CHAPTER-1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Soldering is the process to connect two or more electrical/electronic components with the help of a filler material i.e. solder alloy. Generally, the melting point of filler material is lower than the melting point of adjoining metal. Unlike welding, the work piece doesn't melt in the process of soldering. It provides both electrical and mechanical support, and solder alloys are very extensively used as the linking material in electronic industries for packaging. Most of the solder alloys are basically tin-based. Tin and lead (Sn63/Pb37) alloys are a good combination for soldering material due to their eutectic or near eutectic temperature, low around 183°C, good mechanical and electrical properties, low cost, and Physio-chemical properties [1]–[5].

Despite these benefits, there is a significant disadvantage of heavy metals like lead due to its toxicity. Now, a lot of efforts have been made in recent decades to restrict its use as it could pose an immediate risk to human health and the environment [6], [7]. In many European countries and many countries across the world, Pb was banned in paints, fuels, and plumbing applications. Since many countries have come up with very stringent legislation that mandated the limitation of the use of certain hazardous substances (RoHS) [8]–[10] and the waste electrical and electronic equipment (WEEE) [11], the alloy design and process design of the soldering made a substantial shift in direction. The European Union was the first administrative territory to come up with stringent policies against Pb usage in electronics, enacting the RoHS and WEEE rules. These restrictions have been imposed to control the use of lead in fast-growing electrical and electronic equipment. It is the manufacturer's responsibility to dispose-of safely or recycling of this waste after the end of their useful life. It has been seen that Pb and Pb-containing compounds hold an important place among the top 17 pollutants, which are direct threats to human life and the environment, according to the US Environmental Protection Agency (EPA). The use of lead (Pb) in flame retardants has been phased out under the "Directive on the Restriction of Hazardous Substances in Electrical and Electronic Equipment since, July 1, 2006, in Europe". As a result, researchers have started looking for new alternative solder that is free of lead without compromising its properties [12]–[14]. Before recommending a new lead-free solder, it is essential to critically evaluate the important properties like liquidus temperature, mechanical performance, microstructure, wetting behaviour, corrosion behaviour, pasty range, solderability, dependability, etc. [15], [16]. The cost and reliability of the solder must be considered while producing a new solder. The conventional lead-tin solder has been in use for many decades, and many engineering designs are based on the properties of existing solder alloys. If the characteristics of the solder alloys change, then the changes in design have to be made, which is not that easy. Therefore, developing lead-free solder alloys with similar properties to conventional lead-tin solder is a great challenge. For example, any increase in the melting temperature at which printed circuit boards (PCBs) are processed has a negative impact on component dependability. Due to the limited melting point range, a study is limited to a few different alloys based on Sn with added elements. In addition to the temperature requirements, Sn-Pb has some metallurgical and mechanical qualities that an alternative alloy must match to be a viable replacement.

1.2 Motivation

Eliminating lead (Pb) from the production of electronic devices and electronic waste is crucial due to the well-established toxicity of heavy metals like Pb.. It is also difficult to recycle the Pb from these electronic industries as is done for other sectors due to a small quantity of lead. It has also been seen that lead vapor emission occurs even if it is buried after shredding. Vapor pressure of lead oxide is high in the manufacturing industries and causes hazards by inhalation to workers. Therefore, the world forum needs to reduce the use of lead in many applications seriously. Many countries have brought stringent policies to control the lead in the environment. A multinational decision will lead to the development of lead-free solder alloys based on Sn. As far as the use of lead-tin solder is concerned, there is a huge experience of 1000 years which is not there for lead-free solder. The infrastructure for manufacturing electronics is based on the Pb-Sn solder. One of the beauties of Pb-Sn solder is its thermal efficiency, making it the best choice for the electronic industries. The sizes of handheld electronic objects are reducing daily, putting lots of pressure on the performance of solder alloys.

Researchers are trying hard to find tin-based alloys with melting temperatures similar to tin-lead eutectic. They have not succeeded so far. At the most, they found the melting temperature close to the melting temperature of tin. Change in infrastructure and design is essential for adopting lead-free solders. Further, engineering design decision has to be made based on analytical modeling to predict product reliability. Definitely, some fundamental information is required for reliable analytical modeling for accurate prediction. In addition, it is essential to address the challenges faced by the conventional solder before switching to the lead-free solder, like high current density and electro migration lead to the shrinkage size scale and short circuit due to tin whiskers that are forming spontaneously. The primary issue with adapting a lead-free solder system is the infrastructure requirement. The existing electronic manufacturing industries should be given a stipulated time to get ready with the new infrastructure before implementing the lead-free soldering practice.

1.3 History of Solder

Soldering is a well-known method for joining materials. Many people might be unaware that soldering has been used for thousands of years (referring to **Figure 1.1**). The importance of joining for creating tools and making ornaments purposes led to discovering a primitive kind of soldering. Metal joining for making tools and other materials was a necessity. According to history, soldering was first practiced in Mesopotamia some 5000 years ago [17]. This confirms that the ancient Egyptian goldsmiths knew how to combine gold more than 5000 years ago. Soldering is used to make the legendary Sumerian swords. Soldering was used to build jewelry and cooking items in ancient times. Since then, soldering technology has advanced rapidly around the world. The ancient Romans achieved the incredible feat when they soldered 400 kilometers of lead-based water pipelines.

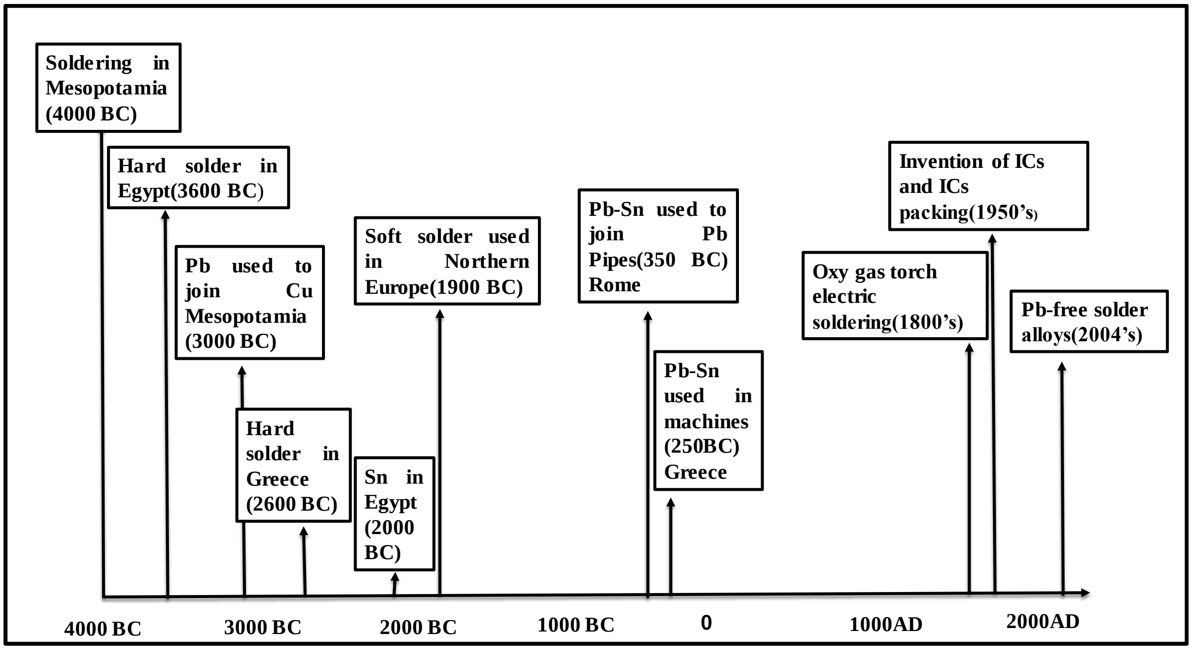

Fig.1.1 History of use of solder [18]

The higher ruling class did not consider such attempts essential and not adequately documented. In King Tut's tomb, in the year 1350 BC, some soft-soldered objects were found. Hard soldering techniques were well developed than soft soldering in Mediterranean cultures. Historians currently assume that Celts and Gauls invented soft soldering in

Northern and Central Europe around 1900 BC. In ancient times, tin-lead solders were utilized mainly in constructing and repairing cooking utensils and metal implements. The Greeks used tin-lead alloys to protect their bronze-based water pumps, air pumps in the year 350 BC. Soft soldering was used to attach the lead sheets lining the water tunnels' interior. The higher cost of tin compared to lead gave the Roman engineers economic incentives to adopt the less expensive tin-lead alloys, just as it does today. From the Iron Age to the Middle Ages, soldering hardly changed. Artisans typically used the method in the creation of jewelry and other crafts. Solders containing tin and lead were used to join copper and brass objects. Soldering technology was dramatically expanded throughout the Industrial Revolution. Soldering first appeared in the electronics sector in the early twentieth century as a dependable method of connecting copper wires for power and signal transmission. In those early applications, the solder joint's primary purpose was to ensure electrical continuity.

