A Comparative Study of the Sn-Ag and Sn-Zn Eutectic Solder Alloy

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

In

Metallurgical & Materials Engineering

By

C SHIV PRASAD(111MM0106)

MANOBES PADHY(111MM0478)

Under the supervision of

Dr. S. N. ALAM

Department of Metallurgical & Materials Engineering

National Institute of Technology

Rourkela

2011-2015

NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA, ORISSA -769008, INDIA

Certificate

This is to certify that the thesis entitled, "A Comparative Study of the Sn-Ag and Sn-Zn Eutectic Solder Alloy" submitted by C Shiv Prasad (111MM0106) and ManobesPadhy (111MM0478) in partial fulfilment of the requirements for the award of Bachelor of Technology Degree in Metallurgical & Materials Engineering to the National Institute Of Technology, Rourkela (Deemed University) is an authentic work carried out by them under my supervision and guidance. To the best of my 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

Dr. S. N. Alam Date:

Assistant Professor

Dept. of Metallurgical & Materials Engineering,

National Institute of Technology, Rourkela

Rourkela, Orissa-769008.

Acknowledgement

I am obliged to Dr. S.N Alam, Assistant Professor of Metallurgical and Materials Engineering Branch, for being my guide and giving me motivation, guidance, and patience throughout the research work. I am grateful to him for his suggestions and constructive criticism which has helped me in this development of this work. I am also grateful to his optimistic nature which has helped this project to come a long way through.

I sincerely thank to Prof S.C. Mishra, Professor and Head of Metallurgical and Materials Engineering Department for providing me required facility for my work.

Special thanks to my family members who always keep me encouraged to go for higher studies all my friends of department for being so supportive and helpful in every possible way.

LIST OF FIGURES

Title **Page No.**

ABSTRACT

The development of lead-free solder alloy has come up as one of the significant issues in the last few decades in the field of electrical and electronic industries. Eutectic composition of Sn–Pb alloys have been used widely for many years owing to their low melting point. They also possess excellent wettability on the surface of base metal. But due to environmental issues and their concerning effects, they have been proscribed lately. An alternative for Sn-Pb having better properties is the need of the hour. Sn–Zn solder is one such alloy that has been considered as one of the most attractive and lucrative lead free system that can replace the conventional Sn-Pb solder with a small increase in the soldering temperature by nearly 30^{o}C. However there are some drawbacks in Sn–Zn lead free system such as poor oxidation resistance, wettability and embrittlement behaviour. The present thesis aims at investigating the properties of Sn-Zn and Sn-Ag solder alloys and extensively focuses on the microstructure, thermal and mechanical properties. The compositions at their eutectic temperatures were weighed carefully in the weighing machine and were prepared after melting the binary system in the furnace at much higher temperatures than their respective eutectic temperatures. The microstructures of both the solder alloys were investigated using a Scanning Electron Microscope (SEM) and optical microscope. The composition and phase analysis of the solder alloys was done using Energy dispersive X- ray spectroscopy (EDX) and X- ray diffraction respectively. Differential scanning calorimetry (DSC) was carried out to find out the melting temperatures of the alloys. Fractography was done to find out the type of fracture under impact testing. Microhardness of the solder alloys were also found out and analysed. The wettability of the samples was observed under Scanning Electron Microscope (SEM) after soldering the alloys on the Copper circuit board. A thorough analysis was done after the experiments were conducted to find out a better solder alloy out of the two.

CONTENTS

LIST OF ABBREVATIONS

Al	Aluminum
Pb	Lead
Cd	Cadmium
Bi	Bismuth
Sn	Tin
Zn	Zinc
Ag	Silver
Cu	Copper
Ni	Nickel
α	Alpha
β	Beta
SEM	Scanning Electron Microscope
XRD	X – Ray Diffraction
DSC	Differential Scanning Calorimetry

CHAPTER 1

INTRODUCTION

INTRODUTION

Solders usually join metal or working material together. They have a lesser melting temperature than working material, typical in the range of 90 to 450 °C (190 to 840 °F). Soldering, unlike welding, does not spatter while joining. This makes it lot easier than welding which requires much higher heat requirement. They have been widely used as an interconnecting material in mostly electronic circuits and assembly of sheet metal parts. They offer both electrical conductivity as well as mechanical strength. Also the ease of use has an added advantage over other joining processes. Eutectic region of Sn-Pb alloys are more preferred in electrical and electronics industry. This is because of its lower melting point which is around 183^{o}C and also better properties at the eutectic composition. Due to low working temperature, it does not affect the microstructure of the base metal. Also it has proved to have superior mechanical properties and wetting tendency [1]. But, due to the hazardous nature of Pb, it has led recently caused widespread opposition and been a concerning factor to the natural habitat. The banning of materials containing Lead in other applications like paints, fuels and plumbing applications has helped in checking a direct exposure to human health and environment. Pb and Pb containing compounds and alloys are considered threat to life on earth and its natural habitats due to its toxicity .

While developing and studying an alternative solder alloy, one needs to take various properties into consideration such as melting point of the solder, oxidation resistance, hardness, microstructure, inter-metallics formed during soldering, wettability, corrosion resistance, feasibility and cost factor [2]. The electrical industry generally works in low melting temperatures not much above the room temperature. The components and solders should withstand soldering temperature associated with this temperature. This is one of the major regulating factors while selecting a better solder to the previous alloy. The new alternative should be identical to the conventional Pb solder alloys in all possible ways. Any rise or fall in the processing temperature of lead free solder alloys can have adverse effects on microstructure and consequently component life and the service life. Sn along with different alloying elements are hence been forced to work with limited alternatives. Apart from considering the temperature constraints, a number of physical and chemical properties of Sn-

Pb solder alloys which the alternative alloys have to prove better in order for it to be used in practical life.

Sn-Zn solder alloys are almost similar in nature when compared to Sn-Pb solder alloys. The Sn-9Zn alloy at eutectic composition has a melting temperature of 198^{o}C. It offers better metallurgical properties with respect to conventional Sn-Pb solders. In addition to this, it is cost effective. Sn-Zn solder alloys lag behind when oxidation resistance and corrosion resistance are considered. The wettability of Sn-Zn solder should also be taken into account. It has are flow temperature of 222^{o}C.During soldering of the metals, the active Zn atoms may get oxidized and create voids in the matrix. Zinc oxide formed during soldering on the surface of the binary solder alloy prevents the solder from wetting. Therefore the Sn-Zn solder is tough to use in day to day life due to its easy oxidation and microvoid formation in the solder surface. Due to these drawbacks traces of alloying elements such as Al, Cu, In, Ni, Ag, Cr can also be added .This can further help in enriching the properties of Sn-Zn lead free system to develop ternary Pb free alloys.

Sn-Ag solder alloys, like Sn-Zn solder alloys, too have better properties than Sn-Pb solders. The Sn-3.5Ag is the eutectic point in the binary alloy system. The temperature at eutectic point is 221^{o}C.The presence of Ag in the binary matrix causes an increase in ductility but the intermetallic formed by Ag and Sn i.e., Ag_3Sn helps in increasing the brittleness of the structure. Due to its lustrous nature, its uses are also found in the field of jewellery. It has good wettability which is a prominent characteristic in determining the quality of a solder. A detailed analysis has been done in the present thesis to come to a conclusion whether Sn-Ag or Sn-Zn is a better solder alternative for Sn-Pb solders.

OBJECTIVE

The objective of the project is to fabricate various alternatives for alloys of Lead-free solders such as Sn-Zn and Sn-Ag alloy and to study their properties of mechanical properties, change in melting point, wettability, microstructure and X-ray diffraction pattern [3]. Following characterisation techniques have been conducted on the above mentioned Lead free alloys:

1. Scanning electron microscope (SEM) and Energy Dispersive X – ray spectroscopy (EDS or EDX).
2. Optical microscopy
3. X – ray diffraction analysis (XRD)
4. Differential Scanning Calorimetry(DSC).
5. Microhardness testing
6. Wettability test
7. Fractography

CHAPTER 2
LITERATURE REVIEW

LITERATURE REVIEW

A GLIMPSE ON SOLDERING PROCESS

Soldering produces coalescence of materials by heating them to soldering temperature (below solidus temperature of base metal) in presence of filler material. The working temperature of soldering is less than 450^{o}C. Unlike soldering, welding involves heating both the base metal and filler metal to its liquidus temperature and should be above 450^{o}c. The difference between soldering process and brazing process is that joining operation temperature is uniquely different for each of them and is higher than 400-450^{o}C in brazing. Both brazing and soldering methods involve a filler material sticks the two work pieces, then freezes and forms a permanent joint, but in case of welding the work materials are melted to fuse together. In soldering, fluxes are used to protect and assist in wetting of base metal and solder alloy. Tendency to warp and burn the metal is very negligible due to low heating. Also residual stresses are not developed. The alloy system usually used in soldering process is Sn and Pb. This eutectic composition has its melting point sharply at 183^{o}C and is used universally to join wires in electronic circuits and assemblies.

ALLOYING ELEMENTS

There is a range of alloying elements that can be used for soldering process to enhance various physical and metallurgical properties. Solder alloys mainly have beta phase tin (Sn) metal and may contain one or more of the given elements depending on the required properties in definite proportions: Lead(Pb), Nickel(Ni), Bismuth(Bi), Zinc(Zn), Antimony(Sb), Cadmium(Cd), Copper(Cu), Silver(Ag), Indium(In) etc. Solder alloys are available in solid, paste or powder form[4].

Tools Used In Soldering

Figure 2.1 Showing tools used in soldering

-Needle Nose Pliers:

Useful for pre-bending solder alloy without any difficulty and pulling out components when soldering is removed.

- Wire Strippers:

In this figure shown above, two types of wire strippers are present. The yellow coloured wire stripper can be adjusted to strip wire of any size (good for small ribbon cable wires). Whereas the red handled stripper have several holes of fixed sizes and can be used according to the requirement.

-Soldering Iron Stands:

These are handy when several joints are being soldered simultaneously. It is a heat resistant stand for the soldering iron to sit in, so as to protect the bench from burning while it is hot.

