A Comparative Study of the Sn-Ag, Sn-Zn, Sn-Cu, Sn-Bi Lead Free Solder Alloys with the Commercially Available Sn-Pb Solder Alloy

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

Master of Technology (Dual Degree)

in

Metallurgical and Materials Engineering

Submitted By

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Department of

Metallurgical and Materials Engineering

National Institute of Technology

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Under the guidance of

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CERTIFICATE

This is to certify that the thesis entitled, "**A Comparative Study of the Sn-Ag, Sn-Zn, Sn-Cu, Sn-Bi Lead Free Solder Alloys with the Commercially Available Sn-Pb Solder Alloy**", submitted by Akella Siva Durga Phani in partial fulfillment of the requirements for the award of Master of Technology Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him 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.

Prof. S. N. Alam

Department of Metallurgical and Materials Engineering

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I express my sincere thanks to my loving parents and friends for providing me the necessary facilities and great atmosphere for my work.

Date: Akella Siva Durga Phani

Abstract

As soldering controls the effective usage and processing of electronic components in applications and devices. Solders are used as interconnect materials in microelectronic packaging. Traditionally Pb-Sn eutectic alloys have been used due to its low melting point and good wettability. However, due to the toxic nature of lead (Pb) and it harmful effect on environment and health the usage of Pb in solder should be avoided. This is why there is a need to develop environmentally benign Pb-free solders (LFS).

In this research work four different lead free solder alloys, Sn-Cu, Sn-Ag , Sn-Bi , Sn-Zn, and Sn-Pb are developed and characterized. Eutectic Sn-0.7 wt. % Cu, Sn-3.5 wt. % Ag, Sn-57 wt. % Bi, Sn-8.8 wt. % Zn and Sn-37 wt % Pb solder alloys have been developed by melting and casting route. A comparative study of all the five alloys was done based on their microstructure and various properties like electrical resistivity, hardness, fractography and wettability on Cu substrate. Their microstructure of the alloys was analyzed using optical microscopy and scanning electron microscopy (SEM). The various phases in the alloys were analyzed using energy dispersive x-ray spectroscopy (EDS) attached to the SEM. The nature of fracture in the alloys was analyzed using SEM. The melting point of the alloys was determined using differential scanning calorimeter (DSC). Hardness of the alloys was determined using a Vicker's microhard ness tester. The wettability of the solder alloys on Cu substrate was analyzed using SEM. Electrical resistivity of all the alloys were determined using a four point electrical probe.

The objective of this study is to find out the solder alloy among the four eutectic solder alloys chosen here which could replace the traditional Sn-Pb solder alloy.

Keywords: Lead free solder alloys, Sn-Ag, Sn-Zn, Sn-Cu, Sn-Bi, Sn-Pb, Microstructure, Electrical Resistivity, Hardness.

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Introduction:

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. 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^{o}C),better wetting behavior and mechanical properties. Despite of all these advantages the toxicity of heavy metallic element Pb has led in recent decades to restrict its use as directed by restriction of certain hazardous substances (RoHS) and the waste electrical and electronic equipment (WEEE) legislations. This urge the development of lead free solders which has emerged as one of the key issues in electronic packaging and industries.

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. 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.

We have developed a binary Pb free solder alloys such as Sn-Zn, Sn-Cu, Sn-Ag, Sn-Bi, and Sn-Pb. In order to overcome drawbacks and to further enhance the properties of binary lead free system small amount of alloying elements such as Bi, Cu, In, Ag, Al, Ga, Sb, Cr, Ni, Ge were can be added to develop ternary and even quaternary Pb free systems as suggested by many researchers. Each binary solder alloy has its own unique advantages and disadvantages for example, although Sn-Bi has very low eutectic melting point (139^{o}C) than Pb-Sn solder (183^{o}C), its high hardness and high electrical resistivity reduces its usage. Sn-Ag, Sn-Cu systems shows best wettability on Cu substrate but formation of intermetallic compounds such as Ag_3Sn, Cu_6Sn_5 creates brittle rich interfacial areas. Sn-Zn eutectic alloy of 198^{o}C melting temperature is non-toxic to human health and environment, but it shows poor wettability and mechanical properties due to its easy oxidation and micro void formation. So selecting an efficient LFS is the challenge ahead for the curious minds.

Table 1: Melting point, Electrical resistivity and Densities of Various Metals

Metals	Melting Point (^{o}C)	Electrical Resistivity (μΩ.cm)	Density (g/cm^3)
Sn	232	45	7.30
Pb	327.5	21	11.36
Ag	961	1.61	10.49
Cu	1084	1.7	8.96
Bi	271.4	115	9.78
Zn	419.5	35	7.13

1. EXPERIMENTAL SETUP AND METHODOLOGY

1.1OBJECTIVE

1. Preparation of basic lead free eutectic solder alloys Sn-Ag, Sn-Cu, Sn-Bi, and Sn-Zn by casting in a suitable furnace.

2. Microstructure analysis of LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb by Optical Microscopy and Scanning electron microscope (SEM).

3. Compositional analysis of LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb by SEM-Energy Dispersive X – ray spectroscopy (EDS/EDAX).

4. Phase analysis of LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb by X – ray diffraction technique (XRD).

5. Determination of Melting point of LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb by Differential Scanning Calorimetry (DSC).

6. Determination of Hardnessof LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb by Micro Vickers Hardness testing machine.

7. Determination of Ultimate Tensile Strength of LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb by Universal Testing Machine (UTM).

8. Fractography analysis on Impact fractured samples of LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb by SEM
9. Determination of Wettability characteristics of LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb by soldering on Cu substrate
10. Determination of Electrical resistivity of LFS alloys Sn-Ag, Sn-Cu, Sn-Bi, Sn-Zn and Sn-Pb.

2.2MATERIALS AND METHODS

❖ Eutectic Composition of the solder materials

S.NO	SYSTEM	COMPOSITION (wt. %)	EUTECTIC TEMPERATURE(^oC)
1.	Sn – Bi	Sn – 57Bi	139
2.	Sn – Zn	Sn – 8.8Zn	198.5
3.	Sn – Ag	Sn – 3.5Ag	221
4.	Sn – Cu	Sn – 0.7Cu	227
5.	Sn--Pb	Sn--37Pb	183

❖ **Purity and supplier of the solder material**

S.NO	METAL	PURITY	SUPPLIER
1.	Sn	99.50%	RANKEM,RFCL Ltd.
2.	Cu	99.50%	NICE Ltd.
3.	Ag	99.00%	RANKEM,RFCL Ltd.
4.	Zn	99.00%	RANKEM,RFCL Ltd.
5.	Bi	99.50%	OTTO Ltd.

❖ Method of Experimental work

Based on eutectic compositions, metals are weighed by electronic weighing machine depending on quantity of sample per say to prepare 10 grams of Sn-57Bi solder 5.7g of Bi and 4.3g of Sn has to be taken. Mostly Sn is available in granules form. Most of our LFS alloys have casting temperature in the range of 400^oC to 600^oC.Furnace is heated to the desired temperature by electrical resistance heating elements. Entire melting is done in a ceramic crucible kept in furnace. First the metal which having high melting point and high amount in eutectic composition is melted, further second element is added to it and melted at its melting point. The molten alloy was held at its casting temperature for 2 hours. After this alloy was furnace cooled to a day or so to get solidified solder.

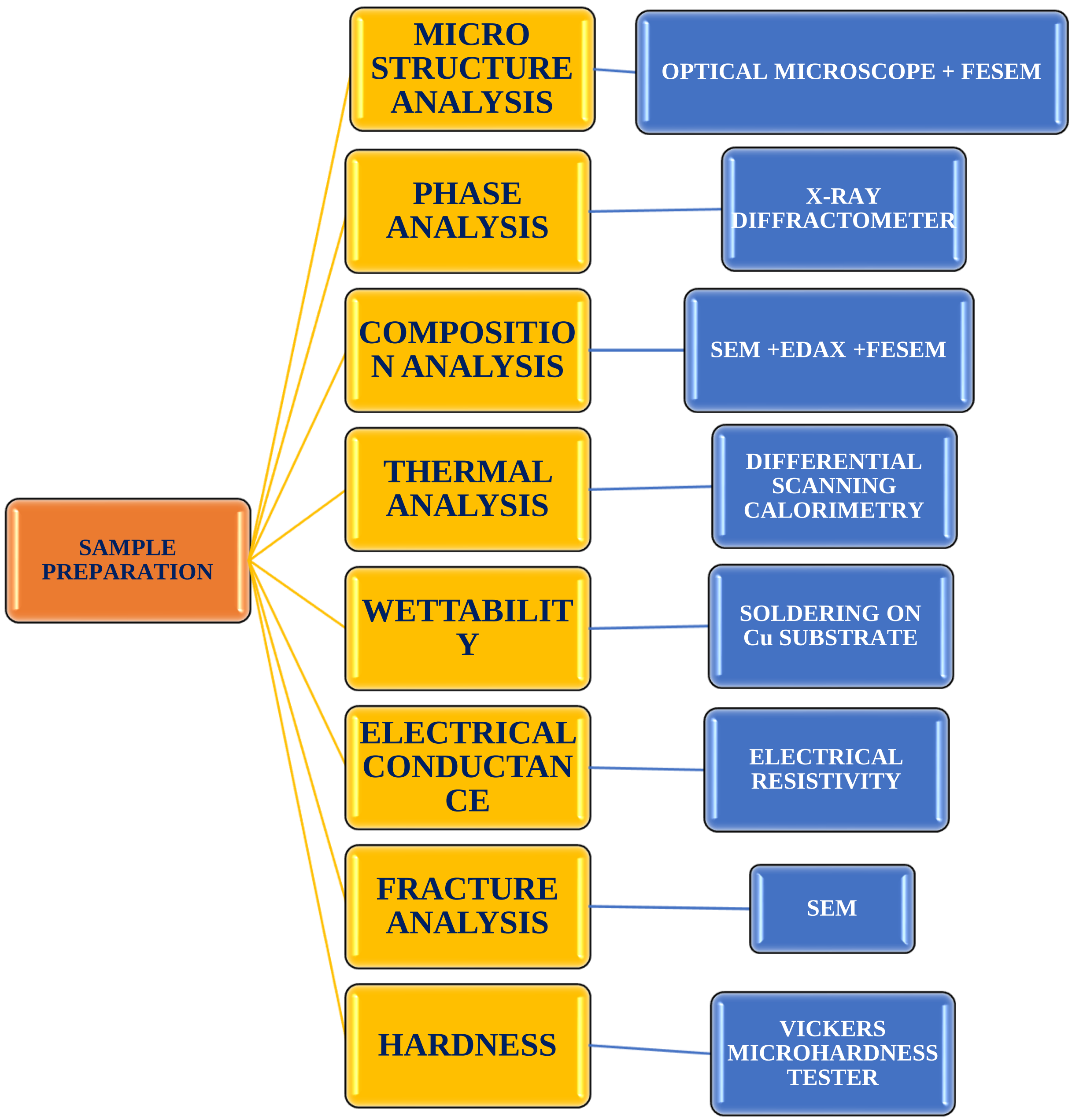
The basic microstructure analysis of our LFS un-etched samples is done by Optical microscopy and FESEM. Morphology and elemental composition of the samples were analyzed using a JEOL JSM-6480LV scanning electron microscope (SEM) equipped with an INCAPentaFET-x3 X-ray microanalysis system with a high-angle ultra-thin window detector and a 30 mm^2 Si(Li) crystal for EDS (energy dispersive X-ray spectroscopy) analysis. X-ray diffraction (XRD) of the alloys was done to find out if any new phases were formed during their development. Differential scanning Calorimeter (DSC) was done in order to determine the melting point of the LFS alloys. The tensile test by UTM and micro Vickers hardness test of the alloys were also performed to find out their mechanical properties. Fractography studies were done using SEM on impact fractured samples. Interfacial analysis is done using FESEM followed by soldering the alloys on Cu substrate to know the wettability. Electrical resistivity tests are done to investigate the electrical conductivity behavior of eutectic LFS.

2.3METALLOGRAPHY

For microstructural studies, samples were cut approximately 20mm height. Samples were ground roughly on a belt grinder. Then they were cold resin mounted to handle it properly throughout the polishing. After this samples were polished with the help of emery papers having different types of finer abrasive grains such as 1/0, 2/0, 3/0 and 4/0 grades. During usage of each polishing paper, the samples were moved perpendicular directions to the existing scratches.

After completion of paper polishing the samples were subjected to cloth polishing in which a rotating wheel covered with special cloth, here aluminum powder in liquid form is preferred for better polishing. For further polishing diamond paste was used. Polishing operation was continued until the surface of samples were becomes plane and free from the surface irregularities such as nicks, inflection, etc. Finally, the polished samples were cleaned thoroughly by the purified water and dried subsequently with the use of drier.

2.4FLOW-CHART OF EXPERIMENTAL PROCEDURE



Above experimental procedures have done for all the samples in this study.

