistance, poor wetting properties and micro void formation. The highly active zinc atoms react and form ZnO which floats on the surface and effects wetting properties. On addition of Bi the wettability of the system improves because there is reduction in the surface tension of the liquid solder and it also reduces the melting temperature of Sn-Zn system to 189 ^{o}C [74].

Sn-zn bi solder pastes are widely used in product like computers, laptop, printers, TV tuners etc.

Bi addition up to a certain extent enhances the properties beyond that it degrades.

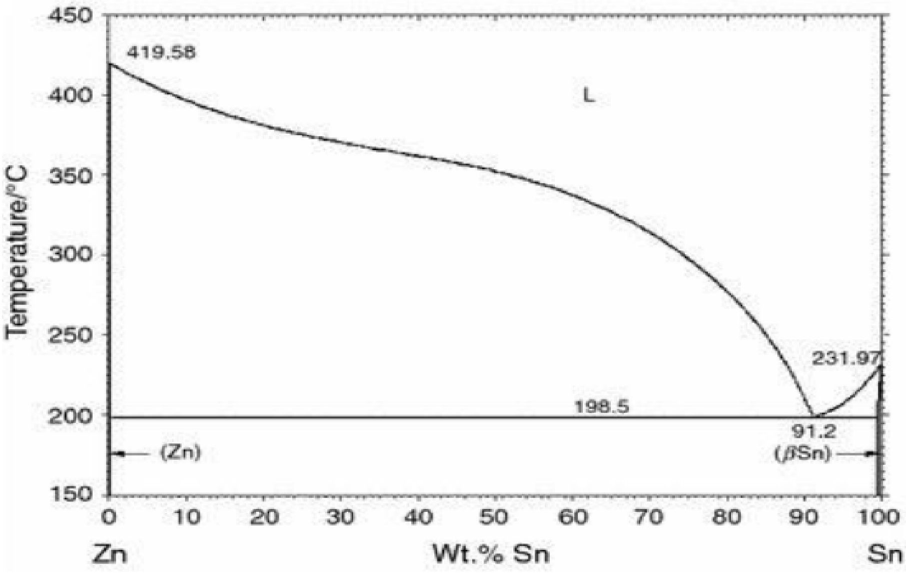

Fig.2.1: Sn-Zn Phase Diagram

2.17.2 SN-CU BASED SOLDERS

Sn-Cu binary solder is also considered as one of the alternates for Sn-Pb solders and has eutectic compositions Sn-0.7Cu and eutectic temperature up to 227^{o}C. Eutectic Sn-0.7Cu is widely used in electronic packaging and shows better creep and fatigue resistance properties as compared to the Sn-Pb solder.

This binary solder is cheapest among all the lead free alternatives and the suitable for high temperature application like automobile industry. But this solder should be properly examined before practical use because addition of Cu enhances gray Sn transformation which leads to decrease in physical and mechanical properties of solder [75].

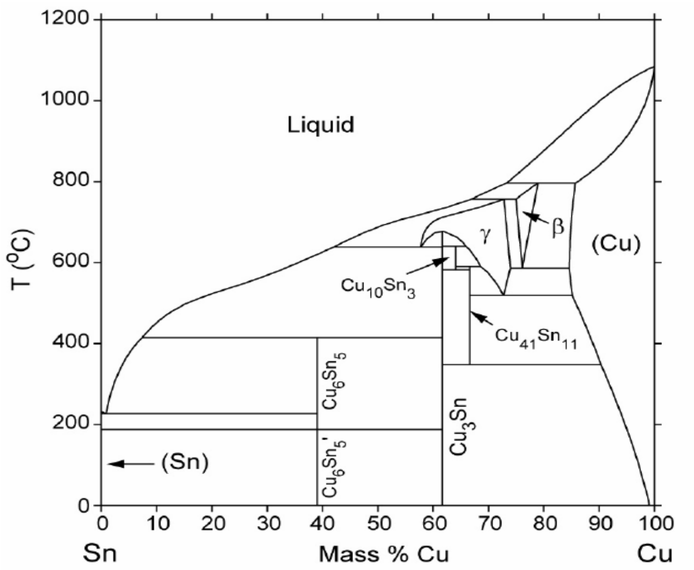

Fig.2.2: Sn-Cu Phase Diagram

2.17.3 SN-AG BASED SOLDERS

Due to the excellent mechanical properties Sn-Ag based solders have been considered as the first choice for lead free alternatives. The eutectic composition for Sn-Ag based solder is Sn-3.5 wt. % Ag and has eutectic temperature of 221^{o}C. With the help of microstructural study it has been confirmed that there is presence of fine Ag3Sn needles and beta Sn matrix and the interfacial bonding between these two phases results in excellent mechanical properties [76]. Ag_3Sn needles are brittle in nature due to which there liability of the solder degrades. On addition of Bi into Sn-Ag eutectic alloy reduces its melting temperature and also enhances its wettability [77-79]. Addition of Cu proves to be advantageous for Sn-3.5Ag binary solder and is widely used in aircraft and automotive industry where the solder joints are subjected to thermal stresses. Researchers found that mechanical properties of Sn-Ag-Cu is better than Pb solder but there is little controversy regarding the exact eutectic composition and the eutectic temperature for this composition is around 217^{o}C [80].

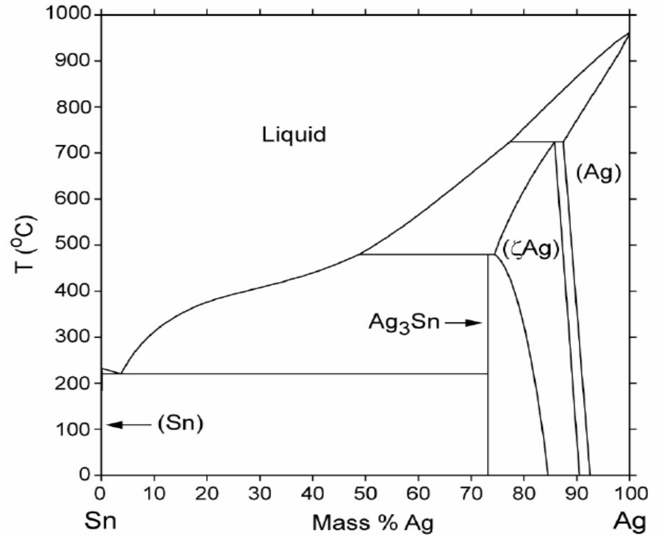

Fig.2.3: Sn-Ag Phase Diagram

2.17.4 SN BI BASED SOLDER

For more than 20 years, Sn-Bi based solder has been used in electronic industry. Eutectic composition of Sn-Bi solder has been found to be 42Sn-58Bi and the eutectic temperature is 139^{o} C. Bi precipitation takes place in Sn matrix and the alloys are allowed to cool and the cooling rate has the great influence on the microstructure as well as the mechanical; properties of the alloy. Slow cooling rate leads to crack formation and large size grain due to which reliability of the solder join degrade. Small amount of Ag addition helps in enhancing mechanical properties [81], [82].

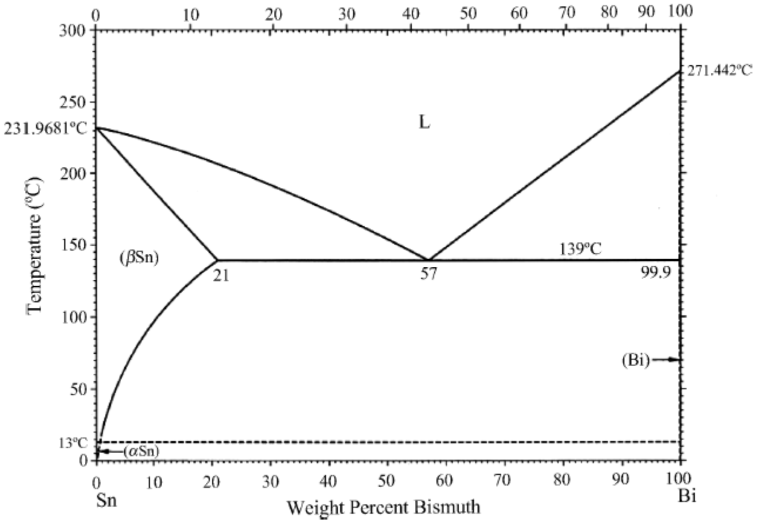

Fig.2.4 Sn-Bi Phase Diagram

Table 2.1: BINARY EUTECTIC SOLDERS

SYSTEM	EUTECTIC TEMPERATURE (°C)	EUTECTIC COMPOSITION (wt.%)
Sn- In	120	Sn-51In
Sn-Bi	139	Sn-57Bi
Sn-Zn	198	Sn-9Zn
Sn-Au	217	Sn-10 Au
Sn-Ag	221	Sn-3.5Ag
Sn-Cu	227	Sn-0.7Cu

2.18 SOLDERABILITY AND WETTABILITY

Solderability is the ability to achieve a clean metallic surface on which a molten solder can wet properly [34]. In other words solderability is the ability of a surface to be wet by a molten solder [83]. Solderability depends on several factors such as the type of flux, the type of solder and the type of surface finish on which soldering will be performed.

The word wettability is basically same as soldering but it is often used as a quantitative measure of solderability. The parameters such as contact angle, the meniscus rise, the capillary depth etc. That can be obtained in soldering tests are often used as measures of the wettability of solders [83]. Success of soldering depends on the wettability of the solder.

In general if wetting angle lies between 0^o to 90^o proper wetting of substrate takes place. The angle should be below 55^o for soldering purpose. Proper wetting will take place if there is net decrease in total free energy at the interface. Surface tension of a liquid is a property which is defined as the amount of energy needed to extend the liquid surface area on solid substrate. Strength, reliability and degree of wetting are decided by this property [84], [85].

2.19 FORMATION OF INTERMETALLICS

Intermetallic compounds are formed when molten solder alloy reacts with a substrate. The most common substrate used for electronic solders is Cu. Due to excellent conductivity Cu is widely used in electronics and Sn- based solders readily wet it. Other potential, wettable substrates are Ni/Fe alloys, Ag and Au, which are commonly coated over Cu contacts. Intermetallic compounds (IMCs) are created when a molten solder wets either Cu or such alternative substrates. They form while the solder is in a molten state but continue grow in the solid state at room temperatures as well as elevated ones via a mechanism which requires diffusion. Strength and wettability of a solder is determined by the formation and growth of interfacial layers.

Formation of intermetallic favor reliability of a solder joint, despite of this there are some disadvantages. Intermetallic are brittle in nature and poor interfacial bonding is the result of formation of thicker intermetallic layer. Soldering will not be successful if there is mismatch of physical properties between substrate and intermetallic. Excessive growth of intermetallic leads to degradation of solder joint strength, thermal fatigue life and fracture toughness of solder.

Formation of intermetallic depends upon the constituents of solder alloy and the manner in which they react with the substrate. There can be a number of intermetallic compound formed but those which are formed first during soldering process plays a vital role in wettability [86].

CHAPTER 3

EXPERIMENTAL

SETUP

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METHODOLOGY

3.1 MATERIALS AND METHODS:

We have procured Sn granules, Zn powder and Bi powder as follows:

TABLE 3.1: Purity and Supplier of the solder material

Sl.No.	MATERIAL	PURITY	SUPPLIER
1.	Sn	99%	Merck
2.	Zn	99%	Rankem, RFCL Limited
3.	Bi	99%	Loba Chemie

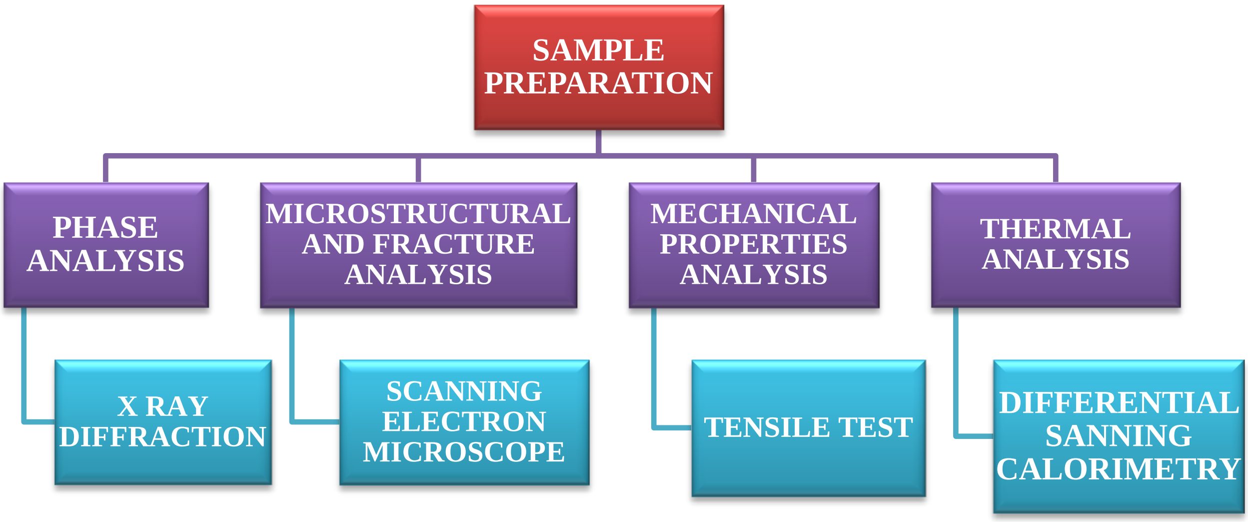
Different alloy compositions which were prepared are near eutectic Sn-8 wt. %-Zn. The modification of the eutectic microstructure by trace element addition like Bi in the eutectic alloy system will also be investigated. Sn-Zn-Bi alloys with different compositions like Sn-8 wt. % Zn-3 wt.% Bi, Sn-8 wt.% Zn-6 wt.% Bi, Sn-8 wt.% Zn-8 wt.% Bi, Sn-8 wt.% Zn-10 wt.% Bi were developed by furnace as well as air cooling.