-Soldering Iron:

It supplies enough heat so that it can melt the solder and join the wires in the circuit board. A soldering iron comprises of a metal tip that heats up and an insulated handle to hold safely.

-Circuit Board

It is a plastic board coated with Copper on the surface. It has many holes for connecting wires. All the circuits are made on the board and then soldered.

- Flush Cutters:

It is used to trim soldering alloy close to the board after soldering is completed.

- Clamps:

The clamps are especially helpful in holding while desoldering or soldering wires together.

- Solder Sucker:

These are used to remove solder alloys from the copper coated circuit board. The sucker is a spring loaded tube that pulls out solder when needed.

Solder Wick:

The wick is a fine thread of flux coated copper that soaks up solder when it is in molten state. When it is heated up by the soldering iron, it melts the solder and then it is drawn out of the joint. It is used for removing the solder from a circuit board.

- Multimeter:

Multimeters have a continuity check that produces alarming sound when a complete circuit is formed. This is very useful for ensuring that the soldering parts are connected when there are a lot of wires and circuit boards.

PROPERTIES OF A SOLDER ALLOY

A good solder is possible if it has the following criteria:

1. Melting temperature of base metal should be higher than working temperature of the soldering
2. Mechanical properties of the material should not be altered after soldering
3. Metallurgically compatible solder with surrounding metal surface
4. Reasonably low rate of intermetallic compounds formation of phases at the service temperature
5. Acceptable wettability
6. Good service life

Sn

CRYSTAL STRUCTURE

Sn is a ductile, malleable and highly crystalline in nature. Its melting temperature is lower when compared to most metals (232^{o}C). Ithas two allotropes:

- "white tin"which is metallic and called beta (β) phase and
- "grey tin" which is semiconductor and called alpha (α) phase.

The beta phase of Sn is stable at temperatures from 13ºC to 232ºC. Below 13ºC,the alpha (α) phase is the one which is found to be stable thermodynamically[5]. But, the intriguing fact is that this alpha phase is not found usually. Transformation temperature between the two phases is 13^{o}C. The transformation of α (white Sn) causes a change in electrical and optical properties in the β (grey Sn). The hardness and tensile strength of Sn is experimentally calculated to be 3.9HV and 11MPa which is very low compared to other metals [6]. However, the ductility is found to be very good i.e., 53% at room temperature[7]. The hardness, creep and tensile values alter greatly when other alloying elements are added to Sn[8][9][10]. The reactivity towards air, water and Nitrogen is found to be very less. It helps in forming a better solder as unwanted inclusions are minimised. However, an oxide layer is formed due to aging of Sn and is called Dross.

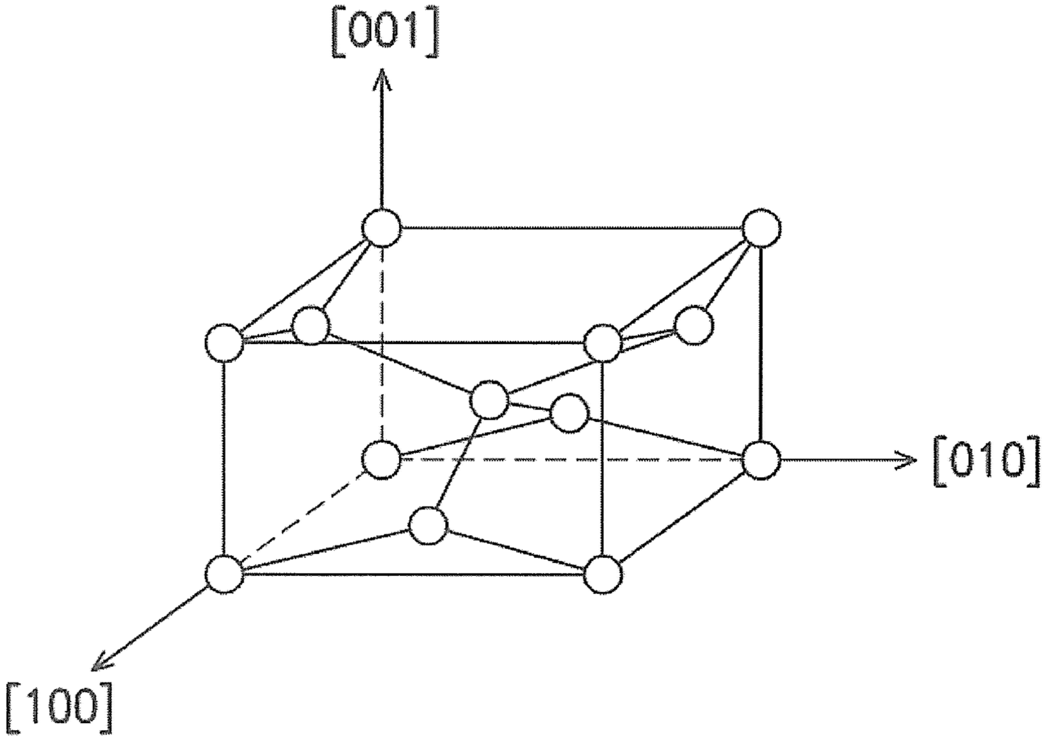


Figure 2.1 Showing β Tin Crystal Structure

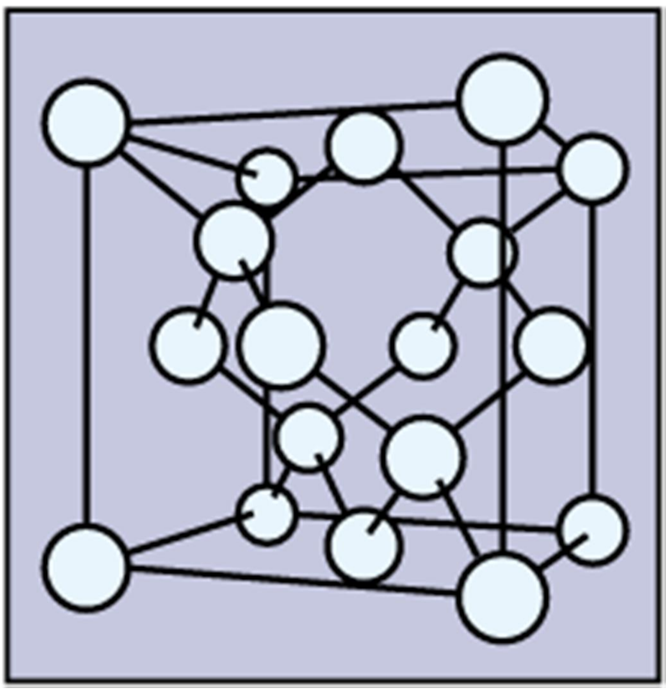


Figure 2.2 alpha (α) crystal structure

Sn-Ag Binary System

The addition of Ag in Sn matrix provides additional mechanical properties to the alloy due to the formation of intermetallic bond. The alloy forms a eutectic composition at Sn-3.5Ag (wt%). The temperature at eutectic point is found to be 221^{o}C which is close to the melting point of Sn (231^{o}C) [11]. It is evident from the experiments that the intermetallic formed is Ag_3Snwhich provides mechanical properties to the beta Sn phase. The needle like structure of the intermetallic and the parent phase has a very strong bond and add excellent mechanical characteristics to the matrix. The strength and hardness value of the alloy increases with the increasing percentage of the intermetallic [12]. However, the intermetallic found is brittle in nature.

The addition of Bi to the Sn-3.5Ag promotes wettability and also helps decrease the melting point of the alloy[13]. The Cu addition is also beneficial and their alloys are used in automotive and aircraft industry where thermal stresses are high. The alloy formed by Sn, Ag and Cu is found to have better properties than Sn-Pb solder alloys. Alternative sources should be developed to counter the high stresses generated in the solder. Laser soldering which has been recently developed can be of some help in such circumstances.

Applications

Sn-Ag solders are used for:

- Electronic Parts
- Integrals of Die
- Applications where lead use should not be used such as joints in pipes that come into contact with water and/or foodstuffs and contaminate it.
- Soldering of precious metals as the alloys have inability to have greater levels of brightness

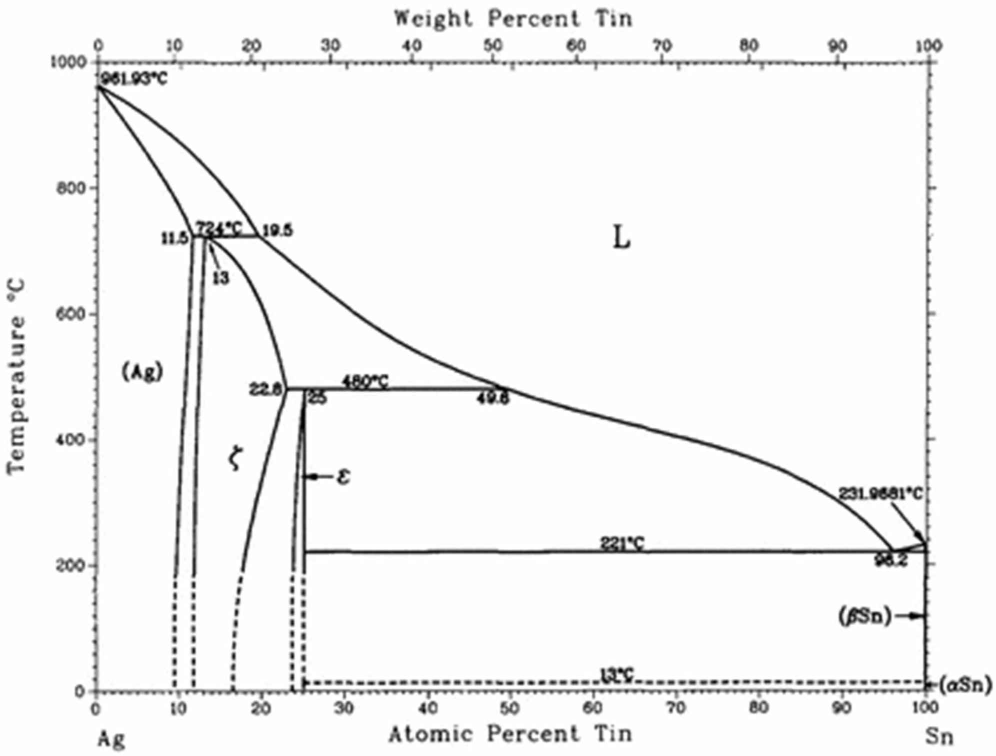


Figure 2.3 Phase diagram of Sn-Ag

Sn-Zn Binary System

The Sn-Zn eutectic composition is obtained at Sn-8.8Zn (wt%). This binary phase is well suited for soldering and is a good alternative for Sn-Pb solder alloys as the melting point at this eutectic composition is very close to that of the Sn-Pb solder alloy composition. The Sn-Zn consists of two matrixes. Zn and Sn are found to be secondary hexagonal and body centered tetragonal respectively. Although they have many advantages, their corrosion resistance and oxidation resistance are very weak and the solder is vulnerable to get attacked by the atmosphere[14][15]. The high reactivity of Zn promotes the formation of ZnO. Apart from these drawbacks, microvoids are also found to be evident in some cases. This can be prevented by addition of Bi to the binary structure. The Bi helps in reducing the surface tension and hence a better structure is formed.The ternary phase is widely used in electronic applications like computers, television tuners, laptops, printers and many more.