At the same time, materials scientists were looking for a solder having better mechanical strength and reliability that could replace lead-tin alloy. Further, it was realized that the lead needs to be replaced in solder alloy due to its toxicity. Therefore, it is essential to remember that the need for a lead-free solder alloy was not only a technological requirement but also a protection of environmental and health concerns. However, in the light of growing environmental and health concerns, the materials science community should carefully look for various new options.

1.4 Soldering Material

Solder alloys are used to solder linkages in a variety of ways. Tin (Sn) alloys with one or more of the following elements are used to make these solder alloys [19]: Lead (Pb), Bismuth (Bi), Indium (In), Silver (Ag), aluminum (Al), Antimony (Sb), Chromium (Cr), Cadmium

(Cd), Zinc (Zn), Copper (Cu), Nickel (Ni), and other metals are examples. A solder alloy is considered eutectic if the solidus and liquidus temperatures are the same; otherwise, it is called non-eutectic. Commercially available solder alloys come in solid, paste, or powder form.

1.5 Issue with lead-based solder alloys

1.5.1 Lead Poisoning

Environmental Protection Agency (EPA) prepared a list of polluting hazardous substances that harm human life and the environment. The pure metal lead and its compound are placed at the 17th position in that list. The Pb has a greater tendency to bind the protein in the body and affects normal functioning. This is the main reason for lead poisoning when the lead concentration is high in the blood. It also affects the Ca and vitamin D metabolism [20]–[24].Plumbism is another name for Pb toxicity. Pb oxide paint is also toxic, putting youngsters at greater risk than adults. According to the World Health Organization (WHO) and the US Centers for Disease Control and Prevention, lead permissible levels in blood 10 μg/dL for adults and 3.5 μg/dL for children, respectively, and can slow down the tissue development [25]–[29].

1.5.2 Adverse Effects of Pb On Human Life

Lead poisoning affects a wide range of physiological functions and organs (referring to **Figure 1.2**). When a person is exposed to Pb, they may experience the following symptoms:

1.5.2.1 Immediate Effects

- Diarrhea, convulsions, vomiting, etc.
- Abdominal pain, appetite loss, Constipation, etc.
- Irritability, sleeplessness, headache, etc.

1.5.2.2 Ultimate Effects

- Continual exposure to Pb can harm the kidneys, liver, and brain.
- Pb is the cause of osteoporosis (a disease that makes bone brittle).
- Excessive Pb exposure can result in convulsions, mental retardation, behavioral abnormalities, anemia, and high blood pressure, among other things.
- Pb can damage the placenta and the unborn child during pregnancy.
- Female employees exposed to high levels of Pb may experience miscarriages and stillbirths.
- Infants' intellectual development, behavior, height, and hearing can all be harmed by a very small quantity of Pb.

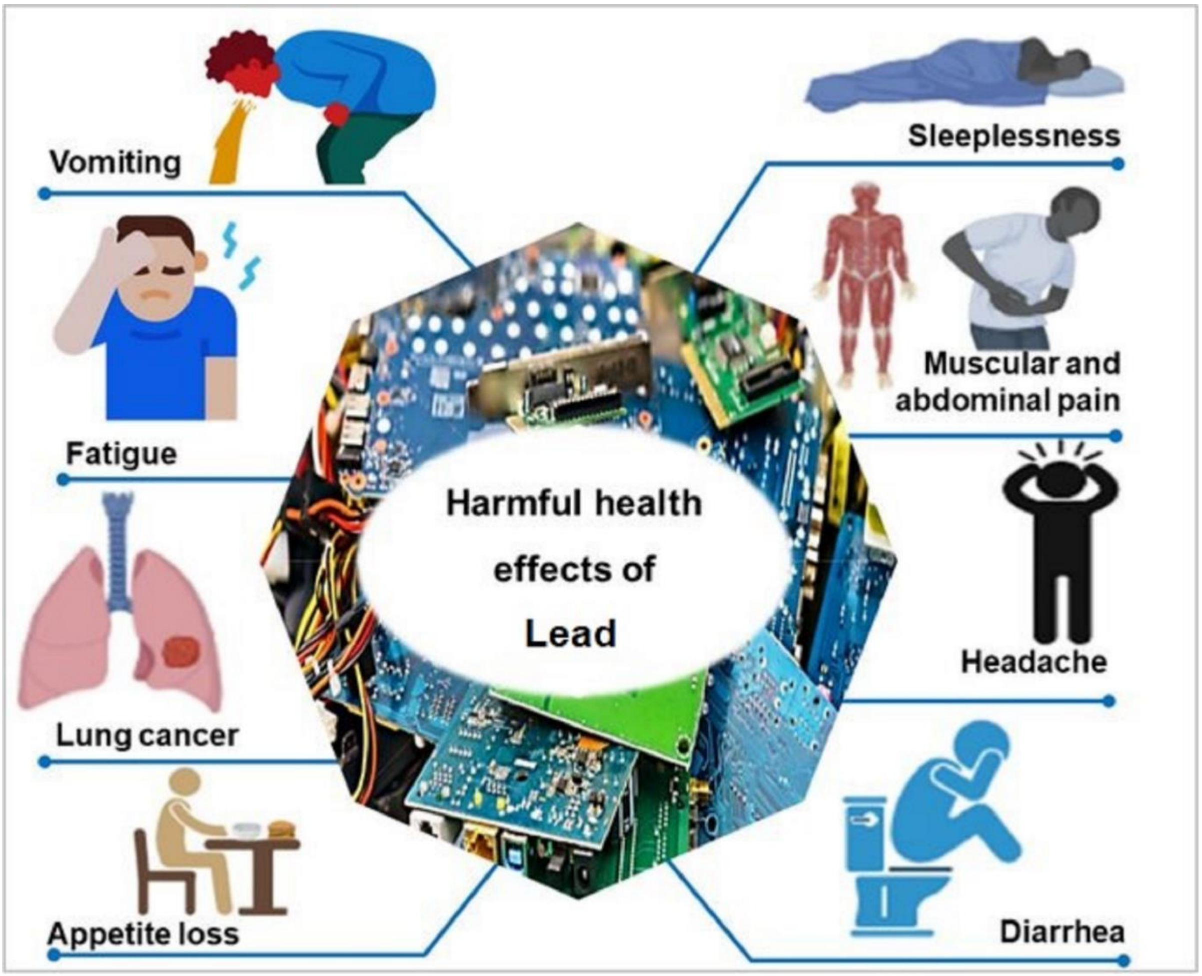

Fig.1.2 Effect of lead

1.5.3 Adverse Effects of Pb on Environment and Other Species

Electronic industries generate a large amount of waste because of the short life of electronic gadgets. These components are disposed of in solid waste dumps. The lead from the landfills getting leached, contaminate the groundwater (referring to **Figure 1.3**). The standard filtration procedure we employ to clean water is insufficient to remove Pb effectively. The bond which lead forms with water is difficult to break. Therefore, it is very difficult to remove by filtration and effective Pb disposal would be a bigger problem in the future. Though recycling Pb can solve the above problem, there are certain drawbacks [30], [31]. The quality of recycled lead depends on the methods used in collection, processing, and purification. Growing industrialization is also another reason for the increasing level of lead in the environment. India's water bodies have been contaminated with significant levels of Pb. Water containing 0.003 mg/L of Pb is considered an average level of Pb [32]. Lead is also found in soil as soluble and insoluble organic salts that readily interact with colloidal organic molecules. Pb toxicity in plants is primarily caused via absorption, transport, and intracellular localization. When Pb reacts with a collection of enzymes, it causes them to slow down. Pb poisoning affects animals with symptoms similar to those experienced by humans, such as gastrointestinal pain, peripheral neuropathy, and behavioral abnormalities. As a result, Pb shots have been outlawed in countries like the United States and Canada [32]–[36].

