

Effect of Ag on Sn-Cu Lead Free Solders

A thesis submitted in partial fulfillment of the
requirements for the degree of

Master of Technology

in

Metallurgical and Materials Engineering

Submitted by

RAJNISH KUMAR

(ROLL NO-212MM1450)



Department of Metallurgical and Materials Engineering
National Institute Of Technology, Rourkela
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Under the guidance and supervision of

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2014



**National Institute Of Technology
Rourkela**

Certificate

This is to certify that the thesis entitled, “**Effect of Ag on Sn-Cu Lead free solders**” submitted by **Rajnish Kumar (212MM1450)** in partial fulfillment of the requirements for the award of Master of Technology in **Metallurgical and Materials Engineering** at the National Institute of Technology, Rourkela is a bonafide research work carried out by him under my supervision.

To the best of my knowledge, the matter embodied in the thesis is based on candidate’s own work, has not been submitted to any other university / institute for the award of any degree or diploma.

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Abstract

Lead free solders are expected to replace the traditional Sn-Pb alloys due to environmental concern. The Sn-Cu lead free solder alloys are found to be a potential alternative to the Sn-Pb alloys compared to other solders. Eutectic Sn-0.7Cu (wt.%) solder has been used for interconnecting and packaging electronic component due to the good wettability between the Sn-Cu solder and the Cu substrates. Three compositions Sn-0.7Cu, Sn-1Cu and Sn-2Cu and three compositions containing Ag, Sn-2Ag-0.7Cu, Sn-2.5Ag-0.7Cu and Sn-4.5Ag-0.7Cu were considered here for the study. Ag was added to the eutectic Sn-0.7Cu composition in order to decrease the melting temperature of the eutectic alloy and to enhance the mechanical properties of the alloy such as hardness. But the amount of Ag was more increases hardness was decreases. The wettability of the Sn-Cu solder on the Cu substrate was also enhanced by the addition of Ag. Structure and morphology of the solder alloys were analyzed using a SEM, XRD and EDX. The microstructural observation reveals the formation of β -Sn matrix and presence of intermetallic phases like Cu_6Sn_5 and Ag_3Sn . Furnace cooling was employed for solidifying the lead free solder alloys. Thermal analysis of the solder alloys were done with the help of a differential scanning calorimeter (DSC). Trace additions of Ag have been found to significantly reduce the melting temperature of these alloys.

Keywords: Sn-Cu, Sn-Cu-Ag, lead free solder, eutectic, differential scanning calorimeter

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Nomenclature

Ag	Silver
Cu	Copper
DSC	Differential Scanning Calorimetry
EDS	Energy-dispersive X-ray spectroscopy
EPA	Environment Protection Agency
FESEM	Field emission scanning electron microscopy
LFS	Lead free solder
Pb	Lead
PCB	Printed circuit board
SAC	Sn-Ag-Cu
SEM	Scanning electron microscopy
Sn	Tin
WHO	World health organization
XRD	X-ray Diffraction

Chapter 1

Introduction

1. Introduction

Eutectic Sn-Pb solder alloys have been considered the most widely used material for interconnecting and packaging electronic components. Pb is a major constituent of solder alloys and traditional Sn-Pb solder alloys have been found to be most popular materials because they have a low melting point, low material cost, good wettability and easily available. But, all these advantages a rapid rise in research for finding a suitable LFS has occurred due to inherent toxicity of Pb, which has proved to be a hazard to environment and human health. As a result attention has been focused on the potential of lead free solder which can provide better mechanical strength as well as reliability. Elements that can be used in lead free soldering are Cu, Ag, Zn, Bi, Sb, Ni, In, Ge, Al and Cr in a combination with Sn by making a binary, ternary or quaternary system [1,2].

Many number of Pb-free solder alloys have been developed, such as Sn-Zn, Sn-Ag, Sn-Sb, Sn-Cu, Sn-Bi and Sn-Ag-Cu alloys. Out all the available alternatives the most suitable lead solder alloys are considered to be eutectic Sn-0.7wt.% Cu (sn-0.7Cu) system. Due to better properties such as, good wettability, relatively low melting temperature and relatively good solderability, low-cost, it has been already introduced in electronics and packaging industry. As a comparison of other LFS alloys, eutectic Sn-0.7Cu alloy systems are a better mechanical property that's why they are used in iron, dip and wave soldering operations [3]. The eutectic Sn-0.7Cu alloy is one of the Sn based, lead-free solder alloys, with small amounts of Cu-Sn intermetallic compound Cu_6Sn_5 precipitated in the Sn matrix. The eutectic Sn-0.7Cu alloy has melting temperature of 227°C . But as a comparison of Sn-Pb solders some disadvantages are there in eutectic Sn-0.7Cu binary alloy system such as high melting

temperature, poor wettability, insufficient oxidation and formation of tin whiskers which prevents the application in electronic packaging industries [4].

. By adding Ag the melting point of system gets lower and increases the wettability of Sn-Cu based solders on Cu substrate. Formation of IMC (Ag_3Sn) can increase if the amount of Ag (wt. %) is more. However Ag_3Sn is of brittle characteristic which may reduce the reliability of the solder joint. It was observed that more amount of Ag_3Sn can effect adversely on the plastic-deformation properties as well as plastic strain localization at the boundary between the Ag_3Sn plates and restricts the formation of β -Sn phase [5]. More amount of Ag_3Sn can also reduce the fatigue life of solder joints. Hence it is recommended that the amount of Ag should not be more than 2-3.9 wt. % in SAC solder alloy. Another important factor is the Cu content in the SAC solder. This is mainly related to the pasty range ΔT i.e. difference between liquids temperature (T_{end}) and solidus temperature (T_{onst}). ΔT is highly sensitive to the copper content, but not more sensitive to silver in SAC solder ternary alloy system. It has been reported that during wave soldering large pasty range increases the vibration. It also increases the fillet lifting phenomena, porosity, differential thermal contraction during solidification and hot tearing due to alloy shrinkage. So the consideration of pasty range the Cu content should not be greater than 0.9wt% in SAC solder [6].

1.1 Objectives of the work

Objective of this work is to manufacture the different type of LFS alloys and to investigate the effects of Ag addition on the microstructure, melting behavior, pasty range and wettability of solidified Sn-Cu solder alloy. Objective of this thesis are –

1. Determination of microstructure and elemental analysis of LFS alloys by scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS or EDX).
2. Phase Analysis by X-ray Diffraction Techniques (XRD).
3. Thermal analysis of LFS alloys by Differential Scanning Calorimetry (DSC).
4. Determination of hardness by Vickers hardness tester machine.

Chapter 2

Literature Review

2. Literature Review

2.1 Definition and metallurgical aspects of Soldering

2.1.1 Definition

Soldering is technically defined as the joining of base metals through the use of heat and a filler metal with a melting temperature well below those of the substrates and typically less than 450°C. Capillary action or capillary attraction draws the molten filler metal in to the joint [7].

2.1.2 Metallurgical aspects

A solder

- Wets the base metals.
- Flows freely over the surfaces i.e., spread and makes contact with the joint opening.
- Is drawn in to the joint by capillary action.
- Solidifies as a sound, firmly adhering film.
- Has adequate mechanical strength.

2.2 Most commonly used soldering methods

- (a) **Soldering iron:** - A soldering iron is consist of a copper rod with a thin tip. It is used for flattening the solder material. Soldering iron is heated by internal electrical resistance furnace. The range of power rating of furnace may vary from 15W for electronic applications and 200W for sheet metal joining. For soldering purpose the soldering iron method is most convenient but as a comparison of other method this method is slow.

(b) Dip soldering: - In dip soldering, a large amount of solder is melted in a closed tank.

Parts that are to be soldered are first cleaned properly. After that, according to the requirement the cleaned parts are dipped in to a flux bath. Now, the parts are dipped in to the molten solder pool and lifted with the soldering complete.

(c) Wave soldering: - Wave soldering method is differ than the dip soldering method. In

this method solder is also be melted in a tank but the parts that are to be soldered are not dipped into the tank. A wave is generated in the tank. Due to this wave solder comes out and makes the necessary joint. Wave soldering method is mainly used in printed circuit board (PCB) assemblies. This is normally a continuous process with the PCB being continuously moving on top of the solder tank and the waves become continuously generated. It is used for mass production of the electronic equipment.

There are also other methods available for soldering, such as torch soldering, oven soldering, resistance soldering, induction soldering and infrared soldering [8].

2.3 Classification and material of solder

Soft or hard are the basic characteristics of solder materials. Soft solders typically contain Tin and lead. Some other materials like Bismuth, indium and cadmium are also the major components of soft solders. While in case of hard solders zinc, gold, copper etc are the major components. Other criteria to deviate the characteristics of soft and hard solders are their melting point. Soft solders melt around 350°C while hard solders melt approximately above 350°C.

Now a day, in the electronics industry lead-tin (Pb-Sn) solder is a very important material but Pb is toxic and has adverse effects on the human beings and environment.

2.4 Adverse effects of lead in human life, environment and other species

2.4.1 Adverse effects of lead in human life

Lead is a useful metal that has been used by the human in daily life, but lead and its compounds have been found to have greatest dangerous of human life according to the Environment Protection Agency (EPA). When the level of Pb in the human blood cells increases more than the normal concentration then it is called the lead poisoning occurs.

Lead comes in contact with the human body over a period of time it forms bond with proteins in the body and retards their normal functions. Lead is the property which absorbed the calcium and interface with the production of blood cell. Calcium is essential for improvement of bones and teeth. It is also be useful for blood vessel function, nerve, and muscle contraction. Red blood cells are damaged by lead and thus decrease the capacity of carrying oxygen which in turn causes anemia. Once lead gets inserted to human body it can be easily spread in the body with the help of minerals like iron, zinc, calcium etc. hence it is treated as dangerous element. Lead is the main factor which affects the major functions of body by affecting major organs like heart, kidney etc. Lead also affects the reproductive system of male and female both. In male when the lead concentration increases more than 40 μ g/dl, then sperm count decreases drastically. In female, lead is more dangerous in the case of pregnant women and may be harmful effect to the child [9]. It has been found that lead exposure increases the high blood pressure, heart rate variability, coronary heart disease and heart attack.

