Chapter-2
Literature Review

2.1 Introduction

Tin-lead solder alloys have been used to join and assemble electronic devices for many years. It has excellent electrical and mechanical properties [11][35]. On the other hand, Pb is a heavy metal poison hazardous to human health and the environment. The investigation of lead-free solder alloys has gotten a lot of attention from academics all around the world [36][4][37][5]. Then, in recent years, Sn-based lead-free solder alloys have been viewed as the most viable options for replacing traditional Sn-Pb solder alloys. The ternary or multi-element solder alloys are designed by alloy element additions to improve the combination properties of lead-free solder alloys further, and the Sn–Ag–Cu ternary lead-free solder alloys have been deemed the best choice for substituting the standard Sn–Pb solder alloys [38][39][40]. The fundamental challenge in developing lead-free solder alloys is finding the right balance of wettability, mechanical performance, electrical properties, corrosion resistance, and cost. The corrosion problem of solder alloys has become a crucial concern in long-term service, especially in high-temperature and high-humidity circumstances, due to the growing miniaturization of electric goods and the deterioration of the service environment[11][41][42][43][44].

2.2 Properties of Sn-Pb Solder alloys

One of the essential characteristics of Sn-Pb is its low melting temperature, which allows soldering to be done safely and without the use of expensive equipment. The reason may be that this low melting temperature enables the soldering procedure to attach small and fragile electronic components without causing heat damage. Aside from this essential property, Sn-Pb is ductile, with elongation frequently exceeding 100 percent and, in some cases, superplasticity after high-temperature deformation [45]. The ductility of Sn-Pb solder junctions allows them to withstand heat and mechanical stresses, which is crucial for attaching fragile and brittle electronic components.

2.3 Role of Pb in Sn-Pb solder

Tin is a filler metal used in the soldering process; the main problem with pure tin is allotropic change at low temperatures. At ambient temperature, white (or β) tin, which has a body-centered tetragonal crystal structure, is transformed to grey (or α) tin at 13.2^0C, comparable to a diamond cubic crystal structure. The rate at which this transformation occurs is incredibly modest, but the lower the temperature (below 13.2^0C), the faster it happens. A 27 % increase in volume accompanies this change from white to grey tin and, as a result, a fall in density (from 7.30 to 5.77 g/cm^3). As a result of this volume expansion, the white tin metal disintegrates into a coarse powder of the grey allotrope. Therefore, electronic components used at the lowest temperature face this problem.

In Sn-Pb solder, Pb contributes remarkable characteristics and reliability, as described below:

1. In addition, Pb decreases the surface tension of pure Sn, increasing its wetting capacity.

2. Pb improves the ductility of Sn-Pb soldiers.

3. Intermetallic compounds between Sn and Cu may be formed through diffusion facilitated by Pb if Cu is present as an alloying element.

4. The addition of Pb hinders the allotropic transformation of Sn, which causes a volume change and lowers the structural integrity. "Sn pest" or "Sn disease" refers to the transformation of β-Sn to α-Sn.

5. Sn-Pb solders have a eutectic temperature of 183^0C for eutectic solder, allowing for low reflow temperatures in the packaging process, ensuring package dependability.

6. In addition to all of these advantages, the cost of Pb is low and abundant [46].

2.4 Role of Sn in Sn-Pb solder

2.4.1 Crystallographic Properties

The base metal in all Pb-free alloys is made up of Sn. White tin and grey tin are the two allotropes of Sn. White tin has a beta phase and is metallic in nature, and grey tin has an alpha phase and is semiconducting in nature. The beta phase of Sn is the most prevalent, and it is stable in the temperature range: of 13-231.9^{0}C. The alpha phase is thermodynamically stable below 13^{0}C; however, it is rarely observed in real life. The transformation from white tin to gray tin takes place at 13^{0}C. Gray tin has excellent electrical and optical properties. Gray Sn has a body-centred tetragonal structure with lattice parameters of a= b= 0.5820 nm and c= 0.3175 nm [47]. The c/a ratio of 0.546 results in extremely anisotropic behaviour in Sn. Sn readily wets and spreads across the substrate. As a result, most solders contain Sn, a substantial component. At around 51 ^{0}C, there may be a growth of whiskers in Sn. The growth of whiskers, known as white Sn, occurs due to internal stress and strain. Short circuits in printed circuit boards can be caused by longer whiskers, which can be prevented by adding Pb [48][49].

2.4.2 Mechanical Properties

The mechanical properties of pure Sn at room temperature are not encouraging. It is found that the tensile strength of pure Sn is just MPa[50] and hardness of 3.9 HB [51]; however, this may be attributed due to its low melting temperature compared to other common engineering metals. The exception is ductility, which allows for up to 53 percent of tensile elongations at ambient temperature [52]. Sn was a creep, hardness, and tensile characteristics are all highly affected by alloying.

2.4.3 Chemical Properties

The reactivity of pure Sn is not high due to its inert behaviour, as it does not react with most of the gases and electrolytes [50]. When Sn-based solders are molten, Sn's oxidation

occurs in the air, and an oxide layer is formed on the molten metal surface, which is most commonly known as dross. Chemical fluxes counteract this and guarantee that surfaces are adequately wetted. Rather than solid solutions, tin forms intermetallic complexes. Sb, and Bi, close neighbors of Sn in the periodic table, have significant solid solubility and develop eutectic mixes.

2.5 Legislation on lead-based solder alloys

There is an important concern about the harmful effects of electronic equipment use hazardous substances. 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. (except for Cd-0.01wt%). 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 had an impact worldwide as everything has been globalized. Although Pb is not yet prohibited in Japan, it cannot be disposed of by landfills but is encouraged for recycling. In India, there are no stringent policies for the disposal of lead ad 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.

2.6 Issues with lead-free solder alloys

There are many issues to be addressed when we have to switch over from lead-tin alloys to pb-free solder alloys concerned with (1) manufacture, (2) cost, and (3) reliability. The following are the issues:

➤ **Increase 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 can replace Pb and have higher melting temperatures (961°C for Ag, 660°C for Al, 1083°C for Cu, and 420°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 utilized, the assembly process will be carried out at a higher temperature during electronic packaging with a PCB. To be suitable for the increased processing temperature, it is essential to change the devices and other associated materials for the assembly process to be carried out successfully.

➤ **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 requiring high connectivity, dependability is debatable. Adhesives

free of lead are environmentally friendly materials that have been successfully used as linking materials in electronic packaging. Adhesives have lower processing temperatures than Pb-free and conventional Pb-Sn solder alloys. On the other hand, Adhesives are more prone to absorb moisture and are extremely sensitive to temperature fluctuations. As a result, adhesives are limited in their application, and their function can be inconsistent when used at high temperatures and humidity.

2.7 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 suitable for use in the field.

- It should meet the metallurgical requirement with the metallization around it.

- 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.

2.8 Lead-free solder alloys for electronic packing

For decades, conventional Pb-Sn alloys have been used as connection materials in electronic packages to provide an electrical link to the PCB. Due to the adoption of the RoHS directive, electronic companies must look for replacements for Pb-based products. Pb free material refers to connection materials that do not contain the dangerous element "Pb"[53].