1.5.3.1 Accidental Cases

- Lead poisoning in Nigeria killed around 400 children in Nigeria on October 5, 2010 (Zamafara state Pb poisoning pandemic) [37], [38].
- More than 1000 youngsters from ten separate villages in China were found to have high levels of lead in their blood near the Yuguang gold and lead-smelting factory. Following the event, 15000 people relocated from the area, and the government halted Pb production at 32 factories [39], [40].

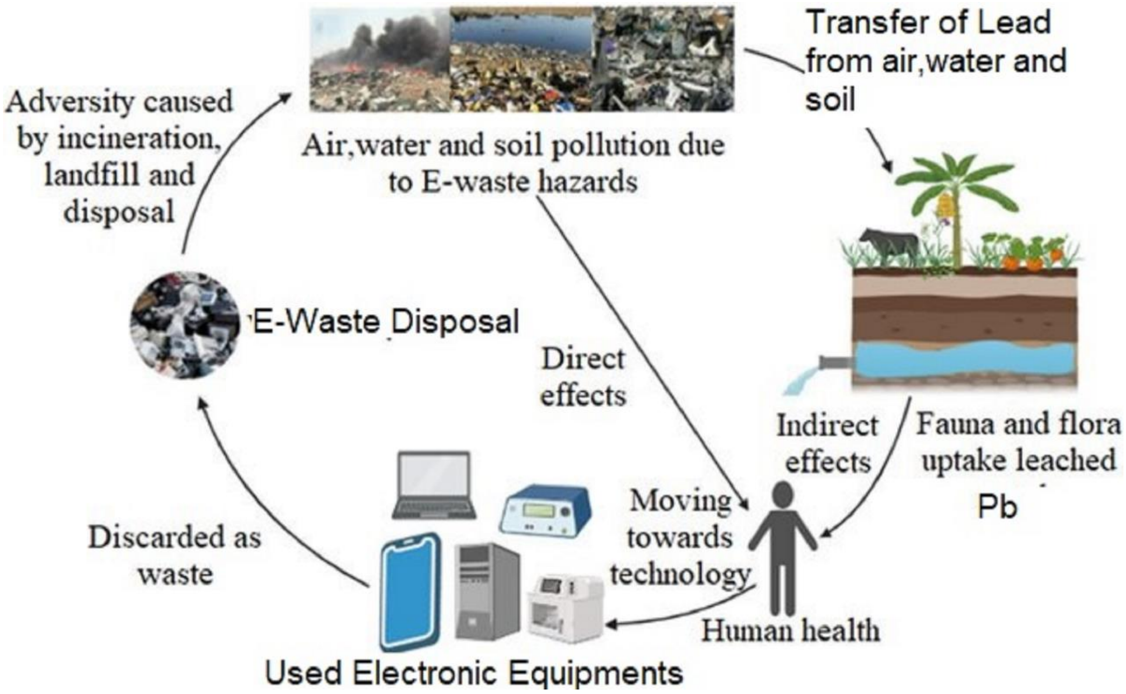

Fig.1.3 Representation of the lead cycle and its impacts on environment.

1.6 Source of exposure of lead

Pb can be found in a variety of places in the environment. The following are the most common:

1.6.1 Electronic waste

The main reasons for the exponential growth of the electrical and electronic industries are increased demand and the quick expiry of gadgets. As a result, a massive quantity of waste is generated [41]–[44]. Electronic and electrical waste (E-waste) is defined as "waste electrical or electronic equipment, including all components, subassemblies, and consumables that are part of the equipment at the time it becomes waste. Globally, 53.6 million metric tons (Mt) of E-waste were produced in 2019, according to the Global E-waste Monitor. By 2030, this quantity is expected to rise to 747 Mt. Asia (24.9Mt) produced the most E-waste in 2019, followed by the Americas (13.1 Mt), Europe (12 Mt), Africa (2.9 Mt), and Oceania (0.7 Mt). An estimated 80% of E-waste from industrialized countries is illegally shipped to LMICs such as China, India, Nigeria, Brazil, Ghana, and Pakistan, where labor costs and disposal are low, and restrictions are non-existent [45].

1.6.2 Drinking Water

The primary sources of Pb in drinking water are lead-containing pipes, faucets, and Pb-containing solder used during pipe repairs. Groundwater pollution occurs by leaching the Pb from the waste landfills. Pb dissolution in water is affected by the acidity of the water, the amount of minerals in the water, the temperature, and the length of time the water stays in the pipes. Drinking water is responsible for 14-20 % of Pb poisoning in the United States [46]–[48].

1.6.3 Lead Paint

Another potential source of Pb is lead paint. Lead carbonate [$PbCO_3/Pb(OH)_2$] is added to the paint to increase durability, expedite drying, and protect the surface from corrosion. Because lead paint dust collects from peeling[49], [50], flaking, and cracking, children are the most affected.

1.6.4 Lead at Work

Adults who work in lead-containing industries such as battery manufacturing, electronic components, pipe fitting, glass production, and smelting activities are prone to lead and have to take some steps to avoid exposure [51], [52].

1.6.5 Contaminated Soil

Contaminated soil can come from leaded gasoline and industrial operations such as smelters.

1.6.6 Lead-based items

Engine oil, jewelry, lunch boxes, and dishwashers are all significant sources of Pb.

1.7 Legislation on lead-based solder alloys

There is an important concern about the harmful effects of using hazardous substances in electronic equipment. The European Commission (EC) imposed the Restriction of Certain Hazardous Substances (RoHS) legislation, which has been in effect in all 25 European Union member states since July 1, 2006. Lead (Pb), Cadmium (Cd), Mercury (Hg), and Hexavalent Chromium (Cr^{6+}) are metals listed in the above list of toxic metals. The use of lead in flame retardants is also banned in Europe. The maximum lead concentration in the above materials list should be 0.1 wt.% max. The RoHS regulation covers a wide range of electronic items; however, some electrical and electronic items used for domestic illumination, transmission, and communications are exempted from the above restriction. The RoHS directive has an impact worldwide as everything has been globalized. Although Pb is not yet prohibited in Japan, it cannot be disposed of in landfills but is encouraged for recycling. In India, there are no stringent policies for the disposal of lead and its components. Pb is still frequently employed in consumer products, despite its negative effects. Due to the negative consequences of Pb, we may only have two options: (a) complete Pb recycling or (b) the use of Pb-free equipment. Because 100% recycling of Pb is prohibitively expensive, finding viable replacements for Pb-containing solders is a significant challenge for the electronic industry.

1.8 Challenges associated with lead-free solder alloys

There are many issues to be addressed when we have to switch over from conventional lead-tin alloys to Pb-free solder alloys considering the following factors (1) manufacturing ease, (2) cost, and (3) reliability. The following are the issues:

- **Higher Production Costs:** It is very difficult to follow the upper limit of the Pb content of 0.1 wt.% during the fabrication of Pb-free material due to lead contamination. The air, the handling production floor, and the equipment can all quickly contaminate the alloy bath. As a result, manufacturing Pb-free materials necessitates a unique enclosed system, which raises the cost of Pb-free materials manufacturing.

- **Higher Operating Temperature:** The melting point of Sn and Pb are 231°C and 327°C, respectively. Ag, Al, Cu, and Zn are all elements that are used today in lead free solder alloys but have higher melting temperatures (961^{o}C for Ag, 660^{o}C for Al, 1083^{o}C for Cu, and 420^{o}C for Zn) than Pb. The furnace temperature must be raised because the melting points of Pb-free solder alloys are more significant. As a result, when a Pb-free alloy is used, the assembly process will be carried out at a higher temperature during electronic packaging. To be suitable for the increased processing temperature, it is essential to design the devices and other associated materials for the assembly process considering the melting point of these solder alloy. When materials have a higher melting point, more energy is needed to heat them to that temperature. If this energy comes from burning fossil fuels, it results in higher carbon dioxide emissions, which contributes to an increased carbon footprint. In our case, there is very slight increase in melting point of alloy.

- **Degradation and Reliability of Joint**: For Pb-free materials, wetting difficulties, greater metallization consumption, and the creation of a thick intermetallic layer are all well-known issues. Metallization plays a very important role in Pb-free solder applications as 100 percent metallization causes an intermetallic layer to form, which is responsible for the package connections to fail because of these considerations, its use in applications requires high connectivity, dependability. Joining materials free of lead are environmentally friendly materials that have been successfully used as linking materials in electronic packaging. These materials have higher processing temperatures than conventional Pb-Sn solder alloys.