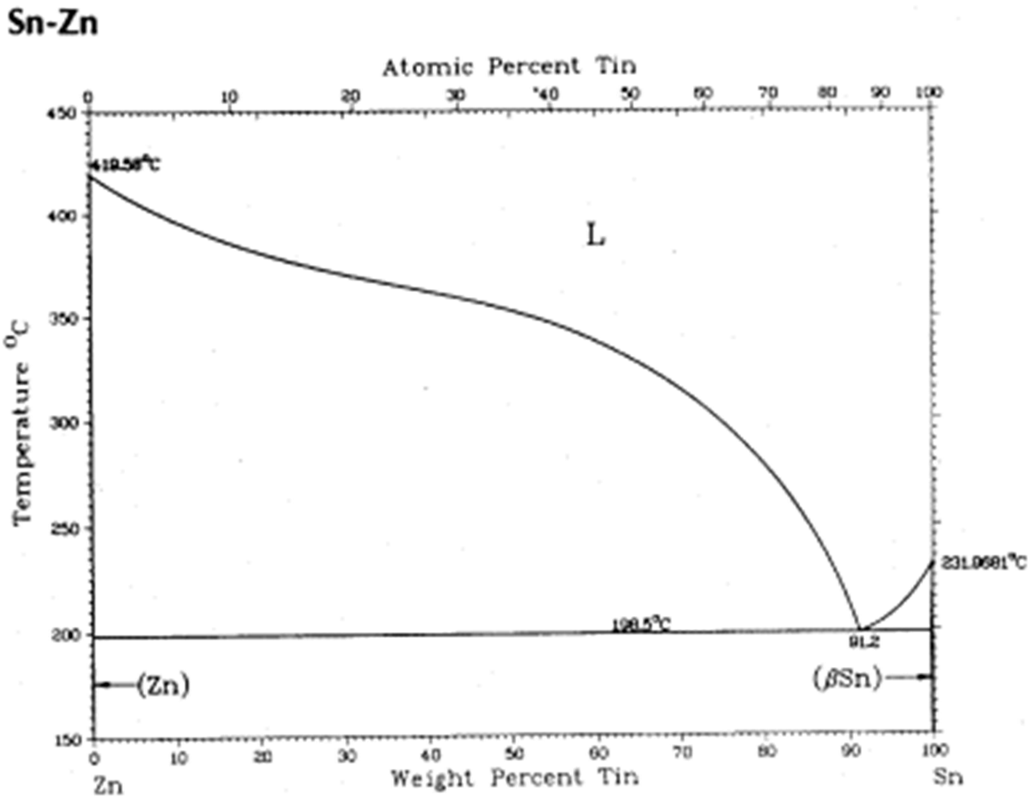


Figure 2.4 Showing Sn-Zn phase diagram

Sn-Pb

The Sn-Pb was commonly used as solder alloys until use of Pb was reduced drastically due to toxic issues. Leaving aside the toxicity, this binary system has most favourable properties that a solder should have. The melting point of the eutectic composition which is used for soldering is 183°C. This low temperature is very good for soldering as the alloy will melt easily and wet the metal surface. The eutectic composition is obtained at 63 Sn/37Pb (wt.%).This is universally used to join wires and circuits in electronic devices and assemblies. The low temperature of soldering prevents any microstructural change in the surroundings of the solder [16]. Another advantage of low temperature soldering of Sn-Pb alloy is that it minimises the risk of handling or operating. Also the cost is lower compared to other joining processes as the elements Sn, Pb and the equipment are cheaper. However, the bonding or the joining of solder is not as strong as compared to other joining processes like welding and brazing.

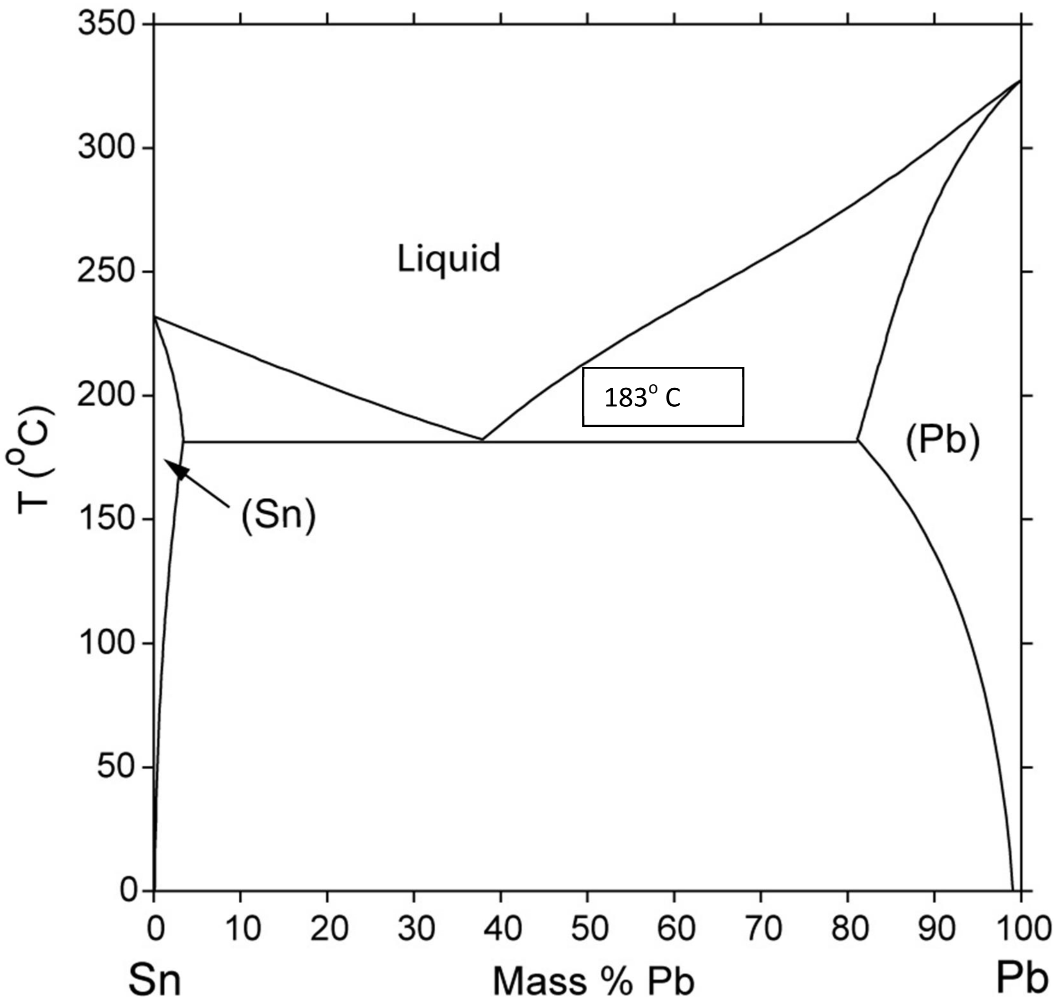


Figure 2.5 Showing Phase diagram of Sn Pb system

The Pb plays an important factor in soldering and imparts many useful properties to the material that is being weld. Some of these properties contributed by Pb are mentioned below:

1. It increases the wettability of the contact surface by reducing the surface tension of Sn.

2. In the ternary phase of Sn, Cu and Pb, it helps in forming the intermetallics of the phases in the solder.
3. In the phase Sn, when temperature is reduced below 13^{o}C, the phase transformation in the structure is observed. The β – Sn changes to α – Sn which is followed by an increase in the volume [17]. This develops stresses in the lattice. But the presence of Pb helps in decreasing the chances of phase transformation.
4. It helps in enhancing the ductility
5. The eutectic of Sn-Pb is lower compared to other solder alloys.
6. Also the element Pb is found in abundance naturally and hence it is very cheap compared to other alternatives.

Lead Poisoning

Lead is one of the 17 chemicals that is toxic in nature and is a threat to living organisms. When contacted at proteins in cellular level, it inhibits its functions. A small amount of Lead in human body can cause tissue damage. Plumbism is another term used for Lead poisoning. Previously, Lead was used as an important ingredient in paints, solders, pipes, batteries and many more. Later when the government realised the rising toxic issues and biodegradation in alarming level, a prohibition was imposed on its use. The World Health Organisation (WHO) has shown serious concerns over this issue [18]. Immediate effects of Lead poisoning are Vomiting, convulsions, abdominal pain, Constipation, headache, etc. Whereas continuous exposure to Lead may cause failure of kidney, liver and brain [19]. It can also lead to seizures, mental retardation, behavioural disorders, anaemia, and high blood pressure. During pregnancy, the effects are also seen in placenta disorders and miscarriages.