Lead containing paint we use in the house is also be harmful, especially children as a comparison of adults. In children lead is most damaging when they are under the six years. It has

been found that when the level of Pb increases in the children blood cells , then it decreases the intelligence, attention, memory, reading, muscle growth, bone growth, behavior issues and arithmetic ability. In the cases of extremely high lead level seizures and unconsciousness will also be there. According to the world health organization (WHO), if the lead level in blood increases more than 10 μ g/dl, it may decreases the tissue development and harmful effect the human health [10].

2.4.2 Lead in environment and other species

The waste disposal of electrical and electronic assemblies containing lead and its compounds are harmful effect to the environment. The lead containing components are disposed in solid waste landfills. These waste components are come in contact with the ground water. The purification methods which are commonly used are not suitable for completely removes the lead content from the water. Technically it is difficult to explain how lead forms bond with water. However a study has been shown that PbO converts to PbCO₃ in presence of CO₂ and Cl. Two major suppliers and users of printed circuit board (PCB) assemblies in the world market is USA and japan. The current research shows that the market of printed circuit board will be double after the ten years duration. So the proper disposal of these components is big issue and doesn't ignore it. Recycling of this component is one of the major solutions to the above problem. But the use of recycled lead is some limitations when we use. If recycled lead is used in the electronics circuit it emits the higer amount of α -particle comparison of pure lead and it affects the performance of electronic circuits [11].

The lead level in our environment is increases day to day due to rapid growth of industry. Lead content in the water is 0.003 mg/l is said to be normal and does not affect the ecosystem. The famous hussain sagar lake is also be contaminated by the lead, this is possibly

due to the industrial waste of the city. During “Green Revolution”, the higher lead containing pesticides is used in the Punjab and Haryana. Resulted high contamination is there in water and soil. Lead is present in soil, in the form of soluble and insoluble salt. Deposition of lead on the ground is transferred to the top layer of the soil surface, where it may be retained for long times. Lead is mixed with soil and reaches in to the root zone. It has been found that lead has been continuously move into the micro-organism and affected the food chains. Pb reacts with some important functional groups of enzymes and retards their normal operation, some of which helps in photosynthesis and nitrogen assimilation. However lead toxicity is not severe in presence of organic and inorganic salts containing potassium and phosphates in a few cases [12].

Animals are also be affected by the lead poisoning. Lead directly affects the central nervous system of the animal and stops their ability to synthesize red blood cells. The hunters which are generally be used lead bullets for hunting wild animals. The predators that eat those hunted animals are also be a big risk. Turkey vultures and California condors, the two critically endangered species are also affected by lead poisoning when they eat dead bodies of animal shot with lead pellets [13]. In many countries like the USA and Canada lead shot has been banned.

2.5 Source of exposure

There are many sources of lead in our environment. The most common sources are following:

- (a) **Lead paint:** - Main source of lead paint is lead. In order to improve the durability, drying speed, and to protect the surface corrosion lead carbonate [$PbCO_3 / Pb(OH)_2$] is added in the paint. It is mandatory to keep it out of the reach from children as it affects more to them. Lead dust from peeling, chipping and cracking will collect on the floors [14].

(b) Drinking water: - The main source of lead in drinking water is lead containing pipes, faucets and lead containing solder which is used during repairing of pipes. In your home if older pipes are there, then before using run the water for 60 seconds every morning. For drinking purpose don't use the hot tap water. Dissolution of lead in water is depends upon the acidic nature of water, amounts of minerals in the water, temperature and time duration of water stay in the pipes. In USA 14-20 % of lead poisoning occurs due to drinking water [15].

(c) Lead at work: - It is advised for the workers who work in lead using industry like battery manufacturing, glass production, pipe fitting etc. must be careful. [16]. They must take shower, change clothes and shoes periodically. Should not contaminate their car.

(d) Contaminated soil: - It is the common source of lead. Leaded gasoline and industrial operations like smelters are the possible sources of contaminated soil. Another common source of lead is engine oil, lunch boxes, dishwasher and jewelry.

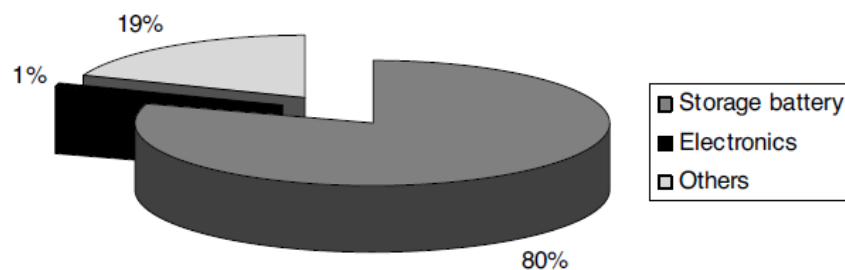


Fig. 2.1 Lead consumption

2.6 Legislation

On Friday October 11, 2002 European Community Members (currently France, Germany, Italy, Austria, Denmark, Belgium, Finland, Spain, Portugal, Sweden, Greece, Holland and the UK) banned the use of some harmful materials or substances in electrical and electronics equipment's. It has been decided that four heavy metals (lead, cadmium, mercury and hexavalent chromium) will not be used further from 1 January 2004. In the US laws have been introduced regarding elimination of Pb [17]. In Japan, the use of lead has not been banned yet. However their laws prohibit lead from being sent to the landfills and other waste disposal yards. Many of Japanese companies have started to respond to this and set their own ideas for producing lead free equipment's. Seiko Epson Corporation ceased using Pb bearing solders in PCBs and other components since March 2002. In India there is no such law that prohibits using lead and its components. But the toxicity and harmful effects of lead on human health should not be ignored. In near future we may only have two options (a) 100% recycling of lead or (b) use of lead free equipment's [18].

2.7 Importance of tin in solder

Tin is silver white color metal with soft, ductile, and nontoxic. It has been found that tin has good corrosion resistance in air, lubricity and transform in to useful alloys. Molten tin is good wettability and adheres readily to clean steel, iron, copper and copper based alloys. That's why tin based solders are excellent.

Tin has exceeded the liquidus range by few metals because low melting point as well as high boiling point. Tin formed the new intermetallic compounds when

melted with other metals. Many metals such as copper, silver, nickel, palladium and gold are completely soluble in tin liquid and form the new intermetallic compound. There are two types of tin such as white (β) and gray (α) tin. White tin is metallic and more useful as compared to β -tin. But β -tin acts as a semiconductor as well as good electrical and optical properties. It has been found that allotropic transformation occurs at 13°C and it is a very slow process. In this transformation such as metal (β -tin or white tin) changes into a semiconductor (α -tin or gray tin) volume will increase up to 27%. Due to large volume changes cracking will propagate in the Sn microstructure. Whisker growth (single crystal growth appears like fine wire) also takes place in tin at 51°C . In whisker growth β -tin is grown due to internal stress and strain. Whisker growth is not affected more in solder properties but long whiskers may cause short circuits in printed circuit assemblies [19].

2.8 Role of lead in Sn-Pb solder

In the electronics industry Sn-37Pb (eutectic composition) or Sn-40Pb solder is mainly used. The addition of Pb in Sn changes the material properties, which are

- Pb decreases the melting temperature of Sn-Pb solder, when its content increases.
- With the addition of Pb thermal and electrical conductivity decreases but density and coefficient of thermal expansion decrease in Sn-Pb solder.
- By diffusion process Pb makes intermetallic compounds with metals such as Sn and Cu.
- Pb decreases the surface tension of pure Sn but improves the wetting property.
- Viscosity of Sn-Pb solder significantly decreases when the content of Pb increases.
- Addition of Pb reduces the whisker growth in Sn.
- Pb inhibits the transformation of white Sn to gray Sn upon cooling.

The above factors make Pb is the most suitable alloying agent for production of solder alloys [20].

2.9 Lead free solders

Lead containing solders are used by the electronic industry for joining purpose because they have many advantages like low melting temperature, good wettability, strength, ductility, reliability, product performance and cost, But hazardous to the health and environment. So the material science community (researchers and manufactures) seriously consider developing the new alternatives to successfully replace the Sn-Pb solders. Many numbers of solders are available in the market but does not full-fill the required properties. Many projects are also be running for developed the LFS like TEIDA project in japan, NCSM project in USA and IDEALS project in European nations [21]. The alloying agents which are use instead of Pb is Cu, Zn, In, Bi, Ni, Sb and Ag. The systems uses for LFS are binary, ternary and quaternary. Several binary LFS are developed such as Sn-Cu, Sn-Zn, Sn-Ag, Sn-Bi and Sn-Sb. For improvement of mechanical and physical property of these binary alloy systems some additional alloying agents are added, due to which the system make the ternary and quaternary.

Most of the LFS are more expensive and poor performance as comparison of Sn-Pb solder. Cost of these solders is two to three times greater than the Sn-Pb solder. However, cost of Sn-0.7wt%Cu eutectic is the same range and better properties to that of Sn-Pb solder. That's why they are used in electronics industries. Addition of rare earth elements like Sb and In in LFS enhance the physical and mechanical properties. Addition of Ag in LFS also increases these properties. However, silver and rare earth elements are more expensive and could not be easily available. According to NCSM report, the addition of In in LFS is restricted up to 0.5wt%. Bi are

also a good rare earth element. It has been increases the mechanical and physical properties when added in LFS. But Bi is not economical beyond 15wt% [22].

2.9.1 Required properties of lead free solders

When we replace the Sn-Pb solder, then it must be focus about the properties of LFS. The properties of LFS are equal or better than the Sn-Pb solder. The major required properties including health and environment stabilities are following

- They must be better mechanical, physical and electrical properties.
- Low melting temperature.
- Good fatigue resistance
- Wetting properties are also be good.
- Corrosion resistance.
- During wave soldering operation low dross formation.
- Solder joint must be strong and reliable.
- Eco friendly.
- Low cost

Properties like yield strength, young's modulus, creep, fatigue, coefficient of thermal expansion, electrical conductivity etc. define the mechanical and electrical properties. In the above properties wettability plays important role for contact between a liquid and a solid i.e. solder joint. Wettability mainly defined the tendency of a liquid to spread over a solid substrate. It is characterized by the degree and rate of wettability. Degree of wetting is depending upon the contact angle and surface energy of the interface. Ability of liquid wets the surface and spreads over the substrate is determined by the rate of wetting. In general, if the wetting angle

lies between 0° to 90° then proper wetting will take place over the substrate. But in soldering process this angle is below 55° . According to thermodynamics proper wetting will take place if there is a net decrease in total free energy at the interface. Wettability is generally affected by the thermal conductivity, viscosity of molten solder and chemical reaction at the interface. Wettability will also depend upon the surface tension of the liquid, which is defined as the amount of energy required to spread the liquid surface area over the solid substrate isothermally. Surface tension decides the degree of wetting, strength and reliability of solder joint [23].