1.9 Lead-free solder alloys as green material

There are several lead-free solder options available on the market. Sn-Zn, Sn-Cu, Sn-Zn-Bi, and Sn-Ag-Cu alloys are now lead-free solders most extensively used. The melting point of the Sn-Zn alloy is 198 ^{o}C, which is similar to that of the Sn-Pb solder. While there are some advantages to utilizing this solder as a lead-free option due to its low melting point, it also has several severe flaws. The most serious flaw with this solder is that the Zn is responsible for excessive oxidation, which results in a large quantity of dross in soldered product. Furthermore, this solder has less wettability than Sn-Pb solders. Bi is most commonly alloyed with Sn-Zn solders to lower the liquidus temperature, increase wetting, and improve corrosion resistance. With melting temperatures of 227 ^{o}C and 218 ^{o}C, respectively, Sn-Cu and Sn-Ag-Cu are extremely promising and widely used lead- free solders. The Sn-Cu solder has the most substantial cost benefit over the Sn-Ag-Cu solder[53]–[55] and several other solders. In addition, this solder uses less copper in the coating process, generates a more stable intermetallic compound layer along the bond line, and has nearly identical dependability to Sn-Pb solders. However, this solder cannot be utilized in various soldering operations because of its high melting temperature. When Ag is added to Sn-Cu solder, the melting temperature drops by around 5-10 ^{o}C, and it becomes costlier by 2.18 times to Sn-Cu solder. Sn-Ag-Cu solder has a greater solder ability than Sn-Cu solder, although it is still inferior to Sn-Pb solder. Sn-Bi-3wt%Sb (T_m = 147˚C) and Sn-Bi-6wt%Sb (T_m = 149˚C), are not still far away from the binary eutectic composition (T_m = 139˚C) of Sn-Bi eutectic alloy, therefore, liquation or phase separation will not become a potential problem for these solder alloys because $T_L – T_s < 10˚C$. In addition, these alloys present a melting temperature that is smaller to the one exhibited by the eutectic alloy Sn-38Pb (T_m = 183˚C). Moreover, the low melting temperatures of this solder alloys may permit to add more elements to further improve their properties in future works [56], [57].

1.10 General criteria for selecting solder alloys

The following criteria should be considered when selecting a solder alloy:

- The melting point is expected to be low and appropriate for the service.
- It should have good mechanical properties[58], [59] suitable for use in the field.
- It should have a low intermetallic compound (IMC) formation rate at the service temperature.
- It should have a wettability that is appropriate to the surrounding metallization.
- It should be stable in its environment.
- It should have good corrosion resistance in the marine environment.

1.11 Importance of thermodynamic study of lead-free solder alloys

Several objectives are achieved by the thermodynamic assessment of the multicomponent solutions. In the first place, multicomponent solutions[14], [60]–[65] are encountered during extraction and refining of metals in extractive metallurgy and in alloy designing in Physical and mechanical metallurgy. For the thermodynamic analysis of these processes, it is essential to know the thermodynamic behavior of the multicomponent solution with high accuracy.

Thermodynamic properties are essential for sizing and designing equipment like heat exchangers, compressors, and reactors. In dynamic process simulation, thermodynamic properties are used to model the time-dependent behavior of systems. This is important for process control and automation, enabling real-time adjustments and optimization. In summary, thermodynamic properties are integral to process modeling as they provide the quantitative basis for understanding and predicting the behavior of systems. Hence, to choose the correct experimental technique is required for the suitable multicomponent solution along with the theoretical models.

Second, the phase diagrams are very important for the materials engineers as far as the choice of materials for the desired application is concerned. It is mandatory to determine the exact position of solidus and liquidus curve in the phase diagram[66]–[69] with very good accuracy which can be done by the careful thermodynamic analysis of the relevant system. The thermodynamic analysis of the phase diagram requires internally consistent data with a high degree of accuracy.

Third, only electrical properties or magnetic properties or X – ray investigation cannot provide all the information about the constitution of the metallic system. Thus authentic thermodynamic data along with above investigations are essential to obtain the deeper insight into the constitution of the multicomponent metallic systems. Lead – tin alloy systems are the most popular among many available solder alloys in electronic circuit and packaging, because of its very attractive physio-chemical, mechanical and many other properties. The use of lead is restricted in many places because of its toxicity. Researchers and scientists are working very hard to develop lead free solder alloys[65], [70]–[73]. They have predicted that the feasible lead free solder alloys must be tin based multicomponent alloys. The design of such alloys needs the accurate evaluation of several properties of those alloy systems. Information like stable and metastable equilibrium between various phases, position of solidus and liquidus in a phase diagram and composition of each phase in a multicomponent solution could be obtained from the phase diagram and thermodynamic data. The information of interfacial reaction between solder and substrate materials could also be obtained from the thermodynamic data. The design and development of lead free solder alloys needs careful understanding and critical analysis of thermodynamic properties and phase equilibria of the multicomponent alloys. The enthalpy of solution, also known as the heat of solution, is defined as the enthalpy change that occurs when a solute dissolve in a solvent to form a solution. It is expressed as the amount of heat absorbed or released per mole of solute dissolved in a specified amount of solvent. The enthalpy of solution can be either positive or negative accordingly.

If the solution process is endothermic at a particular temperature, the heat is absorbed and the molar heat of formation is a positive quantity. In case of exothermic reaction, the heat is evolved. The molar heat of formation is negative quantity for the exothermic process. The enthalpy of solution gives an idea about the nature of bonding. The enthalpy values are small in the case of covalent compounds relative to those of ionic compounds, because a lesser energy change takes place due to the sharing of electron between the atoms. The Gibbs energy of formation of a solution or a compound is an absolute measure of its stability in a given environment. In case the free energy of mixing of the alloy is less than that of the constituent phases, then that alloy is said to be stable one. From the nature of variation of free energy of formation as a function of temperature, one can easily assess the feasibility of formation of alloys. If the free energy of mixing decreases as a function of temperature, thermodynamic stability increases as a function of temperature. The total entropy change in a solution is sum of the entropy changes due to vibrational, configurational, magnetic and electronic and other contributions. The magnetic and electronic contributions are important in case of alloys which involve one or more transition elements. Vibrational and configurational entropies dominate in total entropy. In a crystal, each atom vibrates about a given position and hence there is a randomness associated with the position of an atom at a given time. If each atom is moving in a cell, the vibrational randomness of the system is directly related to the volume of the cell. Larger the volume of the cell, the larger will be the randomness and hence the larger will be the entropy. The other important term, configuration entropy change gives an idea about the degree of order. This entropy becomes zero when the compound is perfectly ordered.

1.12 Calorimetric technique

To find the enthalpy change per mole of a substance A in a reaction between two substances A and B, the substances are added to a calorimeter and the initial and final temperatures (before the reaction started and after it has finished) are noted. Multiplying the temperature change by the mass and specific heat capacities of the substances gives a value for the energy given off or absorbed during the reaction. It does not account for the heat loss through the container or the heat capacity of the thermometer and container itself. A great varieties of calorimeters serve to measure heat and heat capacities in various fields of application. In the following, a classification system for calorimeters and a couple of examples of different types of calorimeters will be presented.

1.12.1 Principle of calorimeter

Calorimetry is the technique of measurement of energy changes in the form of heat;

the apparatus used to measure these changes is known as a calorimeter. The heat or enthalpy of formation of a compound can be directly measured by calorimetry. The enthalpy effect associated with any physical or chemical process or reaction is need to be precisely determined. Calorimetric techniques measure the enthalpy of a reaction, changes in enthalpy or heat content of a substance associated with changes in temperatures, changes in physical state such as melting and boiling, changes in chemical combination such as reaction or alloying, dissolution or changes of physical structure, etc. The successful and versatile use of the calorimetric technique in thermodynamic measurements has encouraged the development of various types of calorimeters.

Since the enthalpy effects are directly measured by the calorimetric technique the corresponding result can be reported with an estimated error which can be relied upon. The quantities obtained directly from other techniques viz. chemical equilibria, vapor pressure, and electrochemical methods are free energies from which corresponding enthalpies can be calculated only when the temperature coefficients of the free energy are known. A small error in the temperature coefficient may result in a large error in the enthalpy.

1.12.2 Classification of calorimeters

For the determination of different parameters, calorimeters have been classified into various main groups viz. adiabatic, isothermal, isoperibol, constant temperature gradient and variable temperature gradient on the basis of the simplified heat flux **Equation 1.1**:

$$\boldsymbol{q = k(T_s - T_c)} \qquad \textbf{(1.1)}$$

Where, **q** (in Watt/m^2), $\boldsymbol{T_s}$(in Kelvin) and $\boldsymbol{T_c}$(in Kelvin) are the heat flux, the temperature of the surrounding and the calorimeter, respectively, and **k** (in Watt m^{-2} K^{-1})is the overall heat transfer coefficient. A number of reviews [74], [75] have appeared in the last two decades on calorimeter highlighting its importance, classifications, experimentation, and instrumentation.