CHAPTER 3

EXPERIMENT SETUP &PROCEDURE

3.1 Materials Needed

Tin granules, Zinc granules and Silver of 99.9% purity were procured and two alloys of weight 10 gms at eutectic composition were prepared. The system chosen for study was Sn-9wt %Zn & Sn-3.5% wt Ag, both being eutectic composition.

S.no	Composition	Sn(gm)	Zn(gms)	Ag(gms)	Total Weight(gms)
1	Sn-9wt%Zn	9.1	0.9	0.00	10.00
2.	Sn-3.5wt%Ag	9.65	0.00	.35	10.00

Different alloy compositions were prepared by mixing the required amount in a silica crucible and was placed in a furnace in an inert atmosphere. The compositions were heated up to a temperature of 500^{o} C held for two hours and then furnace cooled to produce solders.

3.2 Sample Preparation

A small part of the alloy was cut and was carefully weighed in a weighing balance for thermal analysis. For phase analysis by X-ray diffraction, sample was a cut and made flat on a belt grinder following which samples were polished with different grades of polishing papers.

The alloys were also fractured by giving impact, to study the Fractography and fracture surface.

For microstructural analysis, samples were cut and grinded on a belt grinder. Emery papers were used to polish the samples after grinding was done. Emery polishing papers of different grades i.e., 1/0, 2/0, 3/0 and 4/0 were used and on moving from one to another the polishing direction was changed by 90^{o}. Following which the samples were polished on a rotating wheel covered with special cloth. Powdered Alumina and water was used in this process. After completion diamond paste was used during polishing of samples on the cloths. Following which samples were scratch free and had a mirror finish.

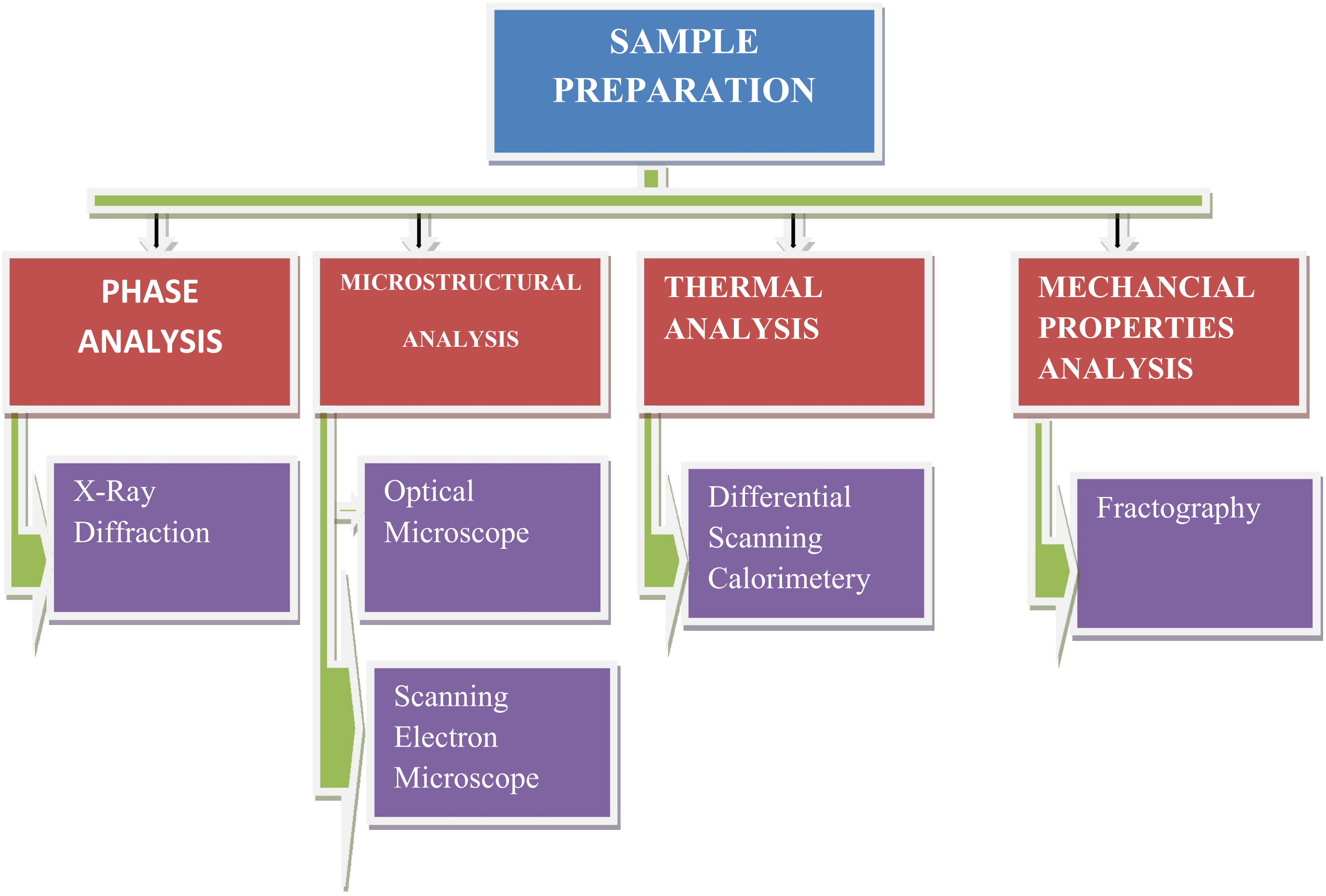


Figure 3.1 Showing Flow chart Experimental Procedure

3.3 Characterization Techniques

3.3.1 Furnace :

Furnace is a device that is used to heat samples. It can be used to melt and simply of heat treatment. The Furnace uses electrical energy and converts it to heat energy. A thermocouple is used to control and maintain the temperature. In this comparative study, Zn, Sn and Ag elements were used, the composition chosen was Sn-9wt%Znand Sn-3.5wt%Ag. These elements were heated in separate silica crucible in the tube furnace in an inert gas atmosphere up to a temperature of around 500^{o}C and the soaking at this temperature was done for almost 2 h. To obtain coarser grains, the alloys were cooled by furnace cooling.

Figure 3.3.2 Tubular Furnace

3.3.2 Scanning Electron Microscope

A scanning electron microscope (SEM) produces highly magnified images of a sample by using a beam of electrons directed towards the sample which is polished carefully with different grades of polishing papers. The samples are usually placed in vacuum chamber, where the electron beams interact on the sample surface producing images. SEM can give a very comprehensive idea about the sample's topography, phase present [20]. It can also measure the dimensions of the various particles present in the sample. The Energy dispersive spectrum an integral part of SEM can be used to find the compositional analysis. It can also tell about the elemental mapping in a sample.

Figure 3.3.3 Scanning Electron Microscope

3.3.3 Optical Microscope

The optical microscope, or the light microscope, uses visible light and a compound combination lenses to focus. It uses objective lens and an eye piece lens to form the image. The magnification and resolution provided by optical microscope is limited [21]. The image obtained can be capture in a camera and using software can be viewed and saved on a computer.

Figure 3.3.4 Optical Microscope

3.3.4 Differential Scanning Calorimetery

Differential scanning calorimetry or DSC is a thermal analysis technique used to find melting point, crystallization kinetics or any phase transformation taking place in a material [22]. DSC measures difference in the amount of heat flow vs. temperature plot[23]. It tells us the amount of difference in heat flow required while increasing the temperature of a sample when compared with a reference.

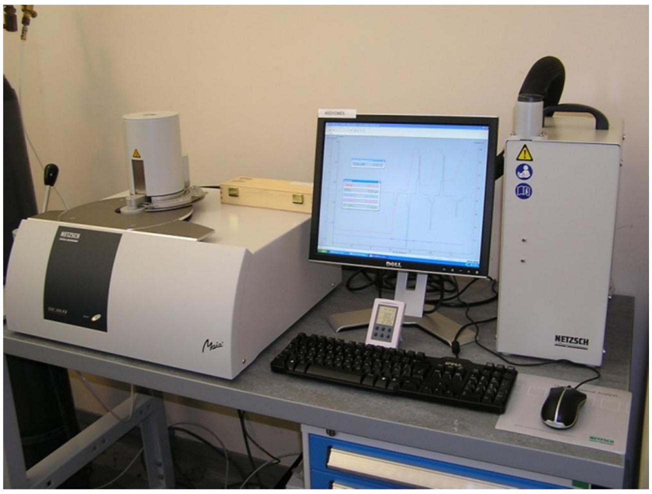


Figure 3.3.5 Differential Scanning Calorimetery

3.3.5 X-ray Diffraction

X-ray powder diffraction (XRD) is used for determining the phase of a crystalline or amorphous material and unit cell dimensions. It uses x- rays incident on the sample at a particular angle and the deflected beams are collected [24][25]. A plot is between 2θ and intensity and compared with the standard values to identify a particular phase.

Figure 3.3.6 X-ray diffraction Machine

CHAPTER 4
RESULTS & DISCUSSION

4.1 Phase Diagram

(i) <u>Sn-Ag</u>

The Figure below shows the phase diagram of Tin and silver binary system. The system shows eutectic behaviour at Sn-3.5Ag. The eutectic temperature is 221^{o} C. It is clear from the phase diagram of the Sn-Ag system the solid solubility of Ag in Sn is very low, the maximum solid solubility of Ag in Sn is about 0.05 wt. %. The phase diagram shows the presence of inter metallic in the form of Ag_3Sn.