2. <u>RESULTS AND DISCUSSIONS</u>

2.1 Sn-3.5wt%Ag Solder alloy

2.1.1 Microstructure Analysis

- **Sn-Ag Binary Phase Diagram**

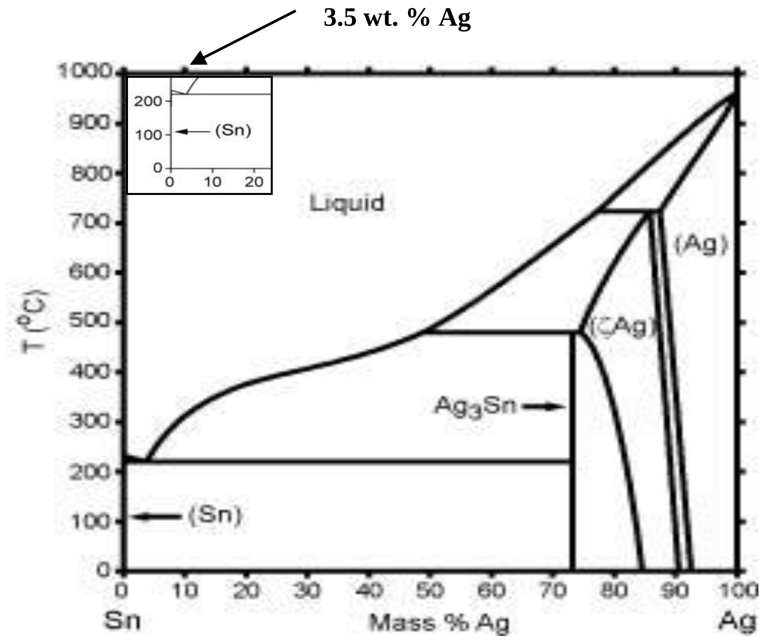


Fig 2.1. Binary phase diagram of Sn-Ag (Insert shows Sn-3.5wt%Ag eutectic)

- In addition to liquid and the two terminal solution phases, (Ag) and (Sn), this system has two intermediate phases, (ζAg) and Ag_3Sn. Both intermediate phases form by peritectic reactions.
- The eutectic reaction in which liquid with 96.5wt%-Sn decomposes into Ag_3Sn and (Sn) at a temperature of 221°C is well established.

- Melting Point of Sn is 231.96^{0}C
- Melting Point of Ag is 961^{0}C
- Eutectic - Composition: Sn-3.5wt%Ag
  Temperature: 221^{o}C

- **Experimental Sample preparation**

- To prepare 10g of Sn-3.5wt%Ag eutectic solder alloy 0.35g of Ag and 9.65g of Sn has to be taken. First, melt Sn at 300^{0}C (because it has high wt%&231.96^{0}C) and then add Ag to it then kept the liquid melt around 500^0C up to 2hrs to homogenize the eutectic solution. After this cool it with in the furnace until to get solidified solder alloy.

❖ Optical Microscopy - Microstructure Analysis

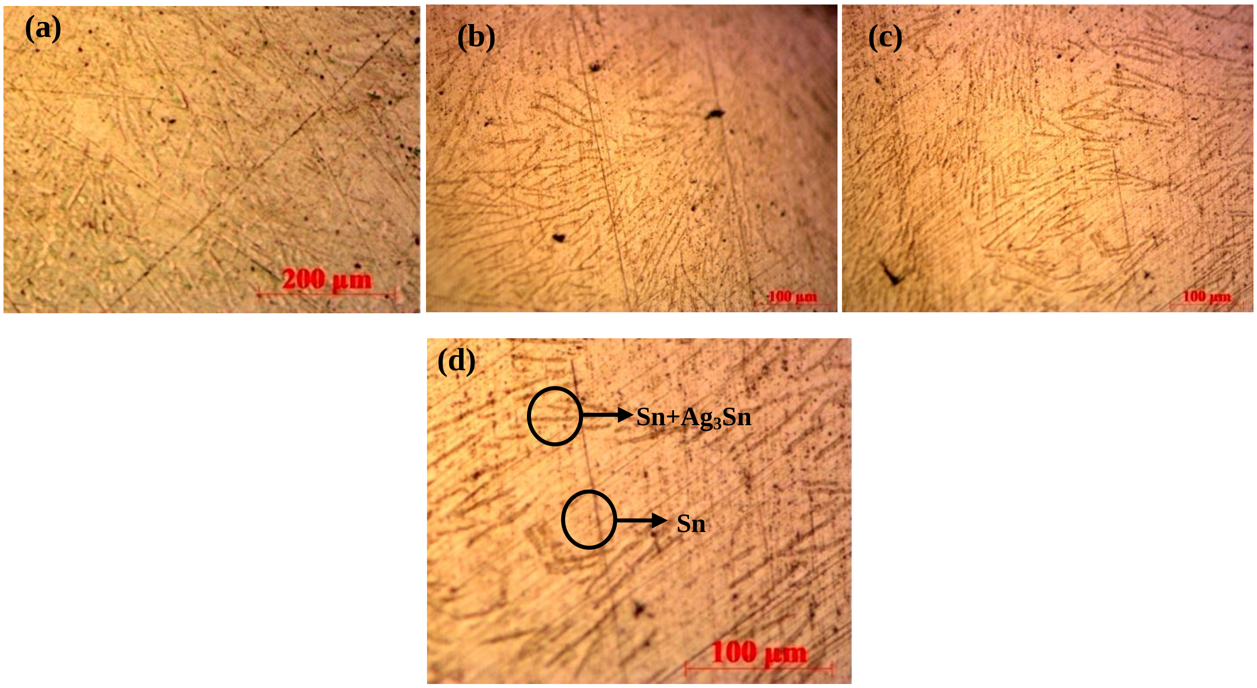


Fig. 2.2 (a-d) Optical micrographs of eutectic Sn-3.5 wt. % Ag solder alloy

- The optical microscopy image shows, soft white matrix and black rod-like structures which are expected to be Sn and Ag_3Sn Intermetallics respectively.

- White colored 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 Sn at room temperature is about 0.05 wt. % only.

2.1.2 XRD - Phase Analysis

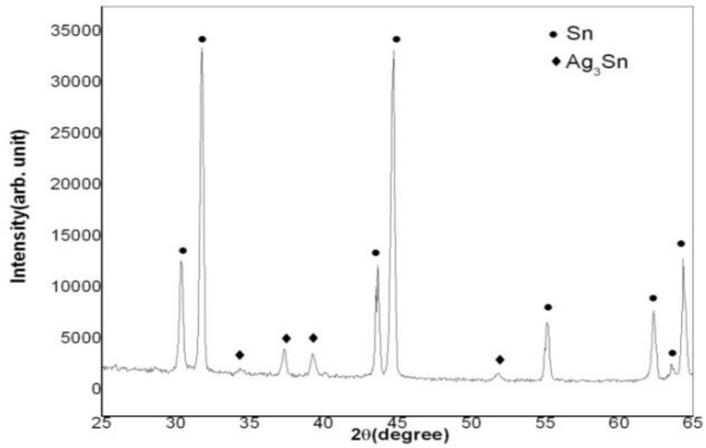
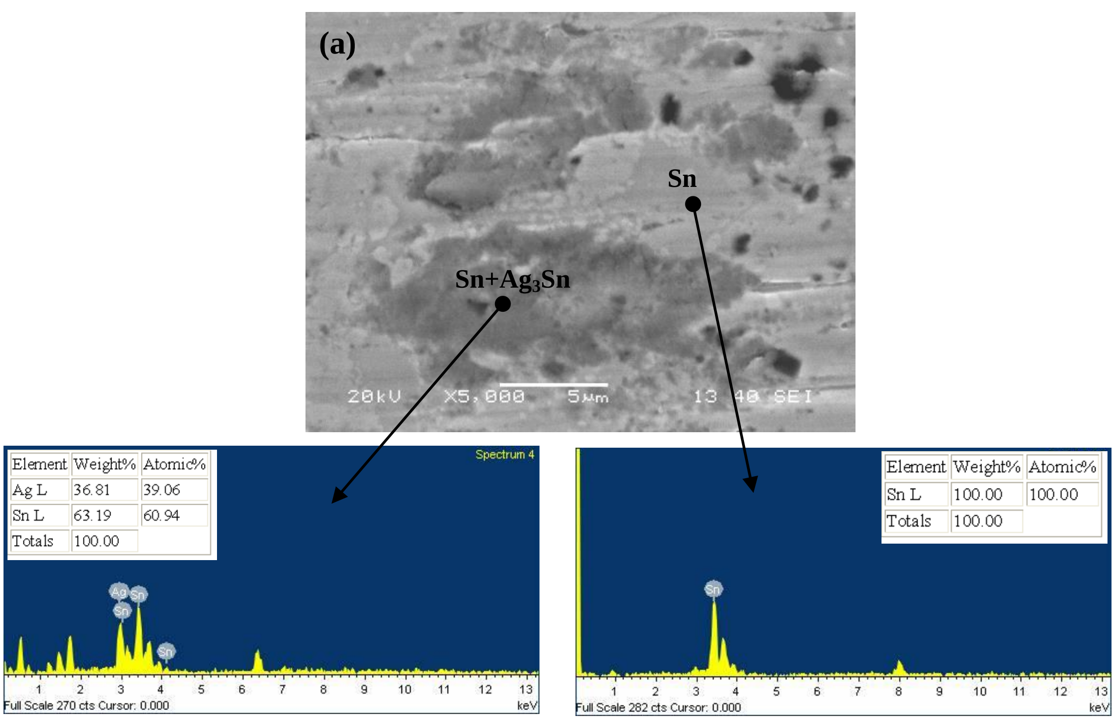


Fig 2.3 XRD peaks of Sn-3.5wt%Ag eutectic solder alloy

- From above XRD peaks, we can confirm the presence of tetragonal β-Sn and orthorhombic Ag_3Sn phases in the Sn-3.5wt%Ag eutectic alloy.

2.1.3 SEM/EDS - Compositional Analysis



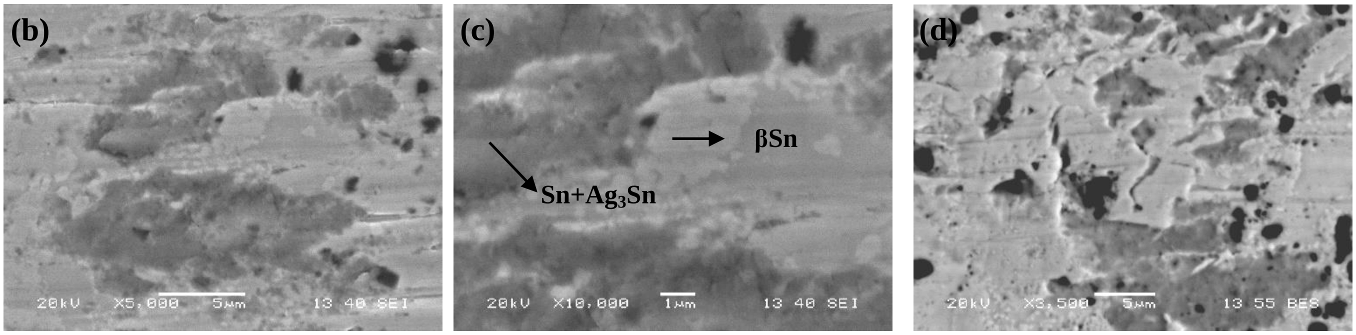


Fig. 2.4 (a-d) SEM and EDS analysis of eutectic Sn-3.5 wt. % Ag solder alloy

- From the above SEM microstructure and EDS/elemental mapping analysis we can conclude that eutectic alloy has White rich phase as β Sn and Black colored region has Sn and Ag3Sn eutectic mixtures.
- The eutectic mixture is composed of both the Ag_3Sn intermetallic and the Sn-rich phase. The Sn rich phase is composed of about 0.05 wt. % Ag. Eutectic
  A mixture containing about 3.5 wt. % Ag is found in inter dendritic regions. The eutectic mixture is formed by a cooperative growth of theses phases.

2.1.4 Thermal Analysis

- ❖ **DSC - Melting point**

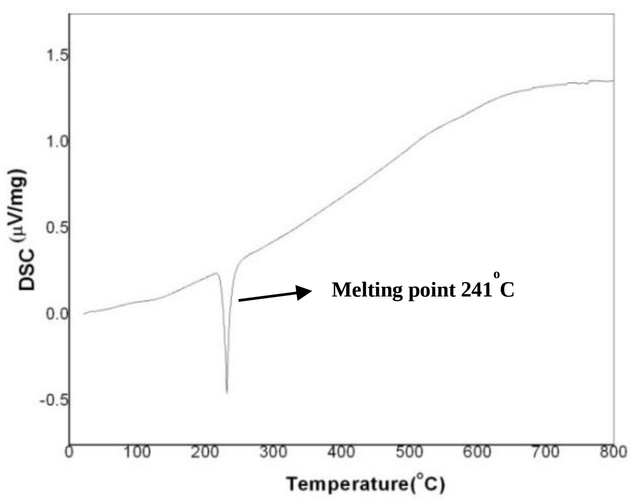


Fig 2.5. DSC analysis of Sn 3.5 wt. %Ag eutectic solder alloy

- Experimental Melting point: 241^{o}C
- Eutectic Melting Temperature from Phase Diagram: 221^{o}C

- From above DSC analysis, we can conclude that melting point is near to eutectic temperature and undercooling is less than 15^{o}C or so, which indicates better solidification and lesser occurrence of the pasty region during processing.

2.1.5 Hardness

❖ Micro Vickers Hardness Test

- It was found that Sn-3.5wt%Ag eutectic solder alloy has the hardness value as 142.5 MPa (14.5 HV).This is mostly because of the presence of Ag_3Sn intermetallic phase.