TABLE 3.2: Chemical Compositions of the solder material (all in wt. %)

Sl.No.	COMPOSITION	Sn	Zn	Bi
1	Sn-8Zn	99.2	0.8	0
2	Sn-8Zn-3Bi	98.9	0.8	0.3
3	Sn-8Zn-6Bi	98.6	0.8	0.6
4	Sn-8Zn-8Bi	98.4	0.8	0.8
5	Sn-8Zn-10Bi	98.2	0.8	1.0

The Sn-Zn and Sn-Zn-Bi solder alloys were prepared from granulated Sn, Zn and Bi powder. The element were mixed in right proportions in a crucible in a tubular furnace in an inert argon (Ar) gas atmosphere and subsequently cooled in furnace as well as air to produce the solders. The furnace is heated to the desired temperature by electrical resistance heating elements. Sn-Zn and Sn-Zn-Bi solder alloys have casting temperature in the range of 400°C to 600°C. The molten alloy was held at this temperature for 2 hours. The morphology and elemental composition of the samples were analysed using a JEOL JSM-6480LV scanning electron microscope (SEM) equipped with an INCAPentaFET-x3 X-ray microanalysis system with a high-angle ultra-thin window detector and a 30 mm^2 Si(Li) crystal for EDS (energy dispersive x-ray spectroscopy) analysis. The microstructure and various phases formed were analysed. The near eutectic composition of Sn-8wt.% Zn was also air cooled and the microstructures of the alloy was compared with the microstructure of the furnace cooled sample. Differential scanning calorimetry (DSC) was done in order to determine the melting point of the alloys. X-ray diffraction (XRD) of the alloys was done to found out if any new phases were formed during their development. The tensile tests of the alloys were also performed to find out their mechanical properties.

3.2 FLOW-CHART OF THE EXPERIMENTAL PROCEDURE:



3.3 METALLOGRAPHY:

For microstructural studies, samples were cut approximately 8mm height. Samples were ground roughly on a belt grinder. Now, samples were moved slowly up and back on the surface of a flat belt grinder. After grinding samples were polished with the help of emery papers. Emery papers contain different type of finer abrasive grains such as 1/0, 2/0, 3/0 and 4/0 grades. During each polishing operation the samples were moved perpendicular directions to the existing scratches. After completion of polishing with the help of emery papers the samples were polished by using rotating wheel covered with special cloths. Diamond paste was used during polishing of samples on the cloths. Polishing operation was continued until the surface of samples became plane and free from the nicks or inflection etc. Finally the polished samples were cleaned thoroughly by the soap solution and dried subsequently with the use of drier.

3.4 EXPERIMENTAL INSTRUMENTS:

3.4.1 TUBULAR FURNACE

Furnace is a device which is used for heating the samples. Source of heat energy to the furnace is directly supplied by fuel combustion, by electricity in electric arc furnace and through induction heating in induction furnace. Tubular furnace is electric heating furnace. Temperature can be controlled via feedback from a thermocouple.

In this experiment work the elements such as Sn, Zn and Bi were in the right proportions. These elements were heated in a crucible in tubular furnace in the presence of inert Argon (Ar) gas atmosphere; the casting temperature is in the range of 400^{o}C to 600^{o}C maintaining the holding time as 2 h. Some samples were allowed to attain room temperature by air cooling and some by furnace cooling.

Fig. 3.4.1: High temperature tubular furnace

3.4.2 SCANNING ELECTRON MICROSCOPE

The scanning electron microscope is a type of electron microscope in which high energy beam of electrons are directed at the specimen. It is used to produce two dimensional image of a specimen of any size and thickness. The electrons produced by the hot filament are accelerated by electric and magnetic fields thus interacting with the sample and producing signals which contain information about the surface or near surface topography, composition and other properties such as electrical conductivity. SEM is primarily used to study the structure of bulk specimens. It can produce very high resolution images of sample surface and give information about less than 1nm in size. The magnification range of conventional SEM is 10x – 200,000x with spatial resolution of 50 – 100 nm can scan areas which vary from 1cm to 5 µm in width. The types of signals produced by a SEM include secondary electrons; back scattered electrons, characteristic X-ray, light (cathodoluminescence). The mode used in SEM micrographs is secondary electron imaging.

SEM has following components

- Electron Gun
- Condenser and Objective lens

- Scan Coil
- Aperture
- Detectors and Display/Date Output devices

In the present work the solder samples work mechanically polish using standard metallography techniques before the examination. The micrographs of the sample were obtained. The mode used in SEM micrograph is secondary electron imaging.

Fig 3.4.2 JEOL JSM-6480 SEM

3.4.3 DIFFERENTIAL SCANNING CALORIMETRY

DSC is a thermo-analytical technique. It gives information about the melting temperature as well as the glass transition temperature of the sample with the help of DSC curve. Using this technique it is possible to observe fusion and crystallisation and can also used to study oxidation as well as other chemical reactions. The basic principle behind its technique is that when a sample undergoes physical transformation such as phase transformation,whether less or more heat is require by the sample then the reference to maintain both at the same temperature depends upon whether the process is exothermic or endothermic.

For example- melting of a solid sample to liquid will require more heat flowing to the sample to increase its temperature at the as same rate as that of the reference due to the absorption of heat by the sample.Andthis undergoes endothermic phase transition from solid to liquid and if the sample undergoes exothermic, less heat is required to raise the sample temperature such as crystallisation. In this experimental work , we have taken the mass of solder 15mg , temprature range 25 ^oC to 300 ^oC and rate of temperature changes 10 ^oC per minute.

Fig. 3.4.3: Differential Scanning Calorimetry

3.4.4 X-RAY DIFFRACTION

XRD is a very useful device to categorise materials for the following information such as phase analysis (elemental phase/ inter-metallic phase/ crystalline phase/ non-crystalline phase) , lattice parameter determination, strain determination, texture and orientation analysis, order- isorder transformation. A phillips Pan analytical PW3040/00 X-ray diffractometer was used to characterise the solder alloys. Radiation used in x-ray diffraction was Ni filtered Cu-Kα. During XRD analysis we have takne the scanning range of 2θ from 20 degree to 90 degree with a scanning speed of 3 degree per minute and accelerating voltage of 30 KV. The peak was analysed by using X-pert high score software to identify different types of phases.

Fig. 3.4.4: X-ray Diffraction Machine

3.4.5 UNIVERSAL TESTING MACHINE

Universal Tester INSTRON 1195 model is being used in the laboratory. UTM is used to evaluate mechanical properties of materials like tensile strength, compressive strength, and flexural strength. Maximum load that can be applied is 100 kN and grip width is maximum to 50 mm. The specimen is placed between the grips and the change in gauge length is recorded during the test. Throughout the tests the control system and its associated software record the load and extension or compression of the specimen.

3.4.6 ENERGY DISPERSIVE X- RAY SPECTROSCOPY

EDX is an analytical technique used for the elemental analysis or chemical characterization. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing set of peaks on its X-ray spectrum.

Primary components of EDX are :

- The excitation source
- The x – ray detector
- The analyzer

CHAPTER 4

RESULT

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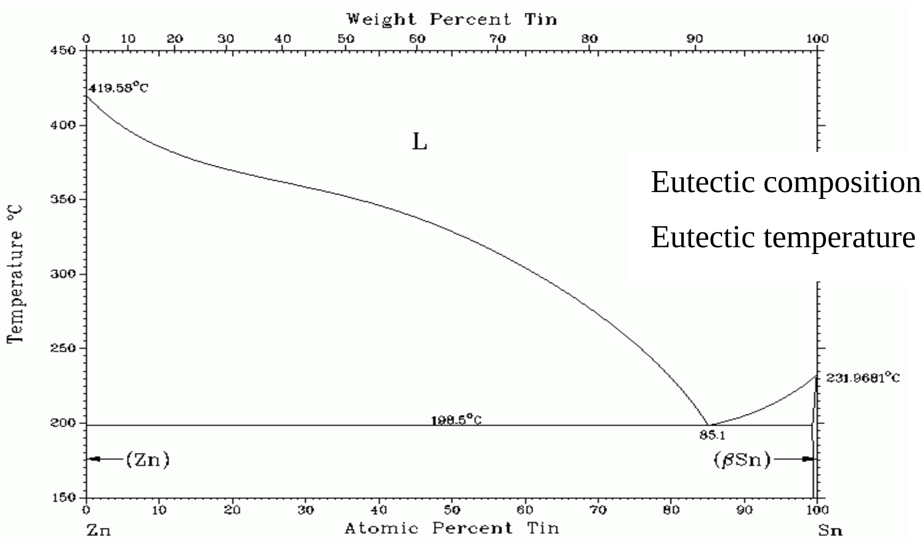
DISCUSSION

4.1 Sn-Zn EUTECTIC PHASE DIAGRAM

Fig.4.1 below shows the Sn-Zn phase diagram. The eutectic composition is Sn – 8.8 wt. % Zn. The eutectic temperature is 198°C. This temperature is very close to the eutectic temperature of Sn-Pb eutectic (183°C) [87].



Eutectic composition Sn-8.8wt. % Zn.

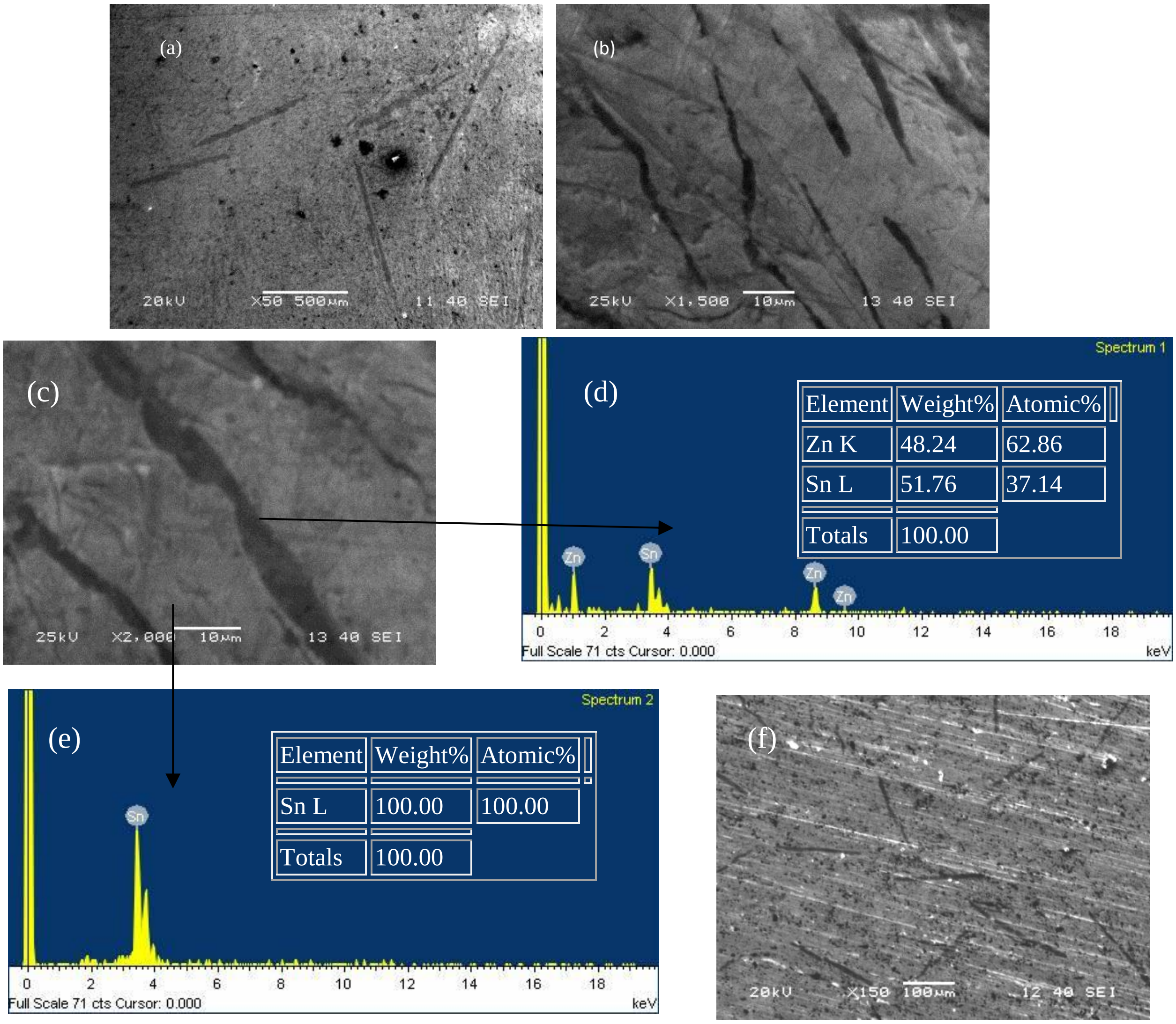
Eutectic temperature is 198°C.