1.12.2.1 Adiabatic calorimeters

When T_s and T_c are equal but not constant, the calorimeter is designated as an adiabatic calorimeter. The temperature of the surrounding, T_s is equalized to that of the calorimeter. The heat effect is obtained from the temperature change and its water equivalent. Such calorimeter is generally, used for the measurement of heat capacities as well as the enthalpy of reactions but due to the requirement, T_s=T_c, its application is limited to slow reactions. The heat capacities of CdS [76], [77] have been measured below room temperature by this calorimeter. Sources of error can include heat loss to surroundings due to imperfect insulation and the sample not reaching thermal equilibrium. To mitigate these issues, it is important to use highly effective insulation materials and designs, calibrate temperature sensors regularly, use high-precision sensors, and allow sufficient time for the sample to reach thermal equilibrium before taking measurements.

1.12.2.2 Isothermal calorimeter

The calorimeter in which T_s=T_c=constant and q varies is known as an isothermal calorimeter. The heat effect due to phase change of a substance at the transformation temperature. The heat effect is calculated from the latent heat of transformation and the quantity of the phase transformed. The use of isothermal calorimeter is limited to slow reaction, hence unsuitable for a study on chalcogenides. It is generally used to study the binding of molecules from small molecules (eg. medicinal compounds) to larger macromolecules (DNA, Proteins etc.). It consists of two cells which are enclosed in a jacket. This jacket is adiabatic, which neither transfer mass nor heat. Sources of error can include heat exchange with the environment, incomplete mixing of the sample, and calibration errors. To eliminate or minimize these errors, it is important to ensure proper thermal isolation of the calorimeter, use effective mixing techniques to ensure homogeneous sample conditions, and regularly calibrate the calorimeter with known standards.

1.12.2.3 Isoperibol calorimeter

A calorimeter where T_s remains constant and T_c changes during the course of a reaction is known as isoperibol type. The heat effect produces a temperature change in the calorimeter which gradually attains thermal equilibrium with its surroundings by exchange of heat. Such calorimeters can be employed for measurement of a number of thermodynamic parameters such as enthalpy of formation, enthalpy of fusion, enthalpy of precipitation etc; hence they have received much attention with regard to the advancement of components. Isoperibol calorimeters are available in different design viz. solution, bomb and drop calorimeter types to suit different investigations. The micro calorimeter developed by Tian and Calvet falls in this category. Sources of error in this calorimeter measurements can include inaccurate measurement of the jacket temperature, heat loss or gain from the surroundings, and incomplete combustion or reaction. To eliminate or minimize these errors, one should use accurate and calibrated thermometers, maintain a stable and controlled environment, and ensure complete combustion or reaction by optimizing experimental conditions.

1.12.2.4 Solution calorimeter

Since the kinetics of most of the solid state reactions or processes are slow, involving a small quantity of net heat changes and very high activation barriers, these heats of reactions cannot be measured with precision by direct reaction calorimeter. In such cases, the heat effect can be measured by following an indirect route e.g. rapid dissolution of the substance under investigation in a suitable solvent. The solvent is so chosen that both the compound and the mechanical mixture of the constituent elements dissolve in it fairly rapidly with a small heat effect. Various types of solvents such as aqueous solutions, liquid metals, liquid oxides, molten salts etc. have been used in solution calorimeters [74], [75]. The process of dissolution of metals, alloys and intermetallic compounds in a liquid metal or alloy is rapid so that the end state of the reaction is not only well defined and reproducible but is also attained quickly. By alternately dissolving a material from the standard state (A^o) and from any other state (A) in a suitable solvent, and then applying Hess's law, the difference in the enthalpy between the two states, $H_A-H_A^o= \Delta H(T)$, is calculated for the dissolution processes. Ticknor and Bever [78] for the first time realized the advantages of liquid metal solution calorimetry and fabricated the first calorimeter in 1951 with molten tin as a solvent. Since then a number of design and modifications have been introduced to increase the degree of accuracy. A liquid metal solution calorimeter of any design has the following essential components, namely, the dissolution chamber with the devices for the temperature measurement and control. Solution calorimeters can be employed for the determination of a number of thermodynamic quantity i.e. enthalpy of formation, the energy of order-disorder transformation, enthalpy interaction coefficient, enthalpy of precipitation, the heat capacity of metallic melts, and excess energy of metastable state and stored energy of deformation [79] has pioneered the design of solution calorimeter. He has developed Calvet type micro calorimeters for thermodynamic studies of refractory borides, silicides, salts and intermetallic etc. Sources of error in this calorimetry can include incomplete dissolution of the sample, heat exchange with the environment, and evaporation of the solvent. To eliminate or minimize these errors, ensure complete dissolution by stirring and allowing sufficient time, use thermal insulation to minimize heat exchange, and cover the solution to prevent evaporation.

1.12.2.5 Bomb calorimeter

In bomb calorimeter, the material, under study, is burnt in excess of oxygen. The conventional oxygen-bomb calorimeter has not been successful for studies on chalcogenides. The results are unreliable because the combustion products cannot be precisely identified. This problem has been overcome by the use of fluorine as the oxidant for combustion. At the Argonne National laboratory, fluorine bomb calorimetry has been advanced for the measurement of molar enthalpies of a number of chalcogenides [80]–[82] have studied the combustion of GeS_2 in fluorine, represented by **Equation 1.2**:

$GeS_2\,(s) + 8F_2\,(g) \rightarrow 2SF_6(g) + GeF_4\,(g)$ **(1.2)**

From the standard values of enthalpy of formation of SF_6 and GeF_4, the enthalpy of formation of GeS_2 has been calculated. Sources of error in bomb calorimeters include incomplete combustion of the sample, heat loss during the transfer of the bomb, and pressure leaks. To eliminate or minimize these errors, it is essential to ensure complete combustion by using excess oxygen and optimizing the ignition method, minimize heat loss by transferring the bomb quickly and efficiently, and regularly check and maintain seals to prevent pressure leaks.

1.12.2.6 Constant temperature gradient calorimeter

In this type of calorimeter, both T_s and T_c varied in such a way that the term (T_s-T_c) remains constant. In this technique, the time required for heating of the known and unknown samples is compared by heating both samples through same temperature interval under the same temperature gradient. A method for determination of heat capacity during heating and cooling has been described by Bullock [83]. Bever [78] and coworkers have advanced the constant temperature gradient calorimeter for determination of enthalpy of fusion and other thermodynamic properties near the melting point of materials. However, in actual practice the maintenance of a zero temperature gradient is an ideal situation which cannot be realized. Sources of error in calorimetric measurements include temperature gradient instability, inaccurate measurement of the temperature difference, and heat loss to the environment. To eliminate or minimize these errors, it is essential to maintain a stable and controlled temperature gradient, use high-precision temperature sensors that are regularly calibrated, and insulate the calorimeter to minimize heat loss.

1.12.2.7 Variable temperature gradient calorimeter

A Variable Temperature Gradient Calorimeter (VTGC) is an instrument based on the differential thermal analysis(DTA) used in thermal analysis to measure heat effects associated with physical or chemical changes in materials as a function of temperature. The principle behind VTGC relies on the measurement of differential temperature variations between a sample and a reference material over a range of temperatures. The operation of a VTGC typically involves subjecting the sample and reference material to a controlled temperature program, during which the temperature difference between the two is continuously monitored. Any heat absorbed or released by the sample during phase transitions, such as melting, crystallization, or chemical reactions, results in deviations in the temperature gradient. Since this technique employs the differential temperature Vs time plot. The main advantages of DTA calorimetry are the simple construction and operation and direct sensing of heat effects. The technique is capable of measuring the enthalpy of formation of a compound, enthalpies of transformation and heat capacity etc. The degree of accuracy depends on the resolution of the peak, hence this technique is not very useful where the evolution of absorption of heat is small or reaction is slow. Its application for heat capacity measurement is also difficult. In recent years a number of such calorimeters have been designed and operated successfully for thermodynamic studies on metals, alloys, intermetallic compounds, salts, and ceramics. In differential scanning calorimetry, it is essential to maintain the same temperature over the sample and the reference. This is possible if the energy supplied to both the sample and the reference is monitored accurately and the same energies are recorded for the heat effect calculation. In the calorimeter, the energies are independently supplied to sample and reference and their difference is plotted against time or temperature. Sources of error include fluctuations in the temperature gradient, measurement inaccuracies, and heat loss to the surroundings. To eliminate or minimize these errors, it is essential to ensure precise control of the temperature gradient, use accurate and calibrated sensors, and properly insulate the calorimeter.