2.9 True definition of lead-free solder alloys

Generally, a Pb-free substance contains no Pb, although a substance with a negligible quantity of Pb can also be termed Pb-free. As per the RoHS directive, a soldering material can be labeled "green" or "Pb free" if it contains less than 0.1 wt. percent Pb. Furthermore, although the ISO 9453 standard allows for less than 0.05-0.10 wt% Pb, the ASTM B32-96 standard considers < 0.1 wt% Pb in general and 0.2 wt% Pb in specific cases to qualify a substance as Pb free.

2.10 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 198^0C, 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 soldering pots.

Furthermore, this solder has less wettability than Sn-Pb solders and lead-free alloys. Bi is most commonly alloyed with Sn-Zn solders to lower the liquidus temperature, increase wetting, and improve corrosion resistance. With melting temperatures of 227^0C and 218^0C, 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 and several other soldiers. 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^{0}C, and it

becomes more costly by 2.18 times to Sn-Cu solder. Sn-Ag-Cu solder has a greater solderability than Sn-Cu solder, although it is still inferior to Sn-Pb solder.

2.11 Importance of lead-free solder alloys

2.11.1 Sn-0.7Cu solder alloys: Sn-Cu binary solder is an alternative to conventional Sn-Pb solders due to its low eutectic temperature of 227°C at a composition of x_{Cu}= 0.7. Eutectic Sn-0.7Cu is commonly utilized in electronic packaging for its excellent creep and fatigue resistance compared to Sn-Pb solder. This binary solder is the least expensive of all the lead-free options and is preferred for high-temperature applications such as the automotive industry[54]. However, before using this solder in a practical application, it should be thoroughly investigated since the inclusion of Cu accelerates grey Sn transition, resulting in deterioration in the physical properties like change in liquidus temperature and mechanical properties like change in tensile behaviour and hardness of the solder.
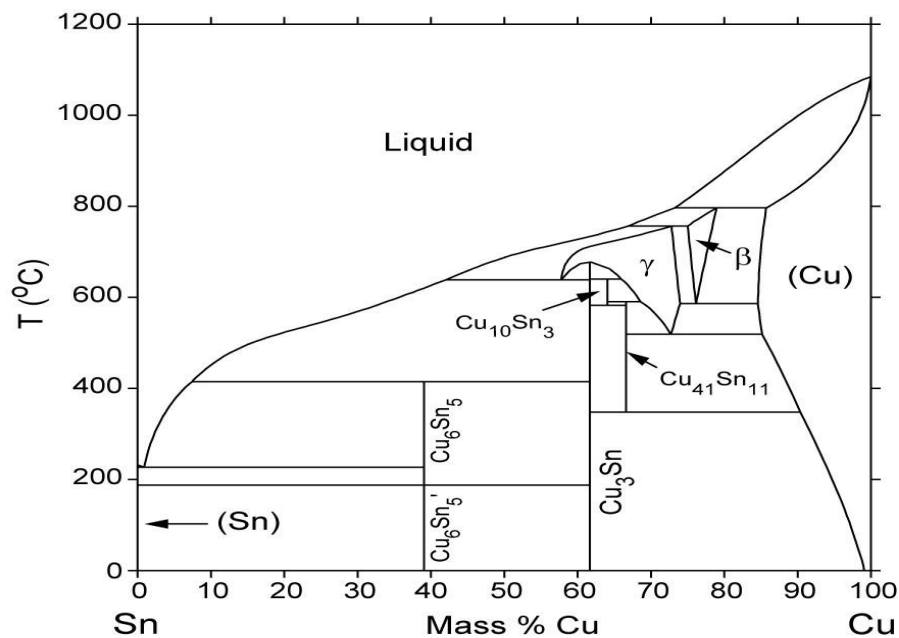

Fig.2. 1 Sn-Cu phase diagram

A galvanic corrosion cell is established between the Sn- matrix, and Cu–Sn intermetallic compounds, which causes corrosion in Sn–Cu solder alloys. The evolution of microstructure suggests that the alloy is susceptible to corrosion. Sn–Pb solder and other lead-free solder alloys (Sn–Cu, Sn–Ag, and Sn–Ag–Cu) were compared in terms of corrosion susceptibility. In 3.5wt.% NaCl solution, lead-free solder alloys exhibit less tendency to corrosion than Sn–Pb solder alloys [55]. However, Sn–37Pb solder alloy has the lowest corrosion tendency when the smoke is produced due to a fire caught in PVC. It has also been seen that Sn–3.0Ag–0.5Cu solder alloy has the most significant tendency among four solder alloys, Sn–37Pb, Sn–0.7Cu, Sn–3.0Ag, and Sn–3.0Ag–0.5Cu to corrode [56].

Furthermore, it was shown that the corrosion susceptibility of four investigated solder alloys increased as smoke concentrations increased. The cooling rate of solidification has a significant impact on the corrosion characteristics of lead-free solder alloy [57][58][4]. In a 0.5 M NaCl solution, Osório et al. [57][58]. They have investigated the tendency to corrosion of Sn–2.8Cu solder alloys produced with varied solidification cooling rates. They discovered that while the cooling rate is approximately 15°C/s, fine and homogeneously dispersed Cu–Sn intermetallic compounds occur in the Sn-rich matrix. The coarsening microstructure appears when the cooling rate is around 1.2 °C/s. The corrosion rate of the IMC is about two times greater than that of a matrix [57]. The corrosion performance of the Cu-Sn alloys at different cooling rates depends on two factors i) Localized stress field existing between matrix and finely distributed intermetallic compounds and ii) cathode/anode area ratios [58]. Fig. 2.2 shows a schematic depiction of the relationship between expected microstructure and corrosion development. Freitas et al.[59] also reported that the cooling rate significantly affects the corrosion rate and mechanical properties of the Sn–0.7Cu solder alloy. Cu_6Sn_5

