A Study of Intermetallics in Cu-Sn system and Development of Sn-Zn Based Lead Free Solders

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

Master of Technology

In

Metallurgical and Materials Engineering

Submitted by

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Roll No. 211MM1201

Department of Metallurgical & Materials Engineering

National Institute of Technology

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Under the supervision of

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CERTIFICATE

This is to certify that Mr. MANAS KUMAR MISHRA, Reg No. 211MM1201 has carried out his project on the topic entitled “**A Study of Intermetallics in Cu-Sn system and Development of Sn-Zn Based Lead Free Solders”** under my supervision and this part of the work has not been presented earlier in Department of Metallurgy and Material Engineering, NIT-Rourkela.

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ABSTRACT

In the electronic industry Pb-Sn solder is a very important material but Pb is toxic and has adverse effects on the environment and human beings. Due to the harmful effects of the Pb the use of the Pb-Sn solder alloys are being avoided and new Pb-free solder alloys are being used for electronic applications. This study is mainly based on the intermetallics that are formed in the Cu-Sn system and development of Sn-Zn based lead free solders. The aim was to understand the solidification of Cu-Sn alloys, the various intermetallics formed and their morphology. Thermal analysis of Sn-Zn based lead free alloys and their wetting characteristics has been analysed. The Pb-Sn solders are being replaced by the Sn-Cu, Sn-Ag, Sn-Ag-Cu, Sn-Zn and Sn-Zn-Bi alloys. Here the intermetallics formed between Cu-Sn during solidification of the molten solder on the Cu electrical contacts are also studied. The intermetallics are brittle in nature and this leads to fracture of the solder. In order to understand the Sn-Cu or Sn-Zn based lead free solder alloys it is essential to is understand the solidification of the molten alloys. This is why a few compositions of Cu-Sn alloy are selected and the various intermetallics formed during the solidification of the molten Cu-Sn alloys are analyzed. At high temperatures diffusion of Cu and Sn increases and as a result intermetallics of Cu-Sn are formed. The common intermetallics formed are Cu_3Sn and Cu_6Sn_5. Sn-8.8Zn and Sn-8Zn-3Bi solder alloys has been developed. DSC analysis of these alloys has carried out to determine their melting points. It has been also observed that the addition of Bi increases the wettability and decreases the melting point of these alloys.

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

In the electronics industry lead-tin (Pb-Sn) solder is a very important material but Pb is toxic and has adverse effects on the environment and human beings. Laws have been proposed to eliminate Pb from electronic devices and components. The harmful effect of lead on human body and environment has promoted many research and experiments on lead free solders for electronic applications. The new lead free solders should have some desirable properties like wettability, low melting temperature, corrosion resistance, good electrical conductivity and good mechanical and material properties. Except these the cost and availability of these solders also play a key role [1]. Several alternate solder alloys are being investigated and their various properties are being studied. Now a day many lead free alloys such as Sn-Cu, Sn-Cu-Ag, Sn-Zn, Sn-Zn-Bi have showed promising characters for replacing traditional Sn-Pb solders [2, 3]. Among these Sn-Cu and Sn-Cu-Ag alloys exhibit higher melting temperature of 216^0-227^0C, which is more than that of the conventional Pb-Sn eutectic alloy (183^0C). According to the international printed circuit (IPC) association Sn-3Ag-0.5Cu and Sn-3.9Ag-0.6Cu, the two near eutectic alloys are going to be most widely used in near future [4].

One of the best alternative candidates for a Pb-Sn solder is the Sn-Zn alloy. The melting temperature of Sn-9wt%Zn eutectic alloy (198^0) is nearer to that of Pb-Sn eutectic solder [5]. Other than this the Sn-Zn alloys are low cost and also non-toxic to human health and environment. Sn-Zn solders are quite capable in terms of mechanical integrity in electronic industries but poor at oxidation and corrosion resistance [6-8].The wettability of Sn-Zn solder has been an important issue as during soldering the highly active Zn atoms get oxidized forming voids at the interface. The ZnO that forms by oxidation of Zn floats on the liquid surface and prevents the solder from wetting the substrate. This decreases the wetting properties of this solder [9, 10]. Therefore the Sn-Zn eutectic solder is difficult to handle due to its poor wettability, easy oxidation and microvoid formation [11]. It has been found that the addition of Bi to the eutectic composition of Sn-Zn system improved the soldering properties. Addition of Bi can lower the melting point of the system and improves wettability of Sn-Zn based solders on Cu substrate [12-14]. The wetting area increases with Bi concentration from 2 – 10wt%. In the same range of process variables, the surface tension of liquid Sn-Bi eutectic alloy is much lower than that of Sn-Zn eutectic alloy. So by adding Bi the surface tension of the liquid solder can be decreased and their wettability can be enhanced. By dissolving a small amount of Bi in the matrix of Sn-Zn solder, the tensile strength and shear strength can also be improved but a slightly higher mass addition of Bi may cause decrease of them. It has been confirmed that the Sn-8Zn-3Bi solder alloy possess less ductility compared to Sn-37Pb but has twice the tensile strength of it at room temperature[15,16].

Most of the packaging and electronic industries use 63Sn-37Pb eutectic composition for soldering purpose. The Pb-Sn binary system gives suitable soldering conditions that are compatible with most substrate materials. Pb plays a key role in deciding the type of joint formed. It reduces the surface tension of Sn and also serves as a solvent, allowing the other constituents in the component being soldered like Sn and Cu to form various intermetallics. The availability and cost of Pb along with above properties make it a suitable alloying element with Sn [17, 18]

We have tried to understand the various intermetallics that are formed when a Pb-Sn solder solidifies on a Cu-rich electrical contact. The molten solder, which is a Pb-Sn alloy, forms intermetallics with Cu in the electrical component. At high temperatures the diffusion of Cu and Sn increases and as a result intermetallics of the Cu-Sn system are formed. The brittle nature of the intermetallics often leads to fracture of the component. The common intermetallics formed are Cu_3Sn and Cu_6Sn_5. Additionally the microstructure of an electrical wire made of a Cu-Sn alloy fused due to the passage of high voltage was also studied [19-22]. Sn-8.8Zn and Sn-8Zn-3Bi solder alloys has been developed. DSC analysis of these alloys has carried out to determine their melting points. The effects of addition of Bi to these alloys have also been studied.

CHAPTER 2

2. LITERATURE SURVEY

2.1Adverse effects of lead on human life

Lead and its compounds are one of the top 17 chemicals having the greatest threat to human life according to the Environment Protection Agency (EPA) [23]. When Pb comes in contact with human body over a period of time it forms bond with proteins in the body and retards their normal functions. If the level of lead in the blood cells exceeds more than normal concentration, lead poisoning is said to occur. In case of hand soldering operations Pb contamination is not a big problem as Pb is less nonvolatile at normal soldering temperature. However the intake of Pb vapour and Pb dust formed during wave soldering operation can have hazardous effects on our health [24]. During wave soldering operation dross formation is common due to surface oxidation at the surface of molten solder. The interesting fact is that 90% of the dross produced can be refined for reuse but the remaining 10% is a waste. The Resource Conservation and Recovery Act (USA) has specified this waste as dangerous to human health and classified that proper care and disposal of this waste has to be maintained [25].

2.1.1 Lead poisoning

Lead Poisoning is also known as Plumbism. Lead is a material which has no biological advantages to human beings. Lead interferes with the metabolism of Ca and vitamin D. Lead toxicity affects variety of body functions and many organs including heart, kidney, bones, intestine and nervous system. It retards the development of nervous system and therefore more dangerous to children. The lead paint we use in house is also harmful. So children are at greater risk of lead poisoning than adults. It has been observed that increased blood Pb level in children correlated with decrease in intelligence, attention, memory, reading and arithmetic ability [26-28]. Lead toxicity is determined by the amount of lead in the blood cells. The US centers for disease control and prevention and the World Health Organization (WHO) states that if lead level in blood increases more than 10 µg/dl, it may retard tissue development and have harmful health effects [29-31].

2.1.2 Source of exposure

The important routes of Pb poisoning include industrial use of Pb (lead-acid batteries, lead wire or pipes and electronic components), metal recycling and foundries. Lead exposure may occur from contaminated water through lead pipes, air and soil [32]. There are several ways of lead contamination in solid which include residues from lead containing gasoline, used engine oil, pesticides, waste landfills or from industries like smelter plants [33]. Water supply pipes which are made up of lead or repaired by lead solder joints and this possess a high level of threat to human life. The amount of lead that may dissolve in water depends on the acidic nature, temperature, water hardness and standing time of water [34]. It has been found that in the US 14-20 % of total lead poisoning is mainly due to drinking water. In 2004 one article from "The Washington Post" published about the lead concentration in the drinking water and was awarded for this work [35].

2.1.3 How lead toxicity affects human health?

Once absorbed lead readily bonds with the proteins and enzymes in the body. It travels with the blood and mainly targets the soft tissues in the body. After several days most of the lead move to the teeth and bone marrow. In adults 94 % of the total lead concentration is confined in the bone and teeth while in case of children 73 % of the total lead content of the body is stored in the bone marrow [36].

(i) Renal system

Higher lead level in human blood cells may cause kidney failure. It can lead to fanconi syndrome which stops the normal function of kidneys.

(ii) Cardiovascular failure

Evidences have been found that lead exposure may cause high blood pressure, coronary heart disease, heart rate variability and heart attack [37].

(iii) Reproductive system

Lead poisoning affects both male and female reproductive system. In men when the concentration of lead is more than 40 μg/dl sperm count decreases drastically. It is more dangerous in case of pregnant women as the elevated blood lead level may lead to miscarriage, prematurity and moreover may be harmful to the child [38].

(iv) Nervous system

The axons of nerve cells degenerate and lose their normal function regarding response to the stimuli due to the lead poisoning. Our brain is the most sensitive organ and it is covered by endothelial cells. These cells act as a barrier between our blood and brain cells. Lead has the ability to pass through this layer because it can mimic calcium ions. In a child's developing brain, lead retards the formation of synapse in the cerebral cortex, neurochemical development and network of ion channels. It reduces numbers of neurons, interferes with neurotransmission and decreases neuronal growth [39].

2.2 Lead in environment and other species

The waste disposal of electronic and electrical assemblies containing lead and its compound are considered hazardous to the environment. The lead containing components are disposed in solid waste landfills. These waste components come in contact with ground water. The normal purification method that we commonly use to purify water is not suitable for removal of lead. Technically it is difficult to explain how lead forms bond with water. However a study has shown that PbO converts to $PbCO_3$ in presence of CO_2 and Cl [40]. In the world market, Japan and USA are considered to be the two major suppliers and users of printed circuit board (PCB) assemblies. The current studies show that this market will be doubled within the period of next 10 years. So the proper disposal of lead containing components is not a small issue and we cannot ignore it. Recycling of lead seems to be one of the major solution to the above problem. But the use of recycled lead has some limitations. It has been reported that the recycled lead displays higher α-particle emission than pure lead and it affects the performance of electronic circuits [41-43].

The lead level in our environment is not stagnant. It is increasing day by day due to rapid industrialization during last few years. Lead content of 0.003 mg/l of water is said to be normal and non hazardous to our ecosystem [44]. In India various water bodies have been reported to be contaminated with high level of lead. The famous Hussain Sagar lake water sample was tested and found to contain high level of lead in it. The lake water is possibly contaminated by the industrial waste of the city. During ''Green Revolution'', the higher consumption of $Pb^{\pm 2}$ containing pesticides in Punjab and Haryana has resulted soil and water contamination upto a high level [45,46]. Lead in soil present in the form of soluble and insoluble organic salts. They easily form bond with colloidal organic molecules. Plants generally absorb them through roots. Lead toxicity in plants depends on mainly its absorption, transport and intracellular localization. It has been observed that the plants growing in urban areas are more susceptible to lead poisoning. 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 [47, 48].

Many tests have been conducted on plants and other animals. These test results show that animals are also affected by lead poisoning. The symptoms are same to that of human race like abdominal pain, peripheral neuropathy and behavioral changes. The hunters generally use lead bullets for hunting wild animals. The predators that eat those hunted animals are also at risk. In many countries like the USA and Canada lead shot has been banned. 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 [49,50].