2.1.6 Fractography

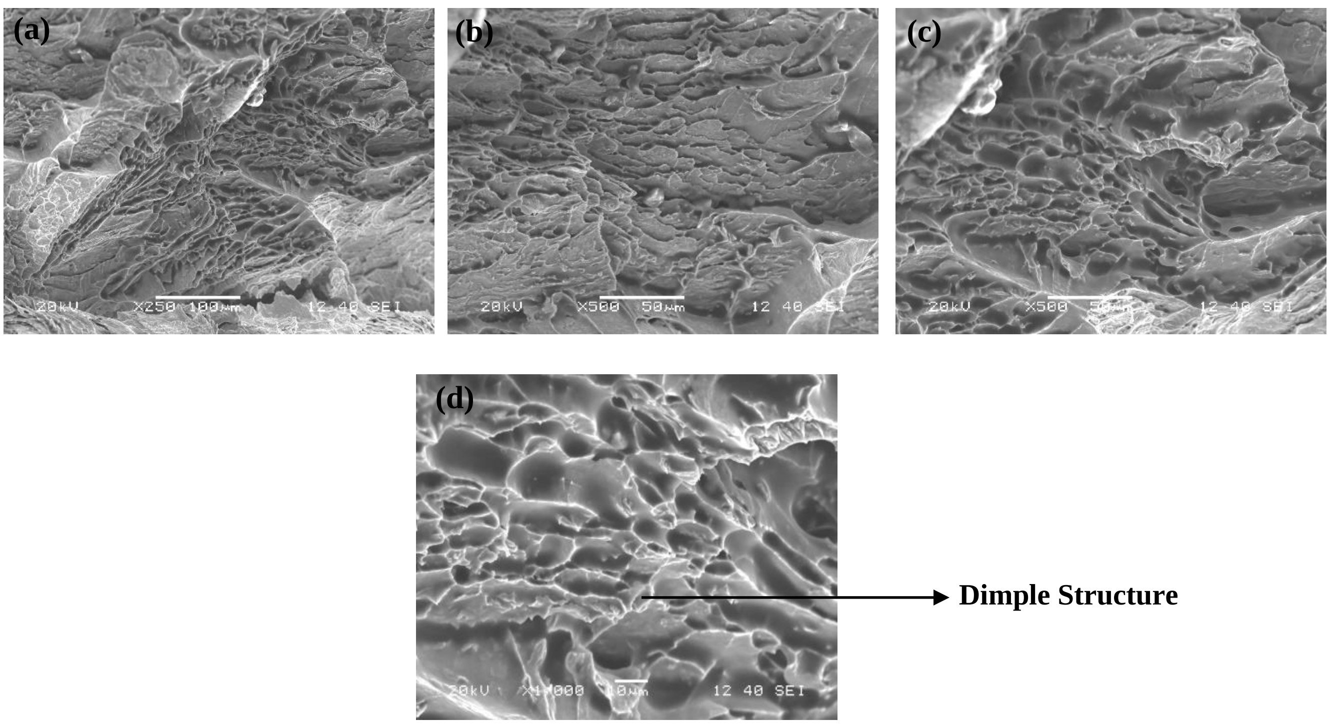


Fig 2.6. SEM image showing fractured surface of Sn-3.5wt%Ag eutectic alloy

- Above SEM image shows the dimple and cleavage like structure under fracture which confirms the ductile nature of Sn-3.5wt%Ag eutectic solder alloy and also supports the micro Vickers hardness value.

2.1.7 Interfacial Analysis

❖ Wettability Test/Soldering

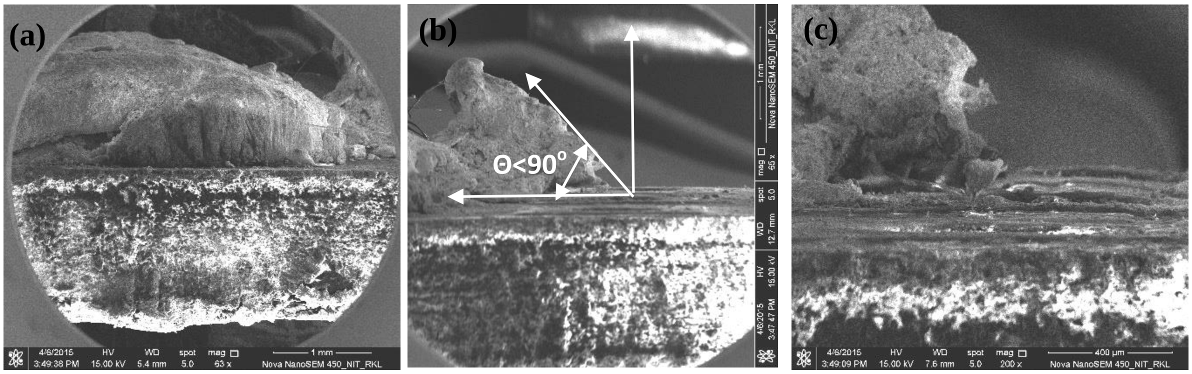


Fig 2.7(a-c). SEM image of Sn-3.5wt%Ag eutectic solder alloy on Cu substrate

- From above figure Sn-3.5wt%Ag eutectic solder alloy has the partial wetting angle ($\theta<90^0$) when it was soldered on Cu substrate which supports the conclusion that it has better wettability and solderability.

2.1.8 Electrical Resistivity Test

Electrical resistivity $(\rho) = R\left(\frac{A}{L}\right)$

R= Resistance of the specimen
A= Cross sectional area
L= Length of the specimen

- It was found that Sn-3.5wt%Ag eutectic solder alloy has the value of Electrical Resistivity is 1.9143 (μΩ-cm).The very low value of 'ρ'among our considered LFSs is attributed to the presence of 'Ag' ,which is the most conductive element among available metals.

Cost

- Sn-3.5wt%Ag eutectic solder alloy is expensive due to the presence of Ag, which hinders the commercial usage.

2.2 Sn-8.8wt%Zn solder alloy

2.2.1 Microstructure Analysis

❖ Sn-Zn Binary Phase Diagram

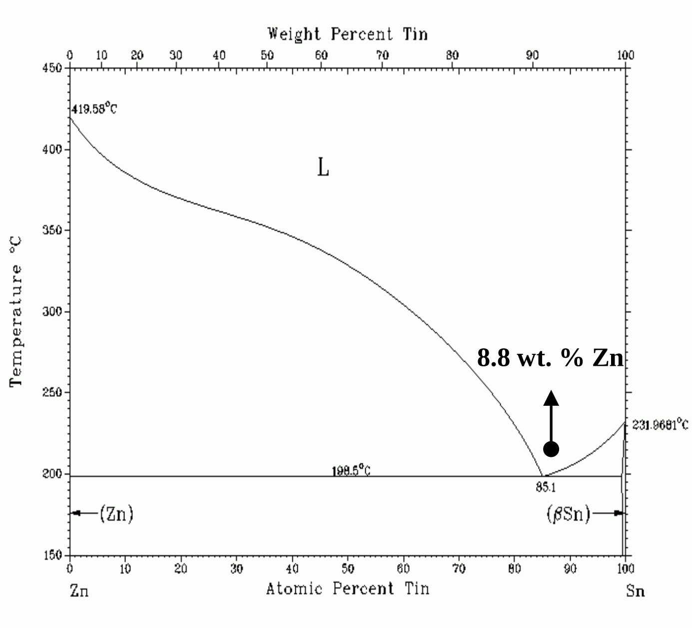


Fig 3.1. Binary Phase Diagram of Sn-8.8wt%Zn Eutectic Solder alloy

- At 198.5°C, the liquid decomposes into the two terminal solid solutions, (Zn) and (Sn). However, the composition reported for the liquid phase at the eutectic temperature varies between 90.6wt%Sn and 92.1wt%Sn.

- Melting Point of Sn is 231.96^{0}C
- Melting Point of Zn is 419.55^{0}C
- Eutectic - Composition: Sn-8.8wt%Zn
  Temperature: 198.5^{o}C

❖ Experimental Sample preparation

- To prepare 10g of Sn-8.8wt%Zn eutectic solder alloy 0.88g of Zn and 9.12g of Sn has to be taken. First, melt Sn at 300^{o}C (As it has high wt% and M.P as 231^{o}C), then add and melt the Zn at 500^{o}C.Then kept the liquid melt around 600^{o}C up to 2hrs to homogenize the eutectic solution. After this cool it with in furnace until to get solidifies alloy.

❖ Optical Microscopy - Microstructure Analysis

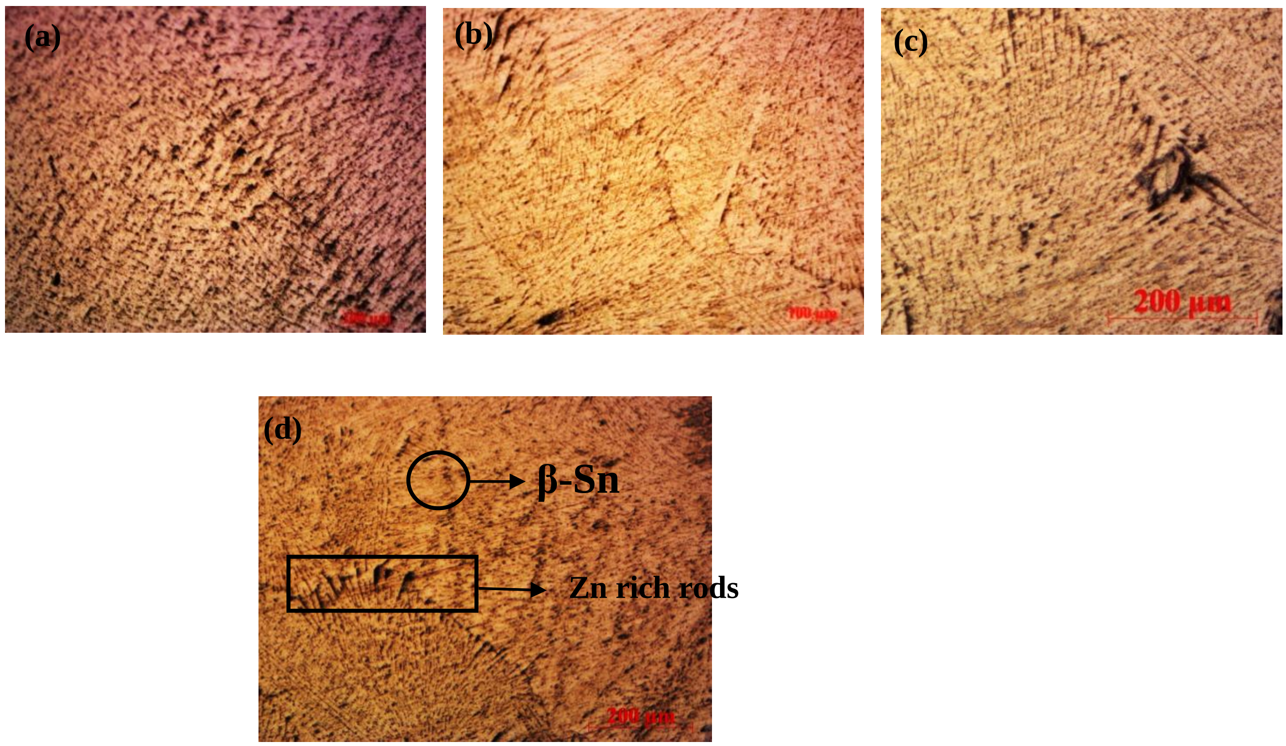


Fig 32(a-d). Optical images of Sn-8.8wt. % Zn eutectic solder alloy

- Optical microscopic figure shows, white soft matrix and black rod like structures which are expected to be Sn and Zn rich phases respectively.

2.2.2 XRD - Phase Analysis

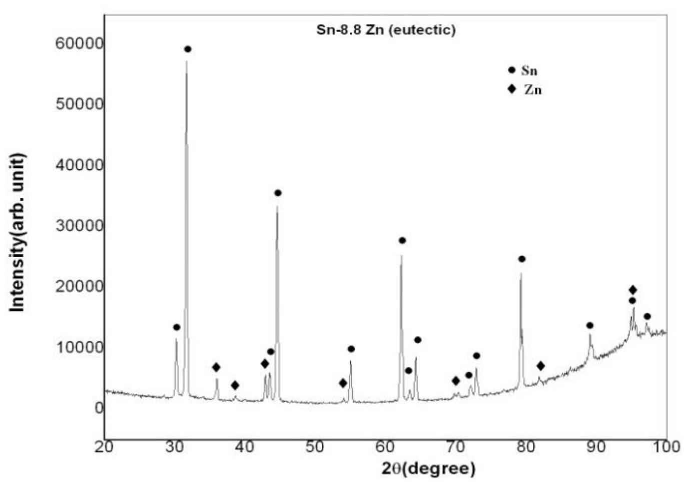


Fig 3.3. XRD peaks of Sn-8.8wt%Zn eutectic solder alloy

- From above XRD peaks, we can confirm the presence of Sn-Tetragonal and Zn-HCP phases in the Sn-8.8wt%Zn eutectic alloy.