intermetallic compound has fine dendritic branches and a fibrous appearance. This is considered to be a disadvantage for the corrosion properties of the Sn–0.7Cu solder alloy but advantageous to the mechanical strength. Table 1 summarizes the specifics of adding alloy components or particles to solder alloys to affect the corrosion tendency of Sn–Cu solder alloys. In a 3.5 wt. % NaCl solution, Jaffery et al.[37] Investigated the effect of adding Fe and Bi on the corrosion tendency of Sn–0.7Cu solder alloy. The development of $FeSn_2$ and Bi-rich phases resulted in a decrease in corrosion resistance following Fe and Bi doping [37]. While the addition of S to an Sn–Sn–0.7Cu solder alloy may enhance corrosion characteristics due to the creation of a passivating corrosion product, $Sn_3O(OH)_2Cl_2$[60]. Yang et al. investigated the effect of adding Ce and La on the corrosion performance of Sn–0.7Cu–0.075Al solder alloy. It was discovered that adding Ce and La to solder alloy improved its corrosion resistance [61]. Huang et al. [62] also looked into the effect of P on the corrosion susceptibility of Sn–0.7Cu solder alloy in harsh environments. It was discovered that P doping reduced the corrosion susceptibility of the Sn–0.7Cu solder alloy. Furthermore, the corrosion rate of the solder alloy is lower in alkaline solution than in acidic solution, according to Yan et al. [63], but the addition of P had no discernible effect on the corrosion tendency of Sn–0.7Cu solder alloy in a simulated maritime environment. Yan et al.[64][63] investigated the effect of Ga doping on the corrosion susceptibility of Sn–0.7Cu solder alloy in a simulated maritime environment. They found that Ga considerably decreased the corrosion tendency of the solder alloy.
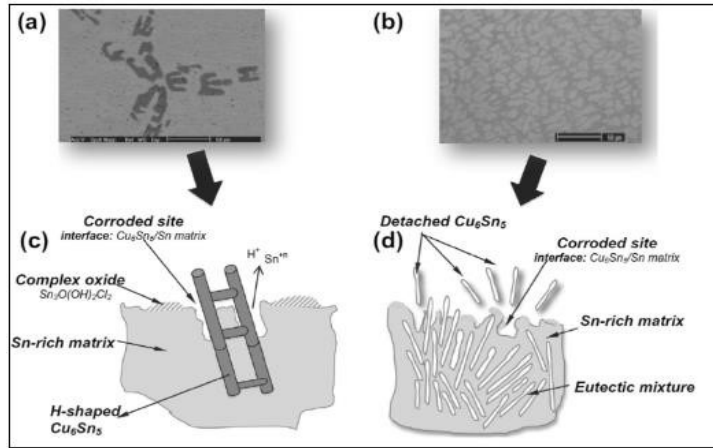
Fig.2. 2 Microstructures of Sn–Cu alloys: (a) Sn–2.8 Cu; (b) Sn–0.7 Cu alloys; (c) H-shaped Cu_6Sn_5 and Sn-rich phase, and (d) eutectic mixture

2.11.2 Sn-Zn Solder alloys: Since the melting point of this alloy is quite close to Sn-Pb eutectic, Sn-Zn-based alloy is one of the most acceptable candidates for Sn-Pb solder. Binary Sn-Zn solder has a eutectic composition of Sn-9Zn and a eutectic temperature of 198^0C. A body-centered tetragonal Sn matrix and a secondary hexagonal zinc phase make up the microstructure of Sn-Zn.
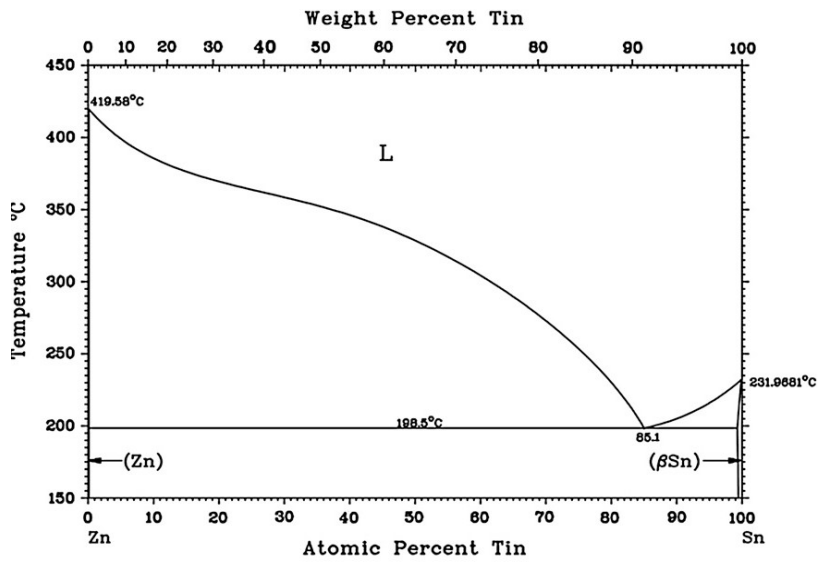

Fig.2. 3 Sn-Zn phase diagram

Sn-Zn solder is more costly, safer, and has better mechanical properties [65]. Aside from these benefits, the Sn-Zn binary system has significant drawbacks, such as poor oxidation and corrosion performance, poor wetting qualities, and the creation of microvoids. Extremely active zinc atoms react to create ZnO, float on the surface, and affect the wetting qualities. The wettability of the system increases with the addition of Bi because the liquid solder has lower surface tension, and the melting temperature of the Sn-Zn system is reduced to 189^0C [66]. Sn-Zn-Bi solder pastes are commonly utilized in computers, laptops, printers, and television tuners. Bi addition improves qualities up to a point, after which it diminishes. Because of its comprehensive features, the Sn–Zn solder alloy is a promising contender for replacing the Sn–Pb solder alloy. The eutectic composition is Sn–9Zn, with a melting temperature of 198 °C [67][68][69], which is similar to the standard eutectic Sn–Pb solder alloy. However, due to the inclusion of Zn, Sn–Zn solder alloy has a greater corrosion tendency in aggressive corrosive environments. As a result, the corrosion resistance of the Sn–Zn solder alloy has received a lot of attention from researchers. In a 0.1M NaCl solution, the corrosion resistance of five Sn-based solder alloys was investigated [70]. Actually, zinc has relatively negative redox potential compared to Na and Cl in NaCl solution. That is why it was discovered that the Sn–9Zn solder alloy had the maximum corrosion susceptibility. Furthermore, Liu et al. [71][72][73] explored the corrosion mechanism of Sn–Zn solder alloy in depth. They described the evolution of the corrosion morphology of Sn–Zn solder alloys with various Zn additions in a 0.5 M NaCl solution [71], as shown in Fig. 2.4.
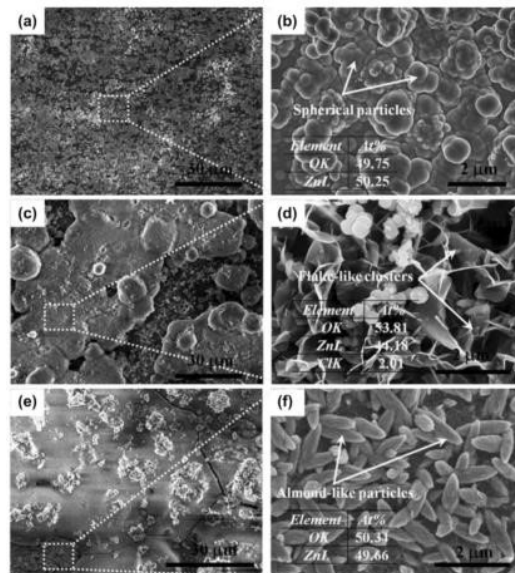
Fig.2. 4 Surface morphology of corroded Sn-Zn alloys in 3.5wt.% NaCl Solution For 7 days of immersion