Accidental cases:-

On October 5, 2010 in Nigeria at least 400 children died from lead poisoning (Zamafara state lead poisoning epidemic). More than 1000 children from 10 different villages living near Yuguang gold and lead smelter plant in China were found to have excess blood lead level. After this incident around 15000 people from that area shifted to other places. The Government has stopped the production of lead from 32 lead plants [51, 52].

2.3 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 certain hazardous substances in electrical and electronics equipments. 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 [53,54]. 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 equipments. Seiko Epson Corporation ceased using Pb bearing solders in PCBs and other components since March 2002[55]. In India there is no such law that prohibits using lead and its components. Despite growing evidence of adverse health effects caused by lead, it is still widely used in consumer products. 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 equipments.

2.4 Role of Pb in Sn-Pb solder:-

The availability and cost of lead are not very big factor to care about. The soldering alloys based on eutectic or near the eutectic composition of Sn-Pb system and have been studied and redefined with many years of experiments by researchers. Their experiences have established a well developed knowledge about the performance characteristics of these solders. In electronic industries the solder used is primarily Sn-37Pb (eutectic composition) or Sn-40Pb. The presence of Pb has many technical advantages, which are

- Pb acts as a solvent, allowing the other materials such as Sn and Cu to form intermetallics by diffusion process.
- Pb if present as a constituent prevents the transformation of white Sn to gray Sn upon cooling. If this transformation occurs it will result in an increase in volume and will affect the structural integrity of Sn.
- Pb reduces the surface tension of pure Sn, which helps in wetting.

The above three factors make Pb the most suitable alloying agent for production of solder alloys [56,57].

2.5 Role of Tin:-

It has been found that white Sn may transform into a gray Sn if it is kept for a long time at a temperature below 0^0C. Thermodynamic data reveals that the transformation temperature between the two phases is 13^0C. It is interesting to note that in this transformation, a metal (white Sn) changes into a semiconductor (gray Sn). There is an increase in volume of 27%. This gray Sn acts as a semiconductor as well as have unique electrical and optical properties. However a large increase in volume change initiates cracking in Sn microstructure [58]. Tin easily wets the substrate and spreads on it. This makes Sn a major component in most of the solder alloys. But the above transformation creates problem for devices that cycle across 13^0C. Under repeated thermal cycling, plastic deformation and crack formation are likely to occur even when no external load is applied. According to previous works Cu, Al, Zn and Ge are the elements which enhance the formation of gray Sn. However addition of elements like Pb, Sb, Cd and Bi has a negative effect on this transformation. Whisker growth (single crystal growth appears like fine wires) in Sn takes place rapidly at about 51^0C. These whiskers are nothing but tetragonal white tin (β-tin) that grow due to internal stresses and strains. Whiskers do not affect solderability but longer whiskers may cause short-circuits in printed circuit assemblies. It has been observed that addition of Pb suppresses the whisker growth in Sn [59,60].

2.6 Wetting characteristics of solders:-

Wetting is a property of liquid to spread over a solid substrate, i.e., the tendency for a liquid solder to wet the substrate. It tells how a liquid and a solid are having an intimate contact between them. Wettability is characterized by the degree and rate of wetting. Degree of wetting depends on the contact angle formed at the interface as well as on the surface energy of interface. The rate of wetting is determined by how quick the liquid wets the surface and spreads over the substrate. Wettability is affected by a number of factors like thermal conductivity, viscosity of the molten solder and the possible chemical reaction at the interface [61]. In general if the wetting angle lies between 0^0 to 90^0 proper wetting of substrate takes place. For soldering purpose this angle should be below 55^0. In terms of thermodynamics proper wetting will occur if there is a net decrease in total free energy at the interface. Surface tension of a liquid is a thermodynamic quantity which is defined as the amount of energy needed to extend the liquid surface area on solid substrate isothermally. This quantity decides the degree of wetting, as well as determines the strength and reliability of solder joints [62,63].

2.7 Lead free solders:-

Lead containing solders are generously used for joining purpose in electronic and other industries because of the advantages they provide like easy handling, low melting point, ductility, reliability and proper wetting on substrate but due to lead toxicity, as well as implementation of laws, the researchers and manufacturers started to develop lead free solders as a replacement. Many commercial lead free solders are now available in the market, but none of them has all the required properties. Many projects have been carried out for the development of the lead free solders. NCSM project in the USA, the IDEALS project in European nations and TEIDA in Japan are few of them [64-66]. In most of the lead free solders tin is the major constituent. The other alloying agents being Zn, Bi, Cu and Ag. The lead free solders may be binary, ternary or quaternary. Some important binary Pb free alloys are Sn-0.7Cu, Sn-3.5Ag, Sn-9Zn, Sn-58Bi and Sn-52In. For better performance some additional alloying elements are added to these binary alloys, as a result of which ternary and even quaternary Pb free solders have came to the picture. Most lead free solders are more expensive compared to the Sn-Pb solders. They cost about two to three times more. However the cost of Sn-0.7Cu eutectic is in the same range to that of Sn-Pb solders, which explains why this composition has been successfully in being used now a days in the production of electronic circuits. Rare earth materials like Sb and In are added to these lead free solders to improve their physical and mechanical properties. However these rare earths are too expensive and are also not easily available. According to the NCSM report, the addition of In is restricted upto 0.5wt%. Also Bi being a rare element, its use for producing lead free solders is not economical beyond 15wt% [67-69].

2.8 Required Properties of lead free solders:-

Lead free solders used in electronic components must have some basic required properties like:

a) They should meet the desired levels of electrical and mechanical performance
b) Low melting temperature
c) They must wet and spread on substrate
d) Strong and reliable solder joint
e) Low assembly cost
f) Eco friendly

When we try to replace a Sn-Pb solder with a lead free solder, we must ensure that the performance of the replacement solder is equal or better than that of Pb-Sn solders. The major performance characteristics include reliability, manufacturability and environment suitability. Properties like yield strength, Young’s modulus, coefficient of thermal expansion, shear strength, fatigue, creep, etc. define reliability of a solder alloy. Manufacturability depends on their melting temperature, density, viscosity, thermal and electrical properties (mainly physical properties). Moreover there should be adequate supply of lead free alloys constituents. According to above requirements, the International Printed Circuit (IPC) association, USA has proposed two choices for lead free solder manufacturers. These two alloys are Sn-3Ag-0.5Cu and Sn-3.9Ag-0.6Cu. These two alloys are believed to be the best candidates for replacing the Pb containing solders. Many research and development has been carried out on these two alloys, especially on their physical and mechanical properties. They have many advantages as a lead free solder but still there is hope to find even better alloys [70].

2.9 Important lead free solders:-

2.9.1 Sn-Zn based solders:-

Sn-Zn based alloy is one of the best alternative candidates for a Sn-Pb solder because of its low melting temperature which is close to the Sn-Pb eutectic alloy. The eutectic composition for Sn-Zn binary solder system is Sn-9wt%Zn and the eutectic temperature is 198^0C. Its microstructure consists of two phases, i.e., a body centered tetragonal Sn matrix and a secondary hexagonal Zn phase. Sn-Zn solders possess better mechanical properties. The solder constituents are inexpensive and non hazardous as compared to lead [71]. However Sn-Zn binary alloy has some limitations like poor wetting, low oxidation, corrosion resistance and microvoid formation. During soldering, the highly active Zn atoms react to form ZnO which float on the surface and affects wetting. It has been found that addition of Bi near Sn-Zn eutectic composition improves the wettability of this system. Bi is a surface active element and its addition could reduce surface tension of the liquid solder. Also addition of Bi reduces the melting temperature of Sn-Zn binary alloy to 189^0C, which is well below the eutectic temperature of this system [72]. Increase in percentage of Zn slightly improves the wettability of Sn-Zn-(4, 6) Bi solder. The diffusion of Zn is more than Sn or Bi while reacting with Cu in the electrical; component. So when Zn% increases, more Zn atoms tend to diffuse into the Cu substrate. This type of diffusion generally affects the interfacial balance between solder and substrate which results in stretching of edges [73].

Sn-Zn-Bi solder pastes are widely used in many consumer products like laptop and desktop computers, printers, TV tuners, etc.. Addition of Bi concentration upto 4wt% sharply increases the ultimate tensile strength (UTS). After addition of 4wt% Bi the UTS value slowly decreases and this implies the elongation of alloys decreases with increase in Bi addition beyond 4wt%. It has been proved that a small addition of Bi to Sn matrix increases the strength of the alloy. It has been also observed that the polyhedral Bi rich phase and the needle like Zn rich phase precipitates in the matrix of Sn-9Zn-6Bi solder. These precipitates lead to cracking in the matrix and degrade the strength of solder alloy. A small addition of Bi can improve the shear strength at the interface of Sn-Zn-Bi solder and Cu substrate. However addition of more than 4wt% Bi decreases the shear strength far below than that of Sn-40Pb/Cu joint [74].

2.9.2 Sn-Cu based solder alloys:-

The eutectic Sn-0.7Cu binary solder alloy is also considered as one of the alternates for Sn-Pb solders. The eutectic temperature is 227^0C. It is the cheapest among all available lead free solders and costs only 30% higher than the eutectic Sn-Pb solder. Eutectic Sn-0.7Cu solder has been widely used in electronic packaging. In 1998 Nortel Network a famous lead free manufacturer in Europe built around 500 lead free telephones using Sn-0.7Cu solder. This composition is also suitable for high temperature applications like the automobile industries. This solder shows better creep and fatigue resistance compared to the Sn-Pb solders [75]. It has been already reported that addition of Cu enhances the gray tin transformation. This leads to decrease in physical and mechanical properties of solders, hence this solder should be properly examined before practical use.

2.9.3 Sn-Ag based solders:-

These solders have been considered as the first choice for a lead free solder due to its excellent mechanical properties. The eutectic composition for this solder is Sn-3.5wt%Ag and the eutectic temperature is 221^0C. Its microstructural studies have confirmed the presence of the fine Ag_3Sn needles and β-Sn matrix [76]. The interfacial bonding between these two phases results in excellent mechanical properties for this alloy. However these Ag_3Sn needles are brittle in nature which may degrade the reliability of the solder joint. It has been found that addition of a small amount of alloying agents can improve its thermal properties. Addition of Bi into Sn-Ag eutectic alloy reduces its melting temperature effectively and also improves the wettability [77-79]. Addition of small amount of Cu has been found to be advantageous for this binary Sn-3.5Ag solder. The eutectic Sn-Ag-Cu solder properly wets the substrate. Now a day it is widely used in aircraft and automotive industries, where the solder joints are subjected to thermal stresses. Its mechanical properties have been found to be better than that of Sn-Pb solders. Researchers have conducted many experiments to find the exact eutectic composition for this ternary alloy, but still there is a little controversy. The eutectic temperature for this composition has been found to be 217^0C [80].