2.2.3 **SEM/EDS - Compositional Analysis**

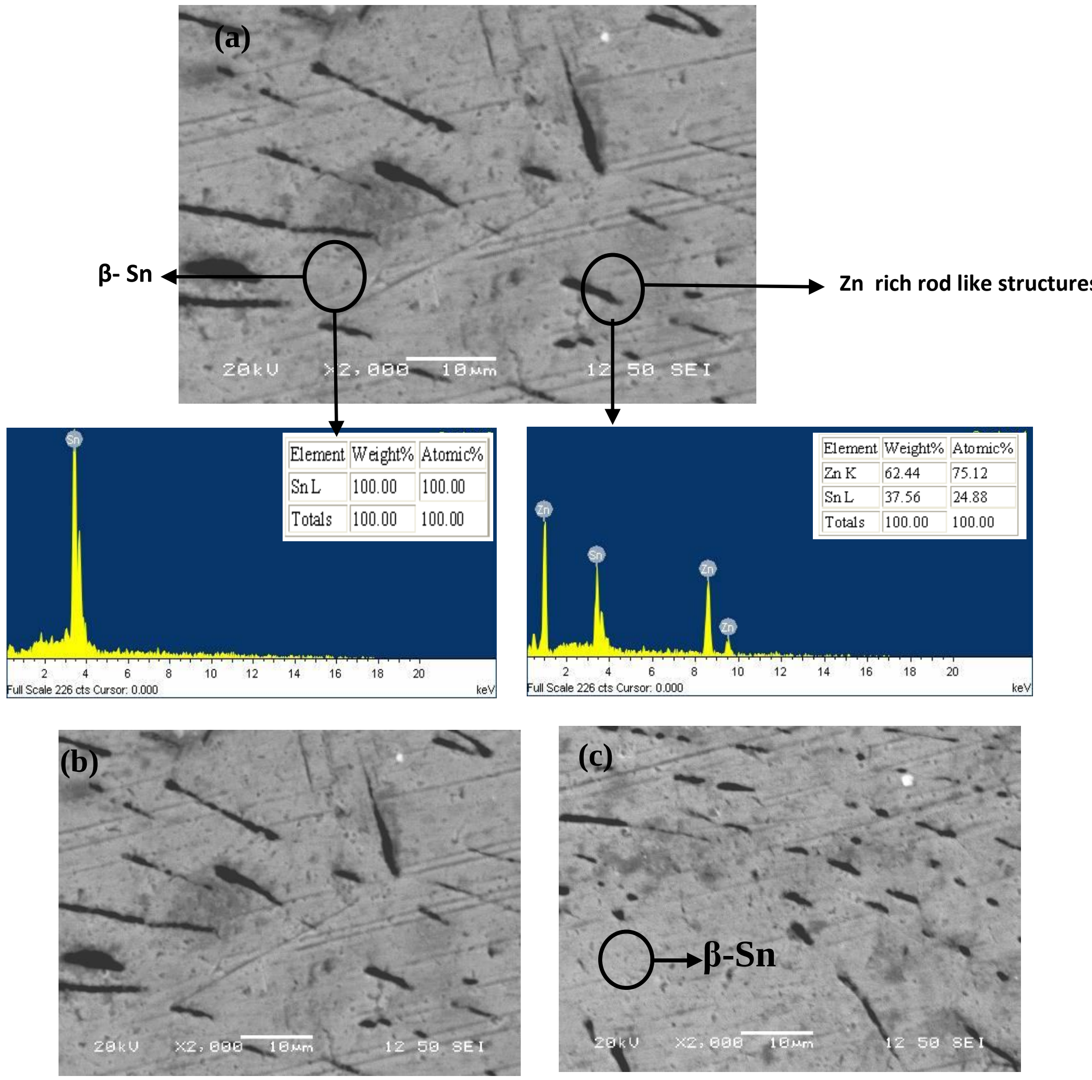


Fig 3.4 (a-c). SEM and EDS analysis of Sn-3.5wt%Ag eutectic solder alloy

- From above SEM microstructure and EDS/elemental mapping analysis we can conclude that eutectic alloy has White rich phase as β-Sn and Black colored region has Sn and Zn eutectic mixtures.
- The eutectic mixture is composed of both the Zn metallic rods and the Sn-rich phase. The Sn rich phase is composed of almost 0.0 wt. % Zn. Eutectic mixture containing about 8.8 wt. % Zn is found in rod like regions. The eutectic mixture is formed by a cooperative growth of theses phases.

2.2.4 Thermal Analysis

❖ **DSC - Melting point**

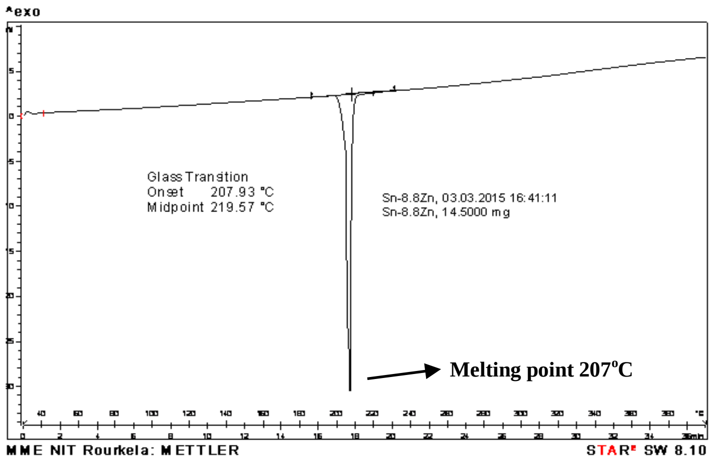


Fig 3.5. DSC analysis of Sn-8.8wt. % Zn eutectic solder alloy

- Experimental Melting point: 207°C
- Eutectic Melting Temperature from Phase Diagram: 199°C
- From above DSC analysis we can conclude that melting point is near to eutectic temperature and undercooling is less than 15°C or so, which indicates better solidification and lesser occurrence of pasty region during processing.

2.2.5 Hardness

❖ **Micro Vickers Hardness Test**

- It was found that Sn-8.8wt%Zn eutectic solder alloy has the hardness value as 162.5 MPa (16.6 HV). This value is higher than the hardness of Sn-Pb (15.1 HV). And it is mostly due to the presence of harder zinc rods.

2.2.6 Fractography

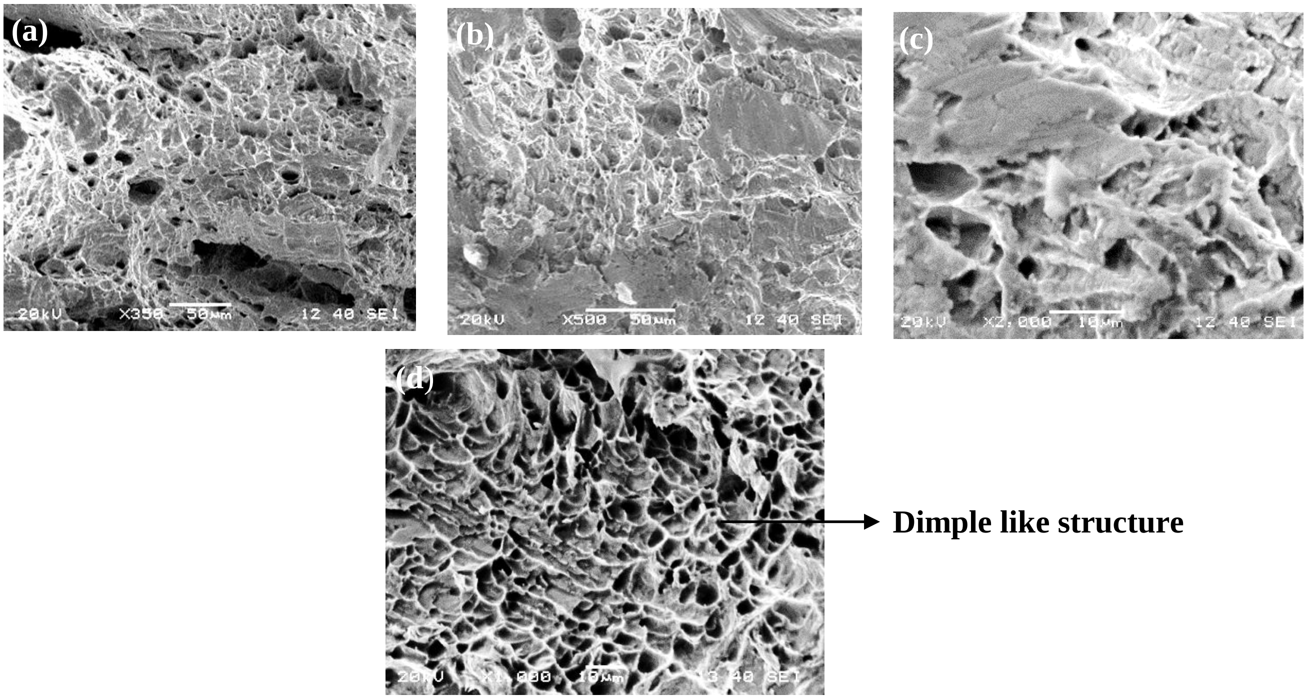


Fig 3.6 (a-d). SEM images showing fractured surface of Sn-8.8wt%Zn eutectic alloy

- Above SEM images shows the dimple and cleavage like structure under fracture whichconfirms the ductile nature of Sn-8.8wt%Zn eutectic solder alloy and also supports the micro Vickers hardness value.

2.2.7 Interfacial Analysis

- **Wettability Test/Soldering**

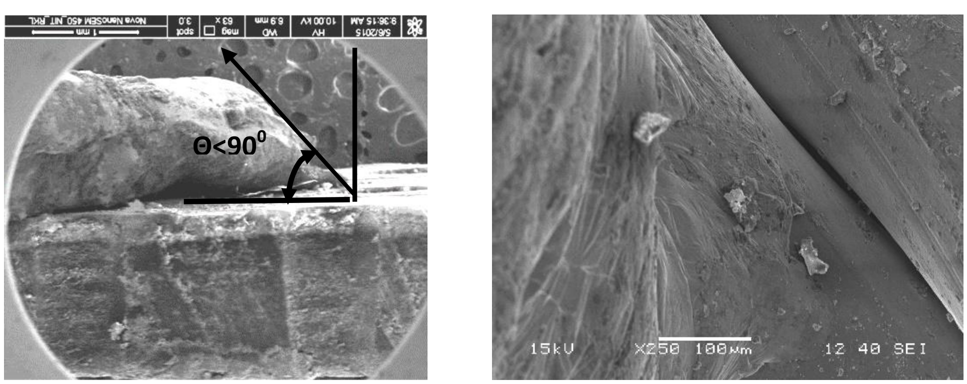


Fig 3.7. SEM image of Sn-8.8wt%Zn eutectic solder alloy on Cu substrate

- From above figure Sn-8.8wt%Zn eutectic solder alloy has the partial wetting angle ($\theta<90^0$) when it was soldered on Cu substrate which supports the conclusion that it has good wettability and solderability.

2.2.8 Electrical Resistivity Test

Electrical resistivity $(\rho) = R\left(\frac{A}{L}\right)$

Where,

R= Resistance of the specimen

A= Cross sectional area

L= Length of the specimen

- It was found that Sn-8.8wt%Zn eutectic solder alloy has the Electrical Resistivity as 2.1934 (μΩ-cm) .This values is lower than the commercial Sn-37Pb (~14 μΩ-cm).

2.2.9 Cost

- Sn-8.8wt%Zn eutectic solder alloy is cheap as compared with other Pb free solders such as Sn-3.5wt%Ag.But poor wettability and poor oxidation resistance limits its application.

2.3 Sn-0.7wt%Cu solder alloy

2.3.1 Microstructure Analysis

❖ **Sn-Cu Binary Phase Diagram**

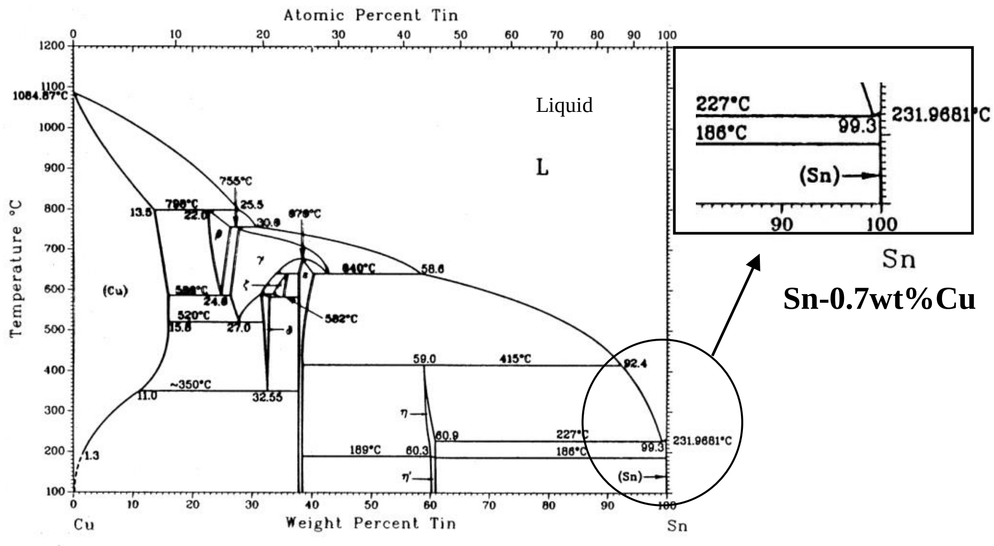


Fig 4.1.Binary phase diagram of Sn-Cu(inset shows Sn-0.7wt%eutectic)

- In addition to liquid and the two terminal solution phases, (Cu) and (Sn), this system has seven intermediate phases, β, γ, $Cu_{41}Sn_{11}$ (δ), $Cu_{10}Sn_3$ (ζ), Cu_3Sn (γ), and Cu_6Sn_5/Cu_6Sn_5' (η/η1, high- and low-temperature forms).

- All of the intermediate phases form by peritectic or peritectoid reactions. All of the copper-rich intermediate phases decompose in eutectoid reactions at temperatures above 350°C and, therefore, only the Cu_3Sn and Cu_6Sn_5/Cu_6Sn_5' phases are of interest for solder applications.
- The temperature of 227°C for the eutectic reaction, where liquid decomposes into Cu_6Sn_5 and (Sn), is well established. However, various evaluations of this system disagree on the exact composition of the liquid phase, either Sn =99.1wt% or Sn = 99.3wt%.

- Melting Point of Sn is : 231.96^{0}C
- Melting Point of Cu is : 1083^{0}C
- Eutectic - Composition: Sn-0.7wt%Cu
  Temperature: 227^{o}C

❖ Experimental Sample preparation

- To prepare 20g of Sn-0.7wt%Cu eutectic solder alloy 0.14g of Cu and 19.86g of Sn has to be taken. First melt Sn at 300^{0}C (As it has high wt% and M.P as231^{o}C),then add and melt the Cu at 900^{o}C.Then kept the liquid melt around 600^{0}C up to 2hrs to homogenize the eutectic solution. After this cool it with in furnace until to get solidifies alloy.