Fig4.1 Sn-Zn phase diagram showing the eutectic composition.

4.2 Sn-8Zn

4.2.1 MICROSTRUCTURAL AND ELEMENTAL ANALYSIS OF EUTECTIC Sn-8Zn

Sn-8 wt. % Zn near eutectic alloy was prepared by heating Sn and Zn mixture at 500°C for 2 h. This temperature is above the melting point of both Zn (419.5°C) and Sn (231.9°C). Zn was added to the molten Sn and mixed thoroughly and held at 500°C for 2 h. After which the sample was allowed to cool in the furnace. Another sample prepared similarly was cooled in air.



Element	Weight%	Atomic%
Zn K	48.24	62.86
Sn L	51.76	37.14
Totals	100.00	

Element	Weight%	Atomic%
Sn L	100.00	100.00
Totals	100.00	

Fig.4.2.1 (a-c) SEM of Sn-8Zn (near eutectic) composition along with (d-e) EDX analysis (f) SEM of air cooled Sn-8Zn (near eutectic) composition.

The microstructure of the Sn-8 wt. % Zn solder alloy cooled in furnace given in Fig.4.2.1 (a-c) along with the EDX analysis in Fig.4.2.1 (d-e) shows that it consists of a primary Sn-phase and a Zn/Sn eutectic mixture. Fine dark coloured Zn-rich phases are dispersed in the lighter coloured Sn matrix.

The size of the needle shaped Zn-rich phase is large having a thickness of 3-4µm as can be seen in the SEM image in Fig.4.2.1 (b-c) and the number of Zn-rich phases are less. This is due to the slow cooling rate during furnace cooling of the samples.

The lighter coloured Sn matrix is almost 100 % Sn containing no Zn at all whereas the dark coloured Zn-rich phase contains both Zn and Sn (48.24 wt. % Zn and 51.76 wt. % Sn). Fig.4.2.1 (f) shows the SEM image of near eutectic Sn-8Zn composition that has been cooled in air. In this case the numbers of fine dark coloured Zn-rich phases dispersed in the lighter coloured Sn matrix are large in number and are also finer in size (1-2µm).

4.2.2 THERMAL ANALYSIS OF Sn-8Zn

The DSC result shows an endothermic peak at 210.1^{o}C which corresponds to the melting point of Sn-8 wt. %Zn near eutectic composition. The melting point of the eutectic Sn-8.8 wt. % Zn composition is 198^{o}C. The difference between above two temperatures may be due to oxide formed during the development of the eutectic alloy or any other impurities in the alloy. Fig.4.2.2 shows the DSC analysis of Sn-8Zn lead free solder alloy.

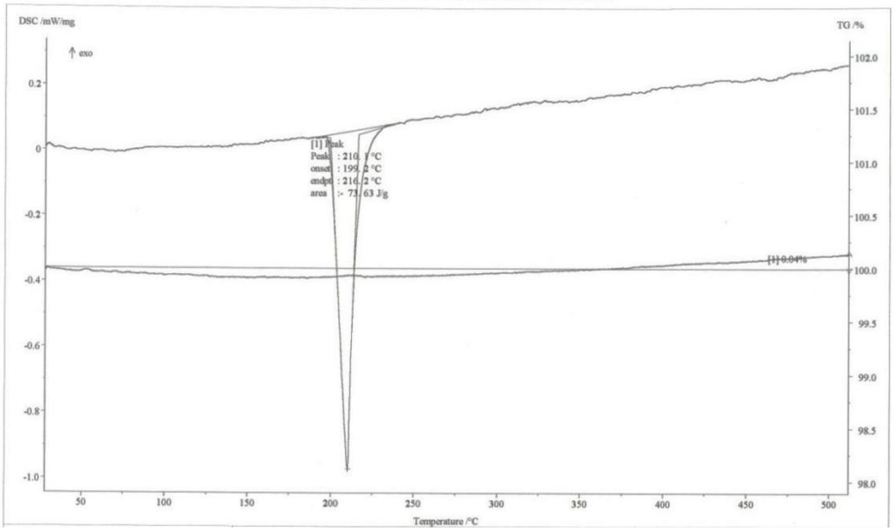


Fig.4.2.2 DSC of Sn-8Zn (near eutectic) composition

4.2.3 WETTING ANALYSIS OF Sn-8Zn

Fig.4.2.3 (a-b) shows how the Sn-8wt. % Zn near eutectic alloy behaves when it is used as a solder on Cu wires. The SEM images show that the Sn-8Zn near eutectic alloy shows good wettability on the Cu substrate.

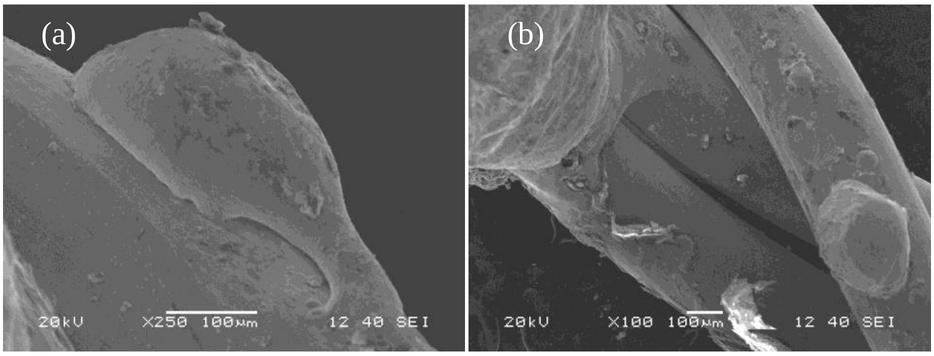


Fig. 4.2.3(a-b) SEM of Sn-8Zn solder on Cu substrate

It has been found that the addition of Bi to the Sn-Zn alloy lowers the eutectic temperature and increases the pasty region. The pasty region is the region between the liquidus and the solidus. The melting temperature of the solder is an important physical property which influences the behavior of the solder with the substrate. A good solder alloy should have a low melting temperature and a narrow pasty region. This is why it is very important to add an optimum amount of Bi to the Sn-Zn eutectic composition [88-90].

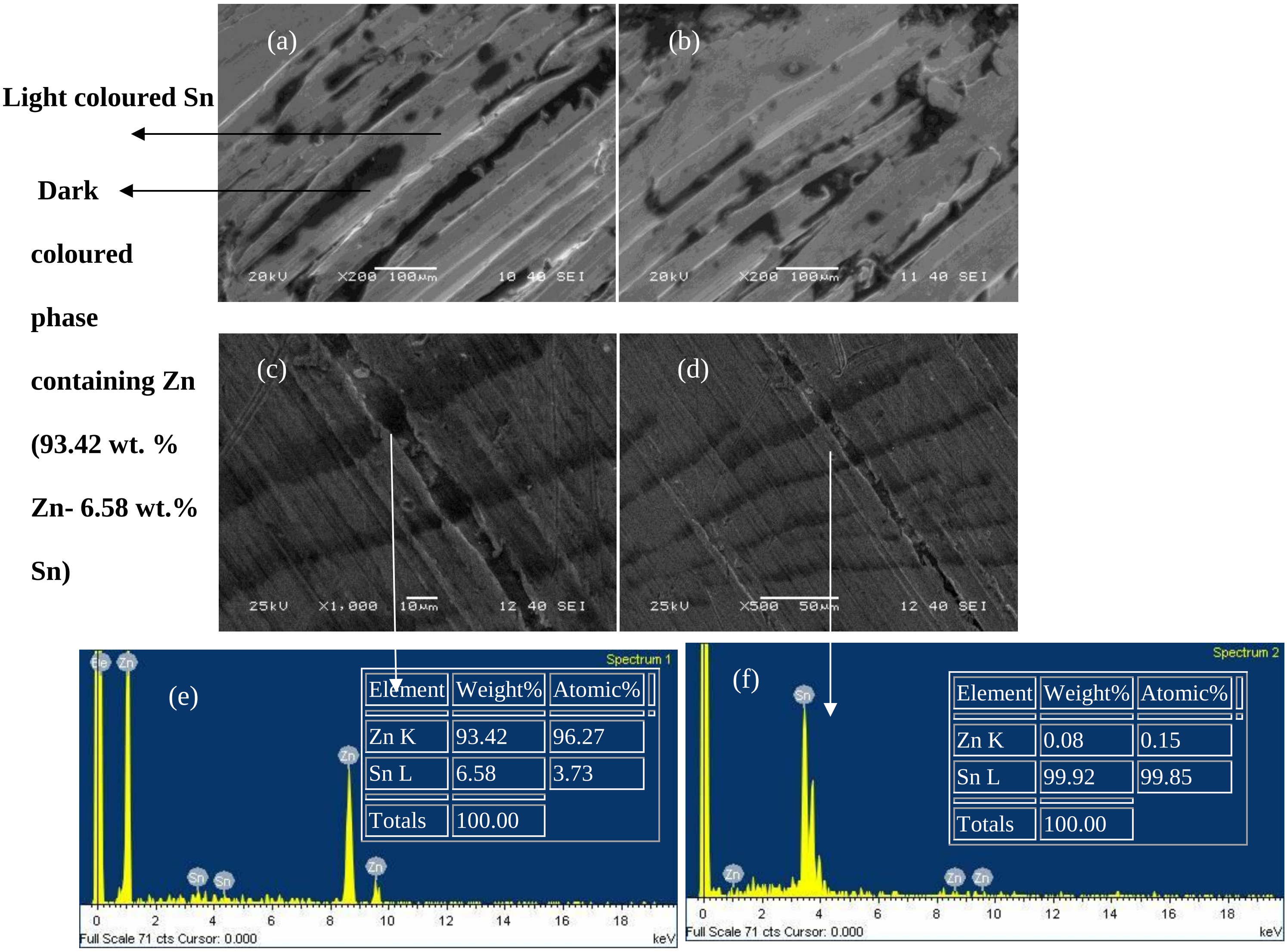
4.3 Sn-8Zn-3Bi

4.3.1 MICROSTRUCTURAL AND ELEMENTAL ANALYSIS OF Sn-8Zn-3Bi

Sn-8Zn-3Bi alloy was developed by adding the desired wt. % of Zn and Bi to molten Sn. After Zn and Bi was added to the molten Sn it was stirred and held at 450^{o}C for 2 h after which it was furnace cooled to room temperature.

In the case of the Sn–8Zn–3Bi solder, the microstructure consists particularly of a Zn/Sn eutectic region with some dark coloured phase containing Zn and a light coloured Sn-rich phase containing almost 100% Sn as can be seen from the SEM images in Fig.4.3.1 (a-d). The fine dark coloured phases containing higher wt. % of Zn are dispersed in the lighter coloured Sn matrix. The EDS analysis in Fig.4.3.1 (e, f) shows the composition of the dark coloured phase containing Zn and the Sn rich matrix. The matrix contains 99.92 wt. % Sn and negligible amount of Zn whereas the dark coloured phase contains 93.42 wt. % Zn and 6.58

wt. % Sn. The dark coloured phase is rich in Zn containing also some amount of Sn. It should be noted that the mutual solubility of Sn and Zn at room temperature is almost nil (Fig.4.1).


Light coloured Sn

Dark coloured phase containing Zn (93.42 wt. % Zn- 6.58 wt.% Sn)

(e)

Element	Weight%	Atomic%
Zn K	93.42	96.27
Sn L	6.58	3.73
Totals	100.00	

(f)

Element	Weight%	Atomic%
Zn K	0.08	0.15
Sn L	99.92	99.85
Totals	100.00	

Fig.4.3.1 (a-d) SEM of Sn-8Zn-3Bi composition along with (e-f) EDS analysis

4.3.2 PHASE DIAGRAM OF Sn-Bi AND Zn-Bi SYSTEMS

Bi could not be traced in the microstructure of Sn-8Zn-3Bi. This is due to the very low percentage (3 wt.%) of Bi in the composition. The maximum solubility of Bi in Sn is around 21 wt.% which takes place at the euctetic temperature of 139^{o}C (refer Fig.4.3.2(a)). The solubility of Bi in Sn is less than 3 wt. % at room temperature and addition of 3 wt.% Bi in Sn-8Zn-3Bi composition possibly forms a solid solution of Bi in Sn. As a result Bi is not visible in the microstructure. The solubilty of Bi in Zn is almost negligible (refer Fig.4.3.2(b)). It has been reported to be less than 0.1wt.% [91] . Therefore all the Bi must be in the Sn-rich region as solid solution in Sn or remain undissolved. In alloys where the conpsition of Bi is higher than 3 wt.% Bi Bi could be seen in the Sn-rich region as bright white spots (Figs.4.4.1(a-c)). The supersaturation of Bi in Sn in alloys where the Bi content in the alloy is higher than 3 wt. % leads to the formation of Bi precipitates. Bi addition could also lead to the lowering of the melting point of the Sn-8Zn-3Bi solder alloy. The result of DSC analysis of Sn-8Zn-3Bi composition clearly indicates reduction in the melting, point to 203.3^{o}C [92].