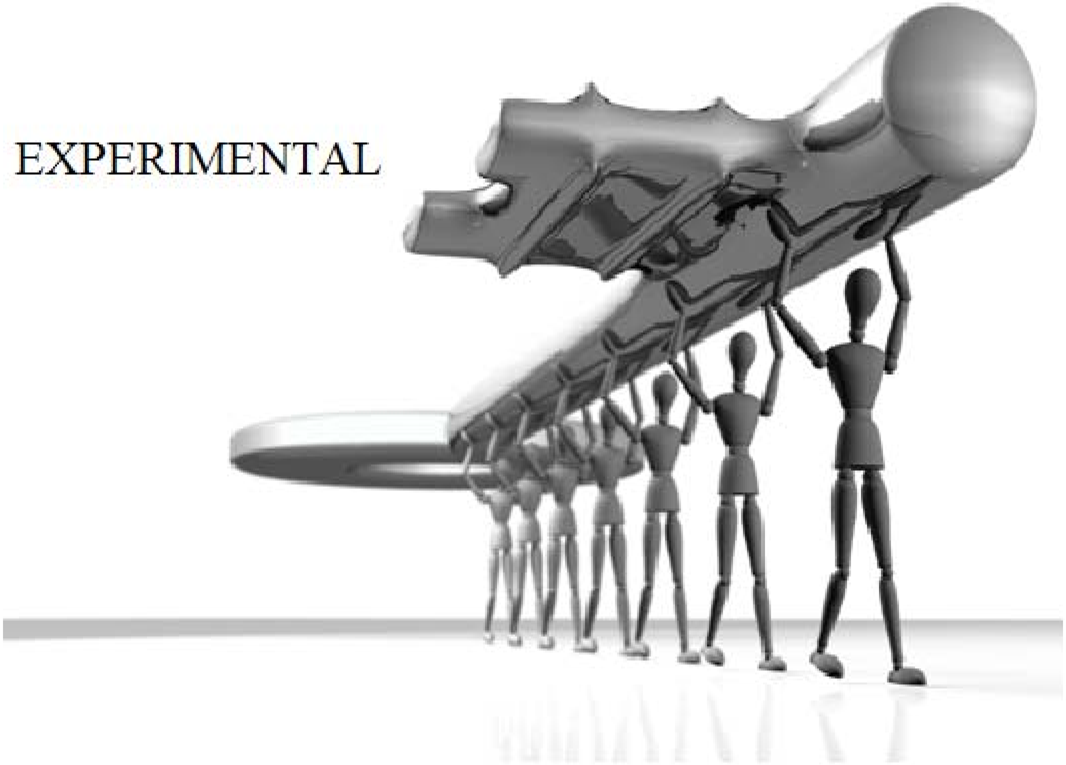
2.9.4 Sn-Bi based solders:-

The eutectic composition has been found to be 42Sn-58Bi and the eutectic temperature is 139^0C. This alloy has been used for more than 20 years in electronic industries. Maximum solubility of Bi in Sn is about 21wt%. As the alloy cools, Bi precipitates in Sn phase. It has been observed that the cooling rate has a great influence on the microstructure as well as mechanical properties of this alloy. Slow cooling rate leads to formation of large size grains and crack formation which ultimately degrades reliability of solder joint. However a small addition of Ag helps in improving the mechanical properties [81,82].

2.10 Solder-substrate interactions and formation of intermetallics:-

The reaction of molten solder alloy with a substrate results in formation of intermetallic compounds. These intermetallics determine the interfacial continuity between the substrate and solder. Intermetallics compounds are produced by the reaction between metals from both the solder and the substrate. The formation and growth of these layers determines the strength and wetting behavior of solder alloy. It lowers the interfacial energy, which indicates that proper wetting has taken place. Although the formation of these intermetallics favor the reliability of a solder joint, but there are some disadvantages. The intermetallics are brittle in nature and formation of thicker intermetallic layer may results in poor interfacial bonding. If there is a mismatch of physical properties of intermetallics and substrate materials, the soldering may fail. It has been observed that the excessive growth of intermetallics degrades solder joint strength, thermal fatigue life, tensile strength and fracture toughness of solder joints. The intermetallics formed at the interface depend upon the constituents of solder alloy and how each of these constituents reacts with the substrate. There can be a number of intermetallics compound formed at the interface but the intermetallics that forms first during the soldering process plays a major role in wetting and solderability [83].

CHAPTER 3



EXPERIMENTAL

3. Experimental

3.1 Materials and Method

We procured Cu power, Sn granules, Zn foils and Bi powder from RFCL Limited (RANKEM), India. The microstructure and the formation of various intermetallics in a Cu-Sn alloy electrical conductor fused due to the passage of high voltage, Cu-20wt.%Sn alloy, Sn-5wt.%Cu alloy, Pb-Sn solder solidified on Cu-Sn electrical wire are studied using a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDX). To analyze the intermetallics formed during solidification of Pb-Sn solder on Cu-Sn electrical wire a commercial solder alloy was wrapped around a Cu-Sn wire and heated to 500^{o}C for 1 h. The microstructure and various phases formed were analyzed. Metallic Sn was oxidized in a muffle furnace at 1000^{o}C for 1 h and 2 h in presence of air in order to study the oxidation behavior of Sn. The oxidized Sn sample was analyzed using SEM and EDX. The Sn-8.8Zn alloy was made to study the melting point and wetting behavior. We have also studied the microstructure and wetting characteristics of Sn-8Zn-3Bi solder alloy by using scanning electron microscope and Differential scanning calorimetry (DSC).

3.2 Experimental Instruments

3.2.1 Scanning Electron Microscopy:

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

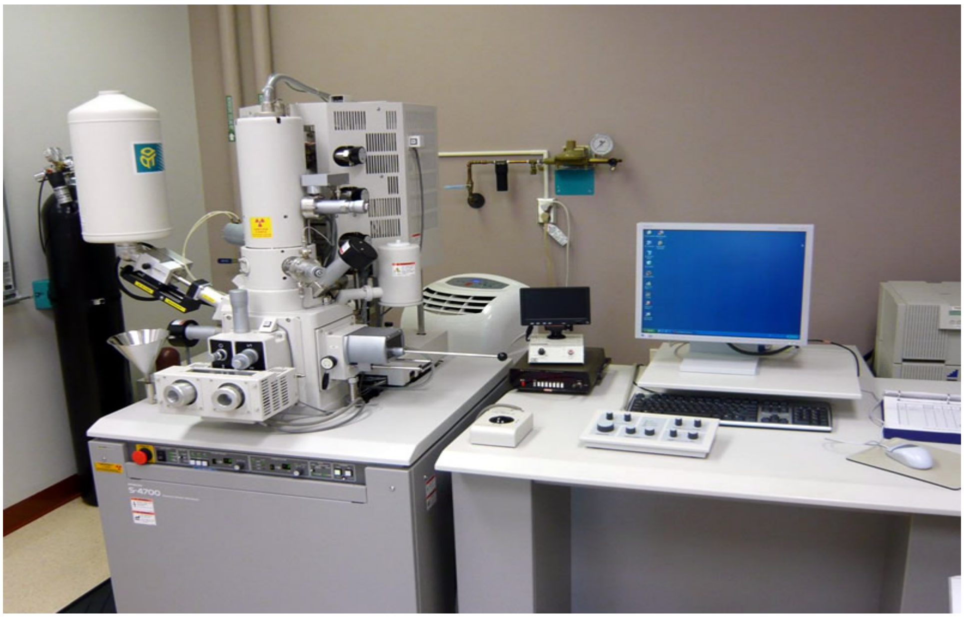


Fig 3.1 JEOL JSM-6480LV SEM

In most of the applications, the data collected is over a pre selected area of the sample surface and following this, a 2D image is generated that shows the various spatial variations. Conventional SEMs with a magnification range of 20X-30000X with a spatial resolution of 50-100 nm can scan areas which vary from 1 cm to 5 µm in width. SEMs also have the ability to analyse particular points as can be seen during EDX operations which help in determining the chemical composition of the sample concerned [84]

SEM has following components

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements

3.2.2 Energy Dispersive X-Ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another [85].

3.3 Differential Scanning Calorimetry:

Differential scanning calorimetry or DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned [86].

Fig 3.2 Differential Scanning Calorimetry

3.4 Furnace

A furnace is a device used for heating. The heat energy to fuel a furnace may be supplied directly by fuel combustion, by electricity such as the electric arc furnace, or through induction heating in induction furnaces. A muffle furnace (retort furnace) is a furnace in which the material is isolated from the fuel and all of the products of combustion including gases and flying ash. Today, a muffle furnace is (usually) a front-loading box-type oven or kiln for high-temperature applications such as fusing glass, creating enamel coatings, ceramics and soldering and brazing articles. These furnaces are usually heated to desired temperatures by conduction, convection, or blackbody radiation from electrical resistance heating elements. Therefore there is usually no combustion involved in the temperature control of the system, which allows for much greater control of temperature uniformity and assures isolation of the material being heated [87].

Fig 3.3 High temperature muffle-furnace

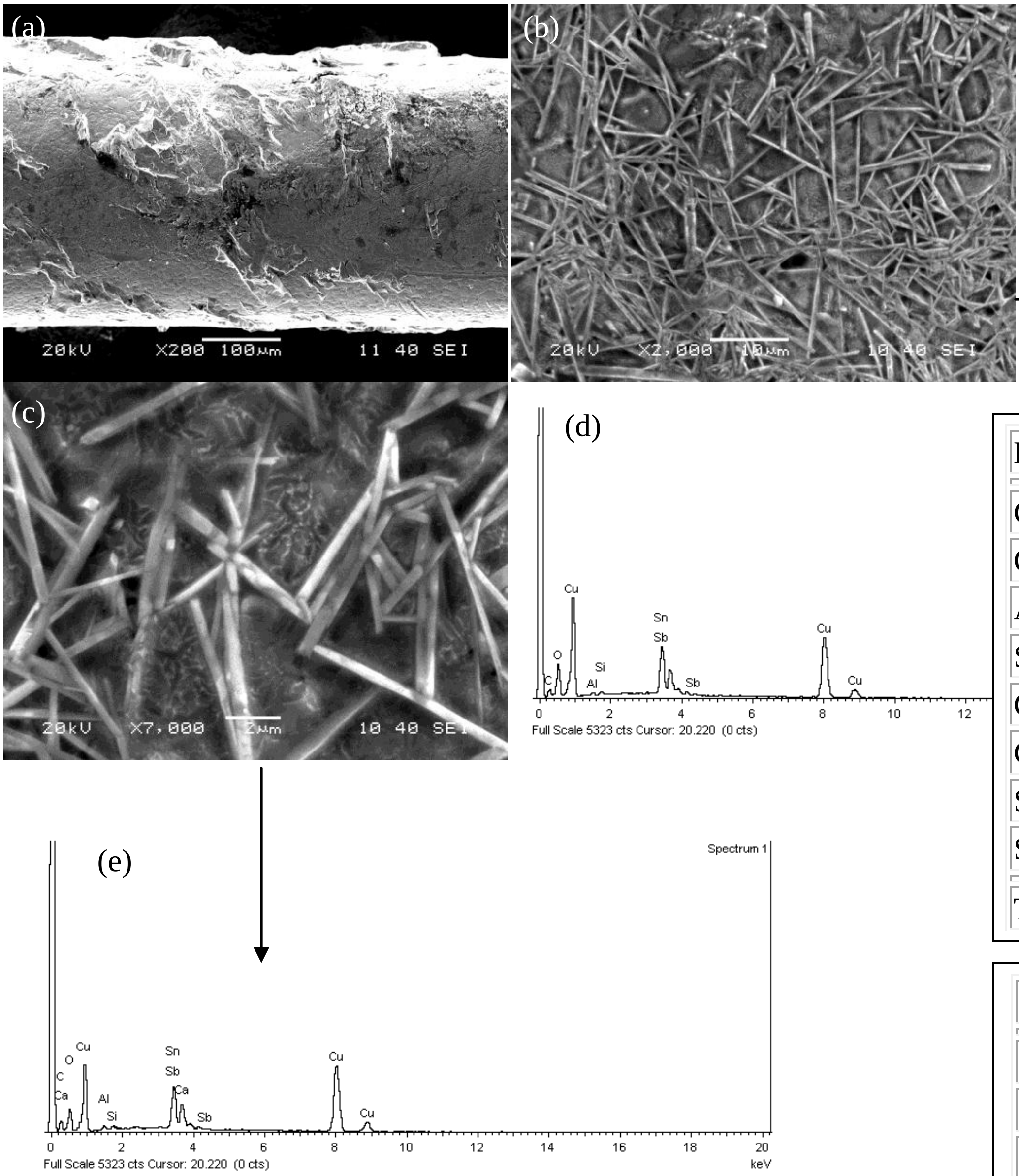
CHAPTER 4

RESULT AND DISCUSSION

4.1 Metals used as electrical contacts and solder

The adverse effects of Pb on environment have led to the need for new solder alloys in order to replace the Pb-Sn solder alloys. Some of the alloys being investigated to replace the Pb-Sn solder alloys are from the Sn-Ag-Cu system. It is important to understand the Cu-Sn system for understanding the Sn-Ag-Cu alloys. The solidification of the molten solder is an important aspect. Intermetallic compounds like Cu_6Sn_5, Cu_3Sn and Cu_5Sn have been found to form during solidification of the molten Cu-Sn alloy. These intermetallics are brittle in nature and failure is likely to take place in this region [88-90].