The corrosion tendency of solder alloy increased as the Zn concentration increased, which was linked to coarsening Zn-rich precipitates. The susceptibility of Sn–Zn solder alloys to metastable pitting is mainly related to passive film characteristics and microstructure evolution, and the susceptibility to pitting rises with increasing Zn concentration [73][72]. Furthermore, the Sn–Zn solder alloy pitting development can be separated into three stages shown in Fig. 2.5; after the Cl⁻ adsorbed onto the passive film for a certain period of time, the Cl gradually permeated the oxide film through the intergranular boundaries; in the second stage, a tiny crack starts to grow on the surface of the passive film and propagate into the interface existing between the film and the Sn–Zn lead-free solder alloy. Finally, increased internal stress resulted in localized disintegration [72]. In neutral NaCl solution, a similar effect was reported in the corrosion of Zn–30Sn solder alloy[74].
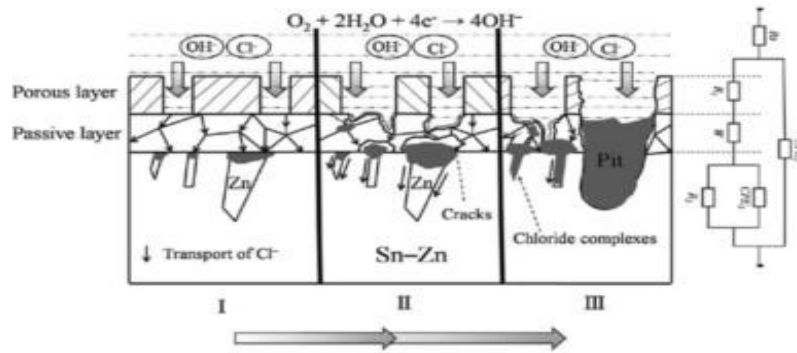
Fig.2. 5 Corrosion mechanism of Sn-Zn solder alloy in NaCl solution

The effect of alloying with different elements, metals, or particles addition on the corrosion performance of Sn-based lead-free solder alloy is summarized in Table 1. It is very important to understand the primary corrosion mechanism in Sn-Zn alloys. Once it is adequately understood, corrosion control will be the next step. Most researchers have proposed that the corrosion tendency can be reduced by altering microstructure with the addition of alloying elements or particles. All Sn–9Zn–0.1x (x = Ni, Cr, Cu, and Ag) solder alloys with doping of these metals significantly enhanced corrosion resistance. The tendency to control corrosion increased in the order of Ag, Cu, Cr, and Ni [75].

Furthermore, it was discovered that the addition of Ti [76] and Mn [77] had a significant impact on the development of corrosion resistance of Sn–Zn solder alloy. Fundamentals behind the corrosion of the alloys could be understood from the concept of evolution of microstructure and the presence of surface film present on the corroded surface [75][77][78]. Wang et al. [79] also found that doping Ti reduced the corrosion tendency of Sn–9Zn due to the alloying of less than 0.1, with 0.05 % being the optimal Ti level. According to potentiodynamic polarization results, the effect of adding Cr content (x = 0, 0.1, 0.3, and 0.5 wt. %) on the corrosion susceptibility of Sn–8.5Zn solder alloy in 3.5 wt. % NaCl solution was also investigated [80]. They showed that Cr doping could cause

anodic polarization characteristics to change. In the NaCl solution, the best corrosion resistance of the Sn–8.5Zn solder alloy was found when Cr was added at 0.3 wt% [80]. Furthermore, the addition of Ag [67], In [78], and Ga[81] to the Sn–9Zn solder alloy reduced its corrosion susceptibility, whereas Al doping had the reverse effect. The above studies entirely focused on the corrosion performance of Sn-based solder alloys in NaCl solutions. In the service of electrical gadgets, an alkaline environment may exist. Nazeri et al. [82] examined the corrosion tendency of Sn–Zn solder alloy in a 6 M KOH solution from the potentiodynamic polarization measurements. When the Zn concentration of Sn–Zn solder alloys was altered from 0 to 12 wt. %, the corrosion potential (E_{corr}) did not vary, but the corrosion current density (i_{corr}) did. After polarization, coexisting corrosion products of ZnO, SnO_2, and SnO developed on the surface of Sn–Zn solder alloy, indicating the production of a passive layer [82]. The ultimate tensile stress of a Cu/Sn–9Zn/Cu solder connection was also shown to be lowered by 26% after polarization in a 6 M KOH solution due to grooves formed by negative Zn dissolving [83]. After the open circuit potential (OCP) experiment, the ultimate tensile stress of the Cu/Sn–9Zn/Cu solder junction similarly dropped [68].

2.11.3 Sn-Bi Solder alloys: Sn-Bi-based solder has been utilized in the electrical sector for over 20 years. The eutectic composition of Sn-Bi Pb-free solder was discovered to be 42Sn-58Bi, with a 139^0C eutectic temperature. It is found that Bi precipitation occurs in the Sn matrix, and the alloys are allowed to cool, with the cooling rate having a significant impact on the alloy's microstructure and mechanical characteristics. Slow cooling causes cracks to grow and big grains to form, lowering the solder join's dependability. The addition of a small quantity of Ag improves mechanical characteristics. In a 0.15 M NaCl solution, Satizabal et al. [36][84] evaluated the

corrosion resistance of Sn–10Bi solder alloy and Sn–2Ag and Sn–22Pb solder alloys.

They pointed out that the solute content determines the microstructural change, eutectic

fraction, and cathode to anode area ratios, which are all connected to corrosion

susceptibility. Three solder alloys are ranked according to their corrosion susceptibility:

Sn–22Pb > Sn–2Ag > Sn–10Bi is in the increasing order. According to Mostofizadeh et

al. [85], rust degraded the mechanical properties of the Sn–Bi solder alloy. Li et al. [86]

also looked into the effect of nanoscale Cu_6Sn_5 particles on the corrosion susceptibility of

Sn–Bi solder alloys. They found that Sn58Bi solder alloys' corrosion rate was
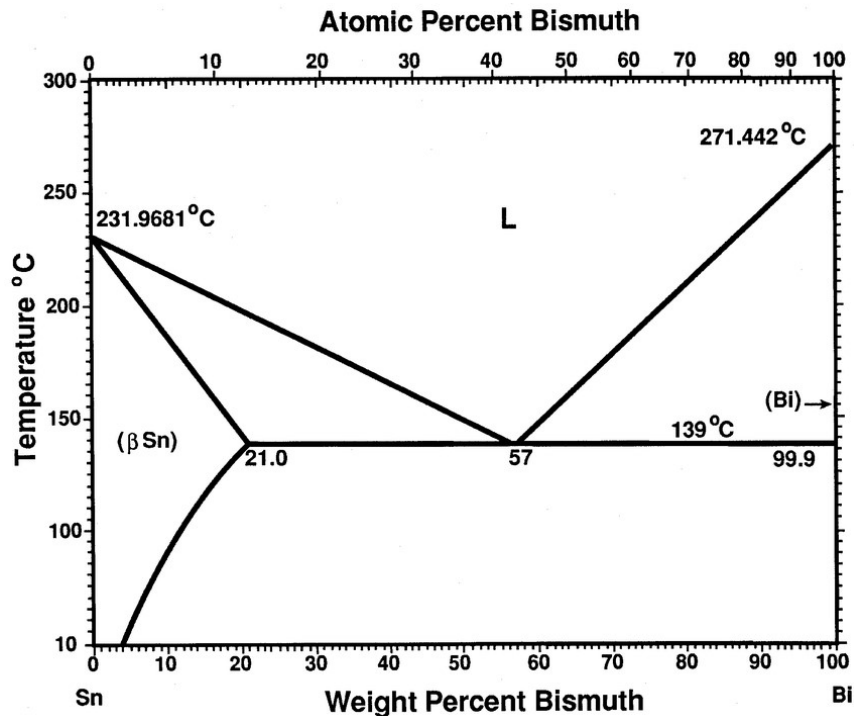
significantly reduced with nanoparticles.