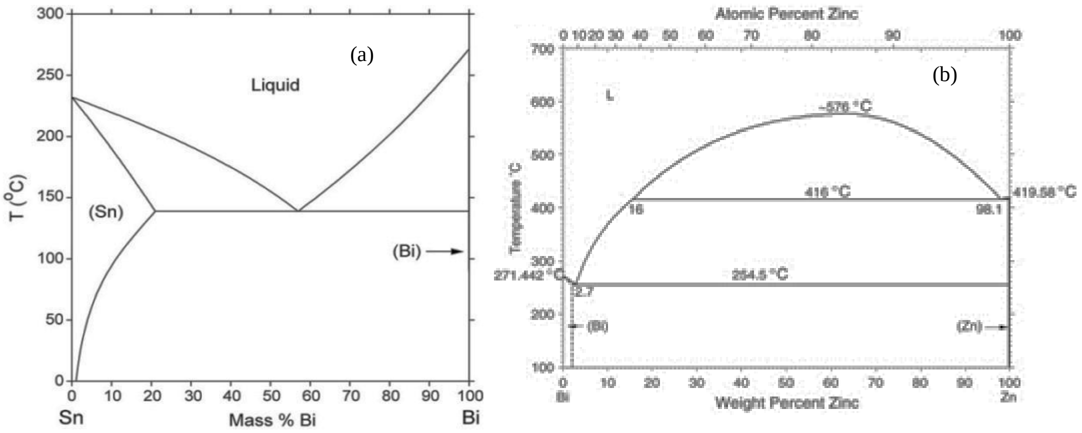


Fig.4.3.2 Phase diagram of (a) Sn-Bi and (b) Zn-Bi systems

4.3.3THERMAL ANALYSIS OF Sn-8Zn-3Bi

The DSC analysis in Fig.4.3.3 shows that the peak indicating the melting of the composition Sn-8Zn-3Bi is at 203.3^{o}C. The DSC result of Sn-8wt. %Zn eutectic composition in Fig. 4.2.2 showed an endothermic peak at 210.1^{o}C which corresponds to the melting point of the near eutectic composition Sn-8Zn. Thus there is a significant lowering of the melting point of the eutectic composition after adding 3 wt. % of Bi

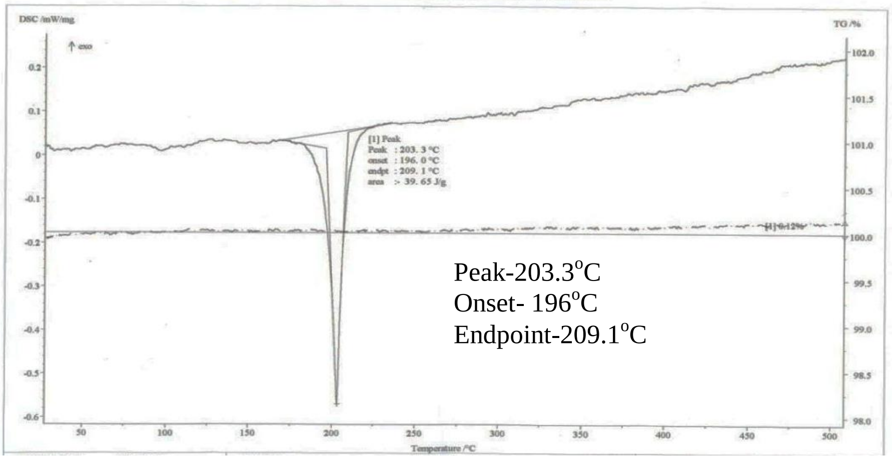


Fig.4.3.3 DSC of Sn-8Zn-3Bi composition

4.3.4 WETTABILITY ANALYSIS OF Sn-8Zn-3Bi

The alloy Sn-8Zn-3Bi has been used to solder a Cu wire. SEM images in Fig.4.3.4(a-b) show that the alloy Sn-8Zn-3Bi has good wettability.

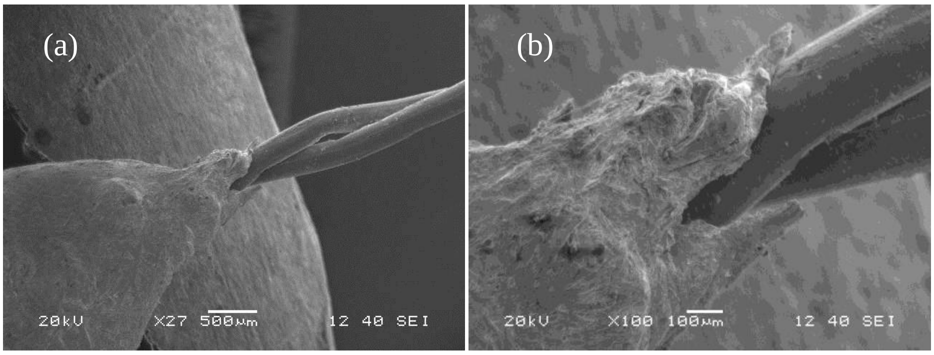


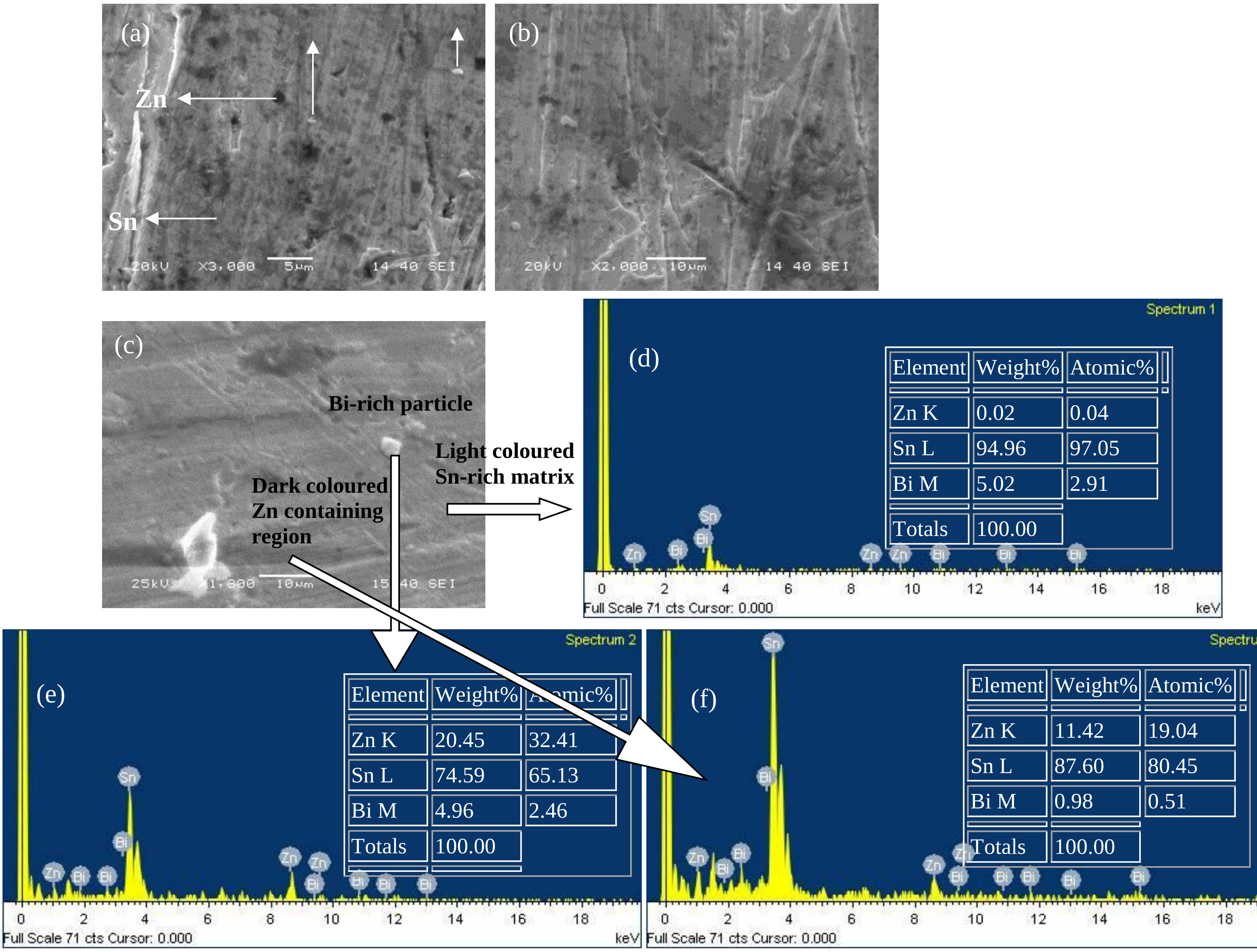
Fig.4.3.4 (a-b) SEM images of Sn-8Zn-3Bi alloy used as solder on Cu substrate

4.4 Sn-8Zn-6Bi

4.4.1 MICROSTRUCTURAL AND ELEMENTAL ANALYSIS OF Sn-8Zn-6Bi

Another system that was developed and characterized was the Sn-8Zn-6Bi. Here we find that the polyhedral Bi rich phase and the needle like Zn rich phase precipitates in the matrix of the Sn-8Zn-6Bi solder alloy. White Bi rich particles could clearly be seen in the Sn rich matrix (Fig.4.4.1 (a-c)). (Fig.4.4.1 (d-f)) is the EDS analysis of the sample. The Sn rich matrix was found to contain as high as 5 wt. % Bi. This suggests that all the Bi is in the Sn matrix and they can be seen as white particles in certain areas of the Sn matrix as the maximum solubility of Bi in Sn is only 3 wt.% and the alloy contains 6 wt.% Bi.

The Zn containing phases are dark in colour the Sn-rich matrix phase is light coloured and the Bi containing particles is white in colour. Here Bi could be seen in the microstructure as 6 wt. % is added. Some voids are also observed at the surface of the Sn–8Zn-6Bi solder alloys. The diffusion of Zn leads to vacancy diffusion in the opposite direction and the accumulation of vacancies lead to void formation.



(d)

Element	Weight%	Atomic%
Zn K	0.02	0.04
Sn L	94.96	97.05
Bi M	5.02	2.91
Totals	100.00	

(e)

Element	Weight%	Atomic%
Zn K	20.45	32.41
Sn L	74.59	65.13
Bi M	4.96	2.46
Totals	100.00	

(f)

Element	Weight%	Atomic%
Zn K	11.42	19.04
Sn L	87.60	80.45
Bi M	0.98	0.51
Totals	100.00	

Fig.4.4.1 (a-c) SEM images of Sn-8Zn-6Bi alloy (d-f) EDX analysis of various regions in Sn-8Zn-6Bi alloy

4.4.2 THERMAL ANALYSIS OF Sn-8Zn-6Bi

The DSC analysis of Sn-8Zn-6Bi alloy is given in Fig.4.4.2. The melting point of the alloy Sn-8Zn-6Bi has been found to be 201.24°C. There is a slight decrease in the melting point with the increase in the wt.% of Bi in the alloy.

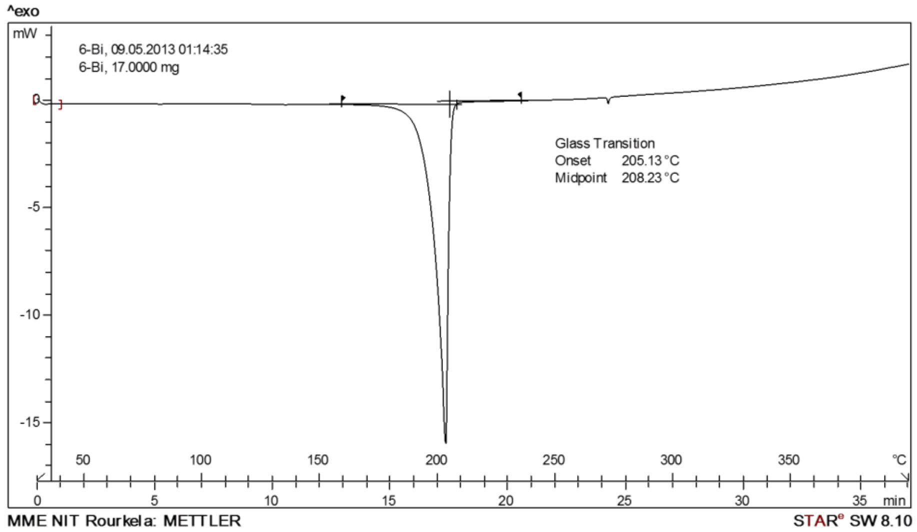


Fig.4.4.2 DSC of Sn-8Zn-6Bi Composition

4.4.3 WETTING ANALYSIS OF Sn-8ZN-6Bi

The SEM images in Fig.4.4.3(a-b) does not show very good wettability between the solder and the Cu wire.