1.12.2.8 Drop Calorimeter

Drop calorimetry is a new method of calorimetry. This technique has been proven to be the best method for the accurate measurement of heat capacity at high temperature according to the literatures. This is very simple technique in which the sample is dropped from outside into the vessel inside the calorimeter at a given temperature. We can determine the enthalpy change associated with the chemical reaction or heating of a substance from one temperature to any other temperature. This method is widely used to measure the enthalpy of mixing, heat capacity and heat of transitions. The technique is also used to determine the specific heat of substances. It is a technique used for calorimetry, or the method of measuring the enthalpy of chemical reactions or phase transition as well as heat capacity. In order to measure the enthalpy, change of a chemical reaction having two reactants A and B, both the substances are dropped inside the calorimeter after that, initial and final temperatures are measured (before and after the reaction). Heat absorbed and given off during the reaction is obtained from the temperature change and heat capacity of the substances dropped. Subsequently, it is converted to energy change per mole of a reactant by dividing of its number of moles. It does not consider the heat loss due to various means like thermometer and reaction vessel etc. Sources of error in drop calorimeter measurements include heat loss during the transfer of the sample, inaccurate temperature measurements, and incomplete thermal equilibrium. To eliminate or minimize these errors, it is important to minimize the time taken to transfer the sample, use high-precision and calibrated temperature sensors, and allow sufficient time for the sample to reach thermal equilibrium before taking measurements.

Drop calorimeter are classified on the basis of operation modes into two types:

1.12.2.8.1 Direct drop Calorimeter

In the direct drop Calorimeter (**Figure 1.4**) the sample is at temperature T_1 outside the calorimeter and the same is dropped into the calorimetric chamber maintained at T_2. The total heat change associated with the increase in the temperature of the substance from T_1 to T_2 is measured.

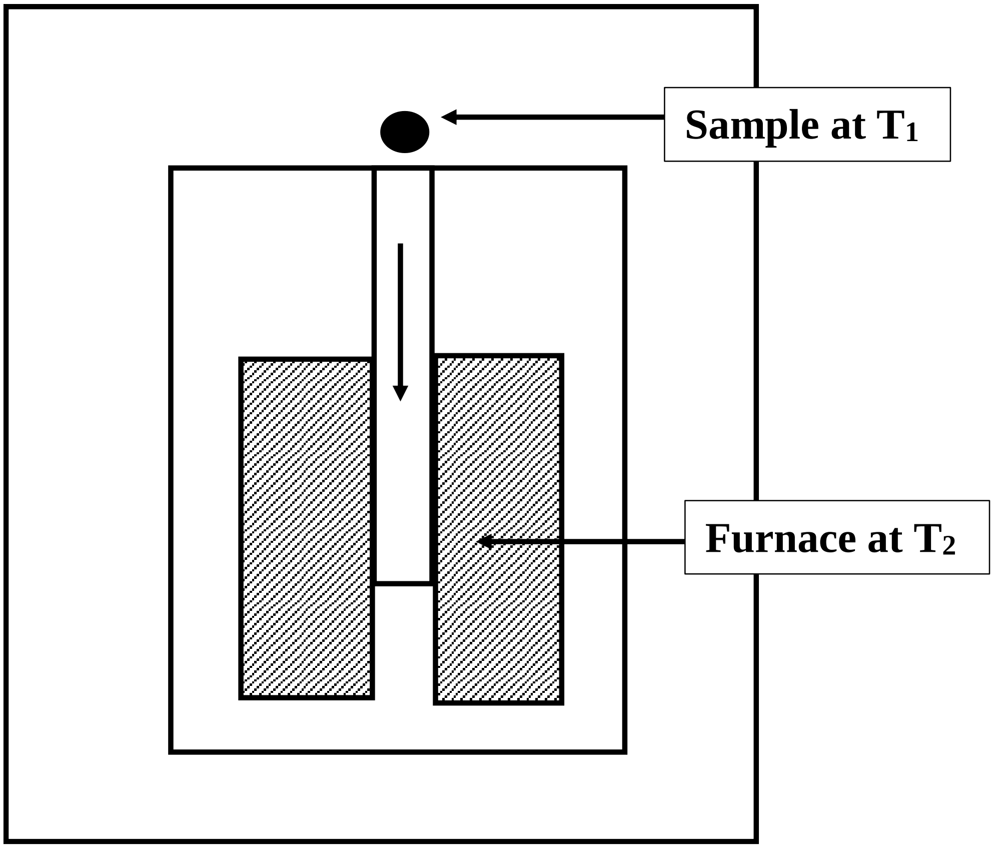

Fig.1.4 Direct drop calorimeter

Applications of Direct Drop Calorimeter:

1.12.2.8.1.1 Determination of heat capacity

For the measurement of heat capacity, the sample is dropped from the initial temperature to the fixed calorimeter temperature. The amount of heat change between these temperature ranges is measured by the calorimeter. The same experiment is repeated at different sample temperatures. Then the heat change is plotted as a function of sample temperature. Heat capacity is obtained from the plot using the following equation. In this method, we measure the mean heat capacity of the material within the temperature range of measurements by using **Equation 1.3**. It is essential to note that no phase transition takes place during heating of the sample from T_1 to T_2.

$$\frac{\partial \Delta H}{\partial T} = C_p \qquad (1.3)$$

1.12.2.8.1.2 Determination of enthalpy of transition

To determine the enthalpy of transition, the sample is dropped into the calorimeter from starting temperature and heating is continued beyond the transition temperature of the substance up to a fixed temperature. Then the heat of transition is obtained by measuring the total heat absorbed (i.e. due to transition and sensible heat of the substance) using the **Equation 1.4**. We need to know the heat capacity of the substance before transition and after transition to calculate the sensible heat.

$$\Delta H_{Total} = \int_{T_1}^{T_2} C_p . dT + \Delta H_{Transition} \qquad (1.4)$$

1.12.2.8.1.3 Determination of heat of reaction by ignition (direct synthesis)

In the case of some alloy synthesis, it is required to carry out the reaction at high temperature which requires very high rate of heating to attain high temperature. The good example is the thermite reaction. In this case, the pellets of both aluminum and ferrites are dropped into the calorimetric vessel and heated rapidly to the reaction temperature. Total heat requirement can be measured by the following **Equation 1.5**:

$$\Delta H_{Total} = \int_{T_1}^{T_2} (xC_{pA} + yC_{pB}). dT + \Delta H_A + \Delta H(A_xB_x)_{formation} \qquad (1.5)$$

It is essential to drop the pure A and B components for the calculation of heat of formation. The term ΔH_A is the latent heat of melting of A that is needed to produce the reaction.

1.12.2.8.2 The solution drop calorimeter

In this technique (**Figure 1.5**), the sample is called solute at T_1 is dropped into the solvent (metal or metal oxide) in the calorimeter vessel at T_2. The amount of heat measured by the calorimeter is on account of sensible heat of solute due to change of temperature and heat of dissolution of solute in the solvent.

Different Applications of solution drop calorimeter are:

1.12.2.8.2.1 Determination of heat of dissolution

In this technique, mostly we measure the heat of dissolution of a metal in multicomponent alloys or oxides. To achieve this, a metal is dropped into a bath of alloy(s) (or oxides(s)) that acts as solvent.