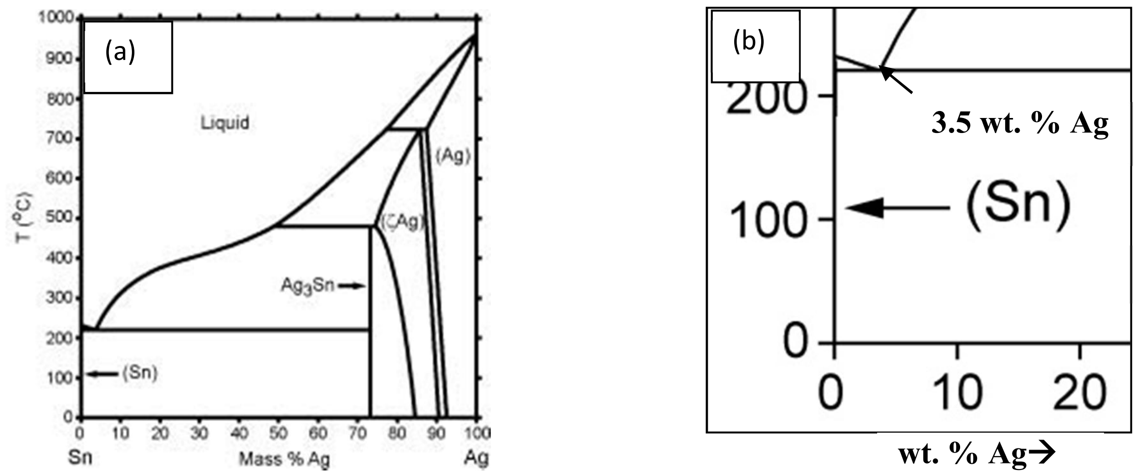


Figure 4.1.1(a) showing the phase diagram (b)showing the eutectic point at 3.5%Ag in Sn-Ag phase diagram

(ii) Sn Zn

The Figure below shows the phase diagram of Tin and Zinc binary system. The system shows eutectic behaviour at Sn-8.8 Zn. The eutectic temperature is 198^{o} C. It is clear from the phase diagram of the Sn-Zn that no inter metallic or new/different phases are formed other than Sn rich phases and Zn phases.

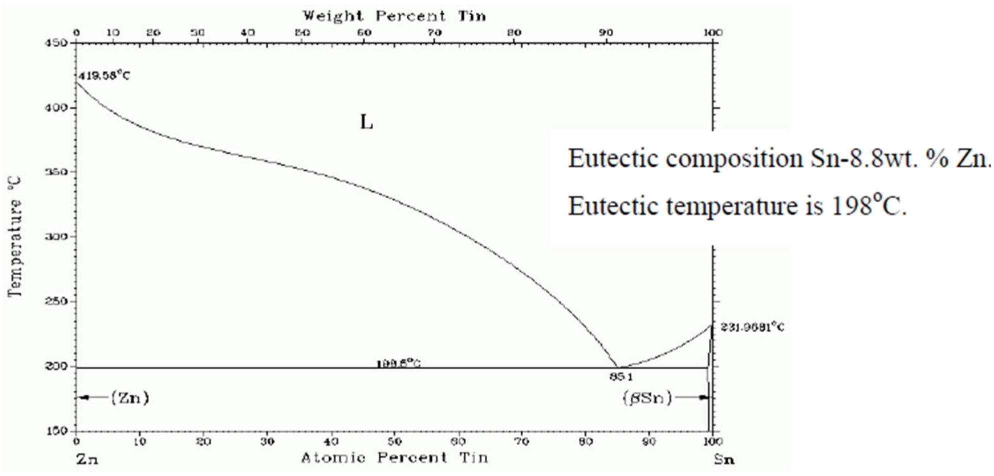


Figure 4.1.2 Showing the phase diagram of binary system of Sn Zn

4.2 X-Ray Diffraction Analysis :

(i) Sn-3.5Ag

The x-ray diffraction plots of the Sn-3.5Ag solder alloy are shown in the Figure given below. The X-ray diffraction graph shows the presence of Sn phases and also the intermetallic compound Ag_3Sn. It was found that no new/different phases are found other than that mentioned above from the X-ray diffraction. It is in complete agreement with the binary phase diagram of the system.

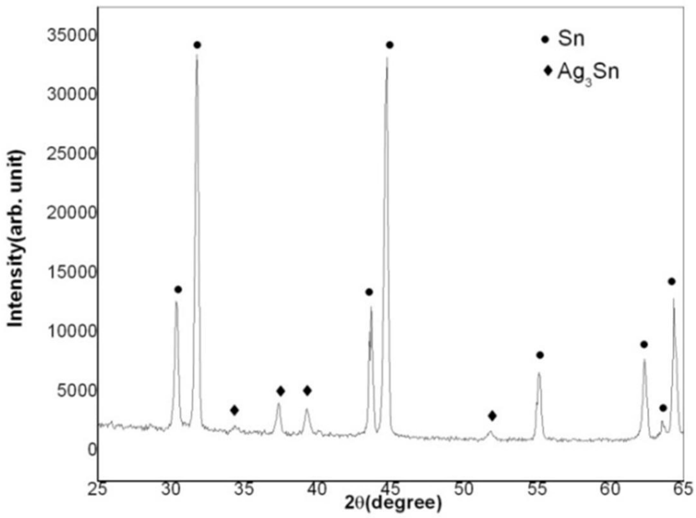


Figure 4.2.1 The XRD of Sn 3.5Ag alloy

(ii) Sn-8.8Zn

The x-ray diffraction plots of the Sn-8.8Zn solder alloy is shown in the Figure given below. The X-ray diffraction graph shows the presence of Sn and Zn rich phases. No new phases found from the X-ray diffraction. This is in complete coherence with the binary phase diagram of the Sn Zn system.

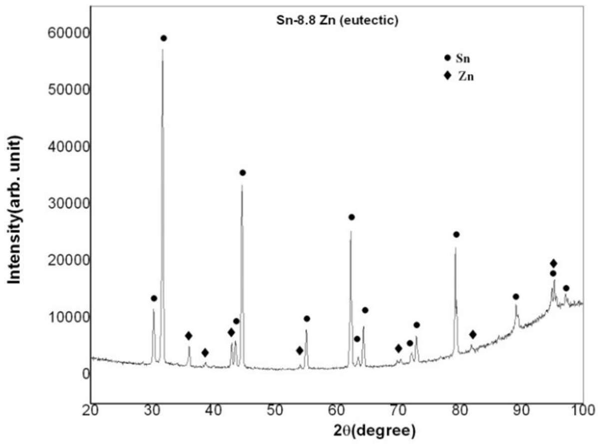


Figure 4.2.2 Showing the XRD of Sn 8.8 Zn alloy

3.Thermal Analysis :

(i) Sn-3.5 Ag

Figure below shows the DSC graph of Sn-3.5Ag alloy. DSC graph tells us that no phase transformation takes place in the alloy. The melting point of the binary alloy was found to be 241^{o} C, while the eutectic temperature from phase diagram was found to be 221^{o}C. The difference in melting point may be due to formation of oxide layer or other impurities present in the alloy during preparation.

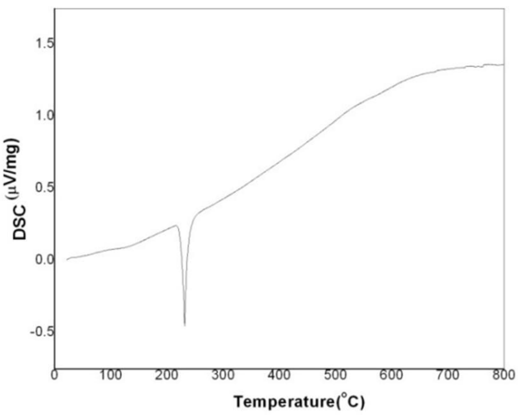


Figure 4.3.1 Showing the DSC of Sn 3.5Ag

Figure below shows the TGA of the Sn-3.5Ag, the graph shows that the alloy has negligible change of mass up to 800^{o} C and hence this implies it has good resistance to oxidation, even at very high temperature.

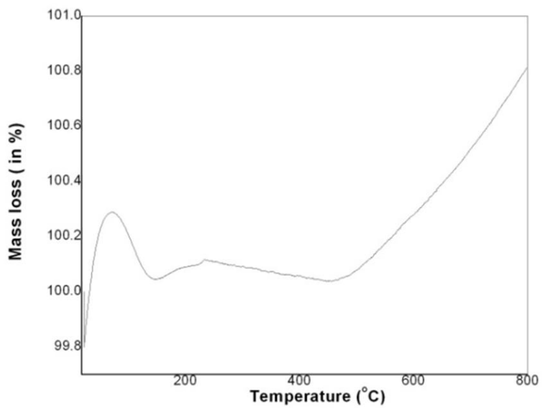


Figure 4.3.2 Showing the TGA of Sn 3.5Ag

(ii) Sn-8.8Zn

Figure below shows the DSC graph of Sn-8.8Zn alloy. DSC graph tells us that no phase transformation takes place in the alloy. The melting point of the binary alloy was found to be 207.93^{o} C, while the eutectic temperature was found to be 198^{o}C. The difference in melting point may be due to formation of oxide layer or other impurities present in the alloy during preparation.

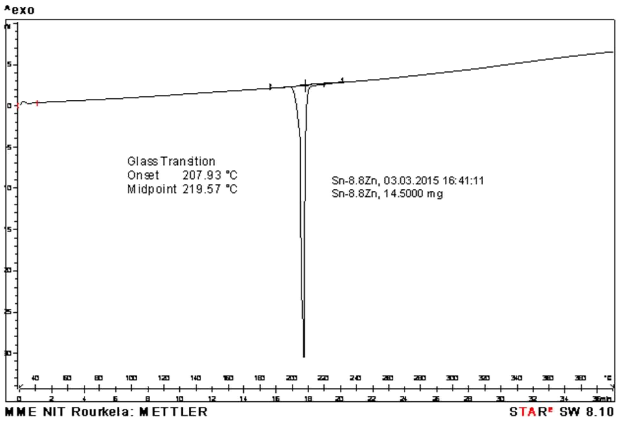


Figure 4.3.3 Showing the DSC of Sn 9Zn

4. Micro Hardness Test

Vicker's microhardnes test was done of the Sn-3.5Ag alloy with an applied load of 50 gf and a dwell time of 10 seconds. The hardness value was found using the relation

$$HV = \frac{F}{A} \approx \frac{1.8544F}{d^2},$$

And found to be 142.5 Mpa. The same was repeated for Sn-8.8Zn alloy and was found to be 161.1 Mpa.