Fig.2. 6 Sn-Bi phase diagram

2.11.4 Sn-Ag Solder alloys: Sn-Ag-based solders have long been regarded as the

preferred choice for lead-free alternatives due to their superior mechanical strength to

typical Sn–Pb solder alloys. Sn–Ag-based solder alloys have been considered attractive

candidates to replace conventional Sn–Pb solder alloys. Sn–3.5Ag with a melting temperature of 221 °C is the eutectic composition for the Sn–Ag binary system [87][88][89]. The galvanic corrosion cell established between the Sn-rich phase and the Ag3Sn intermetallic compound is primarily responsible for the corrosion susceptibility of Sn–Ag-based solder alloys [90][91][92]. The morphology and distribution of Sn-rich precipitates in a matrix and Ag_3Sn solder alloy particles have significantly impacted corrosion performance, mechanical properties, and thermal properties [93].
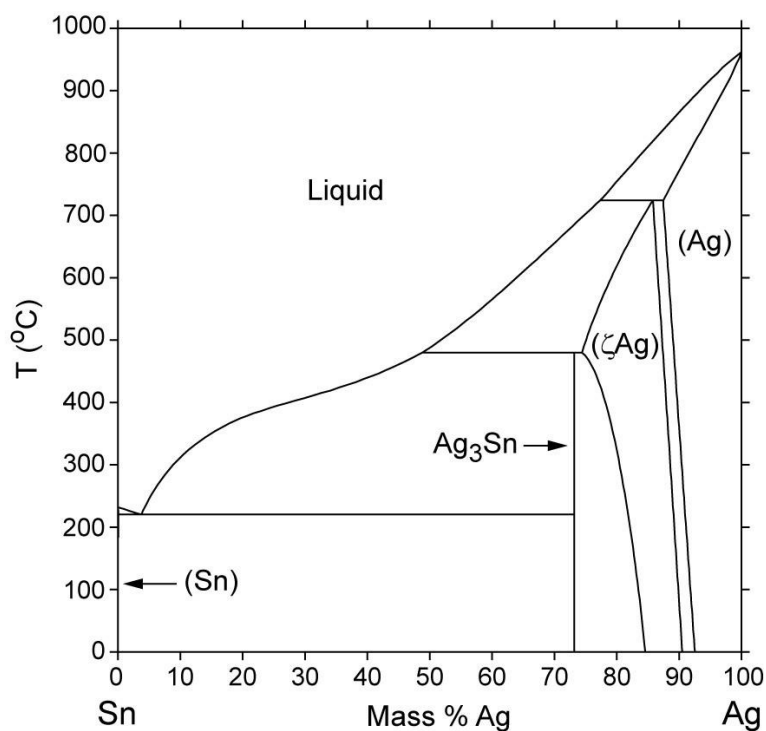
Fig.2. 7 Sn-Ag phase diagram

According to the electrochemical measurement results, the corrosion tendency of Sn–0.3Ag–0.9Zn solder alloy with various cooling procedures was examined in 3.5 wt.% NaCl solution. Water-cooled solder alloys were found to have reduced corrosion susceptibility than the sample cooled in the furnace and air, linked to precipitates' kinds, size, and distribution. It also showed that the barrier properties of passive films generated

using various cooling processes were diverse. Furthermore, Osório et al. [86] confirmed that Sn–2Ag solder alloys with higher cooling rates had reduced corrosion susceptibility than solder alloys with lower cooling rates. They found that the improvement of corrosion resistance was linked to the shape of Ag_3Sn.

Adding alloy components or particles to solder alloy can change the microstructure, resulting in changes in corrosion resistance and mechanical properties. Vuong et al. [94] found that adding Ce to an Sn–1.0Ag solder alloy increased corrosion resistance in a naturally aerated 100 mM Na_2SO_4 with 3 mM chloride ion added separately, which they attributed to Ce speeding up passive film development. Furthermore, it was shown that CeO_2 nanoparticle doping might alter the corrosion tendency of Sn–3.5Ag solder alloy in the electrolyte having 3.5 wt% NaCl solution, with the optimal doping of CeO_2 nanoparticles being around 12 % based on corrosion resistance [95]. Rosalbino et al.[96] Studied the corrosion resistance of standard $Sn_{73.9}Pb_{26.1}$ solder and Sn–Ag–M (M = In, Bi, Cu) solder alloys in 0.1 M NaCl solution. Compared to standard Sn–26.1Pb solder alloys, the Sn–2.3Ag–9.0In and Sn–3.0Ag–10.4Bi solder alloys displayed higher corrosion susceptibility. However, with the addition of Cu, the corrosion resistance of Sn–Ag solder alloy improved substantially, and it is now higher than that of Sn–26.1Pb solder alloy. Bui et al. [90] investigated the evolution of Sn–Ag solder alloy corrosion resistance in Na_2SO_4 solution with varying Ag percentages and discovered that the corrosion susceptibility of the solder alloy increased with increasing Ag content. The volume percentage of the Ag_3Sn intermetallic compound increased as the Ag content increased, increasing the micro galvanic cell. Tunthawiroon et al. [5] found that the Ag concentration of an Sn–Ag solder alloy had minimal effect on its corrosion susceptibility.

2.11.5 Sn-Ag-Cu: The addition of Cu to Sn-3.5Ag binary solder is beneficial. It is frequently utilized in the aerospace and automotive industries, where solder junctions are

subjected to thermal stresses. Researchers found that Sn-Ag-Cu solder has better mechanical properties than Pb solder. However, there is no agreement on the exact eutectic composition and the eutectic temperature for this composition, which is about 217^0C. Ternary Sn–Ag–Cu solder alloys have been used in electronic packaging. The chemical composition of Sn–Ag–Cu solder alloys is currently available worldwide. The National Electronics Manufacturing Association in the United States recommends the Sn–3.9Ag–0.6Cu solder alloy for reflow soldering [97], while Europe recommends the Sn–3.8Ag–0.7Cu solder alloy[98][99]. In comparison, Sn–3.0Ag–0.5Cu (SAC305) solder alloy is often recommended as a candidate for Sn–Pb solder alloy in Japan [100][101].