2.10 Important lead free solders

2.10.1 Sn-Cu based solders

Sn-Cu based alloy system has been found to be amongst the most promising substitutes for lead containing solders. The eutectic composition for Sn-Cu binary solder system is Sn-0.7Cu and the eutectic temperature is 227°C . Fig. 2.2 shows the Sn-Cu phase diagram.

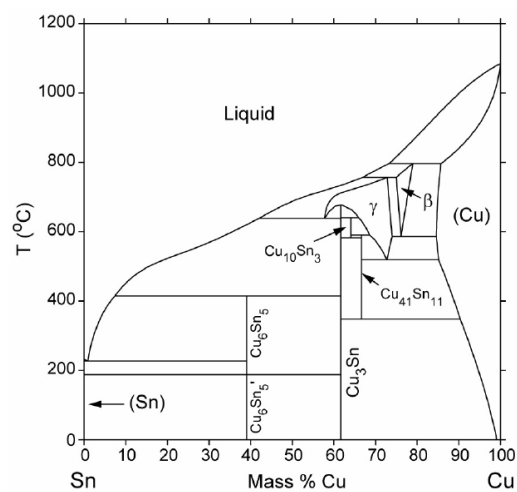


Fig. 2.2 Sn-Cu Phase Diagram

Eutectic Sn-0.7Cu is the cheapest than the other LFS an only 30% higher than the Sn-Pb solder. It is mainly used for electronics industry due to its better mechanical properties, good wettability, low melting temperature and good solderability compared to the other LFS. This solder also shows the better creep and fatigue resistance than the Sn-Pb solder. Eutectic Sn-0.7wt%Cu precipitated the small amount of Cu-Sn intermetallic compound Cu_6Sn_5 in the Sn matrix. The intermetallic compound Cu_6Sn_5 is highly non-stoichiometric and orthorhombic crystal structure. It has been found that Cu_6Sn_5 is brittle in nature and increases the hardness of this binary alloy system. But as comparisons of Sn-Pb solder some disadvantages are there in eutectic Sn-0.7Cu binary alloy system such as high melting temperature, poor wettability, insufficient oxidation and formation of tin whiskers which prevents the application in electronic packaging industries.

It has been found that when the small amount of Ag was added in the eutectic composition of Sn-0.7Cu system improve the soldering properties. It occurs because of the formation of Ag_3Sn and Cu_6Sn_5 intermetallic compounds. Little amount of Ag added can lower down the melting temperature and improves the wettability of Sn-Cu based solder while adding more Ag (in wt %) can increase the formation of intermetallic compound (Ag_3Sn) but it is not considerable because Ag_3Sn is having brittle nature and thus it may decrease the reliability of solder joint. High amount of Ag_3Sn can also decrease the plastic deformation properties of the solder. Hence it is suggested that there should not be more than 2-3.9 % of Ag in Sn-Ag-Cu (SAC) solder ternary alloy. Another imperative factor is the Cu content in SAC solder. This is mainly associated with the pasty range ΔT i.e. difference between liquidus temperature (T_{end}) and solidus temperature (T_{const}). ΔT is highly sensitive to the copper content, but not more sensitive to silver in SAC solder ternary alloy system. It has been reported that during wave soldering large pasty range increases the vibration. It also increases the fillet lifting phenomena, porosity,

differential thermal contraction during solidification and hot tearing due to alloy shrinkage. So the consideration of pasty range the Cu content should not be greater than 0.9wt% in SAC solder

2.10.2 Sn-Zn based solders

There is other substitute for Sn-Pb solder which is Sn-Zn binary alloy system because of its lesser melting temperature which is near to the Sn-Pb eutectic alloy. The eutectic composition of Sn-Zn binary alloy system is Sn-9Zn (wt.%) and having eutectic temperature as 198°C. Microstructure of Sn-Zn eutectic composition consists of two phases out of which primary phase is body centered tetragonal Sn matrix and secondary phase is hexagonal Zn. Sn-Zn solders possess better mechanical properties, inexpensive and non-hazardous as comparisons to the Sn-Pb solder. But Sn-Zn binary alloy systems are some limitations like corrosion resistance, poor wettability, low oxidation and microvoid formation. During soldering operation Zn reacts with the oxygen and formation of ZnO, which floats over the surface and affects the wetting properties. It has been found that these limitations can be removed by the addition of Bi in eutectic Sn-9Zn solder. Bi is surface active element and reduces the surface tension of liquid solder as well as decreases the melting temperature of Sn-Zn binary alloy to 189°C, which is below the eutectic temperature of this system [24].

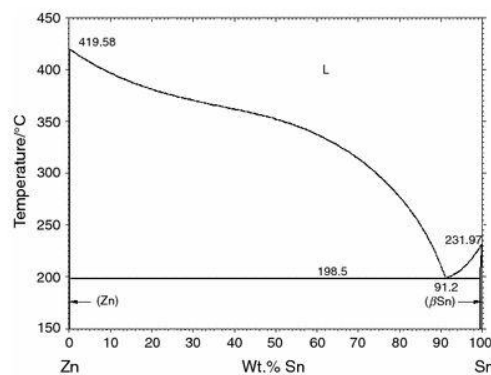


Fig. 2.3 Sn-Zn Phase Diagram

It has been also be found that increases in Zn percentage improves the wettability of Sn-Zn-(4,6)Bi, because diffusion of Zn atom is more than the Sn or Bi, when reacting with Cu in the electrical component. This type of diffusion gives the interfacial balance between solder and substrate which results in stretching of edges. Sn-Zn-Bi pasts are mostly widely used in printers, desktop, laptop, Tv tuners etc. Addition of Bi up to 4wt% increases the ultimate tensile strength and shear strength at the interface of Sn-Zn-Bi and Cu substrate, but after that this value decreases slowly. Microstructure of Sn-9Zn-6Bi solder consists of polyhedral Bi rich phase and needle like Zn rich phase precipitates in the matrix [25].

2.10.3 Sn-Ag based solders

In worldwide the first LFS used was Sn-Ag binary alloy system, because it has better mechanical properties (like ductility, thermal resistance and creep resistance) than Sn- Pb eutectic solder. The eutectic composition of Sn-Ag binary alloy system is Sn-3.5Ag (wt %) at 221°C. Fig. 2.4 shows the Sn-Ag phase diagram.

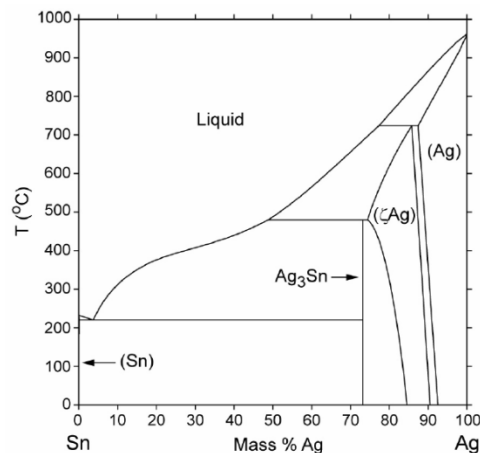


Fig 2.4 Sn-Ag phase diagram

Microstructure of this solder is consisting of fine Ag_3Sn needles and $\beta\text{-Sn}$ matrix. These two phases forms the interfacial bonding between them and gives the better mechanical property. It has been found that Ag_3Sn is brittle in nature which may degrade the solder joint. This solder possess some limitations like higher melting temperature and poor wettability than the Sn-Pb eutectic solder. If we add a small amount of Bi and Cu it has been reducing the limitations. The melting temperature is decreases and the wettability is improved if we add a small amount of Bi in Sn-Ag solder. The properties of eutectic Sn-3.5Ag solder will also enhanced if we add a small amount of Cu. Melting temperature is decreases from 221°C to 217°C . Sn-Ag-Cu solder is most widely used in aircraft and automotive industries, because this solder possess good thermal stress at solder joint and better mechanical properties than Sn-Pb solder. Many exact eutectic compositions has been developed by the researchers for this ternary alloy but still there is a little controversy [26].

2.10.4 Sn-Bi based solders

Sn-Bi solder is also a alternative candidate for Sn-Pb solder. In electronics industries it has been used for more than 20 years. It is most widely used when the requirement of soldering temperatures are low. 42Sn-58Bi is the eutectic composition of this binary alloy system and eutectic temperature is 139°C . Fig. 2.5 shows the of Sn-Bi phase diagram.

Sn-Bi and Sn-Pb have fairly similar microstructure and phase diagram but there is a significant difference in mechanical properties. Sn-rich dendrite matrix is present in the Sn-Bi binary alloy system and the presence of Bi-rich phase and Sn phase formed an eutectic mixture [27]. Eutectic composition of Sn-Bi solder is not more use in electronic industries such as under the condition of impact and rapid stressing, because they are brittle nature. To reduce brittleness

and improve ductility the researcher as well as electronic industry has selected a Sn-3,4wt%Bi alloy. Phase diagram indicates that when Bi is added in to Sn the solubility of Bi is reduced sharply from 21wt% at the temperature 139°C to 4wt% at the temperature 20°C. Bi precipitates in Sn phase when the alloy cools. Microstructure and mechanical properties of these binary alloy systems are greatly influenced by the cooling rate. Rate of slow cooling gives the information of large size grains and crack formation which degrade the reliability of solder joint. Addition of small amount of Ag in eutectic composition improves the mechanical property as well as wettability [28].