5. Optical Microstructure

(a) Sn-3.5Ag

Figure below shows the optical microscope images of Sn-3.5Ag alloy. The images show the presence of bright coloured phase that is the Sn matrix. Microstructure observation shows that the furnace-cooled sample, which had cooling rate of approximately 0.069 K/s, nearly followed the equilibrium solidification process, and hence it exhibits a full eutectic structure consisting of dark needle like phases and white phases. It can be seen that the eutectic structure consists of a mixture of intermetallic compound Ag_3Sn and β-Sn phase and the eutectic reaction is L->Ag_3Sn+β Sn.

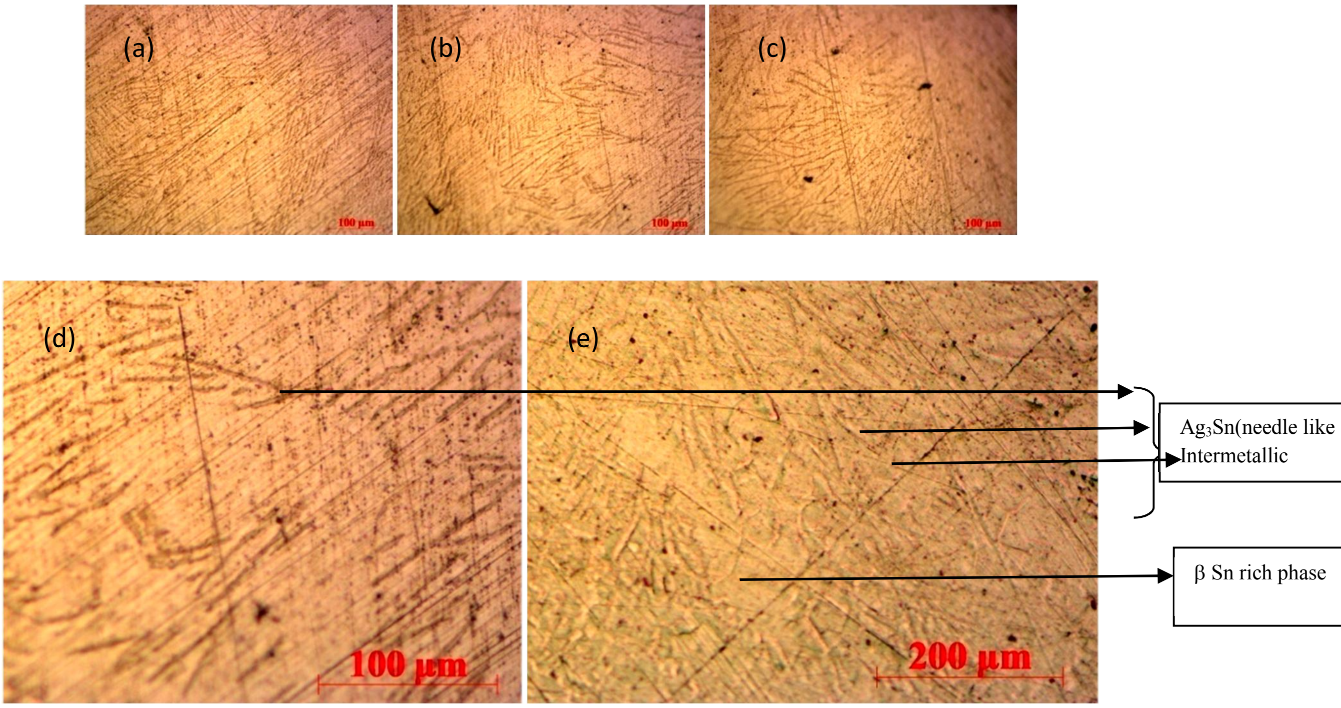


Figure 4.5.1 (a)-(e) showing magnification optical images of Sn-3.5Ag alloy.

The needle like structure seen, is the inter metallic Ag_3Sn embedded in the bright colored Sn matrix. The eutectic mixture is composed of both the beta Sn matrix and the needle like Ag_3Sn intermetallic phase. The beta Sn matrix obtained has 0.05 wt. % Ag. The eutectic compound is formed by a nucleation and subsequent growth of theses phases.

(b) Sn-8.8Zn

Figure below shows optical microscope images of Sn-8.8Zn alloy. The images show the presence the typical lamella of eutectic microstructure. The images show the bright coloured β-Sn phase regions and solidify primarily in the matrix; the dark-coloured and fine needle like Zn-rich phase is embedded in β-Sn matrix. Zn-rich phases are also present in the form of spheroidal.

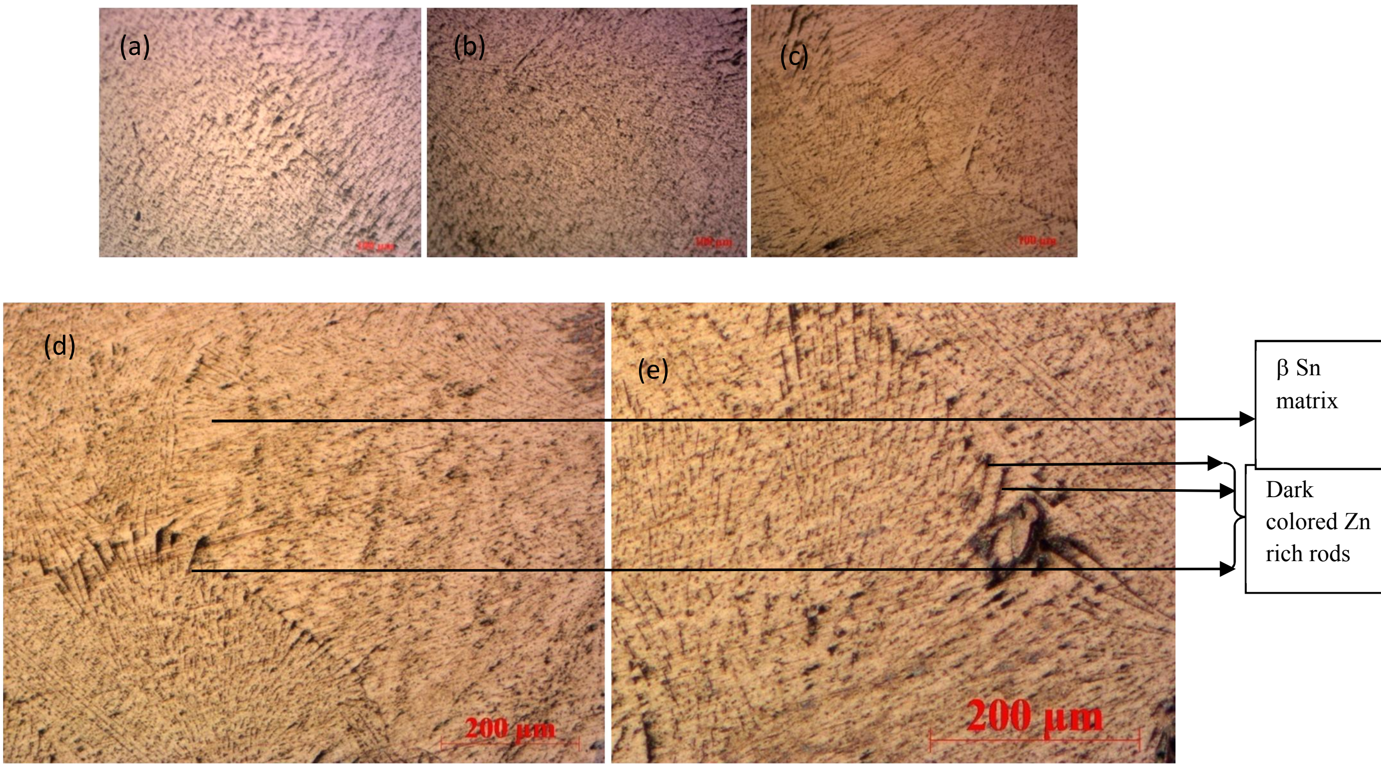


Figure 4.5.2(a)-(e) showing optical images of Sn-8.8Zn alloy.

The matrix has dark colored rod like dark phase which is the Zn rich phase. The eutectic mixture is composed of both the dark phase, i.e. Zn phase and the Sn-rich phase. The eutectic mixture is formed by a cooperative growth of theses phases.

6.Scanning Electron Microscope:

(i) Phase Analysis :

(a) Sn-3.5Ag :

The resulting microstructure of the eutectic Sn–3.5 wt. % Ag alloy is characterized by a Sn-rich phase which is light colored. This phase is almost 100 % Sn. It is clear from the phase diagram of the Sn-Ag system the solid solubility of Ag in Sn is very low. The maximum solid solubility of Ag in S is about 0.05 wt. %. The dark colored phase is the Ag_3Sn. A eutectic mixture containing about 3.5 wt. % Agis found in the in the interdendritic regions. These are the dark coloured regions. The eutectic mixture is composed of both the Ag_3Sn

intermetallicand the Sn-rich phase. The Sn rich phase is composed of about 0.05 wt. %Ag. The eutecticmixture is formed by a cooperative growth of theses phases.