In 0.1 M NaCl solution, the Sn–Ag–Cu solder alloy has a reduced corrosion susceptibility than the typical Sn–Pb solder, which is linked to creating a more compact passive coating on the surface of the Sn–Ag–Cu solder alloy [102]. In addition, they stated that the SAC305 solder had a reduced corrosion susceptibility than the SAC305 solder [103]. Researchers looked at incorporating alloy components or particles into solder alloys to improve corrosion resistance. Subri et al.(104) used a potentiodynamic polarization experiment to assess the effect of Fe and Bi additions on the corrosion resistance of SAC105 solder alloy. They found that adding 1 wt percent Bi and 0.05 wt. % Fe lowered the corrosion resistance of SAC105 in a neutral solution, and immersion corrosion experiments revealed that corrosion mass loss decreased in the following order: Sn–1Ag–0.5Cu–Fe–1Bi < Sn–1Ag–0.5Cu < Sn–1Ag–0.5Cu–Fe–2Bi.The shift in microstructure caused galvanic corrosion to transition from the Ag_3Sn intermetallic compound to the Sn-rich phase, resulting in the evolution of corrosion resistance. Furthermore, Liyana et al.[104] found that increasing the Zn addition content in a 3.5 wt. % NaCl solution improved corrosion susceptibility. Hua et al.[105] Also, adding Zn to the SAC305 solder reduced its corrosion resistance by 3.5 wt. % NaCl salt solution. In addition, it was found

to be damaging to the corrosion properties of solder alloy [105]. There is currently no consensus on the effect of adding Al to the Sn–Ag–Cu solder alloy on corrosion characteristics. According to the electrochemical experiment results of Fayeka et al. [106], the corrosion susceptibility of SAC305–xAl(x =0, 0.1, 0.5) solder alloy increased with the doping of Al in 3.5 wt. % NaCl solution. According to the potentiodynamic polarization and salt spray exposure experiments conducted by Nordin et al.[107], the addition of Al reduced the corrosion susceptibility of SAC105–xAl solder (x = 0.2, 0.5, and 1.0 wt. %) in a 5% NaCl solution. Furthermore, the effect of Ni doping on SAC105 corrosion susceptibility in a 3.5 % NaCl solution was investigated. Compared to Sn–1Ag–0.5Cu–0.5Ni solder alloy, they found that Sn–1Ag–0.5Cu–0.05Ni and Sn–1Ag–0.5Cu–1Ni solder alloys had more excellent corrosion resistance[108].

Nanoparticles are also used to alter the corrosion resistance of Sn–Ag–Cu solder alloys. Xu et al. [109] revealed that adding graphene nanosheets (GNSS) to SAC305 solder alloy enhanced its corrosion resistance, with the optimal addition being 0.03wt.%. Han et al.[110] doping SAC307 solder alloy with Ni-coated carbon nanotubes (Ni-CNTs) inhibited the beginning and progression of corrosion in a 3.5 wt % NaCl solution. In addition, adding Al_2O_3 nanoparticles to the SAC307 solder alloy could improve its corrosion resistance in a 0.5 M NaCl solution[111].

To acquire a precise assessment of corrosion behaviour under real-world situations. Under high-temperature and high-humidity conditions, the corrosion resistance of Sn–Ag–Cu solder alloy was studied. Wang et al.[42][112][113] studied the corrosion properties of SAC305 solder alloy under high-temperature and high-humidity conditions in a systematic manner. Under the requirements of 75 °C and 100 % relative humidity, the corrosion behaviour of air-cooled and furnace-cooled SAC305 solder alloy was identical, which was worse than that of the commercial SAC305 solder alloy. The

coarsening of the Ag_3Sn intermetallic compound generated by the change in cooling rate was linked to the degradation of corrosion resistance of air-cooled and furnace-cooled solder alloy[42][112][113]. With increasing testing temperatures (45, 65, and 75 °C)[113], the thickness of the passive film increased, furthermore, in a 3.5wt. % NaCl solution, the passive behaviour of solder alloy differed at different temperatures (25, 45, and 65 °C)[112]. They also discovered galvanic corrosion between the Sn-rich phase and the Cu pad enhanced corrosion susceptibility, lowering solder joint dependability[100].

The corrosion properties of lead-free solder alloys were influenced by crystallographic roughness and aging treatment [113][114]. The corrosion susceptibility of SAC205 solder alloy solidified by magnet stirring was investigated by Daly et al.[103]. They discovered that permanent magnet stirring reduced the corrosion susceptibility of the SAC205 solder alloy. The change in corrosion susceptibility of solder was related to the modification of microstructure in Fig. 2.8 and crystallographic texture. Furthermore, they established that corrosion always propagated easily along prismatic planes in such crystals [114]. Liu et al. [115] and Lee et al.[116] investigated the long-term stability of SAC305 solder interconnects in wafer-level packages after a 5wt. % NaCl salt spray pretreatment. Fig. 2.8 shows photos of a single SAC305 solder ball. Localized corrosion developed along the solder joint's corner.
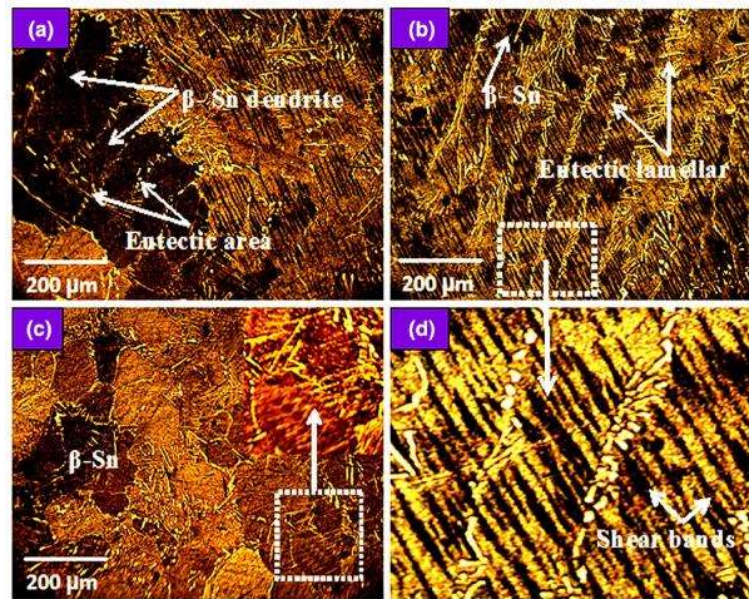
Fig.2. 8 The microstructures of as-solidified SAC205 solder alloy specimens (a) and (b) without permanent magnet stirring (PMS), (c) with PMS and (d) the magnified images of inset in b showing the shear bands in SAC205 solder alloy specimen without applying PMS.