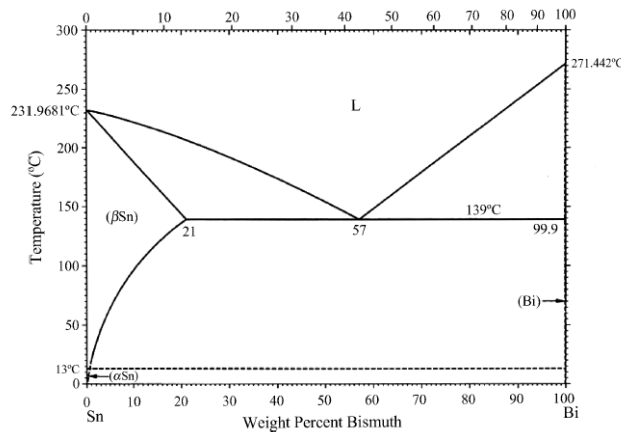


Fig. 2.5 Sn-Bi phase diagram

2.11 Solder-substrate interactions and formation of intermetallics

The reaction between metals from both the solder and the substrate help the formation of intermetallic compounds. Strength and wettability of solder is mainly depending upon the formation of intermetallic compound. It decreases the interfacial energy which indicates the good wetting takes place. Intermetallic compound increases the reliability of solder joint but some drawbacks are there, because intermetallic are brittle in nature. Formation large amount of intermetallic decreases the interfacial bonding between solder and substrate. It also degrades the

strength of solder joint, thermal fatigue life, tensile strength and fracture toughness solder joint. At the interface there are large number of intermetallic compound are formed but the intermetallic that forms first during soldering plays the important role in solderability and wetting [29].

Chapter 3

Experimental

3. Experimental

3.1 Materials and Method

We procured Sn granules, Cu powder and Ag powder as follows

Table 3.1: Purity and supplier of the solder material

S.No.	Material	Purity	Supplier
1.	Sn	99%	Merck
2.	Cu	99%	Rankem, RFCL Limited
3.	Ag	99.9%	Loba Chemie

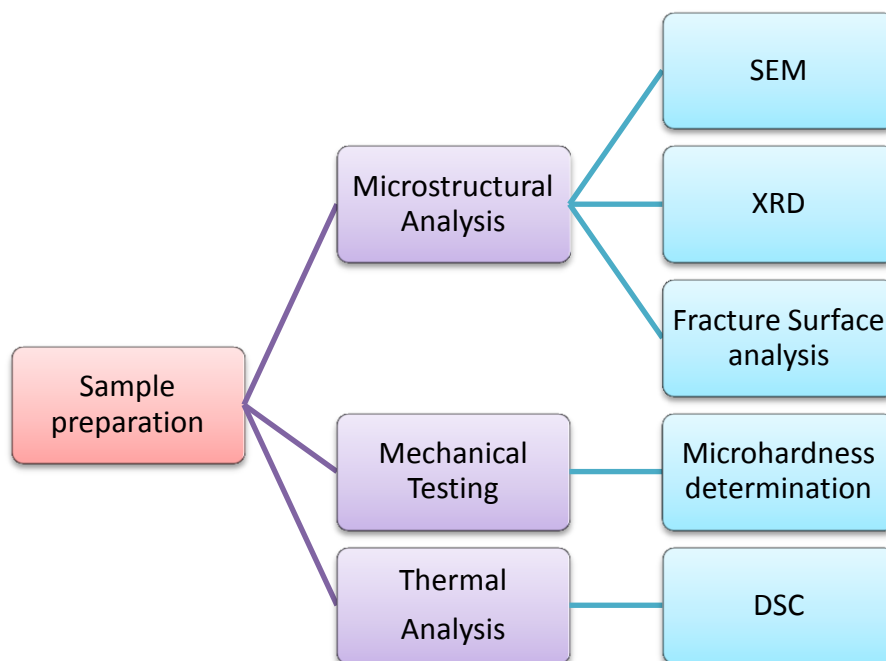
The different alloy compositions that were selected are eutectic Sn-0.7wt.% Cu, near eutectic Sn-1 wt. % Cu and Sn-2wt.% Cu composition. The modification of the eutectic microstructure by trace element addition like Ag in the eutectic alloy system will also be investigated. For this Sn-Ag-Cu alloys like Sn-2 wt.% Ag -0.7wt.% Cu, Sn-2.5wt.% Ag-0.7wt.% Cu and Sn-4.5 wt.% Ag-0.7 wt.% Cu were also developed. Chemical compositions of the solders are as follows

Table 3.2: Chemical compositions of the solder material (all in wt. %)

S.No.	Composition	Sn	Cu	Ag
1.	Sn-0.7Cu	99.3	0.7	0
2.	Sn-1Cu	99	1	0
3.	Sn-2Cu	99	2	0
4.	Sn-2Ag-0.7Cu	97.3	2	0.7
5.	Sn-2.5Ag-0.7Cu	96.8	2.5	0.7
6.	Sn-4.5Ag-0.7Cu	94.8	4.5	0.7

The Sn-Cu and Sn-Cu-Ag alloys were prepared from the granulated Sn, Cu and Ag powder. The elements were mixed in the right proportions and melted in a crucible in a tubular furnace in argon atmosphere and subsequently cooled in the furnace to produce the solders. The furnace is heated to the desired temperature by electrical resistance heating elements. The casting temperature of Sn-Cu solder alloys and Sn-Ag-Cu solder alloys are in the range of 500°C-700°C. The Sn-Cu and Sn-Cu-Ag molten alloys are held at this temperature for 2 h. All the samples were furnace cooled. The morphology and elemental composition of the samples were analyzed using a JEOL JSM-6480LV SEM (SEM) equipped with an INCAPentaFET-x3 X-ray microanalysis system with a high-angle ultra-thin window detector and a 30 mm² Si(Li) crystal for EDS analysis. DSC was done in order to determine the melting point of the various alloys. XRD of the alloys was done to found out if any new phases were formed during their development.

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 move slowly up and back on the surface of a flat belt grinder. After rough grinding these 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 complete the polishing operation through the series of emery papers samples were polished with the help of rotating wheel covered with special cloths which contain the charged. Diamond paste was used during polishing of samples on the cloths. Polishing operation was continued until the surface of samples were 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 Scanning Electron Microscopy (SEM)

The SEM is a type of electron microscope in which high energy beam of electrons directed on the specimen. These electrons strike on the sample and give a signal about the composition, surface topography and other properties like electrical conductivity. SEM is generally used for surface analysis of the specimens. It can give very high resolution images of sample surface i.e., it can gives the information up to 1nm in size. Due to presence of very narrow electron beam SEM micrographs have a large depth of field. The magnification range of conventional SEM is 20X-30000X with spatial resolution of 50-100nm can scan areas which vary from 1cm to 5 μ m in width. SEM also has the ability to analyze particular points as can be seen during EDX

operations which help in determining the chemical composition of the sample concerned. Fig. 3.1 shows the Scanning electron microscopy



Fig. 3.1 JEOL JSM-6480LV SEM

SEM has following components

- Electron gun
- Condenser and objective lens
- Scan coil
- Aperture
- Detectors and Display / Data output devices

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

3.4.2 X-ray Diffraction (XRD)

X-ray diffraction technique was used to identify the different type of phases (elemental phase/intermetallic phase/crystalline phase/non-crystalline phase) present in the sample. A Phillips Pan analytical PW 3040/00 X-ray diffractometer was also used to characterize the solder alloys. Here radiation used in X-ray diffraction was Ni-filtered Cu-K α . During XRD analysis we have taken the scanning range of 2θ value was from 20° to 90° with a scanning speed of $3^\circ/\text{min}$. and accelerating voltage of 30kv. The peak was analyzed by using X- pert high score software to identify the different types of phases. Fig. 3.2 shows the X-ray diffraction machine.



Fig. 3.2 X-ray Diffraction Machine

3.4.3 Differential Scanning Calorimetry (DSC)

DSC is a thermo analytical technique. With the help of DSC curve obtained by this instrument it gives the information about glass transition temperature and the melting temperature. It also gives the information about the heat of fusion. In this experimental work we have taken the mass of solder 14mg, temperature range 25°C to 300°C and rate of temperature changes $10^\circ\text{C}/\text{min}$. Fig. 3.3 shows the differential Scanning Calorimetry machine.



Fig. 3.3 Differential Scanning Calorimetry

3.4.4 Vickers hardness tester

Hardness tests were done by using a Vickers Microhardness Tester (Model: LECO LM 248AT) machine is shown in Fig. 3.4. Samples were hardness measurement firstly make the flat and parallel to each other with the help of a belt grinder to ensure accuracy of measurements. After that the samples were mechanically polished using the procedure above.



Fig. 3.4 LECO LM 248AT Vickers Microhardness

In the present experimental work the hardness was measured at a test load of 100gf and dwell time was 10 second. At least 5 readings were considered for each sample to calculate the average hardness.

3.4.5 Tubular furnace

Furnace is a device which is used for heating purpose of the sample. The source of energy of the furnace is either combustion fuel or the electricity. Tubular furnace is electric heating furnace.

In this experimental work the elements such as Sn, Cu and Ag were mixed in the right proportions. These elements were melted in a crucible in tubular furnace in the presence of argon gas atmosphere. The casting temperature was varied from 500°C to 700°C maintaining the holding time as 2 hour. All samples were allowed to attain room temperature inside the tube of the furnace before exposing to the atmosphere.



Fig. 3.5 High temperature tubular furnace

Chapter 4

Results and Discussions

4.1 Microstructure and elemental analysis of Sn-0.7Cu, Sn-1Cu and Sn-2Cu lead free solders

4.1.1 Sn-0.7Cu solder

The adverse effects of Pb on environment, it must be need for replace the lead containing solders such as Sn-Pb solder. Some of the alloys being investigated to replace the Sn-Pb solder alloys are from the Sn-Cu system. Sn-0.7Cu composition was chosen for experimental work. It was heated in the furnace at 500°C for 2 hour in an argon atmosphere. The molten alloy was cooled in the furnace until they attained the room temperature. At 500°C Sn is completely molten (melting point = 231.9°C). Cu atoms diffuse into Sn resulting in the formation of the intermetallic Cu_6Sn_5 . The microstructure of the as-solidified eutectic Sn-0.7Cu solder is shown in Fig. 4.1(a-b).