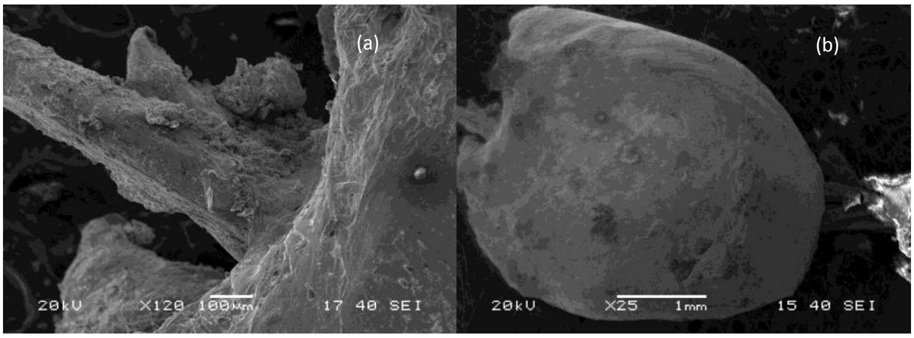
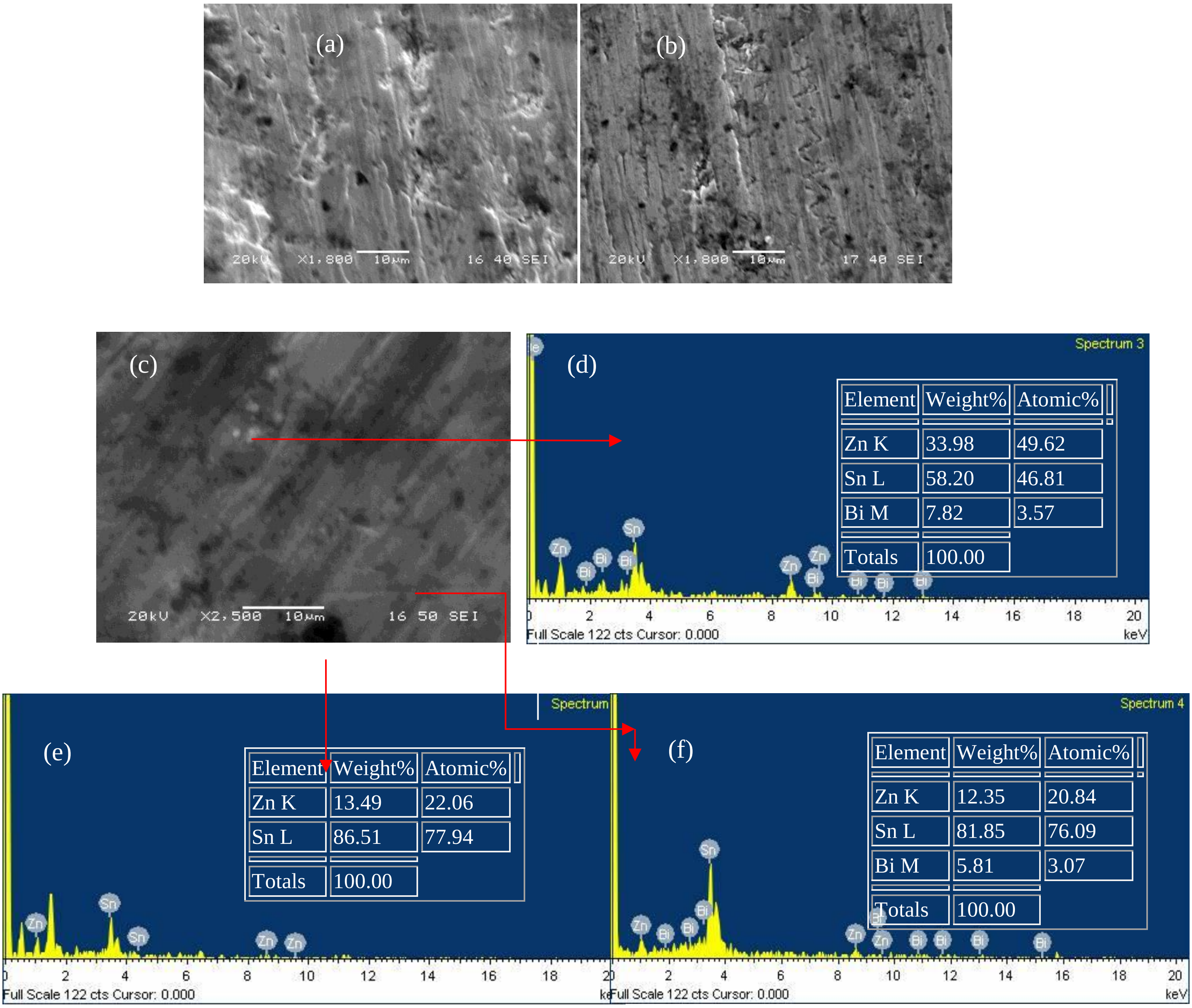


Fig.4.4.3 (a-b) SEM images of Sn-8Zn-6Bi alloy used as solder on Cu wire

4.5 Sn-8Zn-8Bi

4.5.1 MICROSTUCTURAL AND ELEMENTAL ANALYSIS OF Sn-8Zn-8Bi

Sn-8Zn-8Bi alloys showed a large number of white spots. This is seen in the SEM images in Fig.4.5.1 (a-c). These are Bi rich particles which have precipitated in the Sn rich matrix and the contained about 7.82 wt. % Bi. The amount of Bi in the light coloured Sn rich matrix is 5.81 wt. %. It is known that the solubility of Bi in Zn is less than 0.1 wt. %. This can be seen in the phase diagram in Fig. 4.3.2(b). Bi could not be found in the dark coloured Zn containing region. These regions contain 13.49 wt. % Zn and 86.51 wt. % Sn. The light coloured matrix is found to contain only 0.02 wt. % Zn.



(d)

Element	Weight%	Atomic%
Zn K	33.98	49.62
Sn L	58.20	46.81
Bi M	7.82	3.57
Totals	100.00	

(e)

Element	Weight%	Atomic%
Zn K	13.49	22.06
Sn L	86.51	77.94
Totals	100.00	

(f)

Element	Weight%	Atomic%
Zn K	12.35	20.84
Sn L	81.85	76.09
Bi M	5.81	3.07
Totals	100.00	

Fig.4.5.1 (a-c) SEM image of Sn-8Zn-8Bi alloy (d-f) EDX analysis of the various regions in the sample

4.5.2 THERMAL ANALYSIS OF Sn-8Zn-8Bi

The DSC analysis of Sn-8Zn-8Bi alloy is given in Fig.4.5.2. The melting point of the alloy Sn-8Zn-8Bi has been found to be 201.42°C. There is a slight increase in the melting point with the increase in the wt.% of Bi in the alloy. Further addition of Bi to the near eutectic compsoiton of Sn-8Zn does not decrease the melting point of the alloy

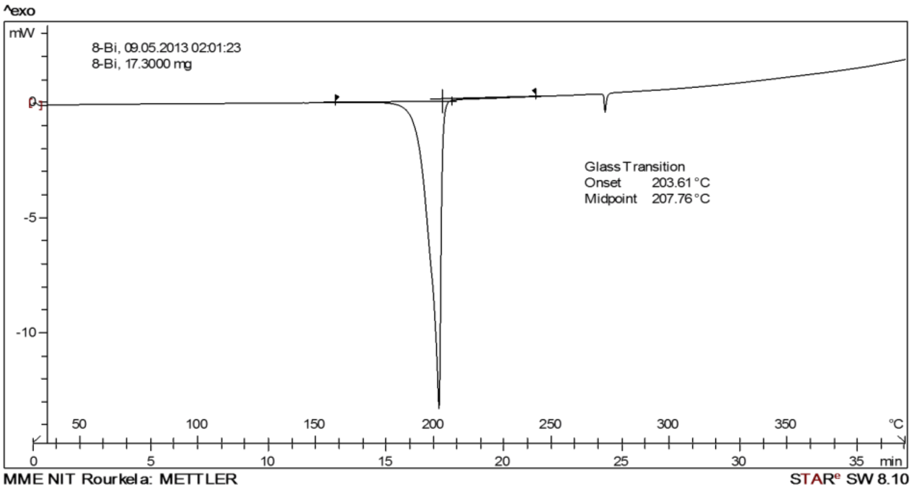


Fig.4.5.2 DSC of Sn-8Zn-8Bi Composition

4.5.3 WETTABILITY ANALYSIS OF Sn-8Zn-8Bi

Sn-8Zn-8Bi alloy was also used to solder Cu wire to find out its wettability. The wettability of this alloy seems poorer than the Sn-8Zn-6Bi alloy. The Sn-Zn-Bi alloys are definitely capable to replace Sn-Pb solder due to its low melting temperature and low cost but the wettability of this alloy is not as good as the Sn-Pb alloy. The compositions of the alloy containing higher Bi wt. % has poorer wettability.

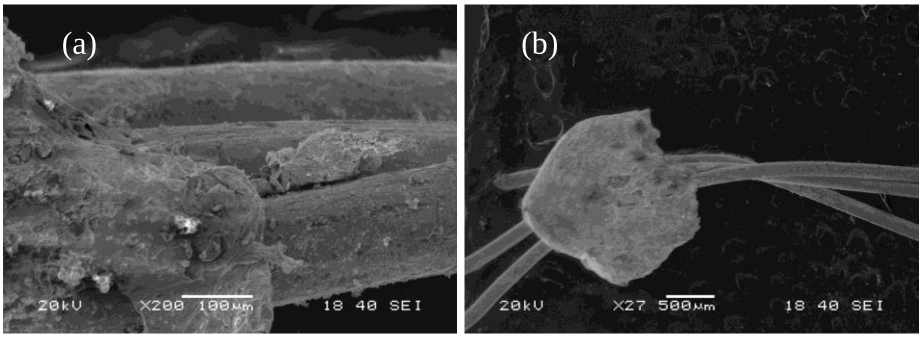
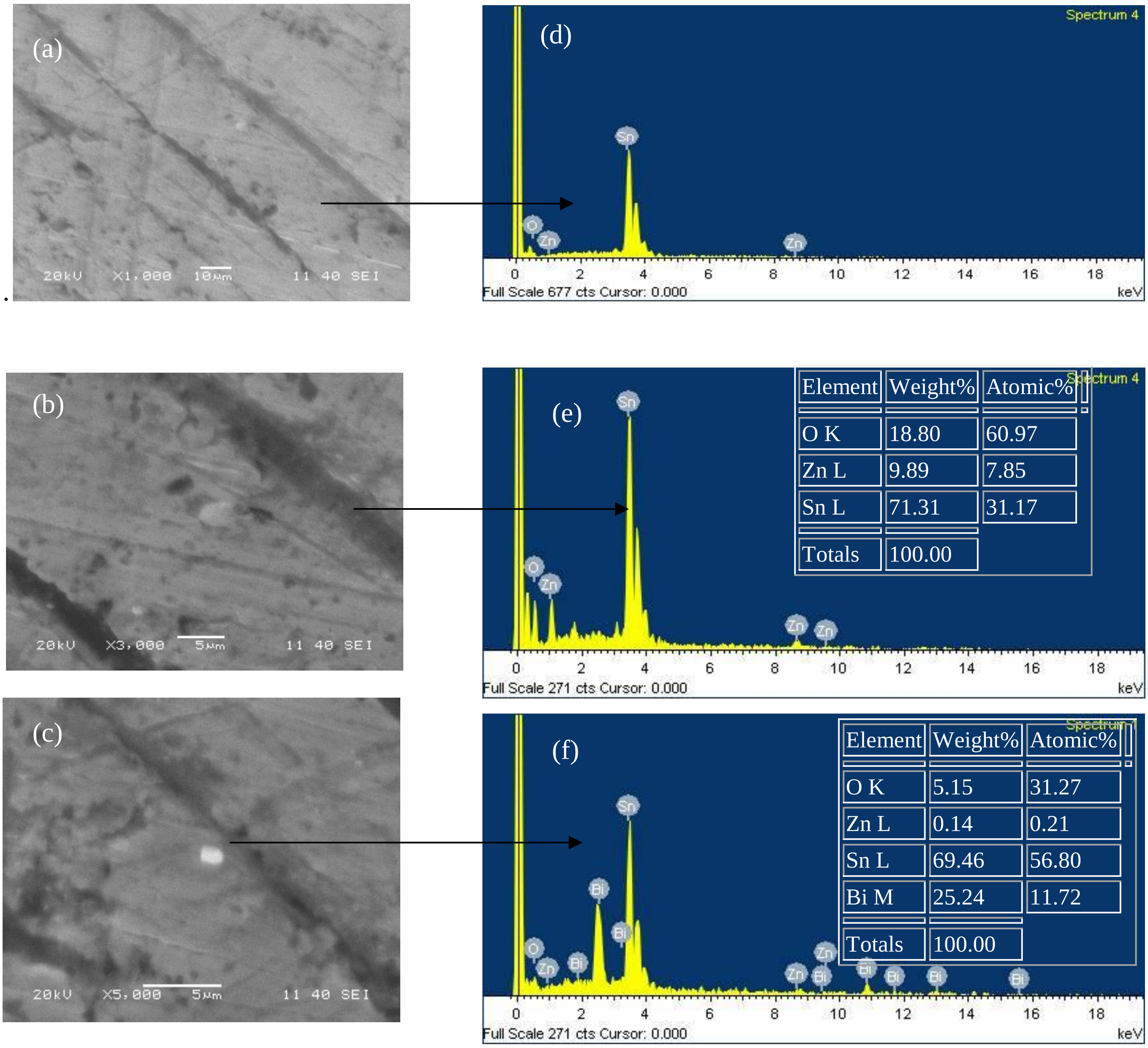