2.11.6 Other Solder alloys: Sn–Zn binary solder alloys are used to create solder alloys. By adding Ag, Al, and Ga to the Sn–8.5Zn binary solder alloy, Mohanty et al.[117][118][119][120] designed five-element solders. The effect of Ag, Al, and Ga doping content on solder alloy corrosion resistance in 3.5wt. % NaCl solution was next investigated using electrochemical experiments. When the Ag content in solder alloys increased from 0.1 to 1.5 wt. %, the corrosion current density reduced, and the corrosion potential changed to the noble direction. A similar change trend was seen in the alteration of polarization resistance and solder alloy corrosion rate [117]. When the Ag content in the Sn–Zn–xAg–Al–Ga solders exceeds 0.1 wt%, the solders passivate [117][118]. And as the amount of Al added to the Sn–8.5 Zn–0.5 Ag–xAl–0.5Ga solder alloys grew from 0.1 to 1.5 wt %, the corrosion susceptibility increased [119]. They also confirmed that Ga doping considerably impacts corrosion resistance of Sn–8.5Zn–0.5Ag–0.1Al–xGa solder

[120]. Chang et al. [121] demonstrated that the addition of In had no influence on the Sn–9Zn–0.5Ag solder alloy's corrosion performance and that it had a lower corrosion susceptibility than Sn–9Zn solder alloy. According to potentiodynamic polarization measurements in 3.5 wt percent NaCl solution, Hu et al. [122] indicated that trace Cr doping could prevent the corrosion of Sn–9Zn–3Bi–xCr solder, and the optimal addition is 0.5 %.

Table 2.1 Corrosion performances of multi-component lead-free solder alloys in various corrosive mediums.

S.No	Solder alloys	Corrosion Medium	Corrosion Resistance	Microstructure
1	Sn-0.7Cu-x(Fe,Bi)[37]	3.5wt. % NaCl	↓	$FeSn_2$ and Bi-rich
2	Sn-0.7Cu-xP[62]	NaOH	↑	Cu_3Sn
3	Sn-0.7Cu-xAl	3.5wt. % NaCl	↑	
4	Sn-0.7Cu-xGa[64]	3.5wt. % NaCl	↑	Ga_2O_3
5	Sn-0.7Cu-xCe		↑	Refine grain and precipitates
6	Sn-0.7Cu-xS[60]		↑	SnS
7	Sn-0.7Cu-0.05Ni[123]	3.5wt. % NaCl	↓	
8	Sn-2.8Cu[57]	3.5wt. % NaCl	↑	homogeneously distributed Cu_3Sn and Cu_6Sn_5
9	Sn-xZn[82]	6M KOH	↓	Zn was sparsely distributed and segregated
10	Sn-9Zn-xBi[124]	3.0wt. % NaCl	↓	
11	Sn-9Zn-xTi[79][76]	3.5wt. % NaCl	↑	Refine Zn-rich precipitates; Sn_3Ti_2 and Sn_5Ti_6
12	Sn-9Zn-xMn[77]	3.5wt. % NaCl	↑	Refine Zn-rich precipitates;

				Zn$_6$Sn$_2$Mn
13	Sn-9Zn-xGa[125]	3.5wt. % NaCl	↑	Refine Zn-rich precipitates
14	Sn-9Zn-xNi[126]	3.5wt. % NaCl	↑	Refine Zn-rich precipitates; Ni$_5$Zn$_{21}$
15	Sn-9Zn-xCr[75]	3.5wt. % NaCl	↑	Refine Zn-rich precipitates; Sn$_2$Zn$_6$Cr
16	Sn-9Zn-xAg[67]	3.5wt. % NaCl	↑	Refine Zn-rich precipitates; AgZn$_3$
17	Sn-9Zn-xAl[119]	3.5wt. % NaCl	↓	Coarse Zn-rich precipitates
18	Sn-9Zn-xIn[78]	6M KOH	↑	Refine Zn-rich precipitates; In$_3$Sn
19	Sn-Zn-xIn[127]	3.0wt. % NaCl	↑	
20	Sn-8.5Zn-xCr	3.5wt. % NaCl	↑	Refine Zn-rich precipitates; Cr$_2$Sn$_2$(Zn)
21	Sn-xAg[90]	0.3 wt% Na$_2$SO$_4$	↑	The volume fraction of the Ag$_3$Sn
22	Sn-xAg[5]	3.5wt. % NaCl	↑	Refine Ag$_3$Sn and Cu$_6$Sn$_5$
23	Sn-In-xAg	3.0wt. % NaCl	↑	
24	Sn-Ag[96]	0.1M NaCl	↑	Coarse Ag$_3$Sn and Cu$_6$Sn$_5$
25	Sn-1Ag-xCe[94]	100 mM Na$_2$SO$_4$+ 3 mM chloride	↑	Refine grains and precipitates
26	Sn-3.5Ag[95]	3.5wt. % NaCl	↑	Refine Ag$_3$Sn
27	Sn-1.0Ag-0.5Cu-	3.5wt. % NaCl	↓	

	xZn[104]			
28	Sn-1Ag-0.5Cu-xNi[108]	3.5wt. % NaCl	↑	
29	Sn-3.0Ag-0.5C-Zn/In[105]	3.5wt. % NaCl	↓	
30	Sn-3Ag-0.5Cu-Al	3.5wt. % NaCl	↓	
31	Sn-1Ag-0.5Cu-Graphene nanosheets[109]	3.5wt. % NaCl	↑	Refine intermetallic compounds
32	Sn-0.3Ag-0.7Cu-Al_2O_3[111]	3.5wt. % NaCl	↑	Refine intermetallic compounds
33	Sn-3.5Ag-0.7Cu-Ni-Coated nanotubes[110]	3.5wt. % NaCl	↑	
34	Sn-8.5Zn-xAg-0.1Al-0.5Ga-Ag[117][118]	3.5wt. % NaCl	↑	
35	NaClSn–8.5Zn–0.5Ag–xAl–0.5GAg[119]	3.5wt. % NaCl	↑	
36	Sn–8.5Zn–0.5Ag–Al–xGa[120]	3.5wt. % NaCl	↑	
37	Sn-9Zn-3Bi-xCr[122]	3.5wt. % NaCl	↑	
38	Sn-9Zn-0.5Ag-1In[121]	3.5wt. % NaCl	↑	

Table 2.2 Binary lead-free solder alloys eutectic composition and temperature.

S. No	Binary Solder alloys	Eutectic Composition	Eutectic Tempereture (^0C)
1	Sn-Al	Sn-3.3Al	228.5
2	Sn-Cu	Sn-0.7Cu	227
3	Sn-Ag	Sn-3.5Ag	221
4	Sn-Au	Sn-10Au	217
5	Sn-Zn	Sn-9Zn	198
6	Sn-Bi	Sn-57Bi	139
7	Sn-In	Sn-51In	120

2.12 Solderability and wettability

The capacity to generate a clean metallic surface on which molten solder can wet effectively is known as solderability. In other terms, solderability refers to a surface's ability to be moistened by molten solder. Solderability is determined by a number of parameters, including the flux used, the kind of solder used, and the sort of surface finish on which soldering will be done. Although the terms wettability and solderability are almost synonymous, wettability is frequently employed as a quantitative measure of solderability. Contact angle, meniscus rise, capillary depth, and other metrics acquired during soldering tests are commonly used as indicators of solder wettability. Soldering success is determined by the solder's wettability. Appropriately wetting of the substrate occurs when the wetting angle is between 0^0 and 90^0. For soldering purposes, the angle should be less than 55^0. Proper wetting will arise if there is a net decrease in total free energy at the contact. The amount of energy required to extend the liquid surface area on a solid substrate is described as the surface tension of a liquid. This attribute determines the strength, dependability, and degree of wetness.