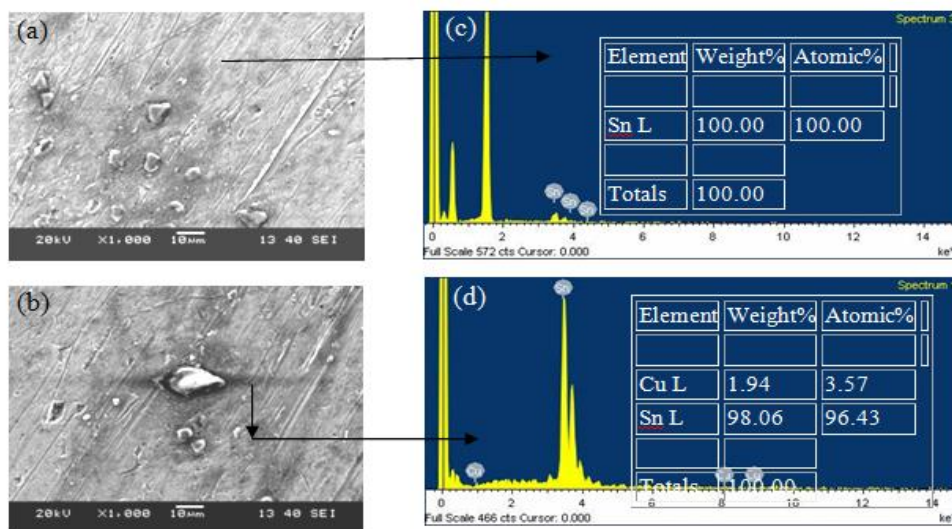


Fig. 4.1 (a-b) SEM and (c-d) EDX analysis of Sn-0.7Cu alloy

The microstructure, as predicted from the phase diagram, consists of β -Sn and the Cu-Sn intermetallic compound Cu_6Sn_5 . With the help of Sn-Cu binary-phase diagram, the volume fraction of intermetallic (Cu_6Sn_5) in eutectic Sn-Cu alloy can found out using the lever rule and

considering the densities of Cu_6Sn_5 (8.28 g/cm^3) and Sn (7.31 g/cm^3). The volume fraction of Cu_6Sn_5 is found to be only 1.6%. This is consistent with SEM image as only a very small amount of dark coloured Cu_6Sn_5 is seen in the SEM images in Fig. 4.1(a, b). The light coloured regions are 100 % Sn containing no Cu.

4.1.2 Sn-1Cu solder

In order to understand the intermetallic that are formed in the Sn-Cu system, Sn-1Cu system was chosen for study. This alloy was prepared at 700°C for 2 hour in an argon atmosphere. Molten alloy was allowed to cool in the furnace. At 700°C Sn is completely molten and Cu atoms diffuse into Sn resulting in the formation of the intermetallic Cu_6Sn_5 . The microstructure of the near eutectic composition of Sn-1Cu solder alloy is shown in Fig. 4.2 (a-b) along with the EDX analysis in Fig. 4.2 (c-d).

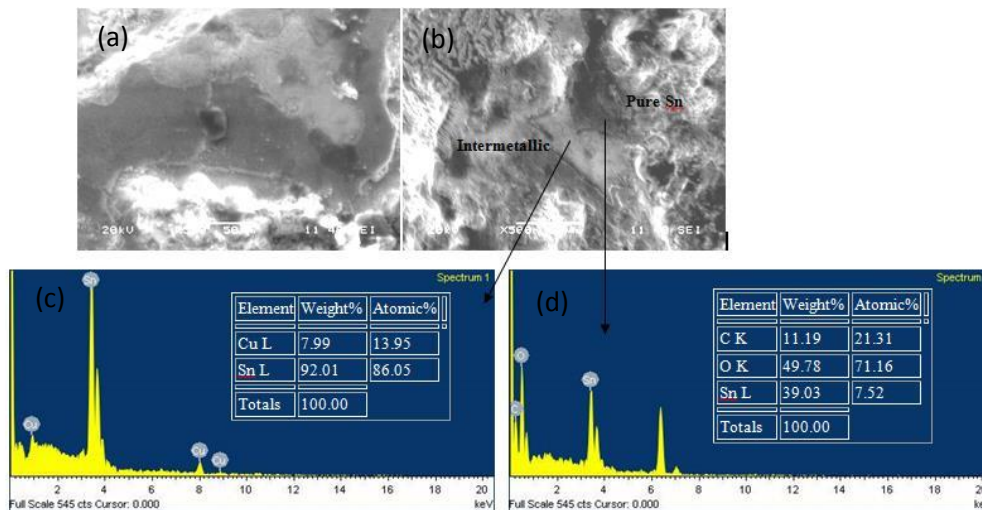


Fig. 4.2 (a-b) SEM images of Sn-1Cu alloy (c-d) EDX analysis of various regions in Sn-1Cu

The SEM images reveal that there are regions which are highly dense containing both Cu and Sn. The grey region containing both Sn and Cu represents the formation of intermetallic,

possibly Cu_6Sn_5 . The intermetallic Cu_6Sn_5 is highly non-stoichiometric. Cu_6Sn_5 is a well-known intermetallic and has an orthorhombic crystal structure. On the other hand the dark regions contain only Sn. The SEM images clearly show the two phase regions of pure Sn and intermetallic Cu_6Sn_5 in the microstructure of the solder alloy Sn-1Cu.

4.1.3 Sn-2Cu solder

Sn-2Cu alloy was also chosen for study. It was heated in furnace at 700°C for 2 hours. The molten alloy was cooled in the furnace. Cu_6Sn_5 could be traced in the solidified alloy. The SEM image in Fig. 4.3 (a) shows the microstructure of Sn-2Cu solder alloy. The microstructure of the Sn-2Cu solder alloy reveals that the dark coloured intermetallic compound Cu_6Sn_5 is finely dispersed in the matrix of β -Sn. EDX analysis in Fig. 4.3 (b,c) reveals the composition of the different phases present in the solder alloy.

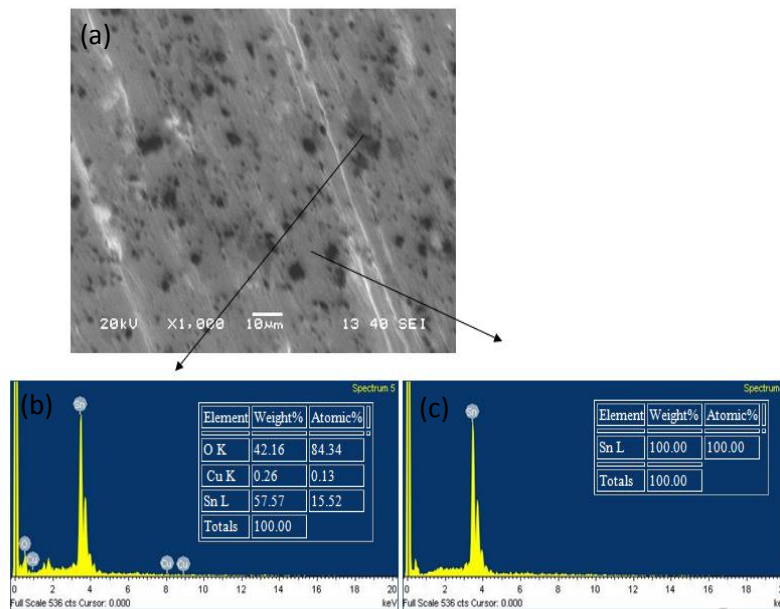


Fig. 4.3 (a) SEM (b-c) EDX analysis of Sn-2Cu solder alloy

Fig. 4.3(b) is the composition of the dark region in the sample and Fig. 4.3 (c) is the composition of the grey region. The grey coloured region contains 100% Sn whereas the dark region contains both Sn(57.57 wt.%) and Cu(0.26 wt.%).

4.2 Wetting characteristics of Sn-1Cu solder

Wettability defines the extent to which a liquid can spread on the solid surface. The present aim of our study also focuses on the wetting properties of the Sn-1Cu alloy. It can be easily seen from the SEM images in Fig. 4.4 (a-b) that near eutectic alloy Sn-1Cu possesses good wettability on the Cu substrate. The region away from the interface contains mainly Sn (93.96 wt.% Sn) as seen in the EDX analysis in Fig.4.4 (d) whereas the region close to the interface between the solder and the Cu substrate shows the formation of intermetallic Cu_6Sn_5 . There is also a very high percentage of oxygen at the interface. This is possibly due to the oxidation of Cu at the soldering temperature.

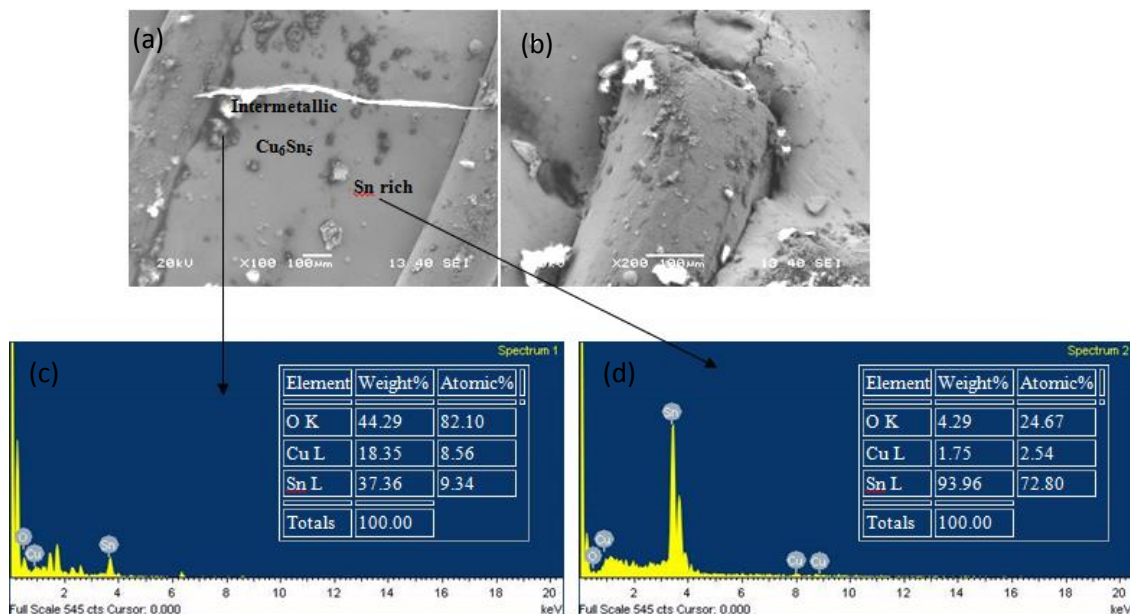


Fig. 4.4 (a-b) SEM of Sn-1Cu solder on Cu substrate (c-d) EDX analysis of the different regions in the solder joint

4.3 Thermal analysis of Sn-0.7Cu, Sn-1Cu and Sn-2Cu lead free solders

4.3.1 Sn-0.7Cu solder

The melting temperature is an important physical property of any solder. Melting temperature of solder has great influence the electronic industries as well as printed circuit board (PCB) assembly. A good solder should have a lower melting temperature and a narrow pasty temperature zone. Fig. 4.5 shows the DSC curve of the solder alloy upon rate of temperature changes $10^{\circ}\text{C}/\text{min}$. DSC result shows an endothermic peak at 234.89°C which corresponds to the melting point of Sn-0.7Cu eutectic composition (227°C). The slight rise in the melting point is possibly due to the presence of impurities or oxidation of the sample during melting.