Electrical wires used in homes are often made of Cu-Sn alloys. We have also tried to study the Cu-Sn alloy system. We have examined a Cu-Sn electrical conductor which has fused due to high voltage. Microstructural analysis of the fused section of the wire shows the formation of rod shaped intermetallic compounds Fig. 4(b-c). The rods like structures were only seen in the fused section of the wire and were not seen in other areas of the wire. Fig. 4(a) is the SEM image of the wire where the rods like structures were not seen. The composition of the rods in both the EDX analysis in Fig. 4(d) and Fig. 4(e) suggests that the possible intermetallic compound is Cu_5Sn. The intermetallic compound has been formed when the conductor attains a high temperature due to excessive flow of current through the wire and then cooling in air. Due to the excessive high temperature the wire also melts. The rod like structure of Cu-Sn intermetallic compound, like Cu_6Sn_5 has also been reported earlier. The sizes of the rods were about 10 µm. The large percentage of oxygen is possibly due to the oxidation of the wire in air at the high temperature. It could be found from the EDX analysis that the atomic percentage of oxygen is very high, which indicates that possibly some amount of Cu and Sn was oxidized.



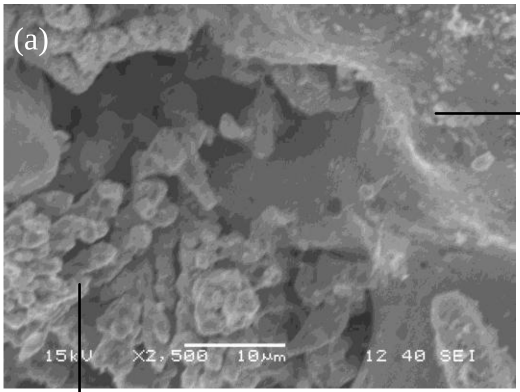
Element	Weight%	Atomic%
C K	10.84	31.64
O K	14.66	32.11
Al K	0.76	0.99
Si K	0.51	0.64
Ca K	0.93	0.81
Cu K	48.72	26.88
Sn L	19.19	5.67
Sb L	4.38	1.26
Totals	100.00	

Element	Weight%	Atomic%
C K	6.96	20.42
O K	20.61	45.39
Al K	0.52	0.68
Si K	0.52	0.65
Cu K	45.40	25.17
Sn L	22.82	6.77
Sb L	3.18	0.92
Totals	100.00	

Figure 4(a) SEM of electrical wire containing Cu and Sn, fused by high voltage application (b-c) SEM images of Cu-Sn intermetallic compound in a fused wire containing Cu and Sn (d-e) EDX analysis of the needle like structures formed in a fused wire containing Cu and Sn

4.2 Cu-20wt. % Sn alloy

In order to understand the intermetallics that are formed in the Cu-Sn system Cu-20wt. % Sn composition was chosen. It was heated at 800°C for 2 h and cooled in the furnace. At this temperature Sn was completely melted as its melting point is 231.9°C whereas Cu remained solid as its melting temperature is 1083°C. The SEM images in Fig. 4.1(a) reveal that there are regions which are highly dense containing both Cu and Sn. This is the intermetallic Cu_6Sn_5 whereas in other areas loose Cu particles could be found. EDX of these areas reveal 100 % Cu and absence of Sn. From the EDX analysis in Figs. 4.1(a-b) the Cu:Sn stoichiometric ratio of the densely solidified region was found to be $Cu_6Sn_{5.79}$ and $Cu_6Sn_{6.83}$ in two different regions. This is very close to the composition of the intermetallic Cu_6Sn_5.

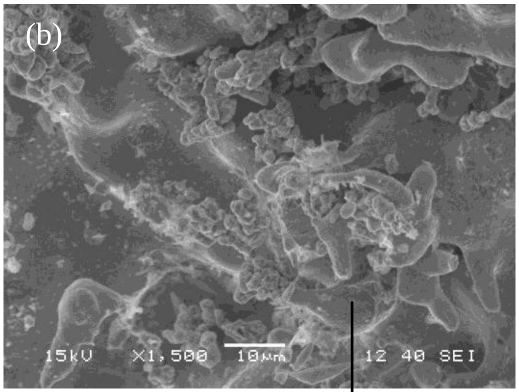


Element	Weight%	Atomic%
Cu K	35.67	50.88
Sn L	64.33	49.12
Totals	100.00	

Intermetallic compound Cu_6Sn_5

Element	Weight%	Atomic%
Cu K	100.00	100.00
Totals	100.00	

Cu rich area



Element	Weight%	Atomic%
Cu K	31.98	46.76
Sn L	68.02	53.24
Totals	100.00	

Intermetallic compound

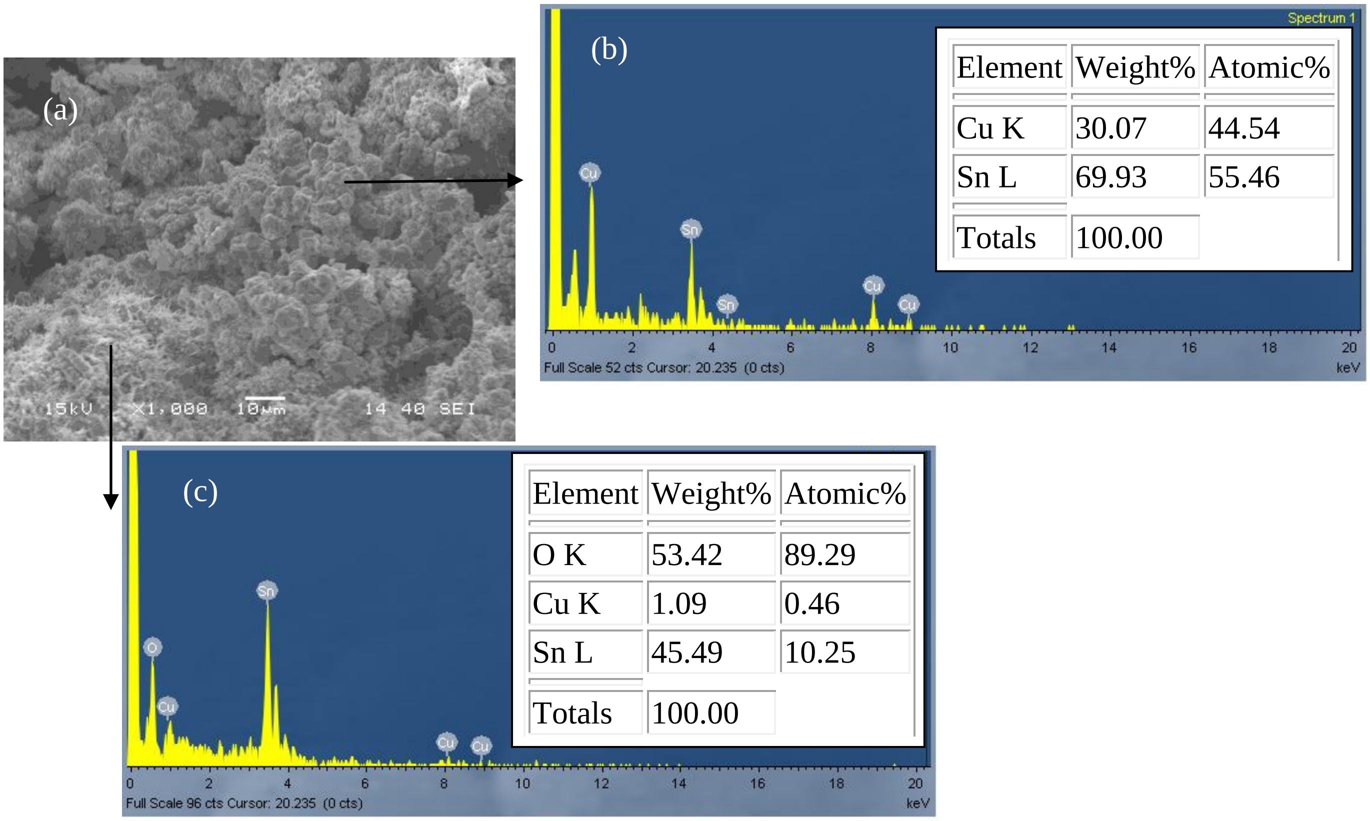
Figure 4.1 (a-b) SEM and EDX analysis images of Cu-20wt. % Sn composition heated to 800°C for 2 h and cooled in the furnace showing the formation of intermetallic Cu_6Sn_5.

The SEM image in Fig. 4.1(b) shows elongated shape of the intermetallic Cu_6Sn_5 seen in the microstructure of Cu-20wt. % Sn alloy. Cu_6Sn_5 is a very well known intermetallic of the Cu-Sn system and has an orthorhombic crystal structure. At 800°C Sn is completely molten. Cu atoms diffuse into Sn resulting in the formation of the intermetallic. The molten alloy was cooled inside the furnace and lower cooling rate has been found to be favourable in the formation of the intermetallic compound Cu_6Sn_5.

Cu_6Sn_5 exists in two crystal structures. At high temperature Cu_6Sn_5 has a hexagonal crystal structure whereas at lower temperature Cu_6Sn_5 has a monoclinic structure. At room temperature the crystal structure of Cu_6Sn_5 is monoclinic. The allotropic transformation from monoclinic $Cu_6Sn_5(\eta')$ which is stable at lower temperature to hexagonal $Cu_6Sn_5(\eta)$ which is stable at higher temperature takes place at 186°C. During cooling the hexagonal to monoclinic transformation leads to volume change and hence cracking of the intermetallic Cu_6Sn_5 takes place. Intermetallics like Cu_5Sn and Cu_6Sn_5 could be found at the Sn-Cu interface. Cu diffuses into Sn to form the intermetallic compound Cu_6Sn_5. Gradually the solubility of Cu in Sn reduces and stops when Sn becomes super saturated with Cu. The excess Cu remains in elemental form around the intermetallic compound Cu_6Sn_5. After a long time the diffusion of Cu will slow down and the growth rate of Cu_6Sn_5 phase will decrease [88-93].

4.3 Sn-5 wt. % Cu alloy

Sn-5 wt. % Cu composition was also chosen for study. It was heated to 500°C for 2 hours. The molten alloy was cooled in the furnace. Cu_6Sn_5 could be traced in the solidified alloy. There is also indication of formation of SnO_2 structures in the solidified alloy. The SEM image in Fig. 4.2(a) shows some areas where Sn was found to be oxidized. The SEM in Fig. 4.3(a-b) also suggests the formation rod like structures of SnO_2. The EDX analysis of Fig. 4.2(b) suggests the formation of intermetallic Cu_6Sn_5. On the other hand the EDX analysis in Fig. 4.2(c) of the few bright regions showed almost the absence of Cu. These rod like structures in this region were found to contain significant amount of O and Sn. The EDX analysis of the rod like structures suggests that the tin oxide structures are highly non-stoichiometric [94-96].