Fig.4.5.3 (a-b) SEM images of Sn-8Zn-8Bi alloy used as solder on Cu wire

4.6 Sn-8Zn-10Bi

4.6.1 MICROSTRUCTURAL AND ELEMENTAL ANALYSIS OF Sn-8Zn-10Bi

The microstructure of Sn-8Zn-10Bi is similar to the Sn-8Zn-8Bi alloys but the white Bi rich regions contained a higher percentage of Bi. The Bi wt. % is found to be 25.24 in the Bi rich region. The microstructure is shown is in Fig.4.6.1 (a-c) along with EDS analysis in Fig.4.6.1 (d-f)



Element	Weight%	Atomic%
O K	18.80	60.97
Zn L	9.89	7.85
Sn L	71.31	31.17
Totals	100.00	

Element	Weight%	Atomic%
O K	5.15	31.27
Zn L	0.14	0.21
Sn L	69.46	56.80
Bi M	25.24	11.72
Totals	100.00	

Fig.4.6.1 (a-c) SEM images of Sn-8Zn-10Bi alloy (d-f) EDX of various regions in the SEM image

The light coloured regions are Sn rich regions having almost no Zn or Bi in it. The dark areas contain higher wt.% of Zn (9.89 wt.%) although they contain significant amount of Sn(71.31 wt.%). The white spots have been identified to be Bi rich and having significant percentage of Sn in it. EDS analysis shows that there is also some amount of oxygen. Bi tries to agglomerate around the Zn-rich phase. The eutectic mixtures are found to be layer type.

4.6.2 WETTA BILITY ANALYSIS OF Sn-8Zn-10Bi

Fig.4.6.2 (a-b) shows the SEM images of soldering of Sn-8Zn-10Bi with Cu wires. There seem to a less wettability of the alloy on the Cu surface.

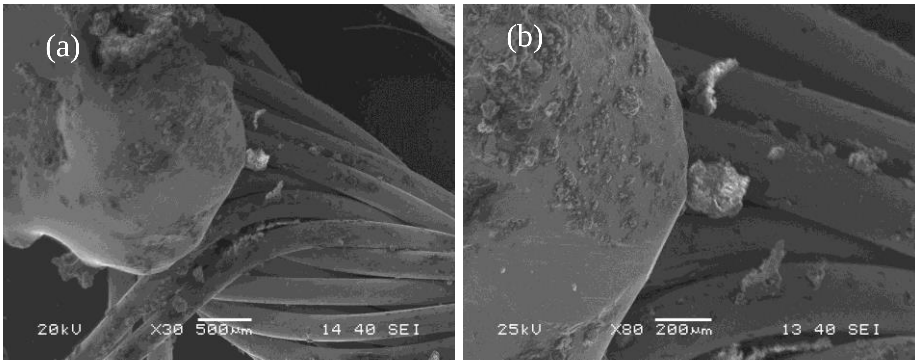


Fig. 4.6.2(a-b) SEM images of Sn-8Zn-10Bi alloy used for soldering Cu wires

4.7 X-RAY DIFFRACTION ANALYSIS

The x-ray diffraction plots of the various solder alloys in Fig.4.7 suggest that no new phase has been formed. The phase diagrams of Sn-Zn in Fig.4.1 and Sn-Bi and Zn-Bi in Figs.4.3.2(a-b) also suggest that no new phase formation takes place between the three elements Sn, Zn and Bi.

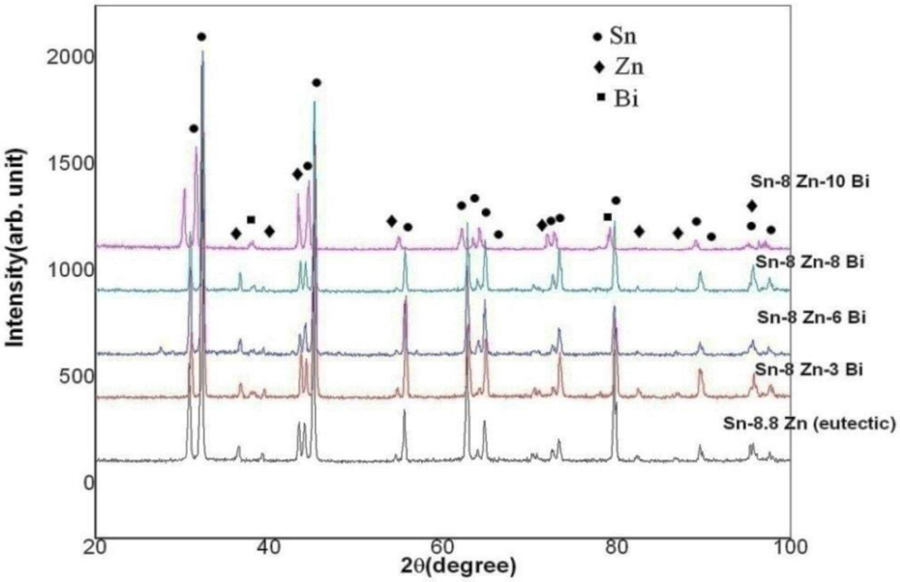
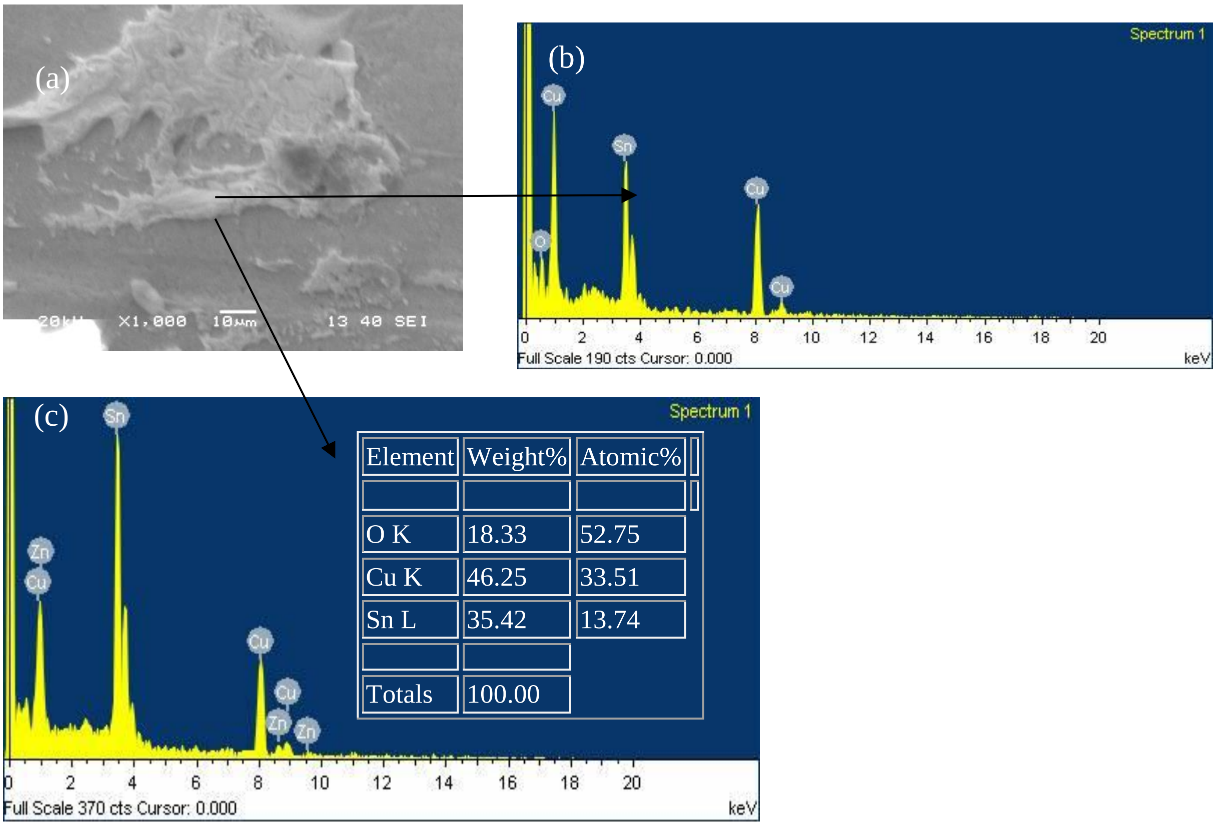


Fig.4.7 XRD plots of the various Sn-Zn-Bi alloys

4.8 FORMATION OF INTERMETALLICS

The SEM image in Fig.4.8 (a) shows the region near the contact of the Sn-Zn solder with the copper substrate. The EDS analysis in Fig.4.8 (b, c) of the Sn-Zn/Cu interface suggests the formation of Cu-Sn intermetallic. There is possibility of formation of intermetallic Cu_6Sn_5 at the interface. The EDS analysis in Fig.4.8(c) shows that there is complete absence of Zn in the layer of the Sn-Zn solder which is in contact with the copper substrate suggesting the formation of intermetallic Cu-Sn compounds in the contact region between the copper substrate and the solder. The intermetallic Cu_6Sn_5 layer that forms at the interface causes the fracture of the solder joints and lead to the degradation of the joint strength [12].



Element	Weight%	Atomic%
O K	18.33	52.75
Cu K	46.25	33.51
Sn L	35.42	13.74
Totals	100.00	

Fig.4.8 (a) SEM of the contact area between the Sn-Zn solder and Cu substrate (b-c) EDX of the layer near the contact.

4.9 VARIATION OF MELTING POINT WITH ADDITION OF Bi

The variation of melting point of the near eutectic coposition Sn-8Zn with addition of Bi is shown in the plot below in Fig.4.9. The graph shows a gradual decrease in the melting point of Sn-8Zn with increase in the Bi content in the alloy upto 6 wt.% addition of Bi to the Sn-8Zn composition

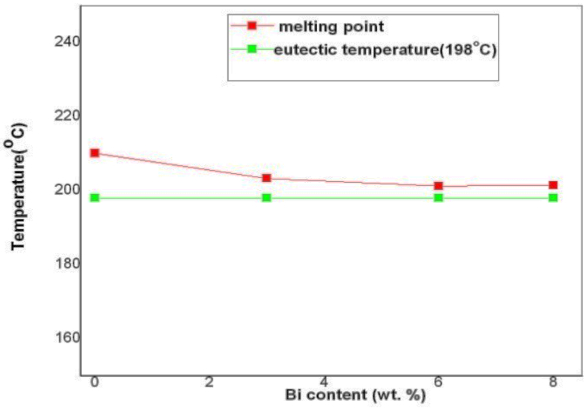


Fig.4.9 Variation of melting point Sn-8Zn with addition of Bi

4.10 VARIATION OF MECHANICAL PROPERTIES

Fig.4.10 (a-b) shows the result of tensile test of the eutectic Sn-Zn, Sn-Zn-3Bi and Sn-Zn-6Bi air cooled samples. The elongation of the sample decreases with increase in the Bi content of the sample. Bi addition also leads to decrease in the tensile strength value. It can be concluded that addition of small amount of Bi (<3 wt. %) could lead to solid solution strengthening of the Sn matrix. When the wt. % of Bi is increased in the alloy it leads to precipitation of Bi in the Sn matrix. It could also lead to the precipitation of needle like Zn phase and this would induce cracks in the matrix and lead to reduction of strength of the alloy.