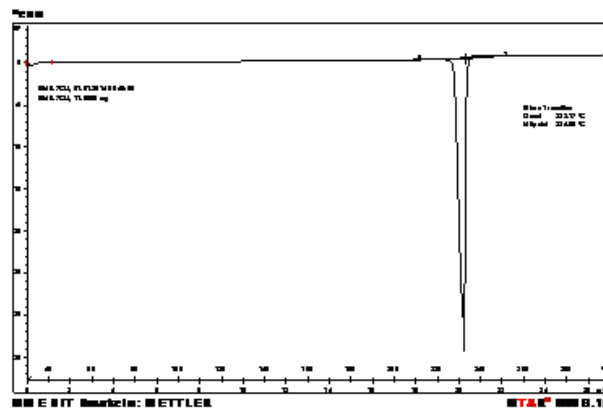


Fig. 4.5 DSC of Sn-0.7Cu solder alloy

4.3.2 Sn-1Cu solder

Fig. 4.6 shows the DSC curve of the solder alloy upon rate of temperature changes $10^{\circ}\text{C}/\text{min}$. DSC result shows that the melting point of the near eutectic composition Sn-1Cu is 236.82°C . The rise in melting point of the near eutectic composition Sn-1Cu (236.82°C) compared to Sn-0.7Cu (234.88°C) may be due to the presence of higher wt.% of Cu.

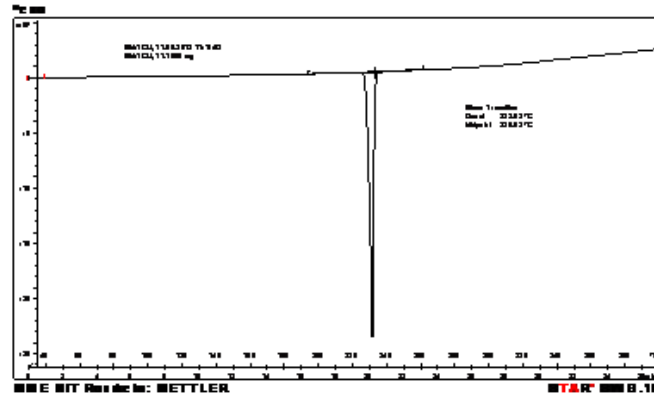


Fig. 4.6 DSC of Sn-1Cu solder alloy

4.3.3 Sn-2Cu solder

Fig. 4.7 shows the DSC curve of Sn-2Cu solder. Rate of temperature changes were $10^{\circ}\text{C}/\text{min}$. DSC result shows an endothermic peak at 237.88°C which corresponds to the melting point of Sn-2Cu composition.

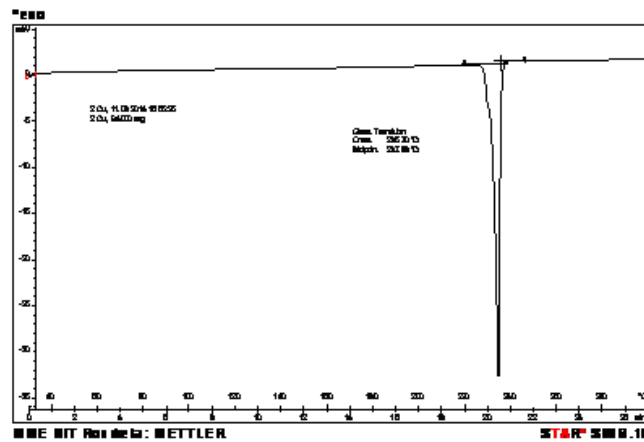


Fig. 4.7 DSC of Sn-2Cu solder alloy

4.4 Microstructure and elemental analysis of Sn-2Ag-0.7Cu and Sn-2.5Ag-0.7Cu lead free solders

4.4.1 Sn-2Ag-0.7Cu solder

To improve the mechanical properties as well as wettability and decreases the melting temperature of eutectic Sn-0.7Cu solder alloys, we have added the small amount (2 wt.%) of Ag in eutectic composition. In this experimental work the elements such as Sn, Cu and Ag were mixed in the right proportions. These elements were melted in a crucible in tubular furnace in the presence of argon gas atmosphere. The casting temperature was 700°C maintaining the holding time as 2 hour. After which the alloy was cooled in the furnace to room temperature. Fig. 4.8 (a) is the SEM of the solidified solder alloy Sn-2Ag-0.7Cu. This sample shows light coloured regions which contains 100 % Sn. The dark coloured regions are surrounded by light coloured spots containing both Sn and Ag approximately in the stoichiometric ratio 3:1. These are possibly intermetallic Ag₃Sn. The formation of Ag₃Sn becomes even more prominent when the wt. % of Ag is increased to 2.5 wt. % in Sn-2.5Ag-0.7 Cu alloy.

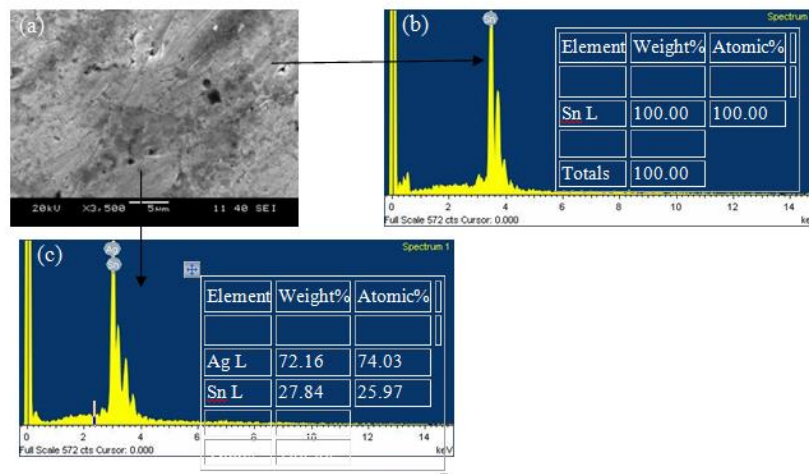


Fig. 4.8 (a) SEM of Sn-2Ag-0.7Cu (b-c) EDX analysis of the sample

4.4.2 Sn-2.5Ag-0.7Cu solder

Sn-2.5Ag-0.7Cu alloy was also chosen for study. It was heated in furnace at 700°C for 2 hours in the presence of argon gas atmosphere. The molten alloy was cooled in the furnace to room temperature. The SEM as well as EDX analysis of solidified alloy in Fig. 4.9 (a-b) shows that the edge of the eutectic region contains intermetallic Ag_3Sn . Intermetallic Ag_3Sn precipitates near the dark regions which are intermetallic Cu_6Sn_5 . The microstructural analysis confirms the presence of the fine Ag_3Sn particles dispersed in β -Sn matrix. The interfacial bonding between these two phases results in excellent mechanical properties of this alloy. However Ag_3Sn is brittle in nature which may degrade the reliability of the solder joint. The dark regions are the intermetallic Cu_6Sn_5 .

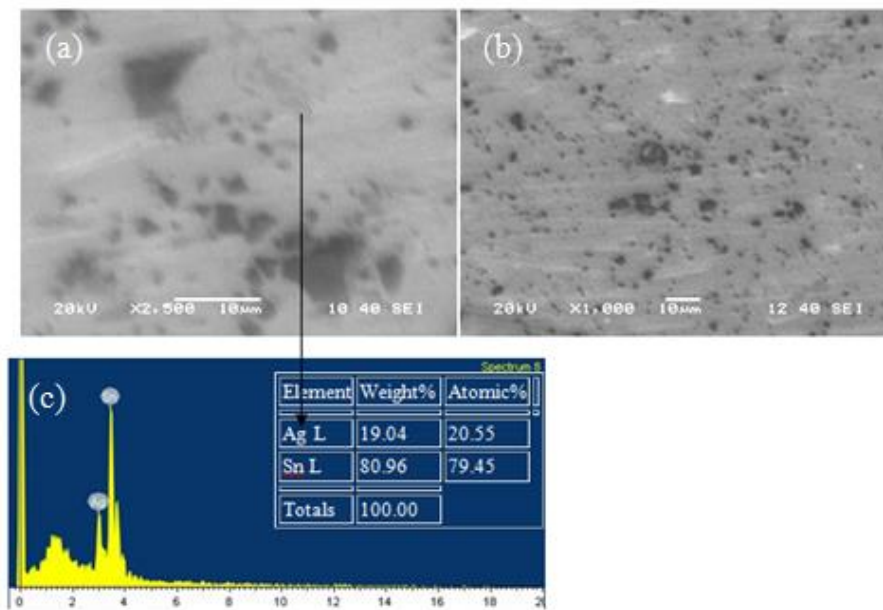


Fig. 4.9 (a-b) SEM of Sn-2.5Ag-0.7Cu (c) EDX analysis of the sample

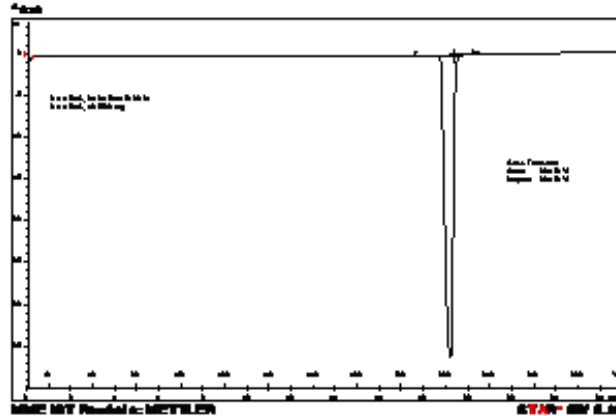


Fig. 4.11 DSC of Sn-4.5Ag-0.7Cu solder alloy

4.6 Reduction of melting temperature with addition of Ag

Fig. 4.12 shows the variation of melting point of the Sn-Cu solder alloy with addition of Ag. There is a gradual decrease in the melting temperature of the solder alloy as the wt. % of Ag is increased in the Sn-0.7Cu eutectic alloy. Initially the melting point increases because the Cu wt. % is raised from 0.7 to 2 wt. % but as Ag wt. % increases in the eutectic Sn-0.7Cu alloy the melting point decreases.