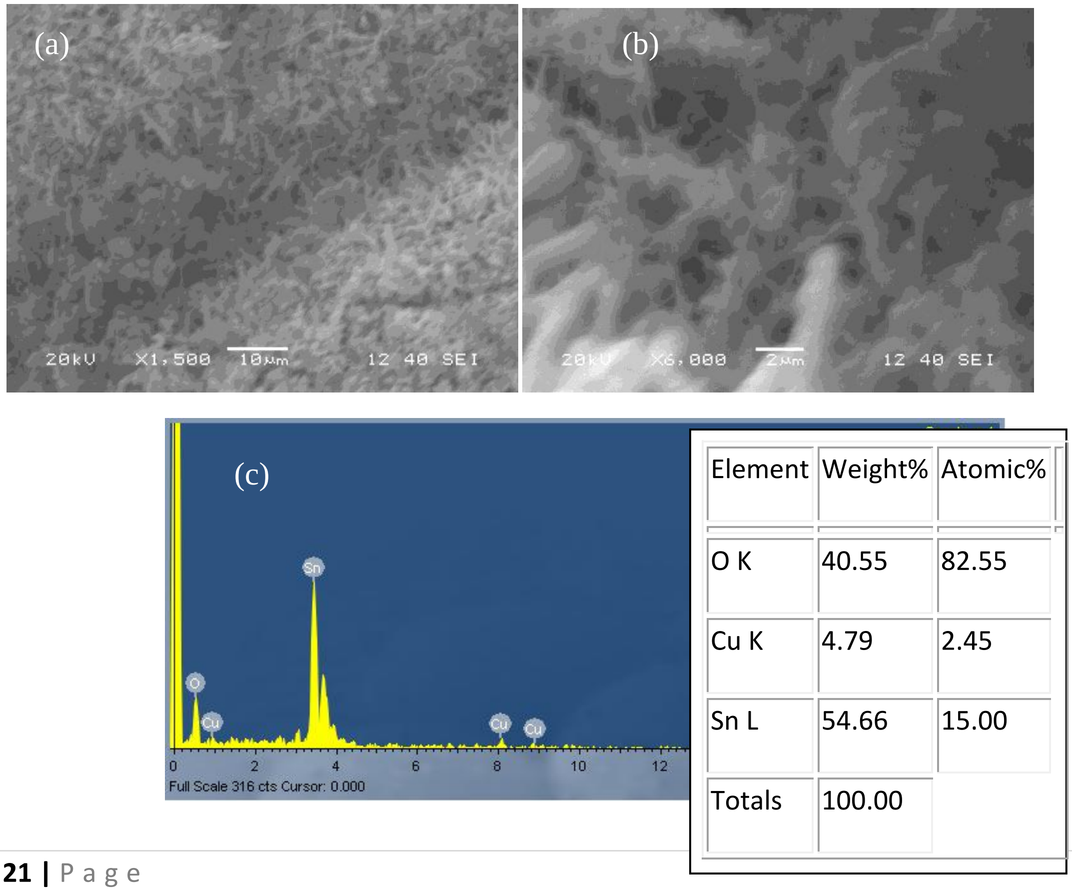
(b)

Element	Weight%	Atomic%
Cu K	30.07	44.54
Sn L	69.93	55.46
Totals	100.00	

(c)

Element	Weight%	Atomic%
O K	53.42	89.29
Cu K	1.09	0.46
Sn L	45.49	10.25
Totals	100.00	

Figure 4.2 (a) SEM and (b-c) EDX analysis of Sn-5 wt. % Cu composition heated to 500°C for 2 hours



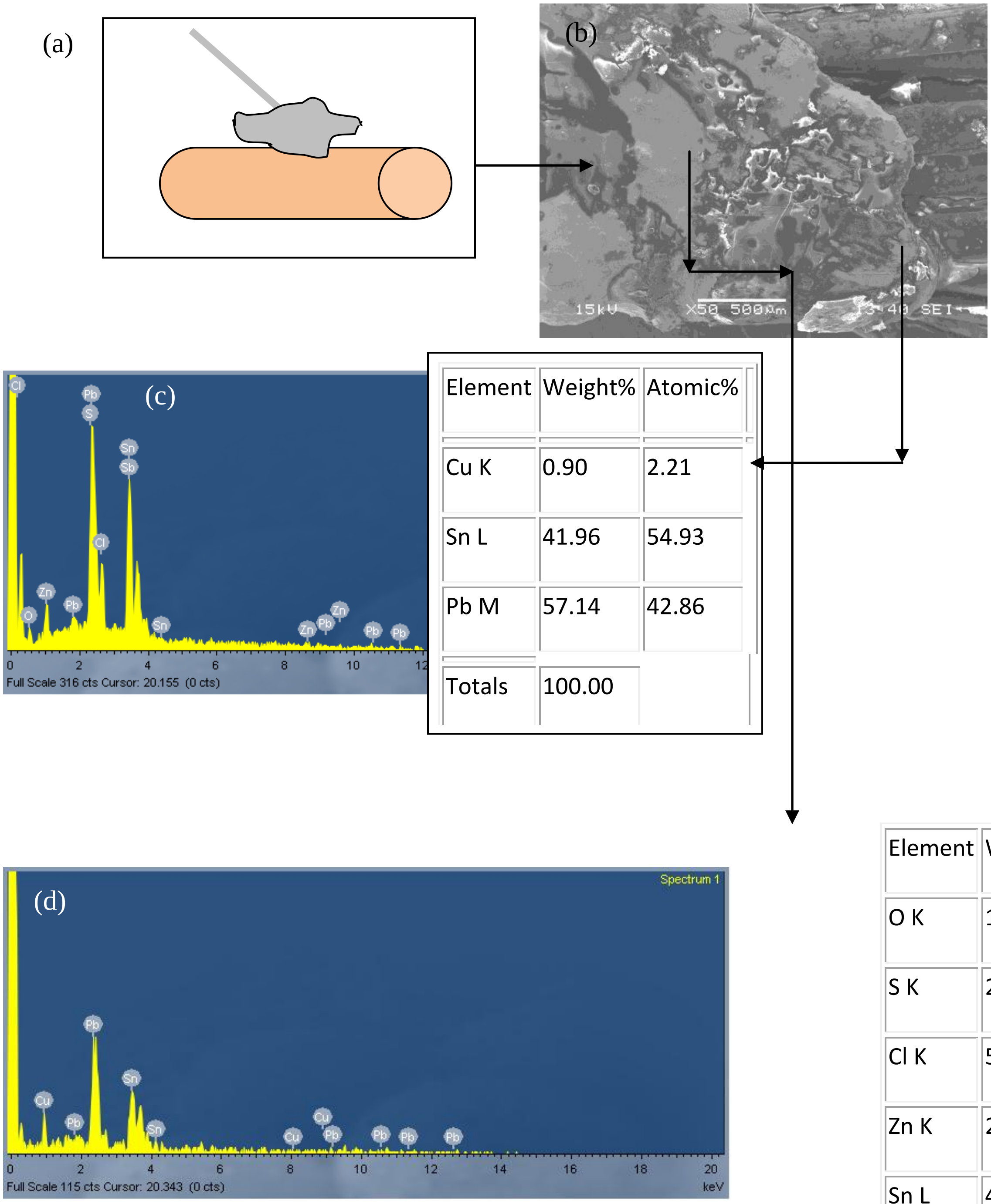
Element	Weight%	Atomic%
O K	40.55	82.55
Cu K	4.79	2.45
Sn L	54.66	15.00
Totals	100.00	

Figure 4.3 (a-b) SEM and (c) EDX analysis of Sn-5 wt. % Cu composition heated to 500^{o}C for 2 hours showing the formation of SnO_2 structures in the solidified alloy

SEM images in Fig. 4.3(a-b) show clearly the rod like structures of SnO_2 that have formed by oxidation of the Sn-5wt.% Cu sample due to the presence of air in the furnace. These structures were not see in the Cu-20wt%Sn composition .

4.4 Solidification of Pb-Sn Solder on Cu

The interfacial reaction between copper and the solder is also studied. Here a copper rich wire is brought in contact with molten Pb-Sn solder. The molten solder was allowed to solidify on the Cu wire in air. Copper from the copper wire diffuses into tin in the Pb-Sn alloy. Similar reaction also takes place when a Pb-Sn solder is used to solder copper rich electrical components. Pb-Sn forms a eutectic system with the eutectic composition being Sn-37 wt. % Pb and the eutectic temperature as 183^{o}C. This composition has the lowest melting temperature in the Pb-Sn system and the Pb-Sn eutectic solder is very commonly used. The EDX analysis of the solder after solidification in air and the copper wire has been given along with the SEM images in Fig. 4.4(a-d). It can be concluded from the EDX analysis in Fig. 4.4(c) that Cu diffused into Sn in the solder only to a very low extent of 2.21 atomic %. There was no trace of formation of intermetallic compounds between Sn and Cu. This was possibly due to the fast cooling of the molten Pb-Sn solder in air. Due to the fast cooling of the molten Pb-Sn solder Cu did not get enough time to diffuse into Sn and form intermetallic with Sn. From the EDX analysis given in Fig. 4.4(d) it can be concluded that in the interior portion of the solidified solder there was no trace of Cu in the solder. The percentage of oxygen in the interior portion of the solidified solder is around 47.30 atomic %. This large percentage of oxygen in the solidified solder suggests that there is possible oxidation of Sn and Pb in the solder.

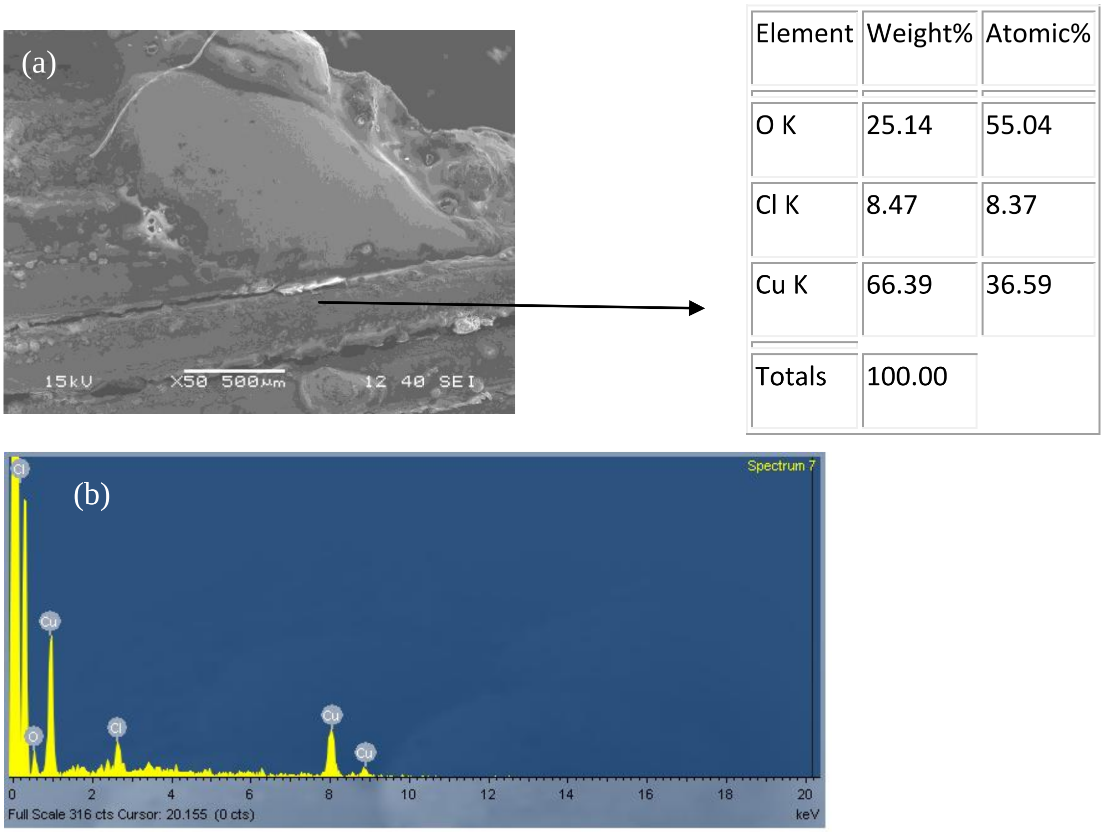


Element	Weight%	Atomic%
Cu K	0.90	2.21
Sn L	41.96	54.93
Pb M	57.14	42.86
Totals	100.00	

Element	Weight%	Atomic%
O K	11.69	47.30
S K	2.35	4.74
Cl K	5.68	10.37
Zn K	2.17	2.15
Sn L	40.43	22.05
Sb L	7.34	3.90
Pb M	30.34	9.48
Totals	100.00	

Figure 4.4 (a) Schematic showing the solidification of Pb-Sn solder on a Cu wire (b) SEM image of the solidified Pb-Sn solder on the Cu wire. EDX analysis of the solidified Pb-Sn solder (c) near the Cu wire (d) in the interior of Pb-Sn solders.

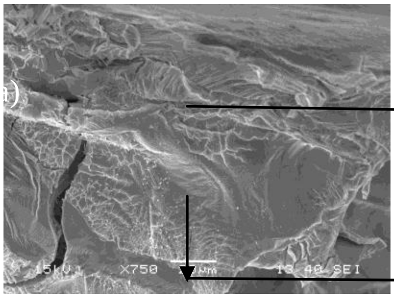
There is also no trace of diffusion of Sn or Pb into Cu. The SEM image in Fig. 4.5(a) shows clearly the interface between the solidified solder and the copper wire. From the EDX analysis in Fig. 4.5(b) we find a large percentage of oxygen in the Cu wire. The percentage of oxygen is around 55.04 atomic %.