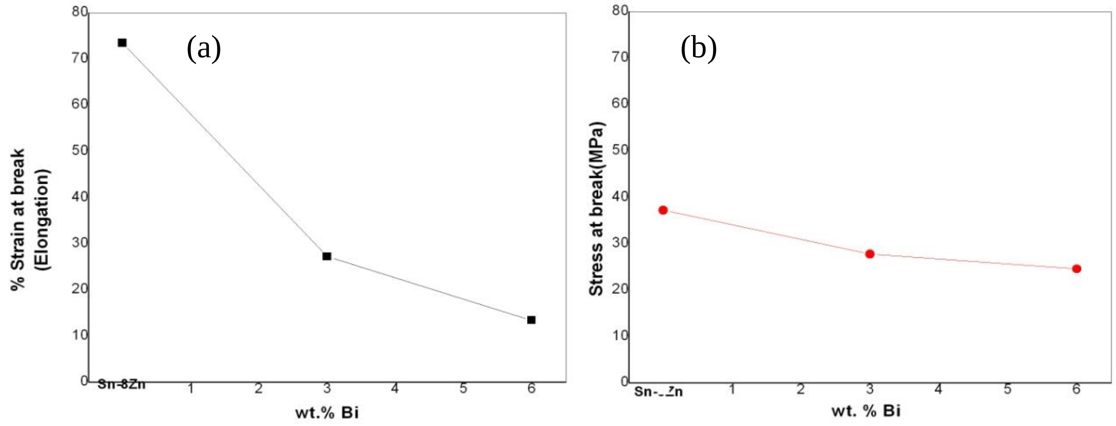


Fig.4.10 Variation of (a) Strain at Elongation and (b) Stress at break of Sn-8Zn alloy with Bi content

4.11 FRACTOGRAPHY

Fig.4.11 shows the SEM images of the fracture surface of the three Sn-8Zn, Sn-8Zn-3Bi and Sn-8Zn-6Bi tensile specimens. All the alloys show a ductile fracture with dimples on the fracture surface. In the case of Sn-8Zn-6Bi (Fig.4.11 (e,f)) the cup and cone fracture size is found to be larger as compared to the Sn-8Zn (Fig.4.11(a,b)) and Sn-8Zn-3Bi (Fig.4.11(c,d)) alloy. This suggests the lowering of ductility of the alloy with addition of higher wt. % of Bi. Sn-8Zn and Sn-8Zn-3Bi show smaller cup and cone fracture size. This suggests ductile failure in these alloys.

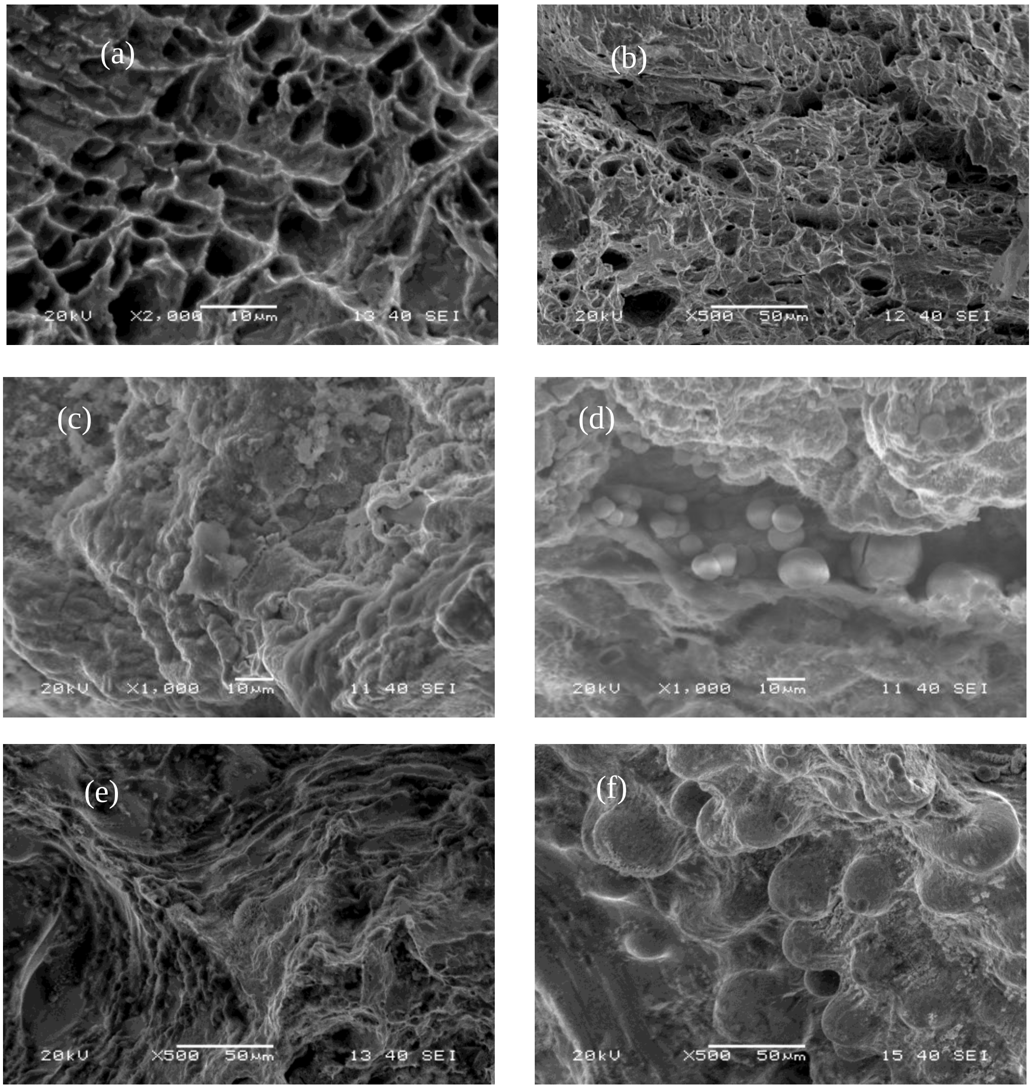


Fig.4.11 SEM images of the fracture surfaces of (a,b) Sn-8Zn (c,d) Sn-8Zn-3Bi (e,f) Sn-8Zn-6Bi alloys

4.12 Sn-Zn-Ag

. We have procured Sn granules, Zn powder and Ag powder as follows:

TABLE 4.12: Purity and Supplier of the solder material

Sl.No.	MATERIAL	PURITY	SUPPLIER
1.	Sn	99%	Merck
2.	Zn	99%	Rankem, RFCL Limited
3.	Ag	99%	Loba Chemie

Different alloy compositions which were prepared are near eutectic Sn-8 wt. %-Zn. The modification of the eutectic microstructure by trace element addition like Ag in the eutectic alloy system will also be investigated. Sn-Zn-Ag alloys with different compositions like Sn-8 wt. % Zn-0.05 wt. %Ag, Sn-8 wt. % Zn-0.1 wt. %Ag and Sn-8 wt. % Zn-0.2 wt. %Ag were developed by furnace cooling.

TABLE 4.13 : Chemical Compositions of the solder material (all in wt. %)

Sl.No.	COMPOSITION	Sn	Zn	Bi
1	Sn-8Zn	99.2	0.8	0
2	Sn-8Zn-0.05Ag	98.9	0.8	0.3
3	Sn-8Zn-0.1Ag	98.6	0.8	0.6
4	Sn-8Zn-0.2Ag	98.4	0.8	0.8

The Sn-Zn and Sn-Zn-Ag solder alloys were prepared from granulated Sn, Zn and Ai powder. The element were mixed in right proportions in a crucible in a tubular furnace in an inert argon (Ar) gas atmosphere and subsequently cooled in furnace to produce the solders. The furnace is heated to the desired temperature by electrical resistance heating elements. Sn-Zn and Sn-Zn-Bi solder alloys have casting temperature in the range of 800^{o}C . The molten alloy was held at this temperature for 2 hours. The morphology and elemental composition of the samples were analysed using a Field emission scanning electron microscope (SEM) equipped with a EDS (energy dispersive x-ray spectroscopy) analysis. The microstructure and various phases formed were analysed. Differential scanning calorimetry (DSC) was done in order to determine the melting point of the alloys. X-ray diffraction (XRD) of the alloys was done to found out if any new phases were formed during their development.