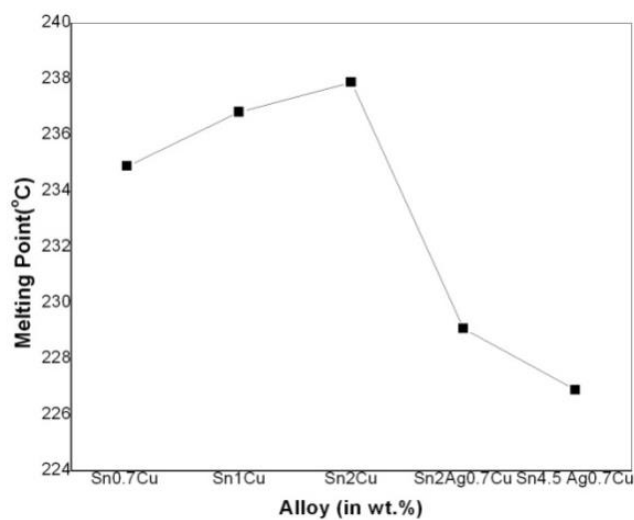


Fig. 4.12 Variation of melting temperature of the Sn-Cu solder alloy with addition of Ag.

4.7 Wetting characteristics of Sn-2Ag-0.7Cu solder

The present aim of our study also focuses on the wetting properties of the Sn-2.5Ag-0.7Cu alloy. It can be easily seen from the SEM images in Fig. 4.13 (a-b) solder is completely spread over the Cu substrate and make the intermolecular interaction between them that means it possess good wettability. According to present experimental works we can say that, addition of Ag in eutectic Sn-0.7Cu alloy improve the wettability.

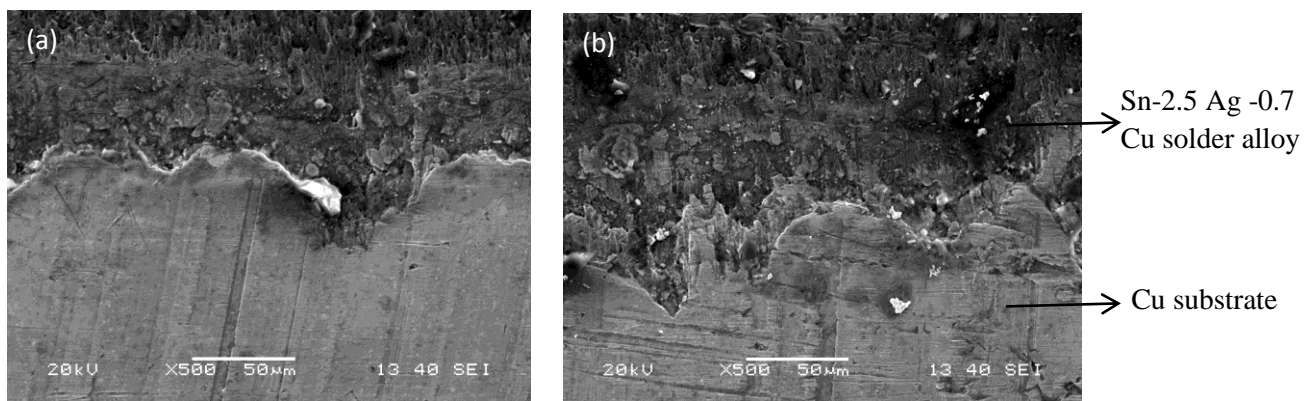


Fig. 4.13 (a-b) Microstructure of Sn-2.5Ag-0.7Cu solder alloy soldered to Cu substrate

4.8 XRD analysis

Fig. 4.14 (a-b) shows the x-ray diffraction pattern obtained for the solidified eutectic Sn-0.7Cu and Sn-2Ag-0.7Cu solder alloys. Fig.4.14 (a) shows the formation of large peaks of β -Sn rich and small peaks of Cu_6Sn_5 intermetallic phase. Fig. 4.14 (b) shows the new diffraction peaks of Ag_3Sn intermetallic phases along with β -Sn and Cu_6Sn_5 phases.

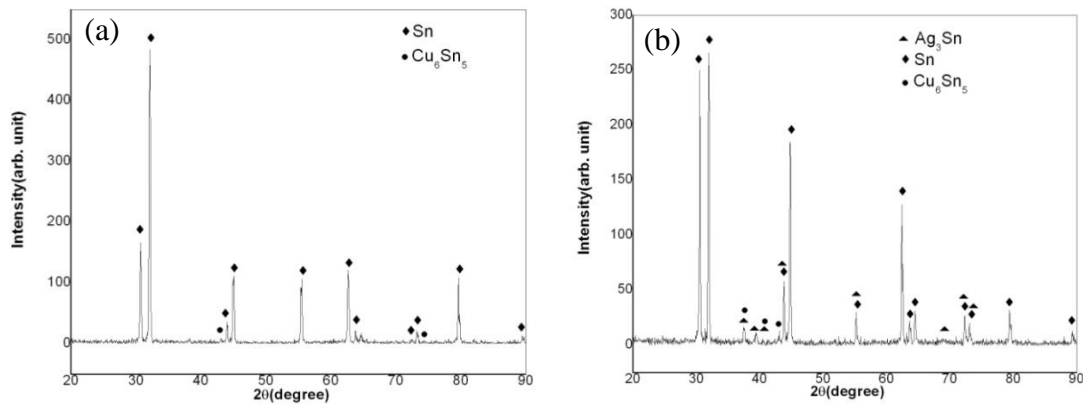


Fig. 4.14 X-ray diffraction plots of (a) Sn-0.7Cu and (b) Sn-2Ag-0.7Cu solder

4.9 Microhardness

The plot in Fig. 4.15 shows the variation of microhardness with increasing wt.% of Ag in the Sn-0.7Cu eutectic composition. It shows that the hardness of the eutectic composition increases initially with addition of Ag up to 2.5 wt.%. This has also been reported by Daly et al. [30]. The hardness of the intermetallic phase Cu₆Sn₅ is greater than the hardness of intermetallic compound Ag₃Sn. This is possibly the reason why on increasing the wt.% of Ag above 2.5 wt.% in the eutectic composition of Sn-0.7Cu the hardness of the alloy decreases.

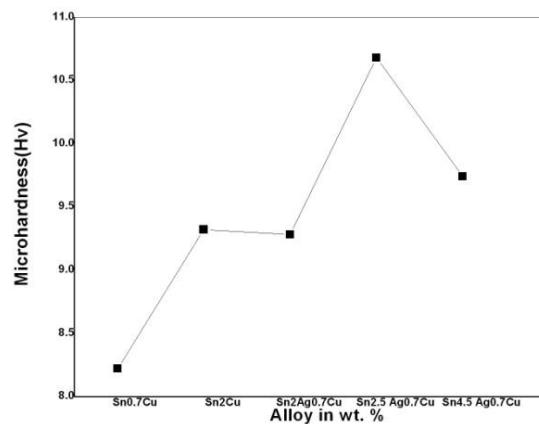
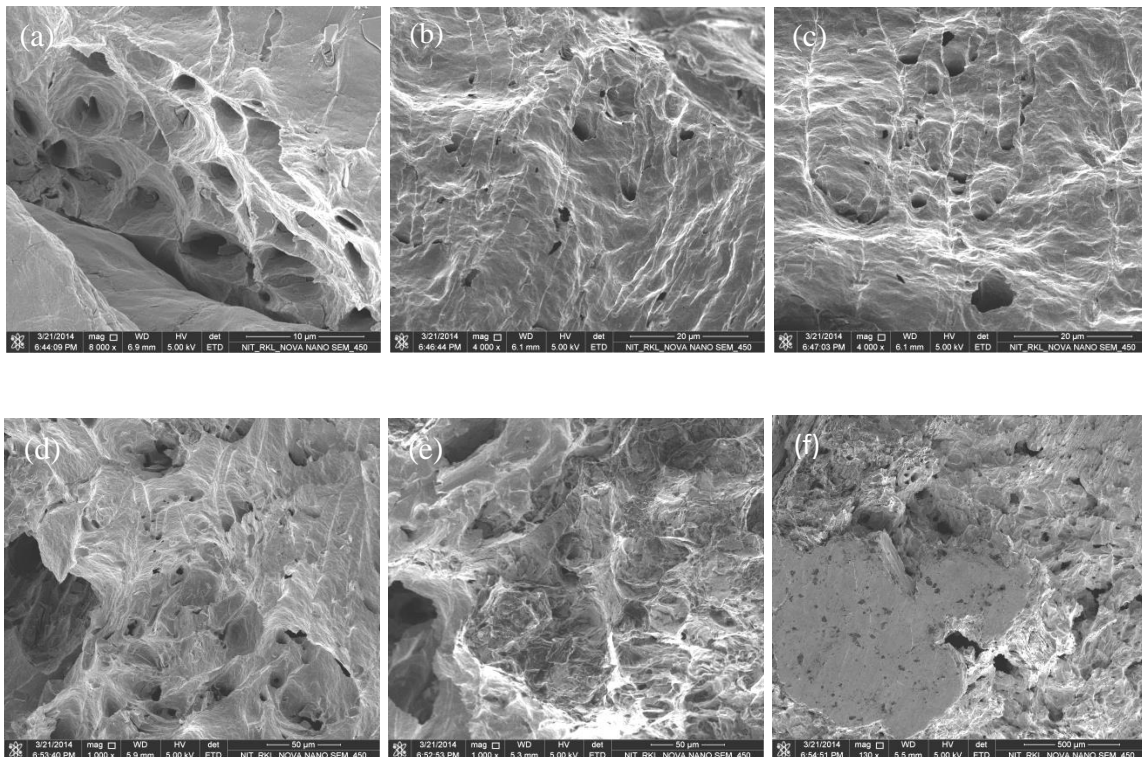