❖ Optical Microscopy - Microstructure Analysis

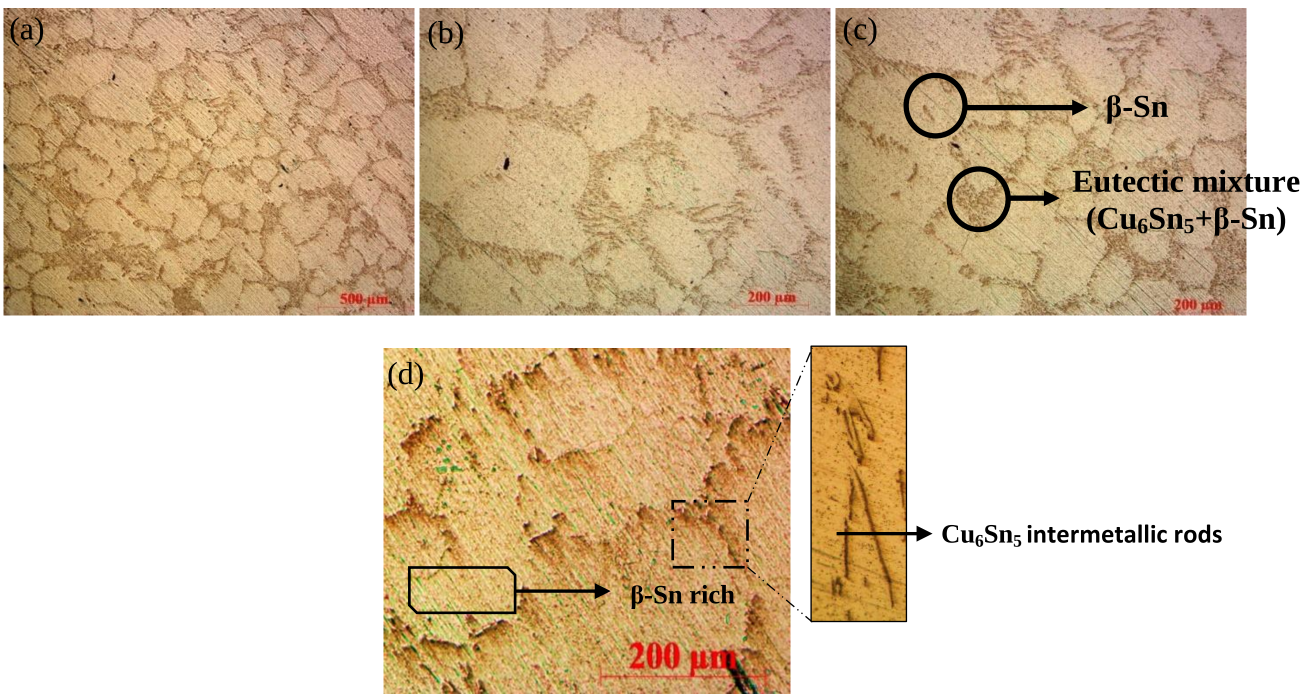


Fig 4.2 (a-d).Optical images of Sn-0.7 wt. % Cu eutectic solder alloy

- Optical microscopic figure shows, white colored soft matrix and black colored rod like structures which are expected to be β-Sn and β-Sn + Intermetallic Compounds(Cu_6Sn_5,Cu_3Sn_{10}) rich phases respectively.

2.3.2 XRD - Phase Analysis

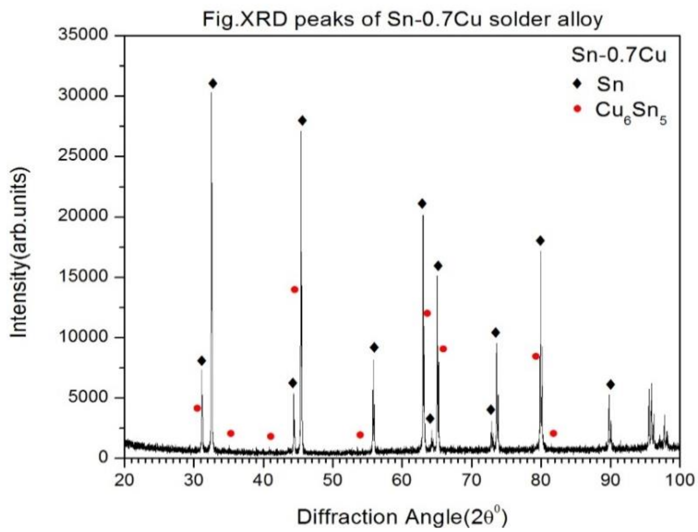


Fig 4.3. XRD peaks of Sn-0.7wt%Cu eutectic solder alloy

- From above XRD peaks we can confirm the presence of β-Sn: Tetragonal and Cu_6Sn_5-Orthorhombic phases in the Sn-0.7wt%Cu eutectic solder alloy.

2.3.3 FESEM/EDS - Compositional Analysis

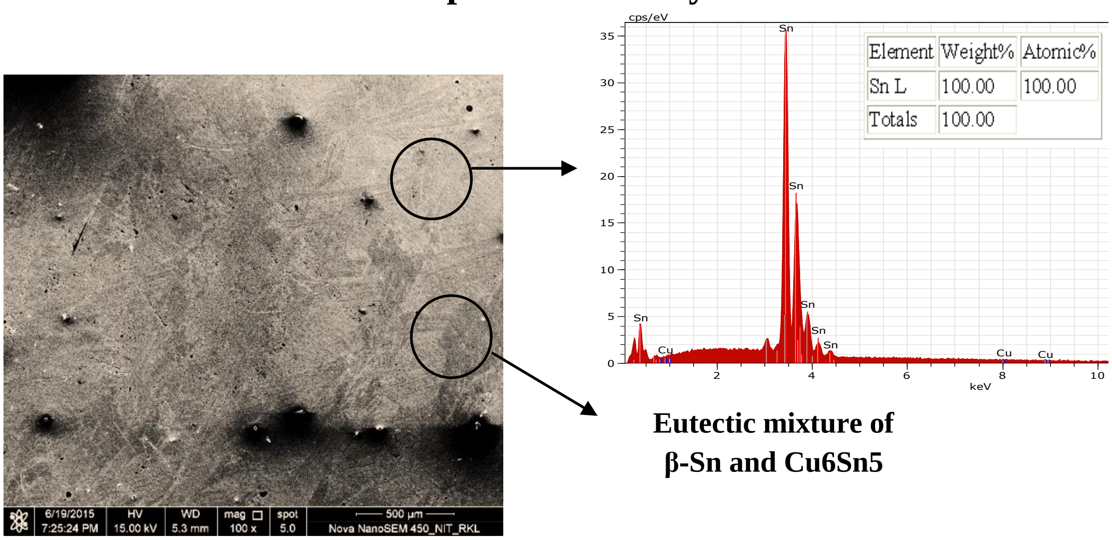


Fig 4.4. FESEM image and EDS analysis of Sn-0.7Cu solder alloy

- From above FESEM microstructure and EDS/elemental mapping analysis we can conclude that eutectic alloy has White rich phase as β Sn and Black colored region has Sn and Cu eutectic mixtures.
- The eutectic mixture is composed of both the Cu_6Sn_5 metallic rods and the Sn-rich phase. The Sn rich phase is composed of almost 0.0 wt. % Cu. Eutectic mixture containing about 0.7 wt. % Cu is found in rod like regions. The eutectic mixture is formed by a cooperative growth of theses phases.

2.3.4 Thermal Analysis

- **DSC - Melting point**

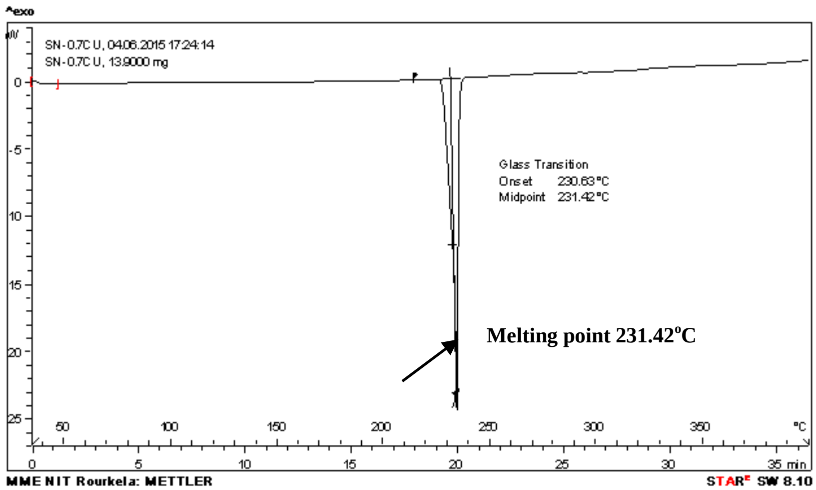


Fig 4.5. DSC analysis of Sn-0.7wt%Cu eutectic solder alloy

- Experimental Melting point: 231.42°C
- Eutectic Melting Temperature from Phase Diagram: 227°C
- From above DSC analysis we can conclude that melting point is near to eutectic temperature and undercooling is less than 10°C or so, which indicates better solidification and lesser occurrence of pasty region during processing.

2.3.5 Hardness

- **Micro Vickers Hardness Test**

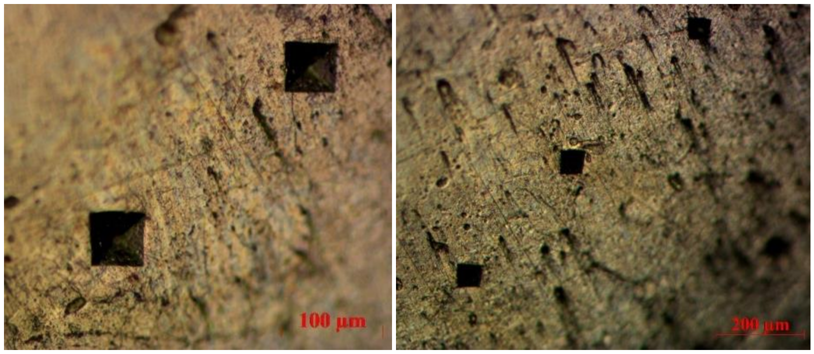


Fig 4.6. (a-b) Shows the Vickers square pyramid indentations on Sn-07Cu alloy.

- It was found that Sn-0.7wt%Cu eutectic solder alloy has the hardness value as 82.2MPa (8.4HV).This hardness is imparted mainly due to the intermetallic phases such as Cu_6Sn_5 etc. The best thing with this solder alloy is its low hardness among all the considering LFS.

2.3.6 Interfacial Analysis

- **Wettability Test/Soldering**

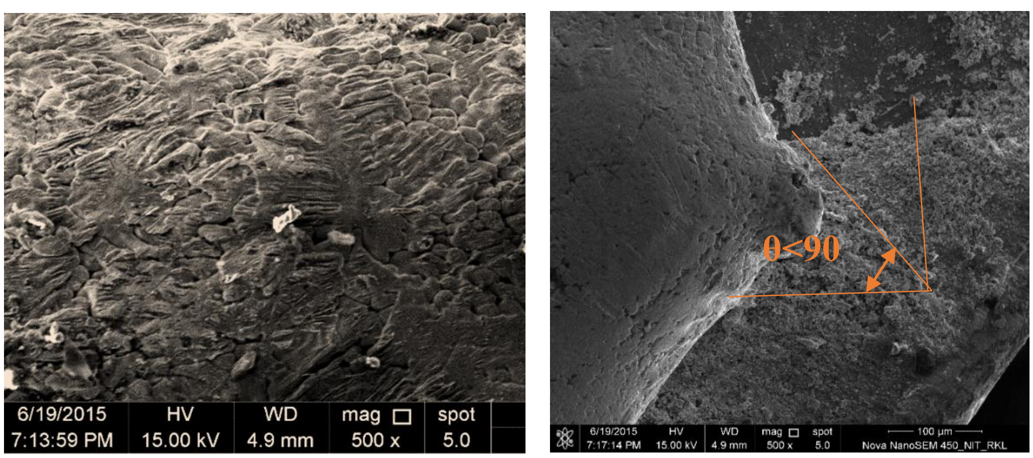


Fig 4.7 (a-b) FESEM image of Sn-0.7wt%Cu eutectic solder alloy on Cu substrate

- Fig a. shows the constructive dendritic growth of Sn and Cu_6Sn_5 inter metallic compounds from the interfacial region between solder and Cu substrate.

- Fig b. Sn-0.7wt%Cu eutectic solder alloy has the good wetting angle ($\theta<90^0$) when it was soldered on Cu substrate which supports the conclusion that it has better wettability and solderability.

2.3.7 Electrical Resistivity Test

Electrical resistivity $(\rho) = R\left(\frac{A}{L}\right)$

Where,
R= Resistance of the specimen
A= Cross sectional area
L= Length of the specimen

- It was found that Sn-0.7wt%Cu eutectic solder alloy has the value of Electrical Resistivity is 2.2948 (μΩ-cm).

2.3.8 Cost

- Sn-0.7wt%Cu eutectic solder alloy is cheap as compared with other Pb free solders such as Sn-3.5wt%Ag.For supposed to make 20g of Sn-0.7wt%Cu it just needs 100/- or so.
- Moreover among all available basic binary Pb free solders Sn-0.7wt%Cu is more ductile in nature, the factor which supports its commercial usage.