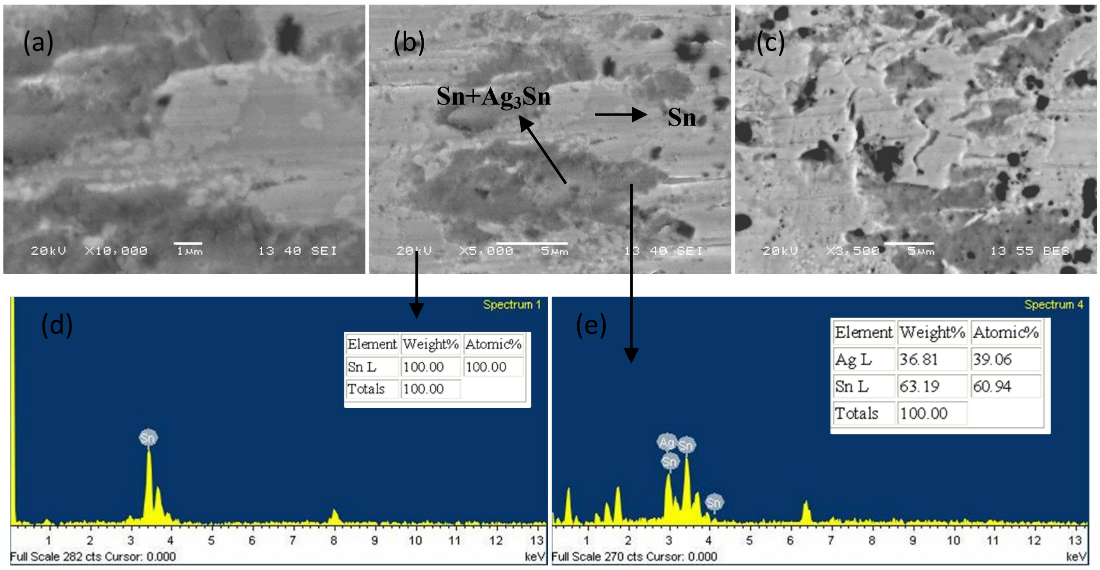


Figure 4.6.1 (a)-(c)showing SEM of Sn-8.8Zn alloy and (d)-(e) shows the EDS analysis

(b) Sn-9Zn:

The following SEM images show the presence the typical lamella of eutectic microstructure. The images show the presence the typical lamella of eutectic microstructure. The image shows, the bright coloured regions as the β-Sn phase which solidified primarily; the darker phases are fine needle like Zn-rich phase embedded in β-Sn matrix. Zn-rich phases are also present in the form of spheroidal.

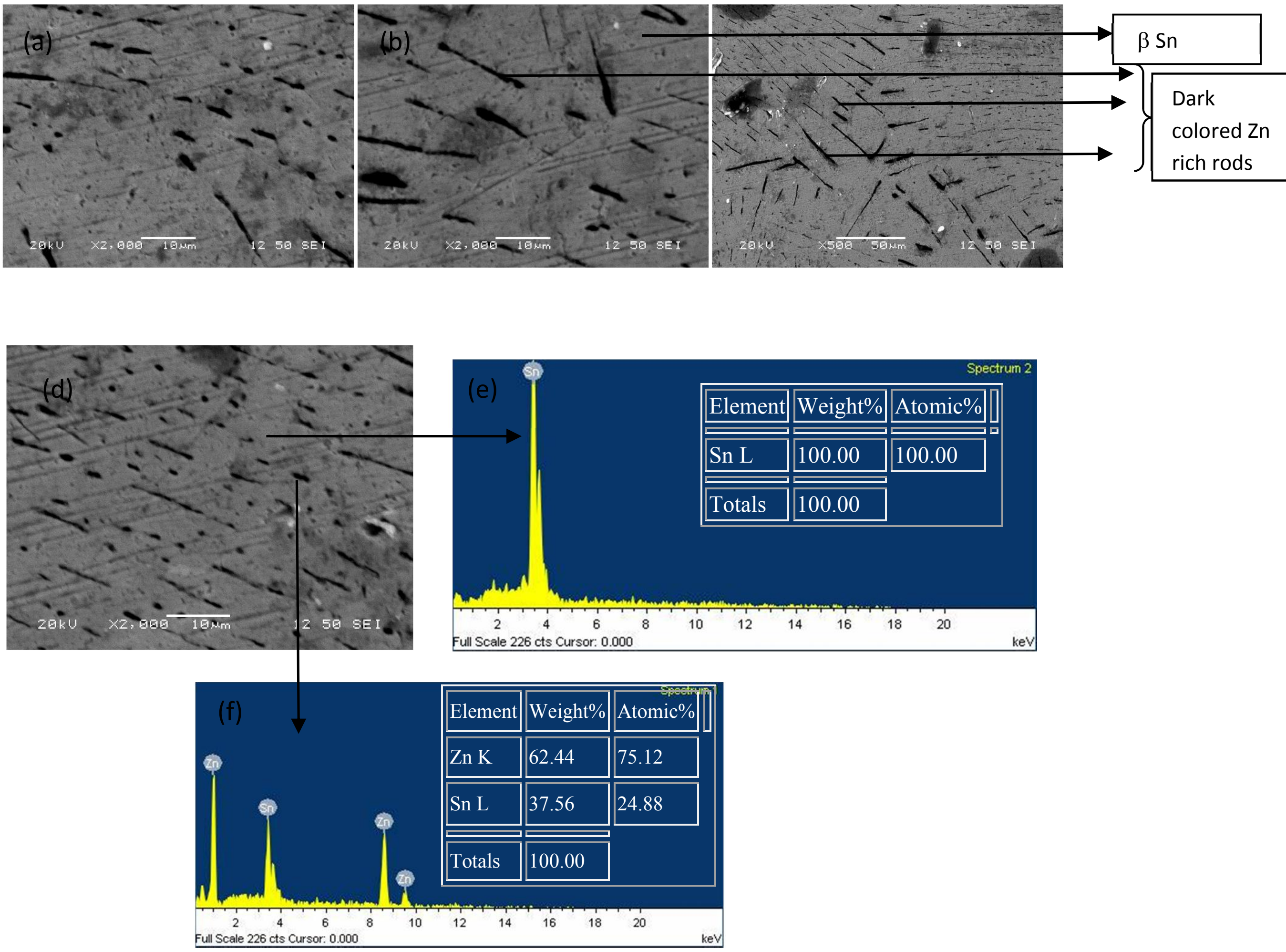
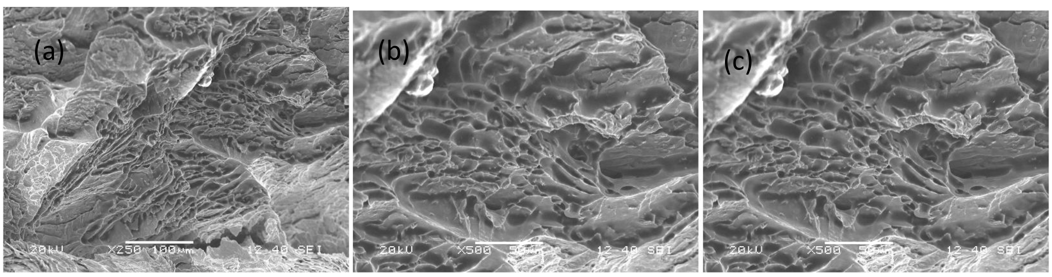


Figure 4.6.2 (a)-(d)showing SEM of Sn-9Zn alloy and (e)-(f) shows the EDS analysis

(ii) Fractography :

(a) Sn-3.5Ag :

The figure below shows SEM images of the fractured surface of Sn-3.5Ag alloy. The alloy shows simple ductile fracture. There is formation of dimples clearly indicating the ductile type of fracture. The figures also show plastically deformed grains due to extensive plastic deformation of beta phase of Tin and Ag_3Sn intermetallic in the eutectic region.



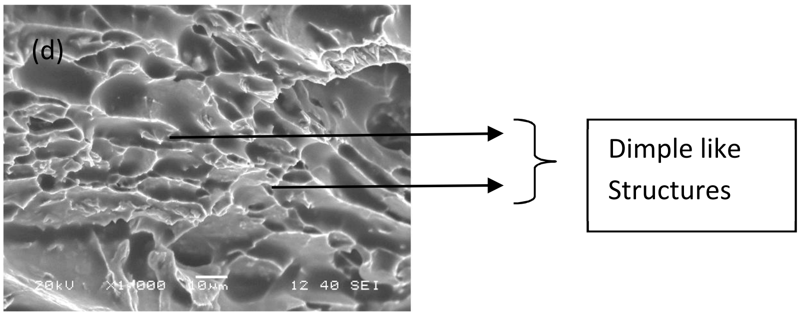
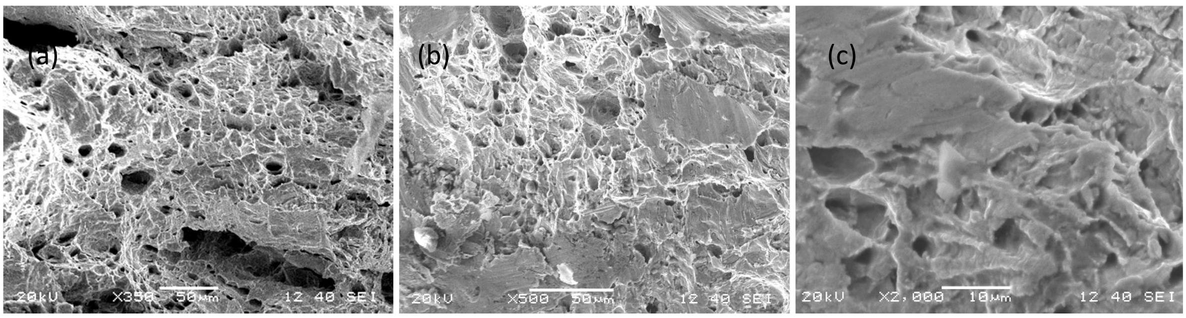


Figure 4.6.3(a)-(d) showing SEM images of fracture surface of Sn-3.5Ag alloy

Here the plastically deformed grains are clearly seen. This type of fracture starts by generation of voids followed by crack formation by formed from coalescence of voids, followed by crack propagation leading to failure of material often leading to formation of a cup-and-cone shaped failure surface.

(b) Sn-8.8Zn

The alloy shows simple ductile fracture. There is formation of dimples clearly indicating the ductile type of fracture. The figures also show plastically deformed grains due to extensive plastic deformation of Sn rich phase and Zn rich rods in the eutectic mixture. Here the plastically deformed grains are clearly seen. This type of fracture starts by generation of voids followed by crack formation by formed from coalescence of voids, followed by crack propagation leading to failure of material often leading to formation of a cup-and-cone shaped failure surface.