Fig. 4.15 Variation of microhardness with increase in wt. % of Ag in Sn-0.7Cu eutectic composition

4.10 Fractography

After tensile tests, the fracture surface of the various alloys synthesized was also analyzed. Fig. 4.16 (a-h) shows the SEM images of the fracture surface of the three Sn-0.7Cu, Sn-2Ag-0.7Cu and Sn-4.5Ag-0.7Cu solder alloys. The fractograph of Sn-0.7Cu shows a ductile nature of fracture of the alloy. The formation of dimples in the fracture surface indicates the ductile nature of the fracture. The fracture surface of Sn-2Ag-0.7Cu alloy shows brittle fracture. Flat smooth fracture surface indicating brittle fracture could be seen in Fig. 4.16 (f). There is also absence of dimples in the fracture surface. The fracture surface of Sn-4.5Ag-0.7Cu alloy shows dimple formation. This indicates that higher wt% of Ag in the alloy leads to increase in the ductile nature of the fracture. Lower wt.% of Ag in the alloys has led to brittle failure of the sample.



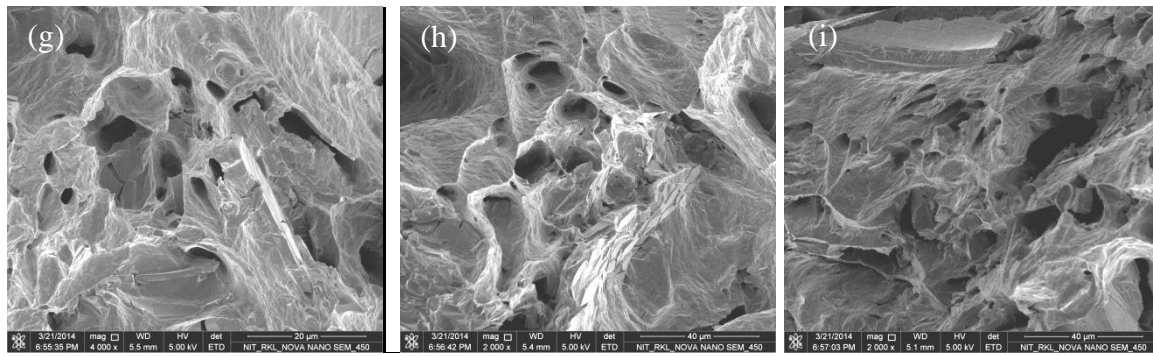


Fig. 4.16 FESEM images of the fracture surfaces of (a-b-c) Sn-0.7Cu (d-e-f) Sn-2Ag-0.7Cu (g-h-i) Sn-4.5Ag-0.7Cu alloys

Chapter 5

Conclusions

5. Conclusions

1. A reduction in melting point was observed on addition of Ag to the eutectic Sn-0.7Cu solder alloy. The melting point of the eutectic Sn-0.7Cu alloy was found to be 234.88°C and it decreased to 226.89°C on alloying with 4.5 % wt% Ag in Sn-4.5Ag-0.7 Cu solder alloy.
2. The wettability of the Sn-Cu solder alloy was enhanced due to addition of Ag.
3. Addition of Ag in Sn-Cu solder alloys led to the formation of intermetallic compound Ag_3Sn . Cu_6Sn_5 was found in Sn-Cu as well as in Sn-Ag-Cu solder alloys.
4. Initially the hardness of the eutectic composition Sn-0.7Cu was found to increase with the addition of low wt. % of Ag but beyond the addition of 2.5 wt.% Ag hardness of the solder alloy decreases.
5. Addition of lower wt.% of Ag in the Sn-0.7Cu eutectic alloy leads to a brittle fracture of the alloy. As the wt.% of Ag in the alloy is increased the nature of fracture is found to be ductile. The absence of Ag in the Sn-0.7Cu eutectic alloy results in a ductile nature of failure.

References

- [1] El-Daly, A. A. and Hammad, A.E., Development of high strength Sn-0.7Cu solders with the addition of small amount of Ag and In. *Journal of Alloys and Compounds* 2011;509(34): 8554-8560.
- [2] Reddy, B., Bhattacharya, P., Singh, B. and Chattopadhyay, K., The effect of ball milling on the melting behavior of Sn–Cu–Ag eutectic alloy. *J Mater Sci* 2009; 44: 2257–2263.
- [3] El-Daly, A.A., Hammad, A.E., Enhancement of creep resistance and thermal behavior of eutectic Sn–Cu lead-free solder alloy by Ag and In-additions. *Materials and Design* 2012; 40:292–298.
- [4] Yu, D.Q., Zhao, J., Wang, L., Improvement on the microstructure stability, mechanical and wetting properties of Sn–Ag–Cu lead-free solder with the addition of rare earth elements. *Journal of Alloys and Compounds* 2004; 376(1-2)170-175.
- [5] Mudryi, S. I., Shtablavyi, I. I., Sklyarchuk, V. I., Plevachuk, Y. O., Korolyshyn, A. V., Yakymovych, A .S. , Structure and electric resistance of Sn–Cu(Ag) solders in the precrystallization temperature range, *Materials Science* 2011; 46(4):464-472.
- [6] Sung K. Kang, Won Kyoung Choi, Da-Yuan Shih, Donald W. Henderson, Timothy Gosselin, Amit Sarkhel, Charles Goldsmith, and Karl J. Puttlitz, Ag_3Sn Plate Formation in the Solidification of Near-Ternary Eutectic Sn-Ag-Cu. *JOM*: 2003.
- [7] Zhang yun, “Tin and tin alloys for LFS” *Modern Electroplating*, Fifth Edition.
- [8] Rao P N, “Manufacturing technology” McGraw hill, volume 1, Fourth Edition.
- [9] Cleveland, LM; Minter, ML; Cobb, KA; Scott, AA; German, VF (2008). "Lead hazards for pregnant women and children: The American journal of nursing .
- [10] Ekong, EB; Jaar, BG; Weaver, VM (2006). "Lead-related nephrotoxicity: a review of the epidemiologic evidence".
- [11] Forstner, U. and Wittman, G.T. *Metal pollution in aquatic environment*, springer-verlag Berlin, Heidelberg, New York (1979).

- [12] Kumar, G., Singh, R.P. & Sushila. Nitrate assimilation and biomass production in *Sesamum indicum* L. seedlings in a lead enriched environment. *Water, Air & Soil Pollute*, 66:163-171 (1993).
- [13] Degernes, LA (2008). "Waterfowl toxicology: a review". *The veterinary clinics of North America. Exotic animal practice* 11 (2): 283–300.
- [14] Woolf, AD; Goldman, R; Bellinger, DC (2007). "Update on the clinical management of childhood lead poisoning". *Pediatric clinics of North America*.
- [15] Maas, RP; Patch, SC; Morgan, DM; Pandolfo, TJ (2005). "Reducing lead exposure from drinking water: recent history and current status". *Public health reports* (Washington, D.C. 1974).
- [16] Mañay, N; Cousillas, AZ; Alvarez, C; Heller, T (2008). "Lead contamination in Uruguay: the "La Teja" neighborhood case". *Reviews of environmental contamination and toxicology*.
- [17] D. Napp, Lead-free interconnect materials for the electronics industry, in: *Proceedings of the 27th International SAMPE Technical Conference*, Albuquerque, NM, 9±12 October 1995, pp. 334±337.
- [18] Industry Aids Environment, *Japan Times*, 14 October 1999, p. 10.
- [19] W.R. Lewis, *Notes on Soldering*, Tin Research Institute, 1961, p. 66.
- [20] T.P. Vianco, Development of alternatives to lead-bearing solders, in: *Proceedings of the Technical Program on Surface Mount International*, 19 August±2 September 1993, San Jose, CA.
- [21] Lead-free solder project final report, NCMS Report 0401RE96, Michigan: National Center for Manufacturing Sciences, 1997.
- [22] E.P. Wood, K.L. Nimmo In search of new lead-free electronic solders, *J. Electron. Mater.* 23 (8) (1994) 709±713.
- [23] H.H. Manko, *Solder and Soldering*, 2nd Edition, McGraw-Hill, New York, 1979.
- [24] R.A. Islam, B.Y. Wu, M.O. Alam, Y.C. Chan, W. Jillek, Investigations on microhardness of Sn–Zn based lead-free solder alloys as replacement of Sn–Pb solder, *Journal of Alloys and Compounds* 392 (2005) 149–158.

- [25] Ramani Mayappan , Ahmad Badri Ismail , Zainal Arifin Ahmad, Tadashi Ariga, Luay Bakir Hussain, Effect of sample perimeter and temperature on Sn–Zn based lead-free Solders.
- [26] Suganuma K, Nakamura Y. Microstructure and strength of interface between Sn–Ag eutectic solder and Cu. *J Jpn Inst Metals* 1995;59:1299–305.
- [27] Jian Zhou, Yangshan Sun, Feng Xue, Properties of low melting point Sn–Zn–Bi solders, *Journal of Alloys and Compounds* 397 (2005) 260–264.
- [28] Ahmed Sharif, Y.C. Chan, Effect of substrate metallization on interfacial reactions and reliability of Sn–Zn–Bi solder joints, *Microelectronic Engineering* 84 (2007) 328–335.
- [29] K.zeng, K.N Tu, six cases of reliability study of Pb free solder joint in electronic packaging technology, *materials science and engg, R* 38 (2002).
- [30] El-Daly, A. A., El-Tantawy, F., Hammad, A.E. , Gaafar, M.S., El-Mossalamy, E.H., Al-Ghamdi. A. A., Structural and elastic properties of eutectic Sn–Cu lead-free solder alloy containing small amount of Ag and In. *Journal of Alloys and Compounds* 2011; 509(26): 7238–7246.