2.4 Sn-57wt%Bi solder alloy

2.4.1 Microstructure Analysis

❖ **Sn-57wt%Bi eutectic Solder alloy Phase Diagram**

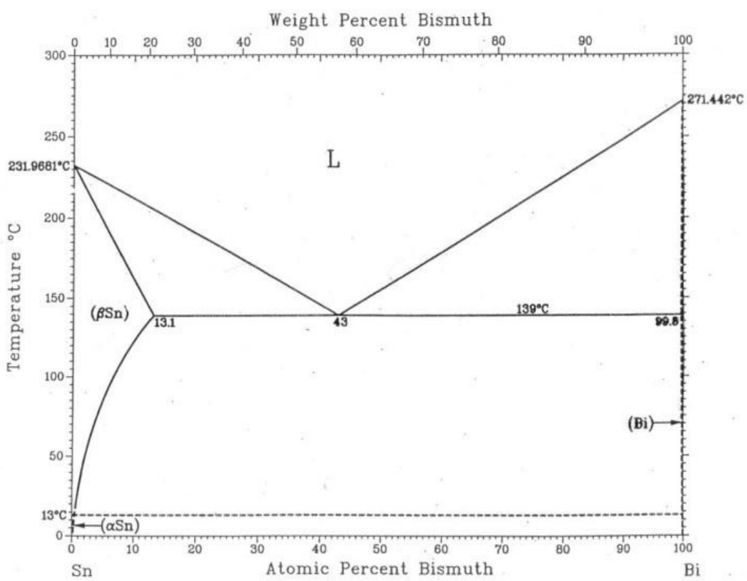


Fig 5.1 Sn-57wt%Bi eutectic solder alloy phase diagram

- Most parts of the phase diagram of this simple eutectic system are well established. At 138°C, the liquid with 43wt%Sn decomposes into the two terminal solid solutions, (Bi) and (Sn).
- However, the solubility limit of Sn in (Bi) is not reliably known although a lower value is preferred.

- Melting Point of Sn is : 232^{0}C
- Melting Point of Bi is : 272^{0}C
- Eutectic - Composition: Sn-57wt%Bi
  Temperature: 139^{o}C

❖ Experimental Sample preparation

- To prepare 10g of Sn-57wt%Bi eutectic solder alloy 5.7g of Bi and 4.3g of Sn has to be taken. First melt Bi at 800^{0}C (As it has high wt% and melting point as 231^{o}C) then add and melt the Sn at 300^{o}C.Then kept the liquid melt around 600^{0}C up to 2hrs to homogenize the eutectic solution. After this cool it with in furnace until to get solidifies alloy.

❖ Optical Microscopy - Microstructure Analysis

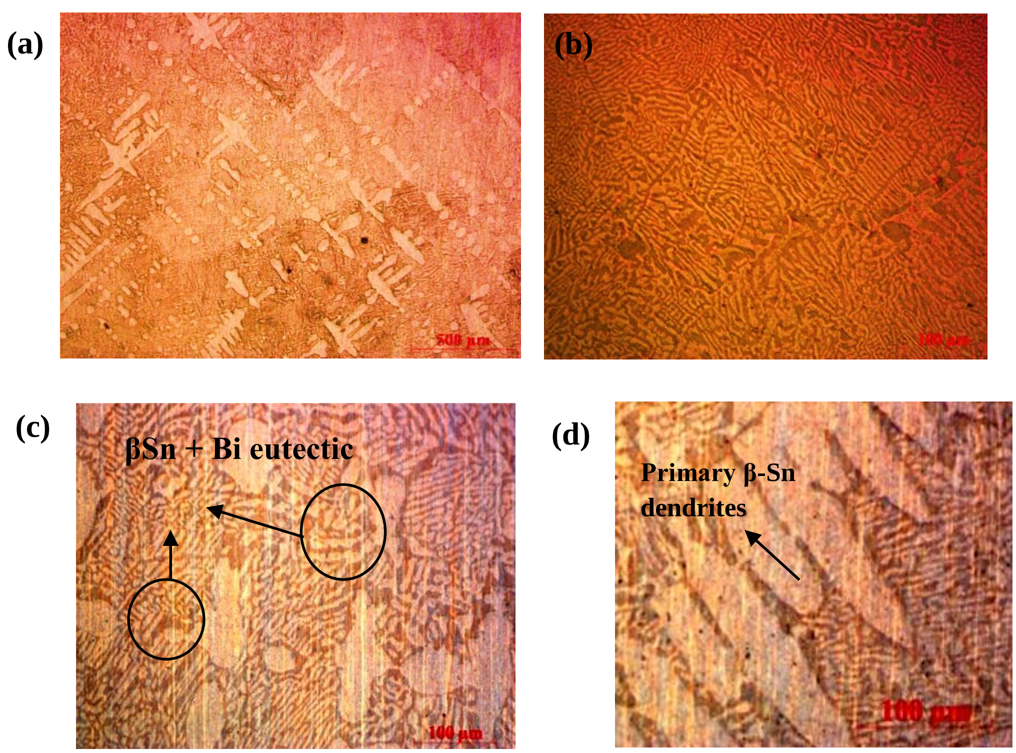


Fig 5.2.(a-d)Optical images of Sn-57wt%Bi solder alloy

- Optical microscopic figure shows, white colored soft matrix and mixture of black and white colored dendrtic structures which are expected to be β-Sn and β-Sn+Bi eutecti rich phases respectively.

2.4.2 XRD - Phase Analysis

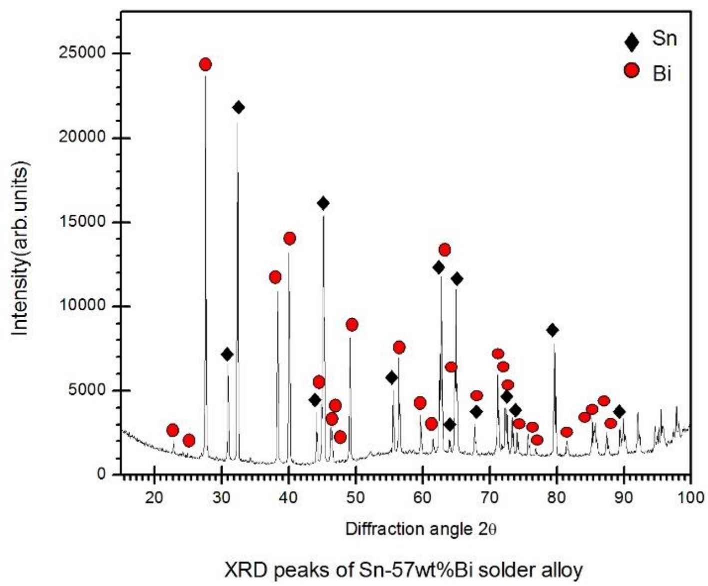
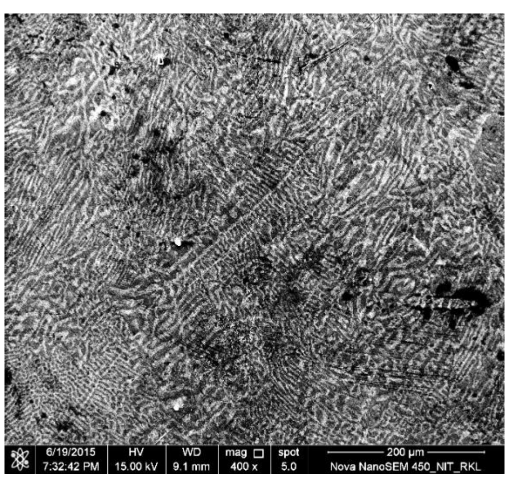


Fig 5. 3. XRD analysis of Sn-57wt%Bi solder alloy

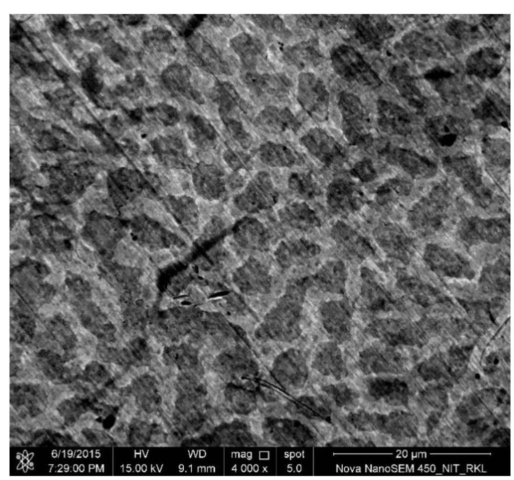
- From above XRD peaks we can confirm the presence of β-Sn: Tetragonal and Bi-Ortho rhombic phases in the Sn-57wt%Bi eutectic solder alloy.

2.4.3 FESEM/EDS - Compositional Analysis

(a)



(b)



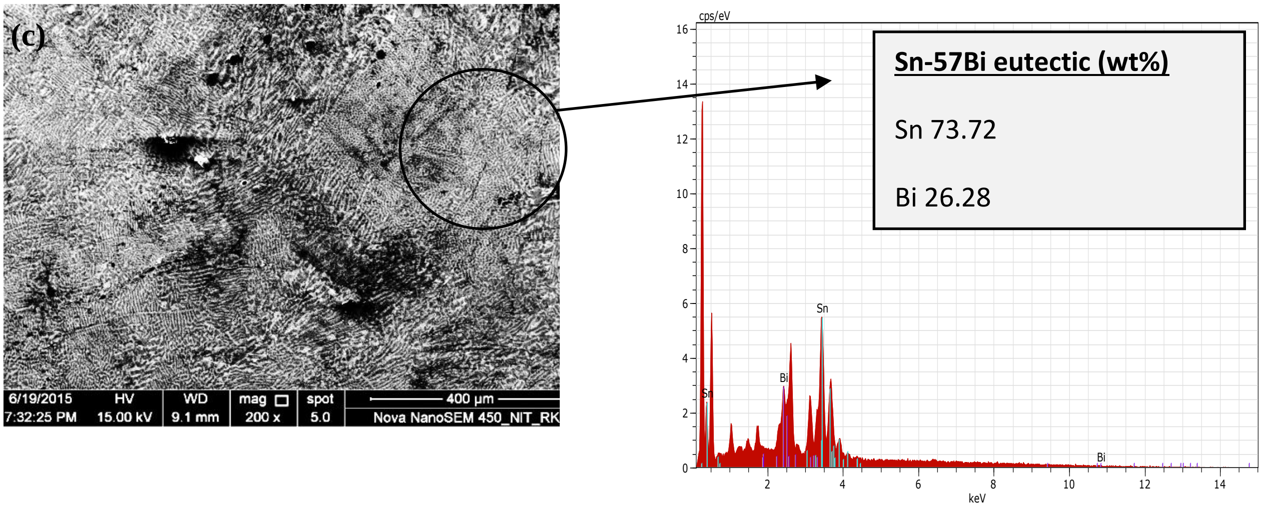


Fig 5.4. (a-b)FESEM and (c) EDS of Sn-57Bi eutectic solder alloy

- From above FESEM microstructures and EDS/elemental mapping analysis we can conclude that eutectic alloy haswhite colored soft matrix as β-Snand mixture of black and white colored dendrtic structures which are β-Sn+Bi eutecti rich phases respectively.
- Dendrites of Sn can be clearly seen in the microstructure of Sn-Bi eutectic solder alloy.
- EDS at eutectic regions shows the 73.72 wt% Sn as well as 26.28 wt% Bi which supports the eutectic composition calculations done by lever rule on Sn-57Bi phase diagram.

2.4.4 Thermal Analysis

❖ **DSC - Melting point**

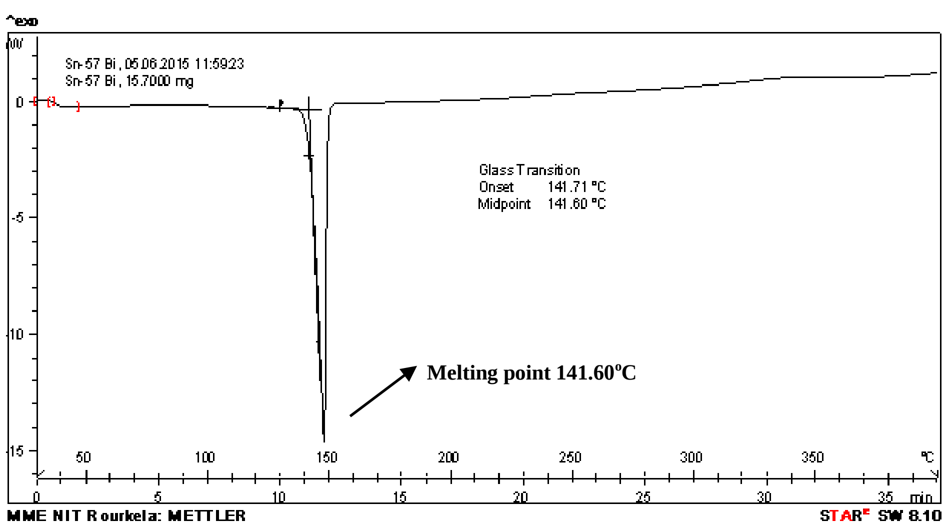


Fig 5.5. DSC analysis of Sn-0.7wt% Bi eutectic solder alloy

- Experimental Melting point: 141.60 °C

- Eutectic Melting Temperature from Phase Diagram: 139^{o}C
- From above DSC analysis we can conclude that experimental melting point value is near to eutectic temperature and undercooling is less than 10^{o}C or so, which indicates better solidification and lesser occurrence of pasty region during processing.