Element	Weight%	Atomic%
O K	25.14	55.04
Cl K	8.47	8.37
Cu K	66.39	36.59
Totals	100.00	

Figure 4.4.1 (a) SEM image of the solidified Pb-Sn solder on the Cu wire (b) EDX analysis of the Cu wire near the solidified Pb-Sn solder

The solidification of molten solder on a copper wire was also studied by melting a commercial solder alloy in a furnace and solidifying the molten solder on the copper wire. A commercial solder alloy was wrapped around a Cu wire and heated to 500^{o}C for 1 h in air in a muffle furnace. At 500^{o}C the solder is expected to be completely molten. The melting temperature of Pb 327.5^{o}C is and that of Sn is 231.9^{o}C. The molten solder was cooled in the furnace. The SEM image in Fig. 4.6(a) shows the surface of the solidified solder. Crack could be seen in the surface of the solder. Fig. 4.6(b) shows the region of contact between the solidified solder and the copper wire. EDX analysis in Fig. 4.6(c) and (e) suggests that there is diffusion of Cu into the solder. The percentage of Cu in the solidified solder was found to be 4.71 atomic % in the interior regions of the solder and 13.67 atomic % near the copper wire. There is indication of oxidation of both the solder and the copper wire. The EDX analysis in Fig. 4.6(d) suggests that there is possible formation of tin oxide as there are regions on the solder where only tin and oxygen could be traced. The atomic percentage of oxygen in both the solder and the copper wire was found to be very high [97].

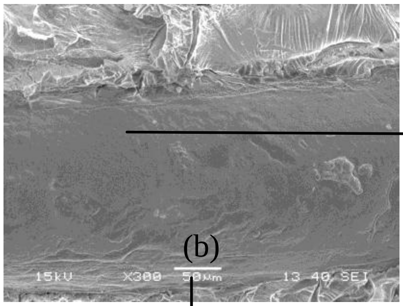


(c)

Element	Weight%	Atomic%
O K	34.19	79.13
Cu K	8.08	4.71
Sn L	43.85	13.68
Pb M	13.87	2.48
Totals	100.00	

(d)

Element	Weight%	Atomic%
O K	48.60	87.52
Sn L	51.40	12.48
Totals	100.00	



(e)

Element	Weight%	Atomic%
Cu K	5.93	13.67
Sn L	37.49	46.30
Pb M	56.58	40.03
Totals	100.00	

(f)

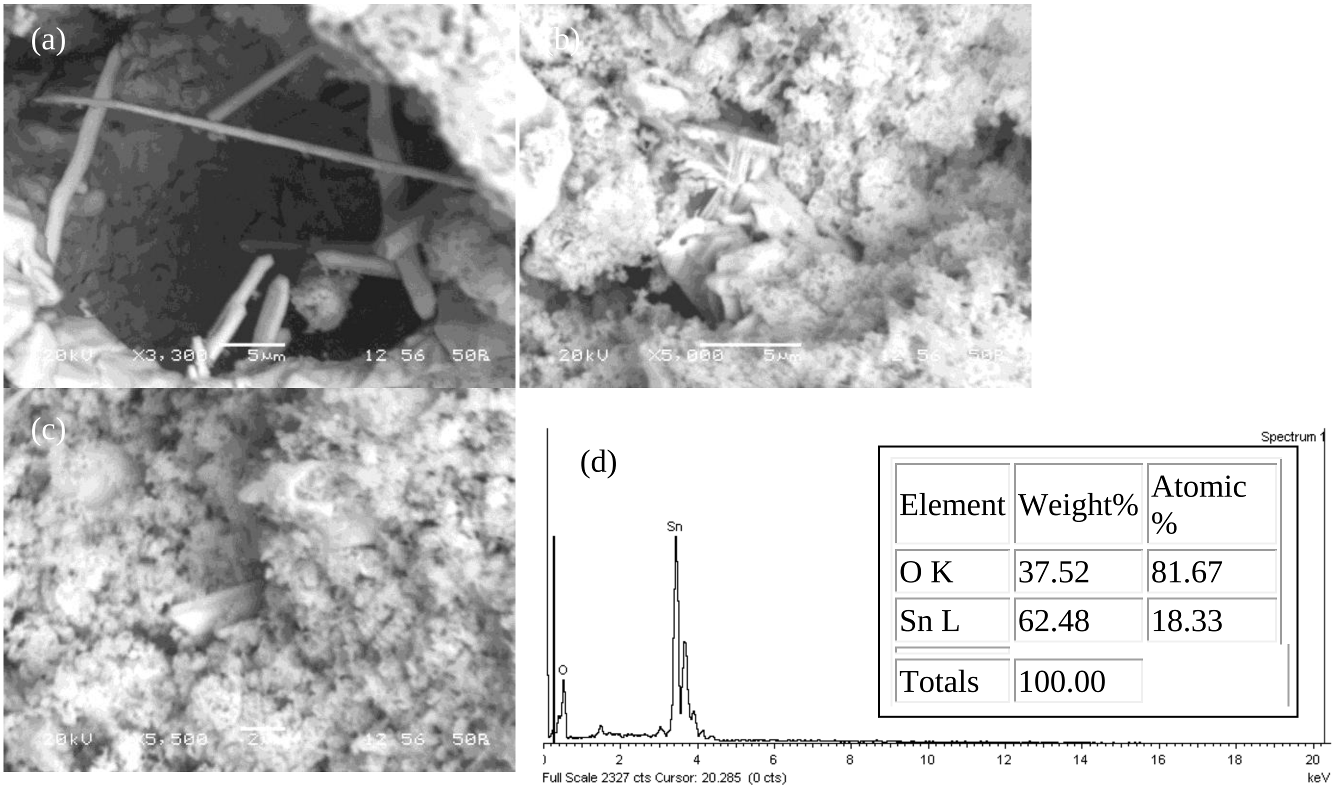
Element	Weight%	Atomic%
O K	32.67	65.84
Cu K	67.33	34.16
Totals	100.00	

Figure 4.4.2 (a-b) SEM images of commercial solder wrapped around a Cu wire and heated to 500^{o}C for 1 h (c-f) EDX of various regions of the sample

4.5 Oxidation Behavior of Sn

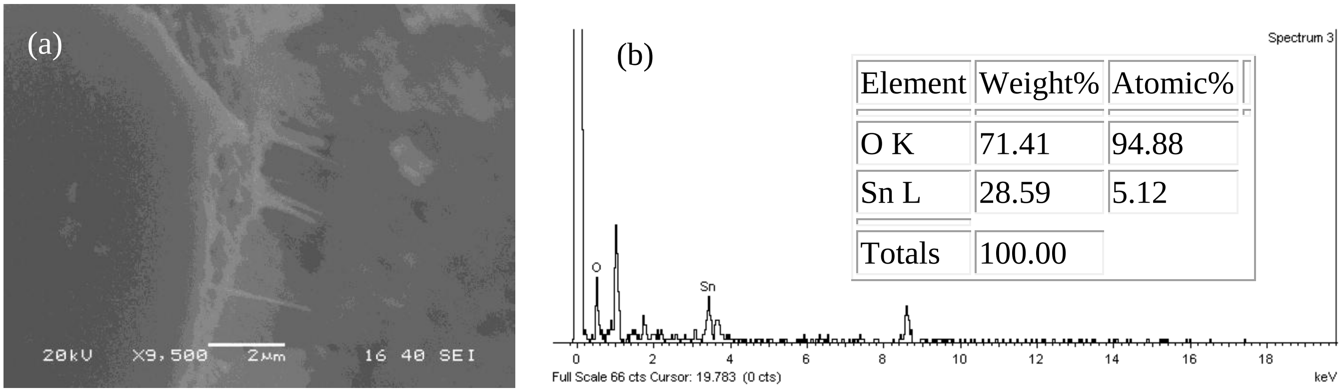
SnO_2 is a material of high technological importance. SnO_2 is a n-type semiconductor having a wide band gap. It has optoelectronic and gas sensing applications. Nanodevices developed from SnO_2 are becoming more and more popular. Tin oxide is chemically very stable. Here SnO_2 has been synthesized by oxidation of tin in a muffle furnace. The objective is to understand the oxidation behavior of Sn. Nanostructured SnO_2 could be seen in the oxidized samples [98,99].

Oxidation of metallic Sn at 1000^oC for 1 h showed the formation of tin oxide rods and nanosturctures. The melting point of Sn is 232^oC whereas its boiling point is 2603^oC. At 1000^oC Sn is expected to melt completely but it will be in the liquid state as it vaporizes at a much higher temperature. The SEM images in Figs. 4.7 (a-c) show the SnO_2 rods that have been formed by oxidation of Sn in a muffle furnace at 1000^oC for 1 h in air. SnO_2 rods have been found to be very long and some of them had lengths of 30-40 µm. The EDX analysis in Fig. 4.7(d) shows that the atomic percentage of oxygen in these tin oxide structures is very high. The tin oxide formed here is not stoichiometric SnO_2. The tin oxide structures formed have been found to be in the form of triangular rods. The formation of triangular rods has been also reported by others [100]. Even at a temperature of 1000^oC and holding time of 1 h the number of tin oxide structures has been found to be very low. Nanostructures of tin oxide could also be seen in the sample. The SEM image in Fig. 4.8(a) shows tin oxide nanostructures on the tin rich particles. The tin oxide nanostructures have a maximum length of around 3µm. The EDX analysis in Fig. 4.8(b) shows that the atomic percentage of oxygen is very high in the tin oxide nanostructures. Sn was also oxidized in a muffle furnace at 1000^oC for 2 h in air. SEM image in Fig. 4.9(a) shows the absence of any tin oxide structures. Oxidation of Sn at 1000^oC for 2 h led to a more stoichiometric tin oxide. EDX analysis in Fig. 4.9(b) shows that the atomic percentages of Sn and O are 30.57 and 69.43 respectively. This suggests that with the increase in time of oxidation at 1000^oC the metallic Sn could be converted to stoichiometric SnO_2 [101-104].



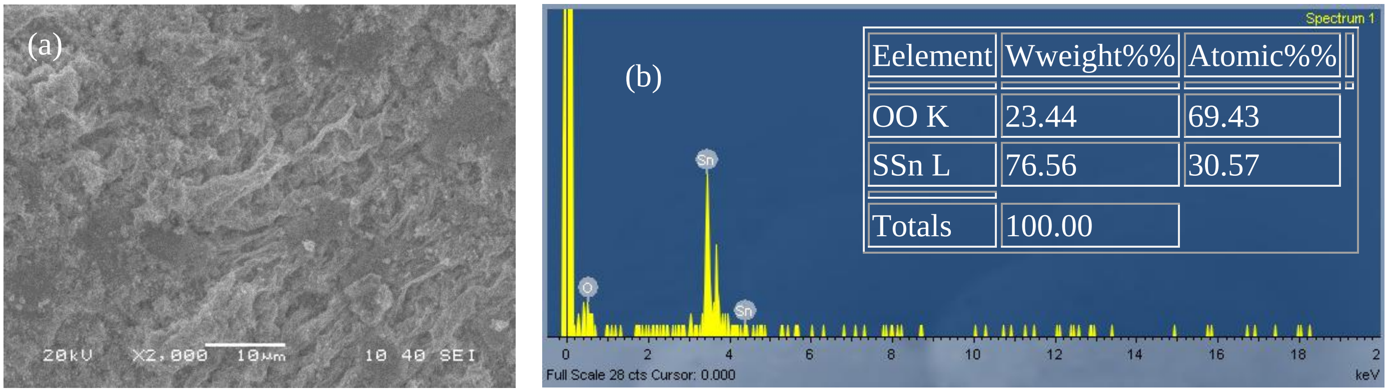
Element	Weight%	Atomic %
O K	37.52	81.67
Sn L	62.48	18.33
Totals	100.00	

Figure 4.5 (a-c) SEM of Sn oxidized in air at 1000^{o}C for 1 h (d) EDX of the rod like structures



Element	Weight%	Atomic%
O K	71.41	94.88
Sn L	28.59	5.12
Totals	100.00	

Figure 4.5.1(a, b) SEM of Sn oxidized in air at 1000^{o}C for 1 h (b) EDX of the rod like structures

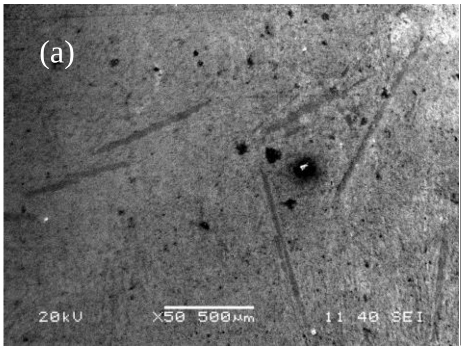


Eelement	Wweight%%	Atomic%%
OO K	23.44	69.43
SSn L	76.56	30.57
Totals	100.00	

Figure 4.5.2(a, b) SEM of Sn oxidized in air at 1000°C for 2 h (b) EDX of the surface

4.6 Microstructure of Sn-8.8Zn and Sn-8Zn-3Bi lead free alloys

The microstructure of the Sn–8.8Zn solder alloy consists of a primary Sn-phase and a Zn/Sn eutectic mixture. Fine Zn-rich phases are dispersed in the Sn matrix near to the interface. In the case of the Sn–8Zn–3Bi solder, the microstructure consists particularly of a Zn/Sn eutectic region with some Zn-rich phase, a Sn-rich phase and very fine Bi precipitates (white in the SEM image). The eutectic mixtures are layer type in the case of both solders. Very fine Bi particles are dispersed in the Sn matrix in the Bi-containing solder. The Bi-rich phase precipitates because the Sn–Bi phase diagram shows that the solubility of Bi in Sn is only about 3wt% at room temperature. The Zn-rich phases and the Bi-rich phases are uniformly distributed in the solder. Some voids are observed at the surface of the Sn–Zn based solder alloys. The diffusion of Zn will lead to vacancy diffusion in the opposite direction, and the accumulation of vacancies will lead to void formation at the upper surface .