4.12.1 MICROSTRUCTURAL AND ELEMENTAL ANALYSIS OF Sn-Zn-Ag SOLDERS

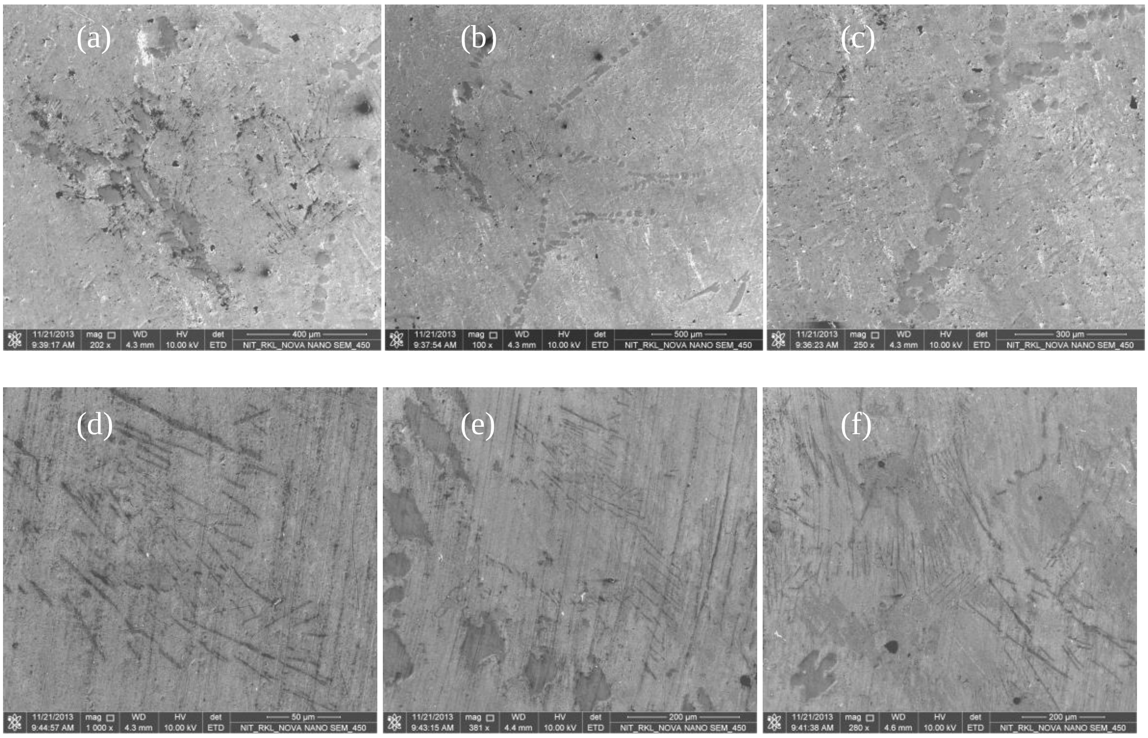


Fig. 4.12.1(A) FESEM images of (a-c) Sn-Zn-0.05wt. % Ag (d-f) Sn-Zn-0.2 wt. % Ag

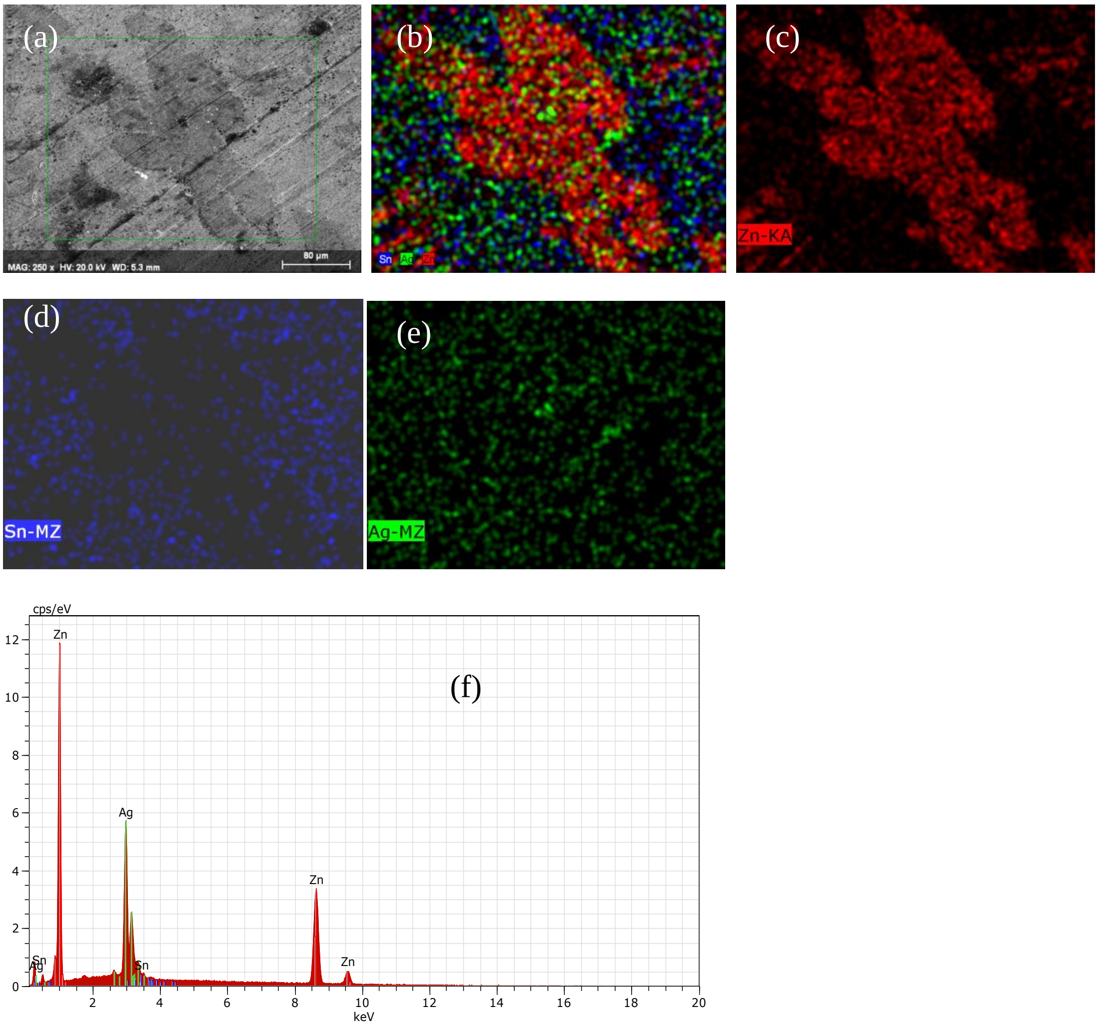


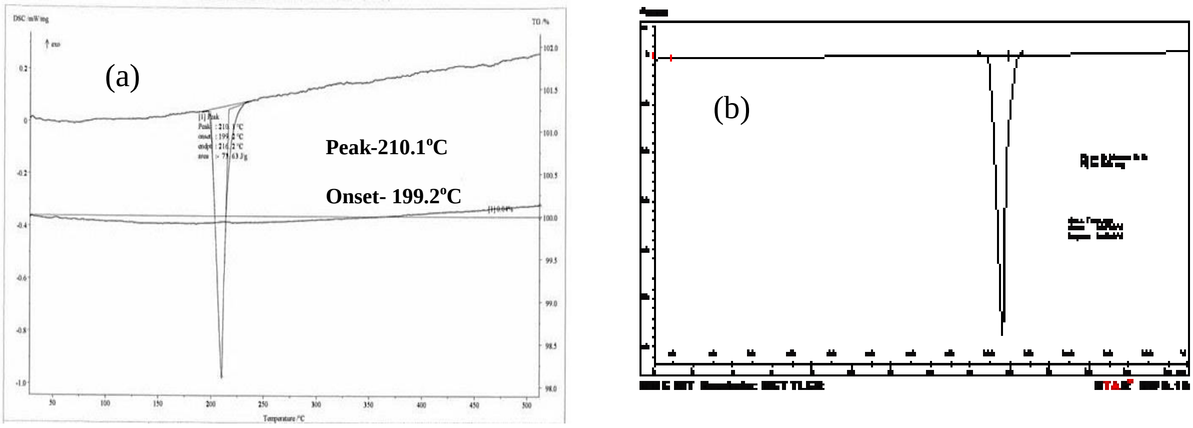
Fig.4.12.1 (B) (a) FESEM image Elemental mapping of (b) Zn, Sn and Ag combined (c) Zn (d) Sn (e) Ag and (f) EDX analysis of Sn-Zn-0.2 wt. % Ag solder alloy

Fig.4.12.1 (A,B) shows the microstructure of the Sn-Zn-0.05 wt. % Ag and Sn-Zn-0.2 wt. % Ag solder alloy along with the elemental maps of Zn, Sn and Ag. It is very clear from the elemental maps that the dark coloured Zn-rich areas are surrounded by Sn rich areas consisting of 100% Sn.

4.12.2 THERMAL ANALYSIS OF Sn-Zn-Ag SOLDERS

The DSC plot in Fig.4.12.2 (a) shows an endothermic peak at 210.1^{o}C. This is the melting point of the Sn-8wt. %Zn eutectic alloy. The DSC plot in Fig.4.12.2 (b) shows a single sharp endothermic peak at 215.48°C This corresponds to the melting point the Sn-Zn-0.05Ag. The melting point the Sn-Zn-0.05Ag is slightly higher than the eutectic point of Sn-Zn system

The DSC of Sn-Zn-0.1Ag solder alloy in Fig.4.12.2(c) shows that the melting point of the alloy is 198.7°C. Thus there is a reduction in the melting point of the eutectic composition after addition of 0.1 wt. % Ag but instead of a single sharp peak now can see two peaks. This is due to the addition of Ag. The liquidus line of the Sn-Zn eutectic alloy rises with the increase of the Ag content in the alloy. This leads to an increase in the pasty region. It can be noted that the height of the first peak decreases with an increase in the Ag content in the alloy. The shoulder was observed at around 220°C in the DSC curves for 0.1 and 0.2 wt. % Ag alloys (Figs.4.12.2(c) and (d)). This shoulder is not present 0.05 wt. % Ag containing solders. The addition of a large amount of Ag in the Sn-Zn-0.1Ag and Sn-Zn-0.2Ag alloys resulted in the formation of larger amount of Ag_3Zn intermetallic compound. This reaction reduced the Zn content of the eutectic Sn-Zn composition which resulted in the formation of a hypoeutectic β-Sn structure. This is why the DSC plots of the solder alloys Sn-Zn-0.1Ag and Sn-Zn-0.2Ag showed two endothermic peaks. The first endothermic peak represents the melting of the eutectic Sn-Zn-Ag ternary system and the other peak is due to the melting of the hypoeutectic β-Sn [93-95].



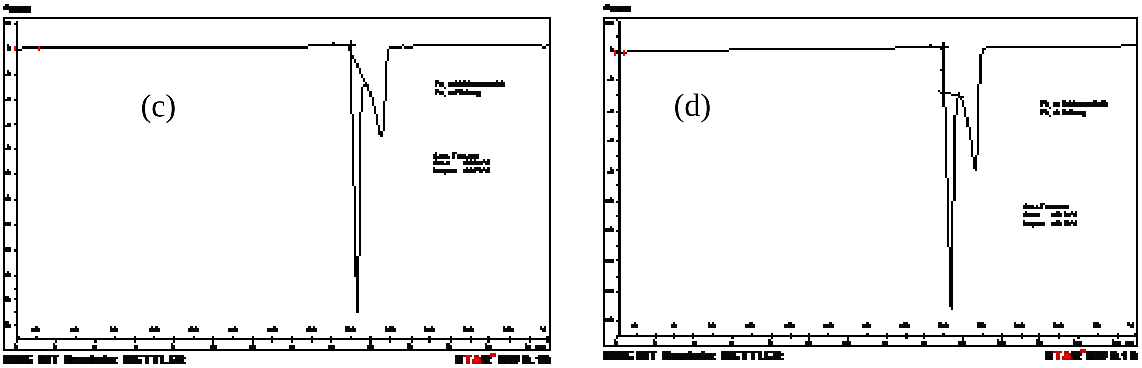


Fig.4.12.2 (a) DSC of Sn-8Zn (near eutectic) composition (b) DSC of Sn-Zn-0.05Ag solder alloy (c) DSC of Sn-Zn-0.1Ag solder alloy (d) Sn-Zn-0.2Ag

4.12.3 X-RAY DIFFRACTION ANALYSIS OF Sn-Zn-Ag SOLDER

The x-ray diffraction analysis in Fig.4.12.3 suggests there is possibility of formation of Ag_3Zn in Sn-8Zn-0.1 Ag and Sn-8Zn-0.2 Ag compositions. The intermetallic phase Ag_3Zn forms as dendrites upon cooling. The Ag_3Zn intermetallic phase depletes the Zn-rich phase and is present in the form of inhomogeneous dendrites. The Ag_3Zn intermetallic is expected to form in the solder alloy at Ag percentage greater than 1 wt. %. The growth of Ag_3Zn nodular compounds is accelerated by the higher wt. % of Ag in the alloy.

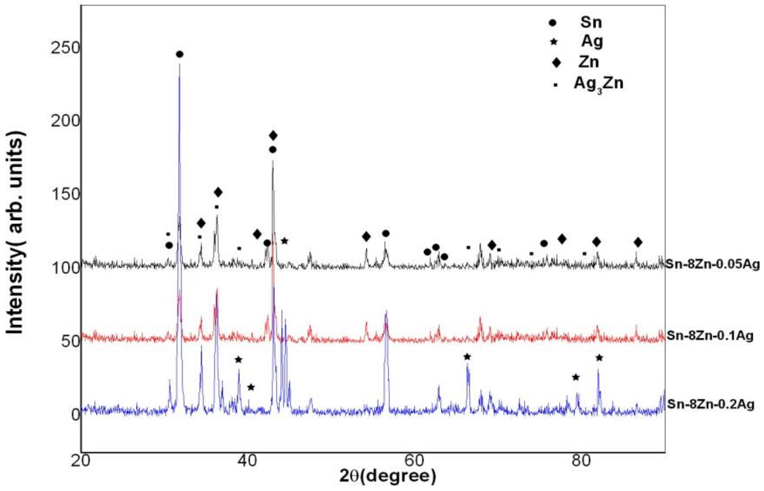


Fig. 4.12.3 X-ray diffraction plots of Sn-Zn-0.05 wt. % Ag, Sn-Zn-0.1 wt. % Ag and Sn-Zn-0.2 wt. % Ag solder alloy

4.12.4 VARIATION OF MELTING TEMPERATURE OF Sn-Zn-Ag SOLDER

The addition of Ag to the Sn-Zn eutectic composition leads to a decrease in the melting point. It should be noted that addition of 0.05 wt. % of Ag has almost no effect on the melting temperature of the eutectic Sn-8Zn solder alloy whereas adding 0.1 wt. % Ag reduces the melting temperature to a great extent. Further addition of Ag (0.2 wt. %) leads to a slight increase in the melting point of the eutectic composition to 199.50^{o}C. Fig.4.12.4 shows the variation of melting point of Sn-Zn-Ag solder alloy with addition of Ag

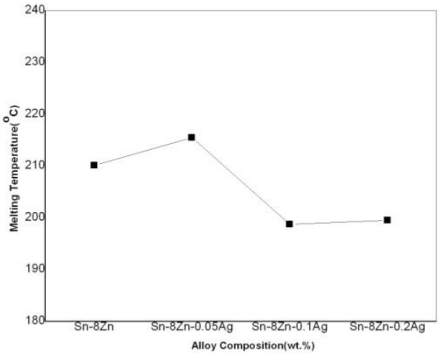


Fig.4.12.4 Variation of melting point of Sn-Zn-Ag solder alloy with addition of Ag

CONCLUSION

1. There is significant lowering of melting temperature due to addition of Bi (upto 6 wt. %) to the Sn-8Zn near eutectic composition. Addition of higher wt. % of Bi leads to increase in the melting point.
2. Sn-Zn-Bi alloys do not form any intermetallic compounds between themselves. No new compound formation was seen in the alloys.
3. Bi showed no solid solubility in Zn. Bi was seen in Sn rich regions only when the wt. % of Bi was higher than 3 wt. %.
4. Very high wt. % of Bi in the alloy led to lower wettability of the Sn-Zn-Bi alloy on Cu Substrate.
5. Addition of Bi leads to the decrease in percentage strain at break of the Sn-8Zn alloy. The tensile strength of the Sn-8Zn alloy was also found to reduce with addition of Bi.
6. Addition of up to 0.1 wt. %Ag to Sn-Zn eutectic composition leads to a reduction in melting point but further addition of Ag (0.2 wt.%) leads to slight reduction in meting point.
7. A shoulder was observed at around 220^{o}C in the DSC curves of Sn-Zn-0.1 wt. % Ag and Sn-Zn-0.2 wt.% Ag alloys. This shoulder is not present 0.05 wt. % Ag containing solders. The addition of a large amount of Ag in the Sn-Zn-0.1Ag and Sn-Zn-0.2Ag alloys resulted in the formation of large amount of Ag_3Zn intermetallic compound. This reaction reduced the Zn content of the eutectic Sn-Zn composition which resulted in the formation of a hypoeutectic β-Sn structure. This is why the DSC plots of the solder alloys Sn-Zn-0.1Ag and Sn-Zn-0.2Ag showed two endothermic peaks.

SCOPE AND FUTURE WORK

1. It was observed that when Ag was added beyond 0.1% there is a possible rise in the melting point of eutectic composition and this can be verified by adding higher wt.% of Ag to the eutectic composition.

2. Electrical resistance of the alloys should be measured to find out their electrical resistivity.

3. Mechanical properties like elongation to failure, hardness, fractographs have to be analyzed in order to ascertain that these alloys are not very brittle. Brittle solder alloy will very easily break at the contact due to the formation of intermetallic

4. Elements like Al (Aluminum) can be added to the alloy to prevent oxidation of the alloys for achieving a good solder.

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