2.4.5 Hardness

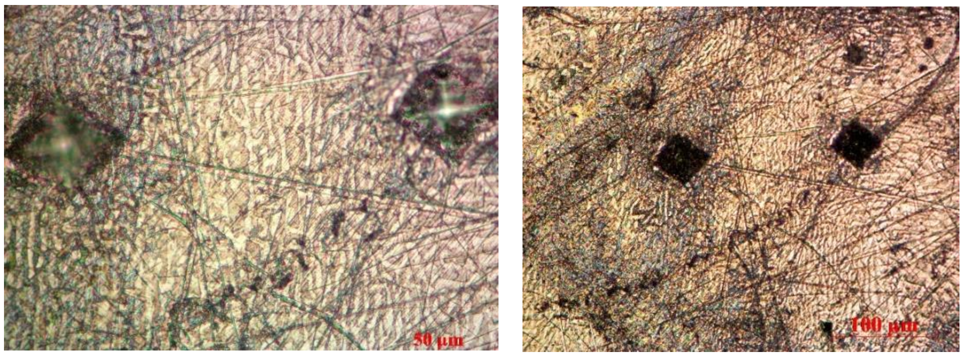
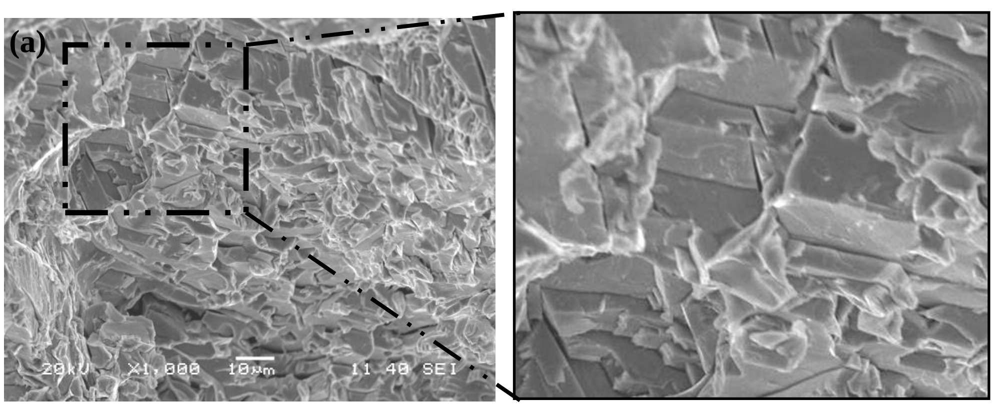


Fig 5.6.Micro Vickers square pyramid indentations on Sn-57wt%Bi eutectic solder alloy

- It was found that Sn-0.7wt%Bi eutectic solder alloy has the hardness value as 193.7 MPa (19.7HV). This high hardness value among basic Pb free solders indicates its brittleness which won't be preferred for electronic soldering applications.

2.4.6 Fractography



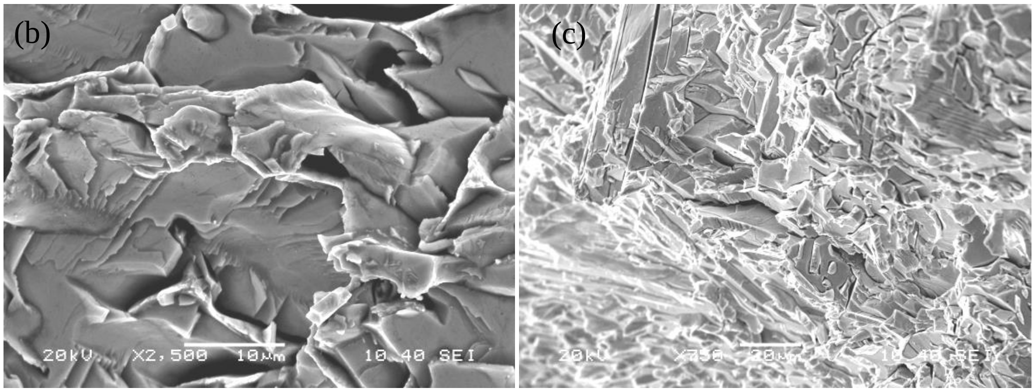


Fig 5.7 (a-c) SEM images of the impact fracture surface of eutectic Sn-57Bi solder alloy

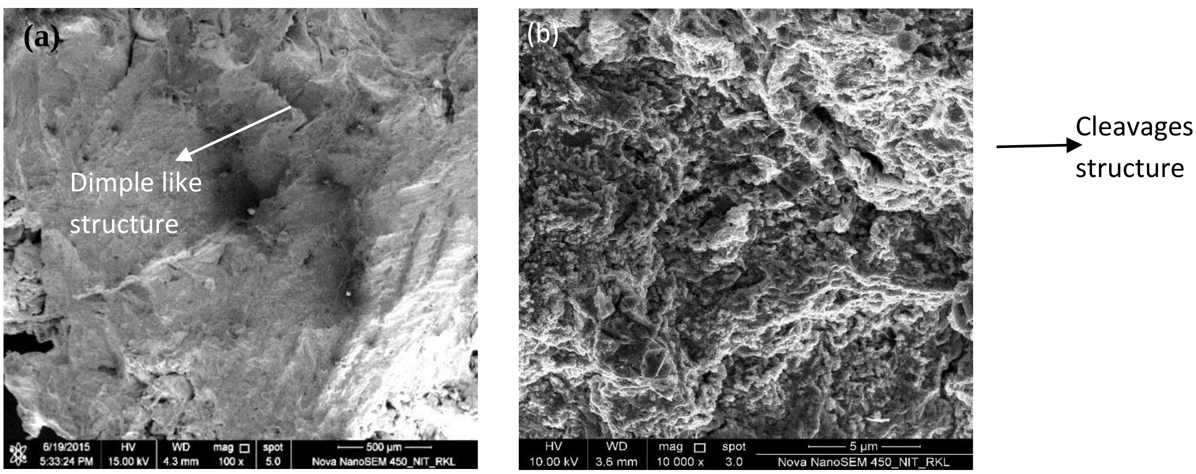


Fig 5.8. (a and b) FESEM images of Sn-57Bi tensile fractured sample

- Above FESEM images shows the cleavages and large dimples structure after fracture which confirms the ductile nature of Sn-57wt%Bi eutectic solder alloy and also supports the micro Vickers hardness value.

2.4.7 Interfacial Analysis

❖ **Wettability Test/Soldering**

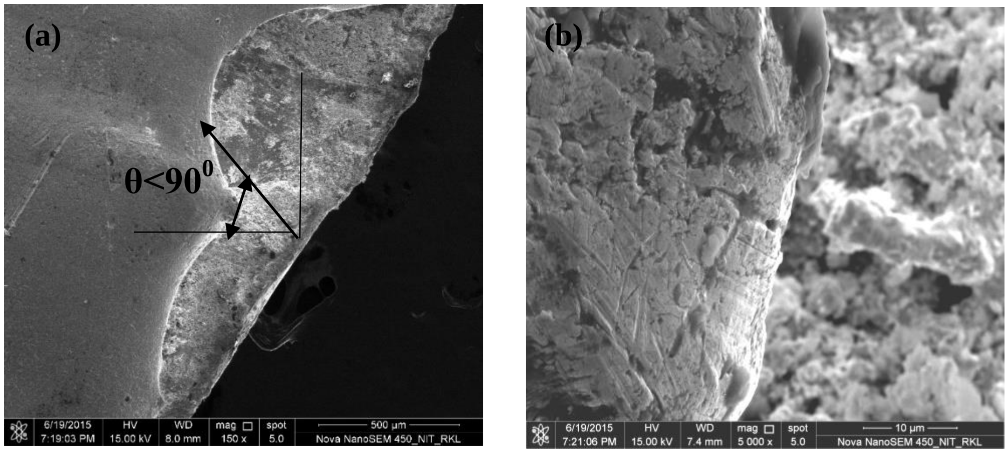


Fig 5.9 (a-b) FESEM image of Sn-57wt%Bi eutectic solder alloy on Cu substrate

- From above figure we can say that Sn-57wt%Bi eutectic solder alloy has the good wetting angle ($\theta<90^0$) when it was soldered on Cu substrate which supports the conclusion that it has better wettability and solderability.

2.4.8 Electrical Resistivity Test

Electrical resistivity $(\rho) = R\left(\frac{A}{L}\right)$

Where,
R= Resistance of the specimen
A= Cross sectional area
L= Length of the specimen

- It was found that Sn-57wt%Bi eutectic solder alloy has the value of Electrical Resistivity is **14.1735 (ρ) (μΩ-cm).** The increase of electrical resistivity in the case of Sn-Bi can be attributed to the high electrical resistivity of Bi. The electrical resistivity of Bi is 115 μΩ.cm.

2.4.9 Cost

- Sn-57wt%Bi eutectic solder alloy is cheap as compared with other Pb free solders such as Sn-3.5wt%Ag but not much than Sn-0.7wt%Cu solder.

2.5 Sn-37wt%Pb Solder alloy:

2.5.1 Microstructure Analysis

❖ Sn-37wt%Pb eutectic lead free Solder alloy Phase Diagram

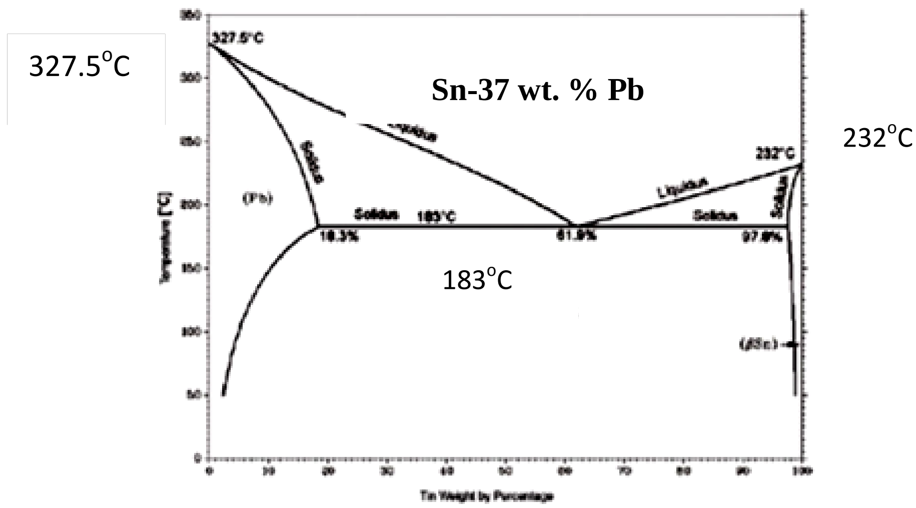


Fig 6.1 Sn-37wt%Pb eutectic solder alloy phase diagram

Eutectic and near eutectic Pb-37 wt. % Sn solder alloys are the most commonly used solder alloys that have been used in the microelectronics industry due to its reliability. The material that has been traditionally used as solder for the electronic packaging is the near eutectic 60Sn/40Pb or the eutectic 63Sn/37Pb solder alloy. Pb/Sn solder alloy has a low melting point (183^{o}C) and has good wetting characteristics. The Pb/Sn solder adheres well to Cu substrates. The Pb/Sn solder is a two phase alloy.

- Melting Point of Sn is : 232^{0}C
- Melting Point of Pb is : 327.5^{0}C
- Eutectic - Composition: Sn-37wt%Pb
  Temperature: 189.04^{o}C

❖ Experimental Sample preparation

To prepare 10g of Sn-37wt% Pb eutectic solder alloy we have taken a Cu substrate and melt the Pb solder wire by soldering method. Drops of liquid melt Pb has poured on the Cu substrate. Then kept the liquid melt around 189.04^{0}C up to homogenize the eutectic solution. After this cool it in room temperature until to get solidifies alloy. Then we will get a solidified and homogenized Sn-Pb solder alloy sample.

❖ Optical Microscopy - Microstructure Analysis

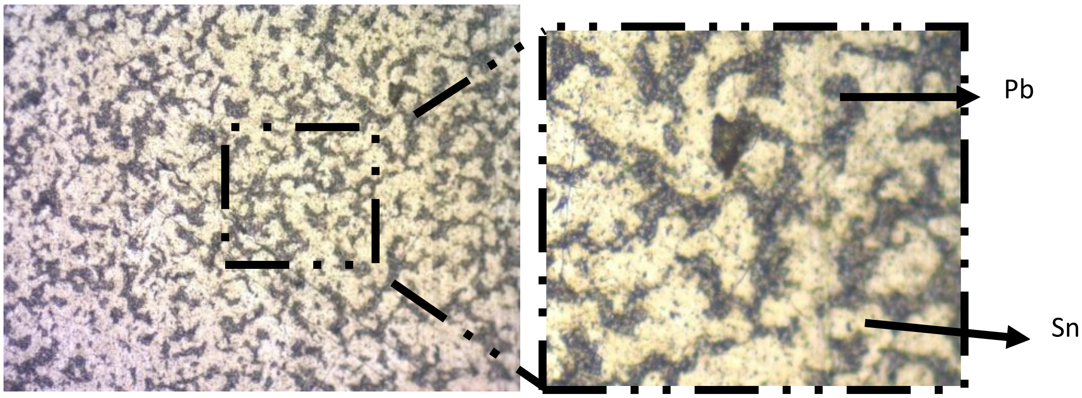


Fig 6.2.Optical images of Sn-37wt%Pb solder alloy

- Optical microscopic figure shows, white colored soft matrix and mixture of black and white colored structures which are expected to be Sn and Pb eutecti rich phases respectively.