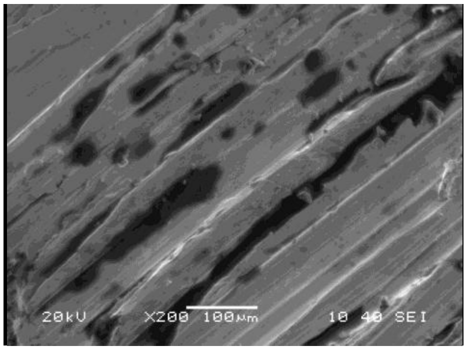
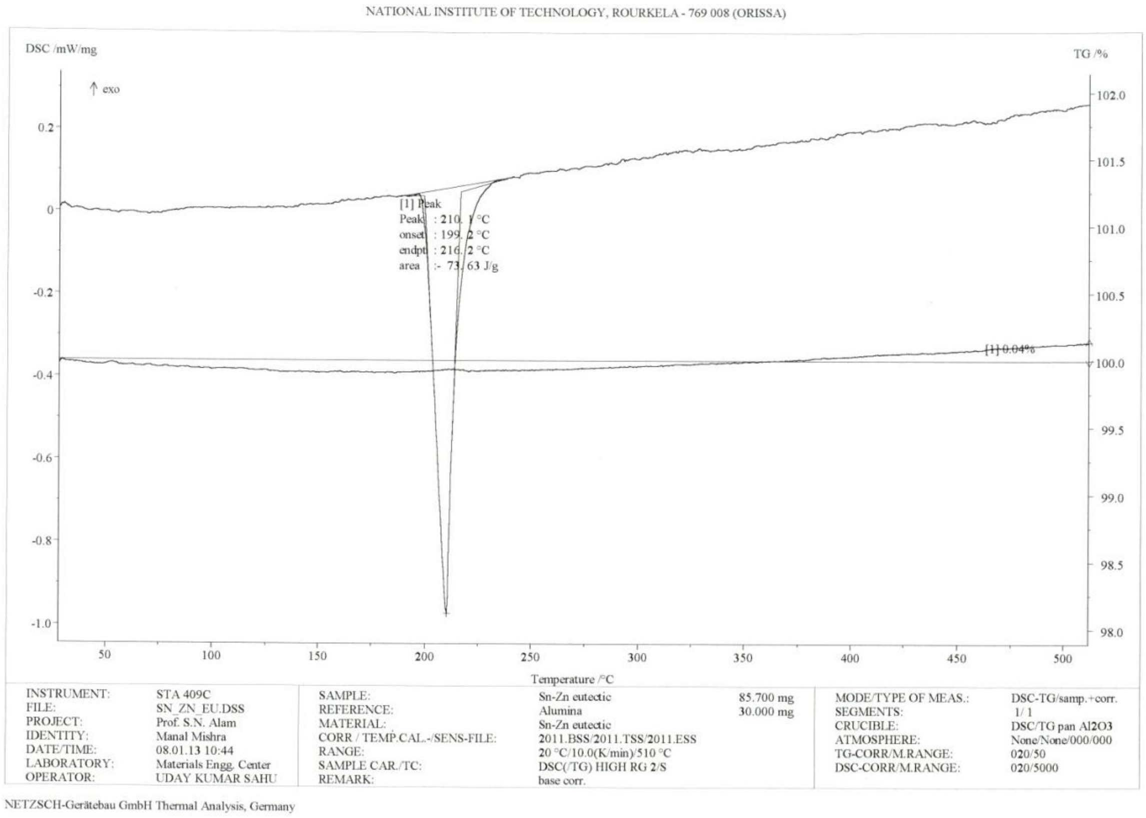


Fig.4.6 (a) Microstructure of Sn-8.8Zn 4.6(b) Microstructure of Sn-8Zn-3Bi lead free alloys

4.7 Thermal analysis of Sn-8.8Zn and Sn-8Zn-3Bi lead free alloys

4.7.1 Sn-8.8Zn solder

The melting temperature (T_m) is an important physical property and has a great influence on printed circuit board (PCB) assembly. A promising solder alloy should have a lower melting temperature and a narrow pasty temperature zone. Sn-8.8Zn eutectic alloy was prepared by heating Sn granules and Zn foils at 500^0C for 2 hour. Fig.4.11.1 shows the DSC curve of the solder alloy upon heating at a scanning rate of 20^0C/min.



INSTRUMENT: STA 409C
FILE: SN_ZN_EU.DSS
PROJECT: Prof. S.N. Alam
IDENTITY: Manal Mishra
DATE/TIME: 08.01.13 10:44
LABORATORY: Materials Engg. Center
OPERATOR: UDAY KUMAR SAHU

SAMPLE: Sn-Zn eutectic 85.700 mg
REFERENCE: Alumina 30.000 mg
MATERIAL: Sn-Zn eutectic
CORR / TEMP.CAL.-/SENS-FILE: 2011.BSS/2011.TSS/2011.ESS
RANGE: 20 °C/10.0(K/min)/510 °C
SAMPLE CAR./TC: DSC(/TG) HIGH RG 2/S
REMARK: base corr.

MODE/TYPE OF MEAS.: DSC-TG/samp.+corr.
SEGMENTS: 1/ 1
CRUCIBLE: DSC/TG pan Al2O3
ATMOSPHERE: None/None/000/000
TG-CORR/M.RANGE: 020/50
DSC-CORR/M.RANGE: 020/5000

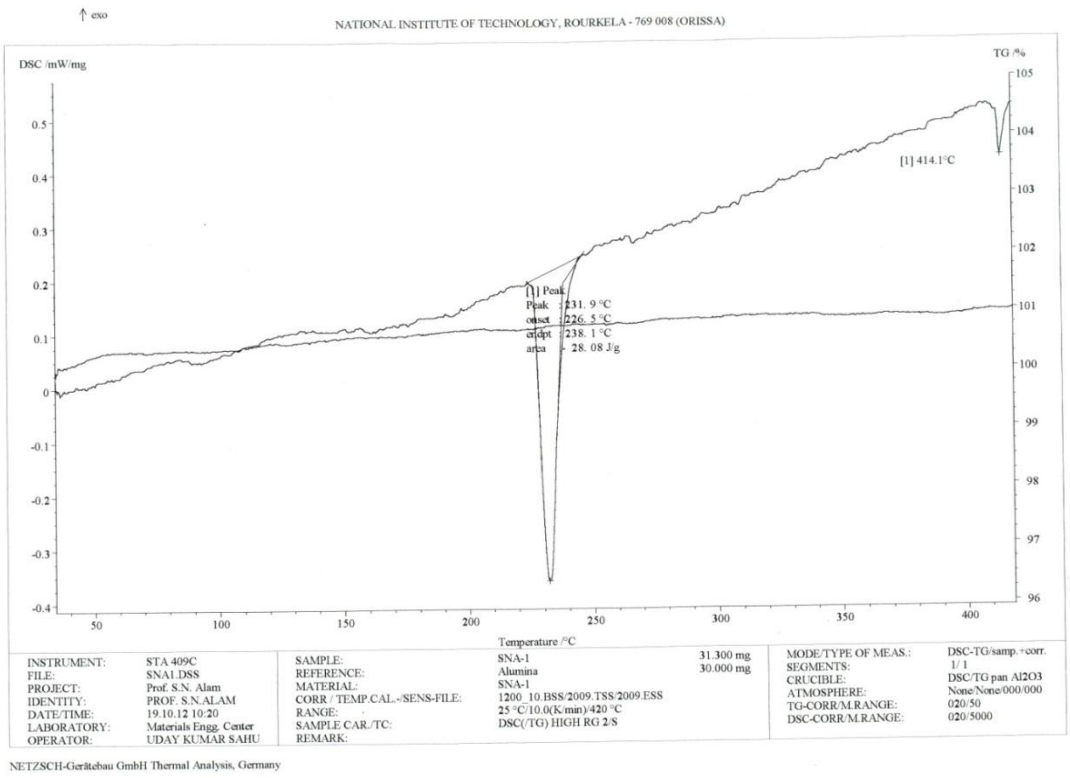
NETZSCH-Gerätebau GmbH Thermal Analysis, Germany

Fig.4.7.1 DSC curve of Sn-8.8Zn eutectic alloy

DSC result shows an endothermic peak at 210.1^oC which corresponds to the melting point of Sn-8.8Zn eutectic composition (198^oC). It confirms that the eutectic alloy has been formed. The difference between above two temperatures may be due to oxide formation. The existence of oxygen is attributed to the absorption of oxygen in the air by the specimen's surface during melting, grinding and polishing.

4.7.2 Sn-8Zn-3Bi lead free solders

Sn granules, Zn powder and Bi powder were taken to prepare this lead free alloy. The mixture was heated at 200^0C for 2 hours. Both SEM and DSC data confirmed that no alloy has been formed at this processing temperature. This may be due to the fact that the powder forms of Zn and Bi. These powder particles readily form oxides when heated. The appearance of some spherical particles in SEM image might have been resulted from sintering. Fig.4.11.2 shows the DSC curve of the Sn-8Zn-3Bi alloy upon heating at a scanning rate of 25^0C/min.