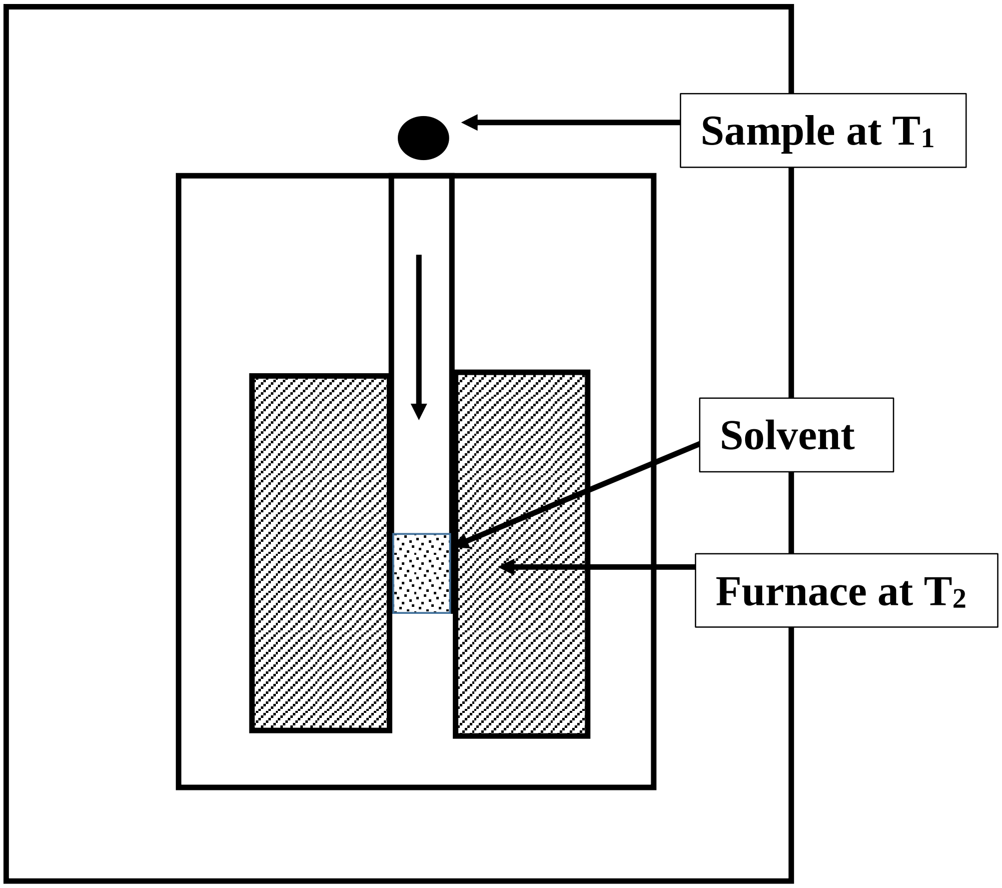

Fig.1.5 Solution drop calorimeter

The following heat relation (**Equation 1.6)** will be used to calculate the heat of dissolution.

$$\Delta \boldsymbol{H}_{\boldsymbol{Total}} = \int_{\boldsymbol{T_1}}^{\boldsymbol{T_2}} \boldsymbol{C_p}.\boldsymbol{dT} + \Delta \boldsymbol{H}_{\boldsymbol{Transition}} + \Delta \boldsymbol{H}_{\boldsymbol{Solution}} \tag{1.6}$$

The first term of the equation is the sensible heat of the dropped metal from T_1 to T_2. The last term is the heat of dissolution of the sample in the solvent. The second term may or may not be there depending on the transformation of sample takes place or not in the temperature range of T_1 to T_2. Samples are dropped into the solvent successively to get the heat of dissolutions of the samples for the entire range of compositions.

1.12.2.8.2.2 Determination of heat of formation

The enthalpy of formation of an alloy (or oxide) can be measured by the indirectly measuring the heat of dissolutions. For measuring the enthalpy of formation of an alloy of A_xB_y type, the following dissolutions are carried out in a suitable solvent:

- First dissolve pure A in the solvent
- Secondly, dissolve pure B in the same solvent
- At last dissolve pure A_xB_y alloy in the same solvent

The heat of formation of A_xB_y alloy is calculated from the following **equation 1.7**

$$\Delta H(A_xB_y)_{Formation} = x\Delta H(A)_{Solution} + y\Delta H(B)_{Solution} - \Delta H(A_xB_y)_{Solution} \quad \text{.......... .(1.7)}$$

1.13 Literature Survey on Calorimetric Measurements of Binary and Ternary alloys

1.13.1 Thermodynamic Investigations of Binary systems

1.13.1.1 Bi–Sn system

Several researchers have conducted experimental investigations on the phase equilibria and thermodynamic characteristics of this system, but there is a significant discrepancy in some of the findings. The specific heat was measured by Nagasaki and Fujita [84] and the heat of mixing was calculated by Oelsen and Golucke [85]. Ohtani and Ishida [86], who tested the eutectic temperature using DSC, more recently released liquidus data. These data generally agree with one another well. Numerous writers have also looked at the mixing enthalpies of liquid Bi-Sn alloys, including [87]–[90]. As noted by Ohtani and Ishida [86], research done prior to the 1940s [87] exhibits significant scatter, but later data [88]–[90] exhibits rather good agreement. Electromotive force (EMF) techniques have been used by numerous authors to measure the activities of Sn in the liquid phase; Asryan and Mikula's contribution[91] is one of the most recent efforts in this area. Bi in the liquid bath of Sn was also measured by Yazawa and Koike [92] at 1100 °C, while Rickert et al. [93] did so between 750 and 1050 °C. The activities were measured by the several authors and there was good agreement among them. The calculated enthalpies, however, revealed significant disparities between them. Only Seltz and Dunkerley's models [94] had good agreement with data that were directly measured [88]–[90]. Enthalpies of formation are also different from Oelsen and Golucke's calorimetric observations[85]. The study by Lee et al. [95] contains a list of other important sources.

1.13.1.2 Sb–Sn binary system

The literature has several calorimetric analyses of the enthalpy of mixing of liquid Sb-Sn alloys. Kawakami[96] was the first to record it at 800°C in 1930. Later, Kleppa [97] at 450°C and 700°C, respectively. All of these facts have been included to Hultgren et al compilation.'s [98]. Later, Sommer et al. [99] and Azzaoui et al. [100] calculated the enthalpy of mixing of liquid alloys in the temperature range of 510°C to 835°C and 619°C ($0.5 \le x_{Sn} \le 1$) and 640°C ($0 \le x_{Sn} \le 0.5$), respectively, to come to the ultimate conclusion that all the experimental results are satisfactory. Sommer et al. [99] proposed a minor but considerable temperature dependence of H_{mix} and the formation of two compounds, SbSn and $SbSn_2$. Frantik and Mcdonald [101] and Vassiliev et al. [102] used EMF methods to calculate the relevant H_{mix} values. Recent research by Chen et al. [103] utilizing a regular solution model and the assumption of temperature-independent heat of mixing defined the liquid phase in the Sb-Sn system. The computed values and the experimental results published by Wittig et al. [88], Sommer et al.[99], and Azzaoui et al. [100] are in good agreement.

1.13.1.3 Bi-Sb binary system

The binary system Bi-Sb, which features an equilibrium between solid and liquid solutions, is only briefly discussed in a few papers. M. Hansen and K. Anderko [104]–[106] established a phase diagram, with a liquidus and a solidus that is somewhat less precisely known. The well-known works R. Hultgren et al.[98] and C. J. Smithells [107] both cite these findings. For alloys with a composition of x_{Sb}=0.21-0.77 and at a temperature of 1073 K, M. Kawakami [96][4] calculated the enthalpy of formation through the direct reaction method. At a temperature of 298 K, O. Kubaschewski and W. Seith [108] founded the mixing temperatures of the constituents in the solid state. Y. E. Geguzin and B. Y. Pines[109] explored solid solutions in the binary Bi-Sb system. For the alloy with $x_{Sb} = 0.63$ in the temperature range of 623 K–823 K, they calculated specific heat.

1.13.1.4 Ga-In system

The Gallium-Indium (Ga-In) system has been studied by various researchers to understand its phase diagram and thermodynamic properties. French et al. [110] conducted a study covering the eutectic compositions in the Ga-In system and presented time-temperature curves. Denny et al. [111] further investigated the constitution of the Ga-In system using thermal and metallographic methods. They discovered that the indium-rich liquidus is concave downward from approximately 70% In to the eutectic point. This result sheds light on the solidification behavior and composition ranges within the system. Svirbely et al. [112] took a different approach and focused on determining the specific resistances of solid and liquid gallium and indium, along with their alloys. Based on resistance measurements, they determined the phase diagram for the Ga-In system. Ansara et al. [113] utilized a Tian-calvet micro calorimeter. Their thermodynamic investigation provided crucial data on the heat capacities and enthalpies associated with the various phases in the system. Anderson et al. [114] also studied the Ga-In system and found that the trend in molar enthalpy closely matched with existing literature data. Continuing the investigation into enthalpies of mixing, Ansara et al. [115] measured the molar excess enthalpies for the liquid Ga-In system at 995 K. Handzlik et al. [106], [116] expanded on the enthalpy measurements by investigating the mixing enthalpy at higher temperatures (1123 K, 1273 K, and 1423 K). This data is crucial for comprehending the thermodynamic behavior of the system across a broader temperature range. Predel et al. [117] determined the enthalpies of mixing for liquid Ga-In alloy systems and identified a maximum value of mixing enthalpy at approximately x_{In} ~0.5.