2.5.2 XRD - Phase Analysis

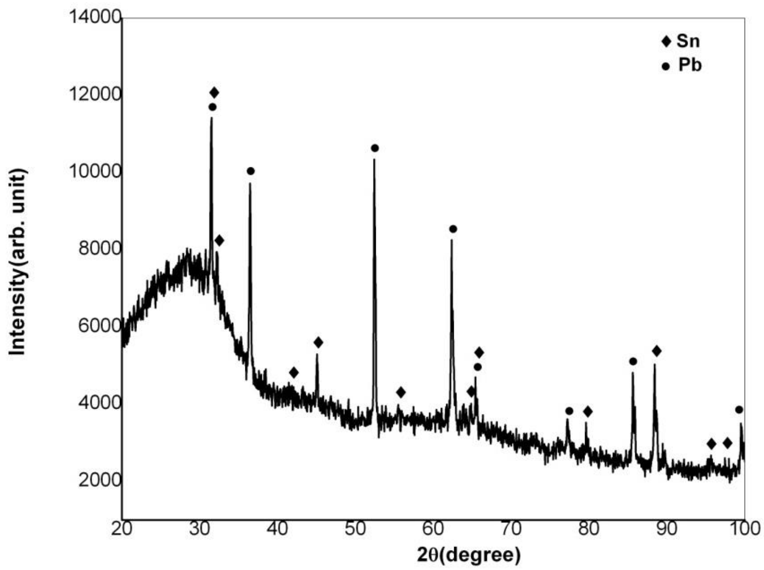
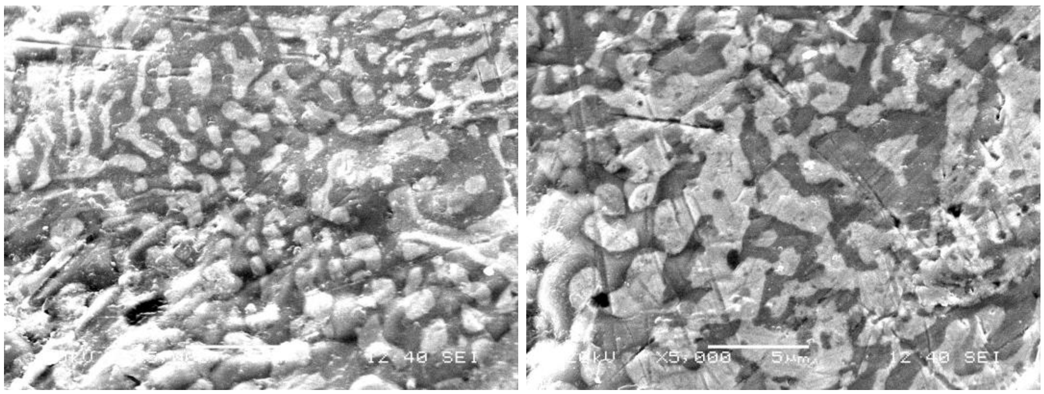


Fig 6.3 XRD analysis of Sn-37wt%Pb solder alloy

- The x-ray diffraction plots of the Sn-37wt%Pb 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 Pb-Sn. 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.

2.5.3 FESEM - Analysis



- From above FESEM microstructures analysis we can conclude that eutectic alloy has white colored soft matrix as Sn and mixture of black and white colored dendrtic structures which are Pb eutectic rich phases respectively.
- Dendrites of Sn can be clearly seen in the microstructure of Sn-Pb eutectic solder alloy.

2.5.4 Thermal Analysis

❖ **DSC - Melting point**

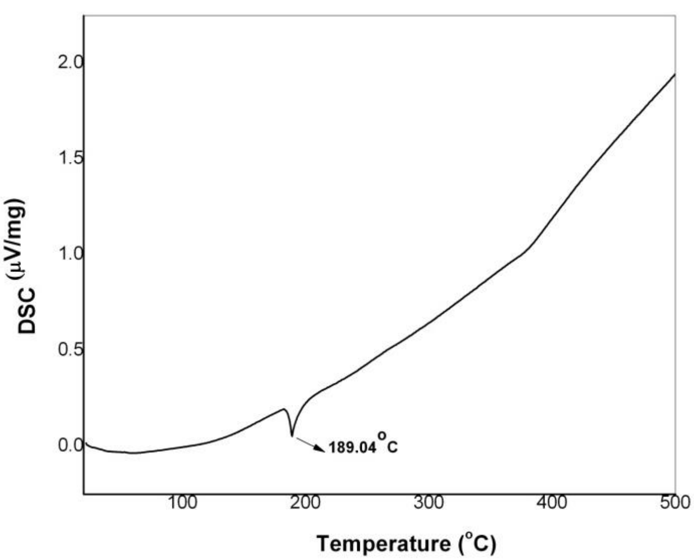


Fig 6.5 DSC analysis of Sn-37wt%Pb eutectic solder alloy

- Experimental Melting point: 189.04°C

- Eutectic Melting Temperature from Phase Diagram: 183°C.
- From above DSC analysis we can conclude that experimental melting point value is near to eutectic temperature and undercooling at room temperature, which indicates better solidification and lesser occurrence of pasty region during processing.

2.5.5 Hardness

- **Micro Vickers Hardness Test**

- Micro Vickers square pyramid indentations on Sn-37wt%Pb eutectic solder alloy.
  - It was found that Sn-37wt%Pb eutectic solder alloy has the hardness value as **108.9**MPa. This high hardness value among basic Pb solders indicates that there is no brittleness which will be preferreble for electronic soldering applications.

2.5.6 Electrical Resistivity Test

Electrical resistivity $(\rho) = R\left(\frac{A}{L}\right)$

It was found that Sn-37wt%Pb eutectic solder alloy has the value of Electrical Resistivity is **6.56(ρ) (μΩ-cm).**The increase of electrical resistivity in the case of Sn-Pb can be attributed to the high electrical resistivity of Pb. The electrical resistivity of Pb is 21 μ**Ω**.cm.

2.5.7 Interfacial Analysis

- **Wettability Test/Soldering**

Sn-37wt%Pb eutectic solder alloy has the good wetting angle ($\theta<90^0$) when it was soldered on Cu substrate which supports the conclusion that it has better wettability and solderability.

4.Conclusions

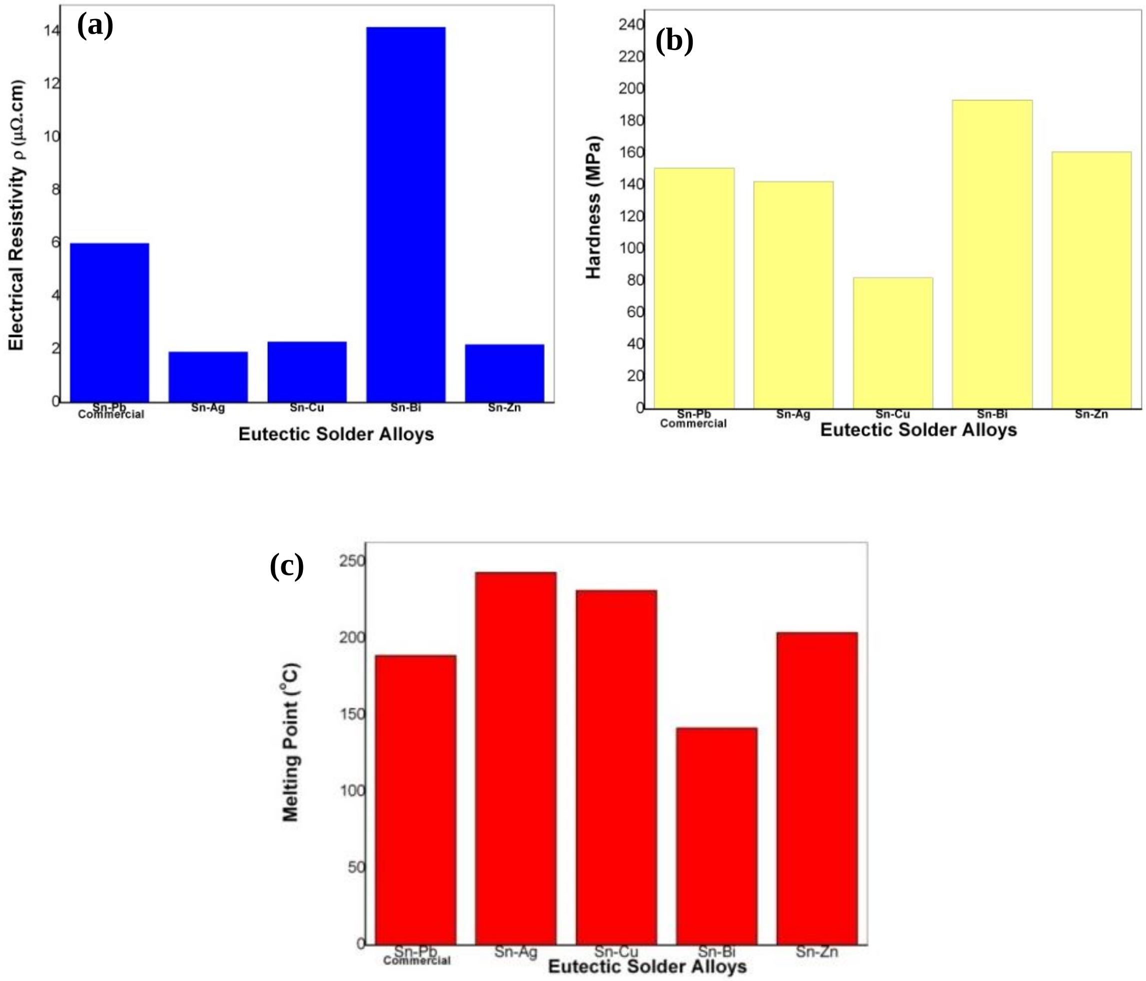


Fig 7.0 Comparison of (a) Electrical resistivity (b) Hardness of eutectic solders (c) Melting Point

Table 2: Melting point, Electrical resistivity, Hardness of the various eutectic solder alloys

Alloy	Melting Temperature (^{o}C)	Hardness (MPa)	Electrical Resistivity (ρ) (μΩ-cm)
Commercial Sn-37Pb	183	150.98	6.016
Sn-3.5Ag	243.28	142.5	1.9143
Sn-0.7Cu	231.42	82.2	2.2948
Sn-57Bi	141.60	193.7	14.1735
Sn-8.8Zn	204.05	161.1	2.1934

- Sn-57wt%Bi has low melting temperature, high hardness and high electrical resistivity than the all considered LFS as well as Sn-37Pb.

- Intermediate phases in Sn-0.7Cu and Sn-3.5Ag are formed by peritectic or peritectoid reactions. Among all of the IMCs of Sn-0.7Cu mostly the Cu_3Sn and Cu_6Sn_5.
- Phases are of interest for solder applications. This is because all of the copper-rich intermediate phases decompose in eutectoid reactions at temperatures above 350°C. Both Cu_6Sn_5 and Ag_3Sn are highly non-stoichiometric, has orthorhombic crystal structure. These have has rod like appearance in microstructure and increases the hardness of respective binary alloy system due to their brittle nature. In case of Sn-8.8Zn and Sn-57Bi no IMCs are found. Sn dendritic eutectic mixtures and Zn rods are observed in respective solder systems. The eutectic mixture is formed by a cooperative growth of the binary phases.

- The reported values of electrical resistivity of eutectic Sn-37Pb alloy is 14.5l μΩ.cm. The increase of electrical resistivity in the case of Sn-Bi can be attributed to the high electrical resistivity of Bi (~115 μΩ.cm.)Both Ag and Cu have very low electrical resistivities as compared to Pb, Bi and Zn. This is why both Sn-Ag and Sn-Cu eutectic solder alloys gives the lowest electrical resistivity among all the solder alloys considered here. It is possible to achieve a lower resistivity in the case of eutectic Sn-Ag, Sn-Cu and Sn-Zn solder alloys as compared to the eutectic Sn-37Pb alloy.

- The obtained value of hardness of the eutectic Sn-37Pb alloy is 151 MPa. Sn-57wt% Bi has higher hardness among all considered LFS as well as Sn-37Pb.Because of the presence of soft and ductile FCC metals Ag and Cu, the solders Sn-Ag and Sn-Cu have low hardness values than Sn-37Pb alloy. In case of higher hardness values of Sn-Zn and Sn-Bi can be attributed to the presence of non-cubic metals Zn (HCP) and Bi (Rhombohedral).Mostly all of the considered LFS shows the dimples and cleavage like fracture surface and it is indicating their ductile nature.

- The experimental melting temperature of eutectic Sn-37Pb alloy is 183^oC. Sn-57wt% Bi has lower melting point (139^0C) among all considered LFS as well as Sn-37Pb.Itcan be due to the existence of higher solid solubility between Sn and Bi. Sn-57Bi shows the excellent mobility in the molten state and zero shrinkage upon solidification and it is also more compatible for step soldering process. Both Ag and Cu have very high melting temperatures as compared to the Pb, Sn, Bi and Zn. Along with this formation of intermetallics having higher free energies than the system leads to the higher melting temperature of the Sn-Ag and Sn-Cu eutectic solder alloys. Even though no IMCs are present in eutectic Sn-Zn, lower solubility and higher oxidation tendency of Zn contributes the somewhat higher melting point than the Sn-Bi as well as Sn-37Pb.

- The intermetallic that forms first during soldering plays the important role in solderability and wetting. The solder alloys Sn-Ag and Sn-Cu shows better wettability on Cu substrate. Their intermetallic compounds such as Cu_6Sn_5, Ag_3Sndecreases the interfacial energy which helps in good wetting and increases the reliability of solder joint. But the formation of large amount of brittle IMCs decreases the interfacial bonding between solder and substrate. Sn-Bi and Sn-Zn shows the lower degree of wettability on Cu substrate as compared to other LFS this because of the presence of hard Bi phase and poor oxidation resistance of Zn and Sn respectively. Sn-57wt%Bi solder paste with suitable RMA(Rosin Mildly Activated) flux wets Cu matrix with a wetting angle of 35^0 and had a 15^0C under cooling during solidification which may comparable with Pb-Sn solder.

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