INSTRUMENT: STA 409C
FILE: SNA1.DSS
PROJECT: Prof. S.N. Alam
IDENTITY: PROF. S.N.ALAM
DATE/TIME: 19.10.12 10:20
LABORATORY: Materials Engg. Center
OPERATOR: UDAY KUMAR SAHU

SAMPLE: SNA-1 31.300 mg
REFERENCE: Alumina 30.000 mg
MATERIAL: SNA-1
CORR / TEMP.CAL.-/SENS-FILE: 1200_10.BSS/2009.TSS/2009.ESS
RANGE: 25 °C/10.0(K/min)/420 °C
SAMPLE CAR./TC: DSC(/TG) HIGH RG 2/S
REMARK:

MODE/TYPE OF MEAS.: DSC-TG/samp.+corr.
SEGMENTS: 1/ 1
CRUCIBLE: DSC/TG pan Al2O3
ATMOSPHERE: None/None/000/000
TG-CORR/M.RANGE: 020/50
DSC-CORR/M.RANGE: 020/5000

Fig.4.7.2 DSC curve of Sn-8Zn-3Bi solder alloy

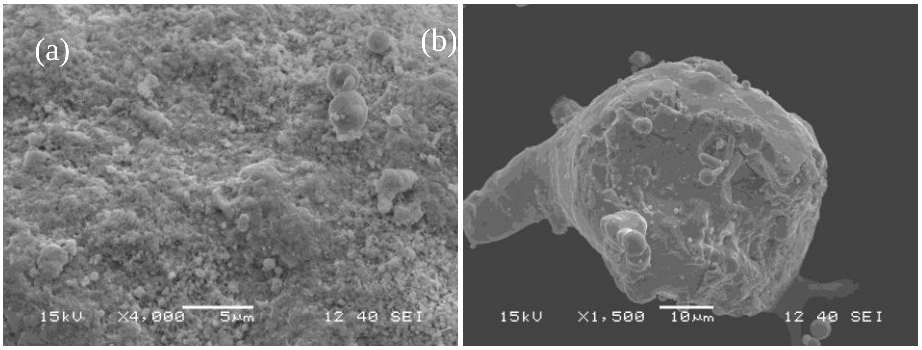
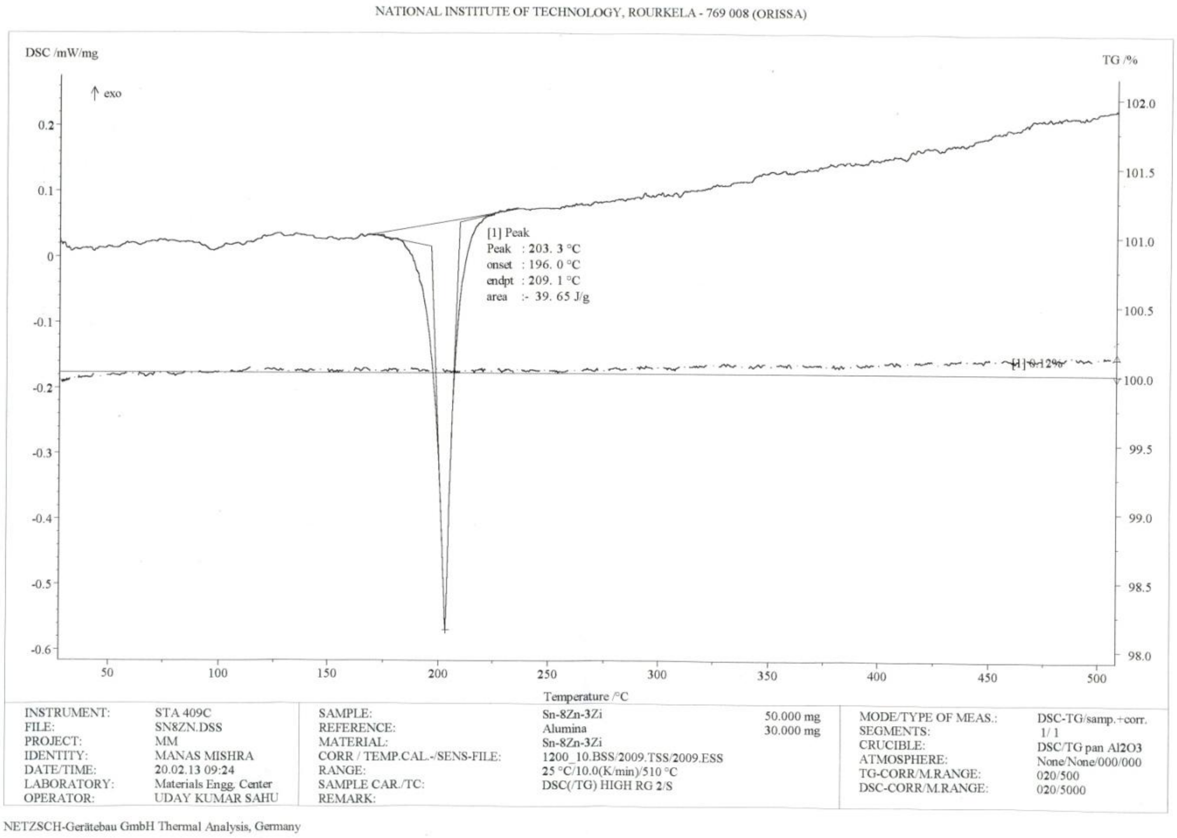


Fig. 4.7.3(a,b) microstructure of Sn-8Zn-3Bi at 200^0C for 2 hour

DSC result shows an endothermic peak at 231.9^oC which corresponds to the melting point of Sn(231.9^oC). Another endothermic peak at 414.1^oC was also found which corresponds to the melting point of Zn (419.5^oC). The existence of the two separate melting peaks of Sn and Zn suggests that the processing temperature of 200^oC is very low for the formation of the alloy and the two elements melt separately. Therefore a higher processing temperature of 450^oC was chosen.

Zn foils and Bi powder were taken along with Sn granules to develop Sn-8Zn-3Bi lead free solder alloy. The composition was heated at 450^0C for two hours. Fig.4.11.3 shows the DSC curve for this alloy upon heating at a scanning rate of 25^0C/min. DSC result shows an endothermic peak at 203.3^oC which corresponds to the melting point of Sn-8Zn-3Bi composition (189^oC). It confirms that the eutectic alloy has been developed.



INSTRUMENT: STA 409C
FILE: SN8ZN.DSS
PROJECT: MM
IDENTITY: MANAS MISHRA
DATE/TIME: 20.02.13 09:24
LABORATORY: Materials Engg. Center
OPERATOR: UDAY KUMAR SAHU

SAMPLE: Sn-8Zn-3Zi 50.000 mg
REFERENCE: Alumina 30.000 mg
MATERIAL: Sn-8Zn-3Zi
CORR / TEMP.CAL.-/SENS-FILE: 1200_10.BSS/2009.TSS/2009.ESS
RANGE: 25 °C/10.0(K/min)/510 °C
SAMPLE CAR./TC: DSC(/TG) HIGH RG 2/S
REMARK:

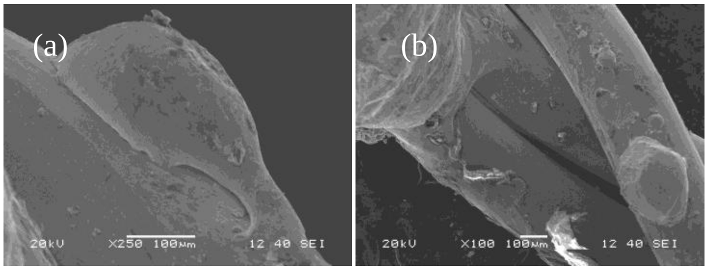
MODE/TYPE OF MEAS.: DSC-TG/samp.+corr.
SEGMENTS: 1/1
CRUCIBLE: DSC/TG pan Al2O3
ATMOSPHERE: None/None/000/000
TG-CORR/M.RANGE: 020/500
DSC-CORR/M.RANGE: 020/5000

Fig.4.7.4 DSC curve for Sn-8Zn-3Bi alloy

From above DSC data (fig.4.12) it has been observed that the addition of 3% Bi decreased the melting temperature from 210.1^{0}C to 203.3^0 C. This suggests that the Bi addition achieves a melting temperature closing to 63Sn–37Pb. However, the addition of small amount of Bi expands slightly the temperature interval of the pasty range (T_{end} $-T_{onset}$), which is the difference between the liquidus (T_{end}) and solidus (T_{onset}) temperature. According to Sn-Bi binary phase diagram, 1% Bi addition may form solid solution with Sn. Besides, the eutectic temperature of Sn-Bi alloys is 139^{0}C, which could lower the melting point of the Sn–8Zn–3Bi. Since the solubility of Bi in Sn is less than 3% at room temperature, the high supersaturation of Bi at low temperature is relived by the formation of Bi precipitates and/or SnBi IMC, which brings down the melting temperature of the Sn–8Zn–3Bi alloy [105,106].

4.8 Wetting characteristics of Sn-8.8Zn and Sn-8Zn-3Bi solders

The addition of Bi could improve wettability of Sn–Zn based solders on Cu substrate. Soldering has been done on a Cu wire by using the above two solder alloys. It has been observed that proper wetting does not take place in case of Sn-8.8Zn solder



However the wetting area is more in case of Sn-8Zn-3Bi solder. As shown in Fig. 5(a, b), wetting area increases with addition of Bi. Bi is one of the surface-active elements. Surface tension of liquid Sn–Bi eutectic alloy is far lower than that of Sn–Pb or Sn–Zn eutectic alloy in the same state. Hence, the addition of Bi could decrease surface tension of the liquid solders, and accelerate their spreading on Cu wire [107,108].

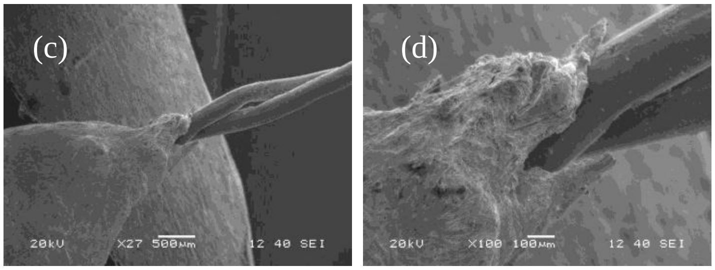


Fig.4.8 (a,b) soldering of Sn-8.8Zn on a Cu wire and (c,d) Soldering of Sn-8Zn-3Bi on Cu wire

CHAPTER 5

CONCLUSION

CONCULSIONS

Intermetallics like Cu_6Sn_5, Cu_5Sn could be formed in the various Cu-Sn alloys. Needle like structures of intermetallic Cu_5Sn could be seen in fused Cu-Sn alloy electric wire. Elongated shape of the intermetallic Cu_6Sn_5 could be seen in the microstructure of solidified Cu-20wt. % Sn alloy. In the solidified Sn-5 wt. % Cu alloy formation of Cu_6Sn_5 intermetallic could be traced.

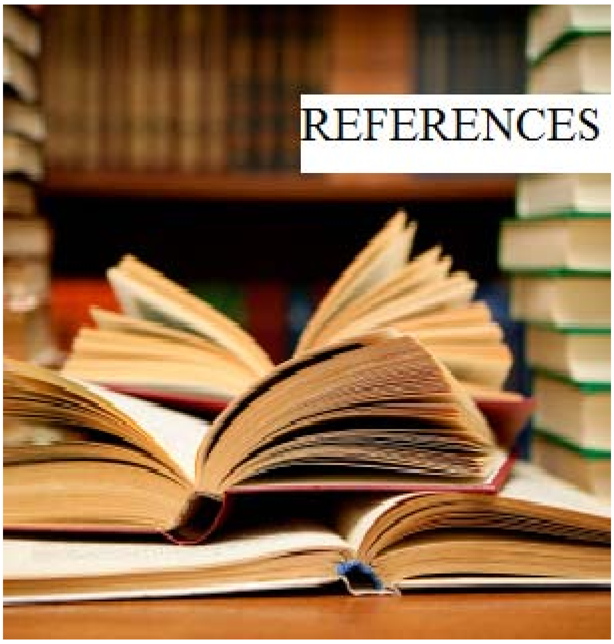
Solidification of Pb-Sn Solder on Cu electrical wires did not show any formation of intermetallics although there was diffusion of Cu into Sn which could be seen in the solder in contact with the copper wire. There was no indication of diffusion of Sn into Cu.

Oxidation of Sn led to the formation of SnO_2 structures. Rod like SnO_2 structures could be seen in the solidified Sn-5 wt. % Cu alloy. Tin oxide nanostructures could be formed when metallic Sn was oxidized in air at 1000^oC for 1 h. The SnO_2 that was formed was highly non-stoichiometric. Triangular rods of SnO_2 could be formed. Oxidation of metallic Sn for a period of 2 h at 1000^oC led to the formation of more stoichiometric SnO_2.

No alloy has been formed by heating Sn granules, Zn powder and Bi powder at 200^0C for 2 hours. This may be due to the fact that the powder forms of Zn and Bi. These powder particles readily form oxides when heated. The existence of the two separate melting peaks in DSC data suggests that the processing temperature of 200^oC is very low for the formation of the alloy.

We find the melting point of Sn-8.8Zn eutectic composition i.e. 210.1^oC and for Sn-8Zn-3Bi it is 203.3^oC. The addition of 3wt%Bi decreases the melting point of Sn-Zn lead free solder but it increases the pasty range. By soldering the above two solder alloys on a Cu wire, it has been observed that proper wetting does not take place in case of Sn-8.8Zn solder but the wetting of substrate is more in case of Sn-8Zn-3Bi solder.

CHAPTER 6



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