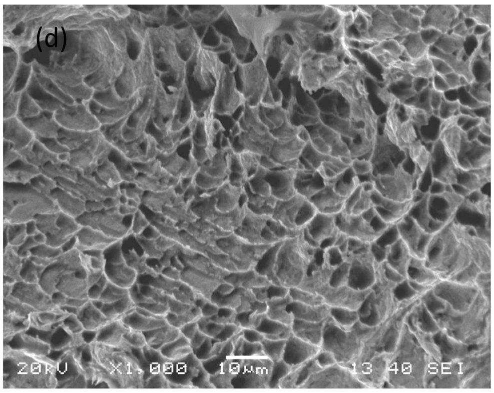


Figure 4.6.4(a)-(d) showing SEM images of fracture surface of Sn-9Zn alloy

(iii)Wettability :

(a) Sn-3.5Ag :

The figure below shows the Sn-Ag solder alloy on Cu substrate. The wettability of the alloy on Cu substrate was found to be moderately good. The alloy shows partial wettability on the Cu substrate with contact angle made being less than 90^{o}.

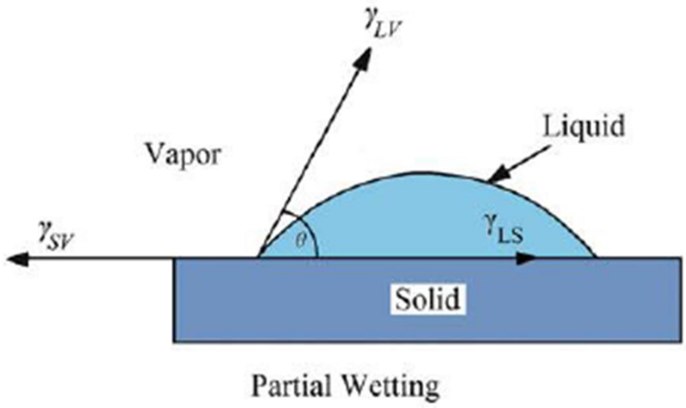
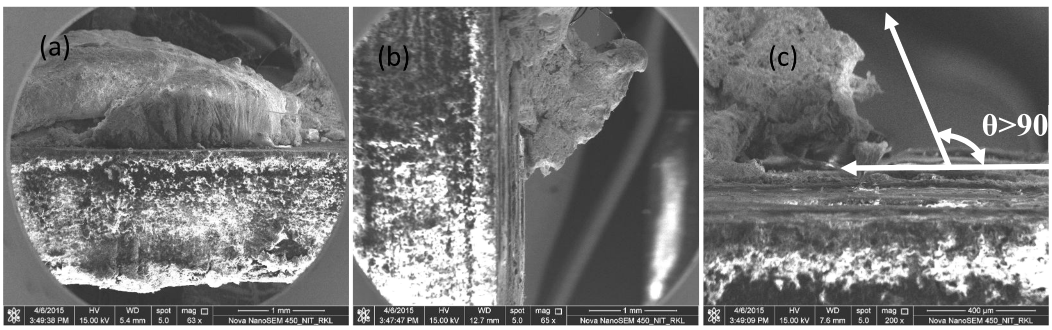


Figure 4.6.5 showing partial wettability of a liquid on solid



(b) Sn-8.8Zn

The figure below shows the Sn-9Zn solder alloy on Cu substrate. The wettability of the alloy on Cu substrate was found to be moderately good. The alloy shows partial wettability on the Cu substrate with contact angle made being less than $90^{o.}$

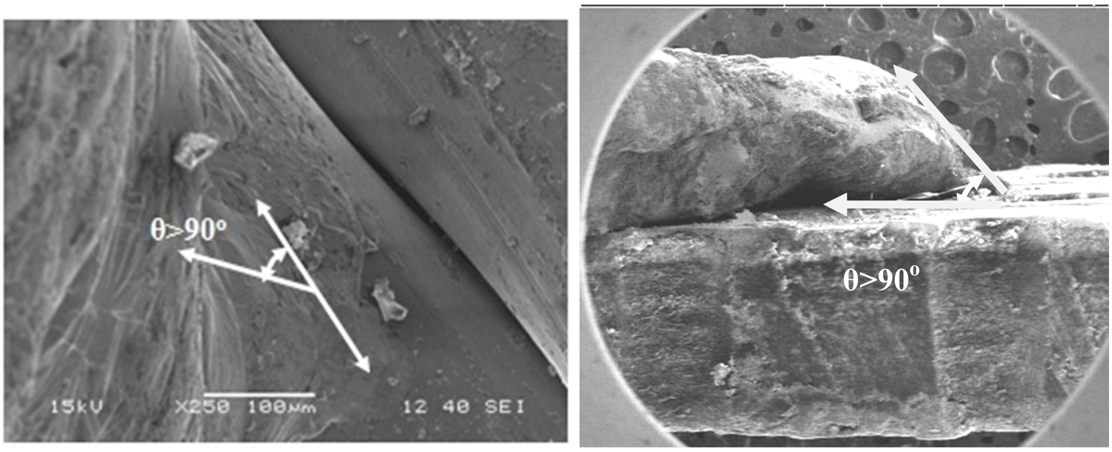


Figure 4.6.7showing high magnification SEM image of Sn-9Zn solder alloy on Cu substrate

CHAPTER 5
CONCLUSION

Conclusion

Sn 9Zn lead free solder alloy was found to better than Sn3.5 Ag because:

1.) Sn 9Zn has a lower melting point than Sn 3.5Ag
2.) Sn 9Zn has a higher hardness compared to Sn 3.5Ag
3.) Sn 9Zn doesn’t have any IMC formations in its phase
4.) Sn 9 Zn has decent wettabilty on Cu substrate
5.) Sn9 Zn is cheaper than Sn 3.5 Ag

Hence, from the above it is clear that Sn 9Zn is a better solder alloy compared to Sn 3.5Ag.

REFERENCE

1. Prerna Mishra, S.N. Alam, Rajnish Kumar, "Determination and Characterisation of Lead free solder alloys" Submitted to National Institute of Technology, Rourkela on 2014-05-21,

2. Abtew, M.. "Lead-free Solders in Microelectronics", Materials Science & Engineering R, 20000601

3. Osorio, W.R.. "Electrochemical behaviour of a lead-free Sn-Ag solder alloy affected by the microstructure array", Materials and Design, 201112

4. Chang, T.C.. "Solderability of Sn-9Zn-0.5Ag-1In lead-free solder on Cu substrate", Journal of Alloys and Compounds, 20060928

5. Li, W.L.. "Microstructure and adhesion strength of Sn-9Zn-1.5Ag-xBi (x=0wt% and 2 wt.%)/Cu after electrochemical polarization in a 3.5wt% NaCl solution", Journal of Alloys and Compounds,

6. Das, S.K. "Influence of small amount of Al and Cu on the microstructure, microhardness and tensile properties of Sn-9Zn binary eutectic solder alloy", Journal of Alloys and Compounds, 20090729

7. Wu, C.M.L.. "Properties of lead-free solder alloys with rare earth element additions", Materials Science & Engineering R, 2004040120080811

8. Chang, T.C.. "Solderability of Sn-9Zn-0.5Ag-1In lead-free solder on Cu substrate", Journal of Alloys and Compounds, 20060928

9. Osório, Wislei R., Leandro C. Peixoto, Leonardo R. Garcia, Nathalie Mangelinck-Noël, and Amauri Garcia. "Microstructure and mechanical properties of Sn–Bi, Sn–Ag and Sn–Zn lead-free solder alloys", Journal of Alloys and Compounds, 2013.

10. H. T. Lee. "Effects of *in situ* nickel particle addition on the microstructure and microhardness of Sn–Ag solder", Science and Technology of Welding & Joining, 06/01/2005

11. Lin, C.T.. "Interfacial microstructures and solder joint strengths of the Sn-8Zn-3Bi and Sn-9Zn-lAl Pb-free solder pastes on OSP finished printed circuit boards", Journal of Alloys and Compounds, 20080714

12. Li, D.. "Characteristics of intermetallics and micromechanical properties during thermal ageing of Sn-Ag-Cu flip-chip solder interconnects", Materials Science & Engineering A, 20050125

13. Kang-I. Chen. "The microstructures and mechanical properties of the Sn-Zn-Ag-Al-Ga solder alloys—the effect of Ag", Journal of Electronic Materials, 08/2002

14. Chang, T.C.. "Microstructure and adhesion strength of Sn-9Zn-xAg lead-free solders wetted on Cu substrate", Materials Science & Engineering A, 20060815

15. M. McCormack. "New, lead-free solders", Journal of Electronic Materials, 07/1994

16. Chen, K.I.. "Effects of small additions of Ag, Al, and Ga on the structure and properties of the Sn-9Zn eutectic alloy", Journal of Alloys and Compounds, 20060608

17. "Abstracts of forthcoming manuscripts", IEEE Transactions on Electronics Packaging Manufacturing, 7/2002

18. Freitas, Emmanuelle S., Wislei R. Osório, José E. Spinelli, and Amauri Garcia. "Mechanical and corrosion resistances of a Sn–0.7wt.%Cu lead-free solder alloy", Microelectronics Reliability, 2014.

19. Tao-Chih Chang. "Thermal properties and interfacial reaction between the Sn-9Zn-xAg lead-free solders and Cu substrate", Metallurgical and Materials Transactions A, 11/2005

20. Zhang, H.. "Synthesis of Sn-Ag binary alloy powders by mechanical alloying", Materials Chemistry and Physics, 20100701

21. El-Daly, A.A.. "Thermal and mechanical properties of Sn-Zn-Bi lead-free solder alloys", Journal of Alloys and Compounds, 20090918

22. Wenxue Chen. "Solderability and intermetallic compounds formation of Sn-9Zn-xAg lead-free solders wetted on Cu substrate", Rare Metals, 12/2009

23. Fredriksson, . "Microsegregation in Alloys - Peritectic Reactions and Transformations", Materials Processing during Casting Fredriksson/Materials Processing during Casting, 2012.

24. Wufeng Feng. "Electronic structure mechanism for the wettability of Sn-based solder alloys", Journal of Electronic Materials, 03/2002

25. Mayappan, R.. "The effect of crosshead speed on the joint strength between Sn-Zn-Bi lead-free solders and Cu substrate", Journal of Alloys and Compounds, 20070614