1.13.1.5 Ga-Sn system

The Ga-Sn system has been the subject of numerous thermodynamic investigations aimed at understanding its eutectic composition and mixing behavior. Anderson et al. [118] conducted a study on the eutectic composition of the Ga-Sn system using thermal analysis techniques at temperature of 693 K. In a separate study, Ansara et al. [119] evaluated the thermodynamic data of both the Ge-Sn and Ga-Sn systems. Their investigation likely involved the determination of phase diagrams, phase equilibria, and other thermodynamic properties of these binary systems. Li et al. [120] employed a calvet type calorimeter to measure partial and integral mixing enthalpies of the Ga-Sn system at a specific temperature of 803 K, but only for compositions where $x_{Sn} < 0.35$. Fornaris et al. [121] presented a relationship between enthalpy data available in the literature to predict the behavior of the more complex system at temperature of 473 K , 518 K & 743 K. Katayama et al. [122] evaluated the partial and integral mixing enthalpy of liquid Ga-Sn alloy at a higher temperature of 1073 K, with a noteworthy observation of a minima occurring at $x_{Ga} \sim 0.5$. Kulawik et al. [123] displayed mixing enthalpy data and compared it with data available in the literature. Their work likely involved a comprehensive review and comparison of enthalpy data from various sources to identify potential discrepancies or inconsistencies. Zivkovic et al. [124] performed a thermodynamic investigation of the Ga-Sn system at three different temperatures (1000 K, 1073 K, and 1200 K). This multi-temperature study may have provided a more comprehensive understanding of the thermodynamic behavior of the Ga-Sn system across a wider temperature range.

1.13.1.6 In-Sn system

The In-Sn binary alloy has been the subject of various thermodynamic investigations aimed at understanding its behavior and properties. Rechchach et al. [125] conducted an investigation of the binary In-Sn alloy at a specific temperature of 500°C using a calvet type micro calorimeter. Korhonen et al. [126] focused on optimizing available data from the literature to predict the thermodynamic behavior of the In-Sn binary system. This approach suggests that they collated existing data from various sources, possibly including phase diagrams, mixing enthalpies, and other thermodynamic parameters, to develop models or correlations that can estimate alloy behavior without the need for additional experimental work. Lee et al. [95] undertook a thermodynamic evaluation of the In-Sn binary system using thermodynamic models. By utilizing thermodynamic parameters derived from experimental data, they likely compared their model predictions with actual experimental results. Luef et al. [127] conducted measurements of the partial and integral mixing enthalpy of the In-Sn binary system at a higher temperature of 900°C, employing a calvet type micro calorimeter. Zivkovic et al. [128] used oelsen calorimetry to calculate thermodynamic parameters for the liquid In-Sn system at 600 K.

1.13.2 Thermodynamic Investigations of Ternary systems

1.13.2.1 Sn-Bi-Sb ternary system

Katayama et al. [129] employed the fused salt EMF method to get the activity of tin between 700 K and 1000 K along pseudo-binary sections of Sn (x_{Sb}/x_{Bi} = 1/3, 1/1 and 3/1) and in binary alloys of Sn-Sb and Sn-Bi systems. Based on these findings, Darken's equation was used to determine the concentration dependence of the excess Gibbs energy of mixing. D. Manasijevic et al .[130] examined phase equilibria in the Sn-Bi-Sb ternary system using phase diagram calculations as well as experimental results.

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Studies by Wang et al. [131] have shown that adding small amounts of Sb to Sn-Bi solder improves its wettability and mechanical strength, making it more reliable for electronic applications. This is particularly important for surface mount technology, where solder joints must withstand thermal cycling without failing. Another promising area of research involves the development of quaternary and higher-order systems incorporating Sn-Bi-Sb. Wang et al. [131] investigated the addition of silver (Ag) to Sn-Bi-Sb solders, finding that this quaternary alloy offers improved mechanical properties and better thermal stability. This opens up new possibilities for creating high-performance solders that meet the stringent demands of modern electronic devices.

The addition of Sb has also been found to enhance the thermal stability of the solder joints. Research by Nan et al. [132] demonstrated that Sb-containing solders exhibit slower growth rates of intermetallic compounds at the solder-substrate interface, which is beneficial for maintaining joint integrity over extended periods and under high temperatures.

Microstructural analysis is crucial for understanding the mechanical properties of Sn-Bi-Sb alloys. Studies by Cao et al. [133] revealed that the distribution of SnSb intermetallics within the solder matrix plays a significant role in determining the alloy's strength and ductility. These intermetallics help to refine the grain structure, thereby enhancing the overall mechanical performance.

In addition to microstructural benefits, the presence of Sb has been shown to improve the fatigue resistance of Sn-Bi solders. According to Li et al. [134] , Sn-Bi-Sb alloys exhibit better resistance to thermal and mechanical fatigue compared to their Sb-free counterparts. This makes them particularly suitable for applications where long-term reliability is critical.

Recent research has focused on optimizing the Sn-Bi-Sb alloy for new applications, such as in flexible electronics and high-performance solder joints. Studies by Zhang et al. [135] explored the use of Sn-Bi-Sb in flexible printed circuit boards (FPCBs), demonstrating that these solders can maintain excellent mechanical properties even when subjected to bending and stretching.

1.13.2.2 Sn-Ga-In alloys

Evans et al. [136] performed a comprehensive thermal analysis, identifying key eutectic points and phase transitions. Their study revealed that the eutectic composition, where the alloy exhibits the lowest melting point, is crucial for applications requiring liquid metals at near room temperatures. The eutectic temperature and composition were determined to be essential for understanding the alloy’s melting and solidification processes, which are critical for its practical applications.

Liu et al. [137] employed advanced thermodynamic modeling techniques to simulate the phase behavior of the alloy under various conditions. These models help in predicting the alloy’s response to different thermal and mechanical stresses, which is essential for designing materials with tailored properties for specific applications.

Koh et al. [138] investigated the phase change behavior of the eutectic Ga-In-Sn alloy, commonly known as Galinstan, which is liquid at room temperature. The alloy solidifies at around -10°C and melts at approximately 10°C, revealing a significant hysteresis between these two temperatures. This hysteresis is crucial for applications requiring stable phase change materials (PCMs). One of the prominent applications of the Ga-In-Sn alloy is in flexible electronics. The low melting point and liquid state at room temperature make Galinstan an ideal candidate for use in flexible circuits and wearable devices. The alloy's ability to maintain electrical conductivity in its liquid state, combined with its non-toxic nature, broadens its applicability in biomedical devices and soft robotics.

Recent studies by Yang et al. [139] have focused on developing new Ga-based alloys with improved properties by doping with other elements. These efforts aim to enhance the thermal and electrical conductivity while maintaining a low melting point, broadening the alloy’s applicability in advanced technological field.

1.14 Research Gap

The literature review suggests that there is no calorimetric data available for the Sn-Ga-In and Sn-Bi-Sb system. There is no systematic investigation of many binary systems in the literature. Determination of binary and ternary interaction parameters and their temperature dependencies should be computed accurately. Therefore, we have undertaken to investigate the above ternary system along with their boundary binary systems using drop calorimetric technique.

1.15 Objective

- The primary objective of this thesis work is to explore the thermodynamic properties of the lead-free solder alloys for the replacement of lead from the conventional Pb-Sn solder alloy system, aiming to mitigate the environmental and health hazards associated with lead usage.
- The research aims to develop a comprehensive database of enthalpy values across the composition spectrum of the lead-free solder alloy system: Sn-Ga-In and Sn-Bi-Sb. This database will serve as a valuable resource for understanding the thermodynamic behavior of the alloy under varying conditions, aiding in the optimization of its properties for specific applications.
- One of the objectives is to compute the interaction parameters for binary and above ternary systems and study the effect of temperature on those.
- This work will involve comparing the experimental data obtained with theoretical predictions from various geometrical models.
- Overall, this thesis endeavors to contribute to the advancement of lead-free solder technology by providing insights into alloy design, thermodynamic properties, and performance evaluation, thereby supporting the ongoing efforts towards sustainable and eco-friendly manufacturing practices in the electronics industry.