2.12 Formation of intermetallic

When molten solder alloy interacts with a substrate, intermetallic compounds occur. Cu is the most often used substrate for electronic solders. Cu is commonly employed in electronics because of its strong conductivity, and most Sn-based solder alloys readily wet it. Ni/Fe alloys, Ag, and Au, which are typically coated over Cu connections, are other suitable wettable substrates. When molten solder wets Cu or other alternative substrates, intermetallic compounds (IMCs) are formed. They originate while the solder is still molten, yet they continue to grow even in the solid-state at ambient and increased temperatures thanks to a diffusion process. The creation and growth of interfacial layers influence strength and wettability. Although intermetallic formation improves the solder junction's stability, there are certain drawbacks. Intermetallic are fragile by nature, and the bonding quality depends upon the thickness of the intermetallic compound present at the interface due to its growth over there. If the physical parameters of the substrate and intermetallic parameters do not match, soldering will fail. Excessive intermetallic growth degrades solder joint strength, thermal fatigue life, and solder fracture toughness. The intermetallic formation is determined by the elements of the solder alloy and how they react with the substrate. Various intermetallic compounds may be created, but the ones that develop initially during the soldering process play an essential role in wettability.

2.13 Corrosion of lead-free solder

2.13.1 The Fundamentals of the corrosion of lead-free solder alloys

The evolution of corrosion characteristics in Sn-based solder alloys is mainly linked to microstructure variations. Galvanic corrosion occurs due to electrochemical cells forming between the Zn-rich and Sn-rich phases in Sn–Zn lead-free solder alloys[71][75]. The potential difference between the Zn-rich and Bi-rich phases is responsible for the corrosion of Sn–Bi solder alloys. The galvanic corrosion takes place due to

electrochemical cells formed between the Zn-rich phase and intermetallic compounds in Sn–Cu, Sn–Ag, and Sn–Ag–Cu solder alloys, and the intermetallic compounds generally consist of Ag_3Sn and Cu_6Sn_5, which are nearly insoluble in corrosion media due to chemical stability [42][112] Different experimental methods are used to investigate the corrosion performance of Sn-based lead-free solder alloys[64][128][129].

2.13.2 Formation of corrosion products

The dissolution of the Sn-rich and Zn-rich phases leads to the development corrosion products in Sn-based lead-free solder alloys. In Sn–Zn solder alloys, ZnO, $Zn(OH)_2$, and $Zn_5(OH)_8Cl_2H_2O$ are the main corrosion products.
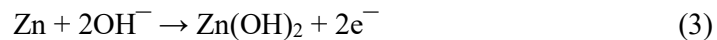
The corrosion process begins with the dissolving of Zn in the NaCl solution at an anodic site reaction.

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad (1)$$

The cathodic reaction

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad (2)$$

The formation Of $Zn(OH)_2$ and ZnO

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^- \qquad (3)$$
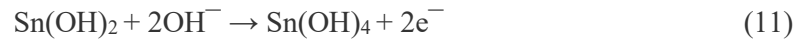
$$Zn(OH)_2 \rightarrow ZnO + H_2O \qquad (4)$$
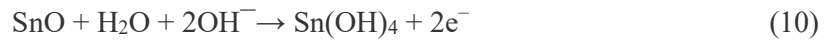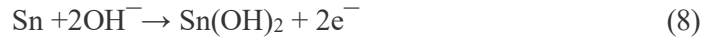
The corrosion product of $Zn_5(OH)_8Cl_2H_2O$ formed when the concentration of Cl was increased, and the formation mechanism was as follows:

$$4ZnO + Zn^{2+} + 5H_2O + 2Cl^- \rightarrow Zn_5(OH)_8Cl_2.H_2O \qquad (5)$$
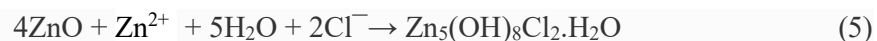
The corrosion products for Sn–Cu, Sn–Ag, Sn–Bi, and Sn–Ag–Cu solder alloys have been determined to be mostly SnO, SnO_2, $Sn(OH)_4$, and $Sn_3O(OH)_2Cl_2$. The dissociation of Sn at the anodic location initiates the corrosion process.

$$Sn \rightarrow Sn^{2+} + 2e^{-} \tag{6}$$

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^{-} \tag{7}$$

According to the reaction, the cathodic reaction occurs (2). Then SnO, SnO^2, and $Sn(OH)_4$ were created, with the following details:

$$Sn + 2OH^{-} \rightarrow Sn(OH)_2 + 2e^{-} \tag{8}$$

$$Sn(OH)_2 \rightarrow SnO + H_2O \tag{9}$$

$$SnO + H_2O + 2OH^{-} \rightarrow Sn(OH)_4 + 2e^{-} \tag{10}$$

$$Sn(OH)_2 + 2OH^{-} \rightarrow Sn(OH)_4 + 2e^{-} \tag{11}$$

$$Sn(OH)_4 \rightarrow SnO_2 + H_2O \tag{12}$$

Because of the presence of Cl^{-}, the corrosion product $Sn_3O(OH)_2Cl_2$ was produced, as shown below.

$$3Sn + 4OH^{-} + 2Cl^{-} \rightarrow Sn_3O(OH)_2Cl_2 + H_2O + 6e^{-} \tag{13}$$

2.13.3 Researches for corrosion resistance of lead-free solder.

Contaminants, particularly Cl, play an essential role in the corrosion of solder alloys. As a result, extensive research on the development of lead-free solder alloy corrosion susceptibility in NaCl solution has been conducted. Immersion corrosion tests are used to determine how susceptible solder alloys are to corrosion in a NaCl solution. This method can be used to examine the corrosion resistance of solder alloys before they are put into service, as long as the actual service circumstances are different. Then, to further replicate the service environment, the salt spray service environment, as well as the high-humidity and high-temperature service conditions, are constructed[42][112][113][130]. However,

the corrosion that occurs in electronic equipment service is classified as atmospheric corrosion, in which electrochemical processes occur beneath a thin electrolyte layer [131][132]. As a result, the corrosion resistance of solder alloys under a thin electrolyte layer is examined[128][129]. The above-mentioned experimental methods can only detect the evolution of solder alloy corrosion morphology; electrochemical experiments should be used to investigate the corrosion mechanism. Electrochemical experiments always include open circuit potential, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) studies. The corrosion mechanism is next explored in view of the electrochemical parameters collected by electrochemical experiments.

2.14 Motivation

The motivation to eradicate Pb from manufacturing electronic gadgets and electronic waste is essential as the toxicity of heavy metals like Pb is well established. 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. Vapour pressure of lead 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 soldiers.

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 electromigration lead to the shrinkage size scale and short circuit due to tin whiskers 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.

2.15 Scope of the Present Work

After an extensive literature survey, it has been observed that there are many areas where very little literature is reported. Few researchers have carried out a research gap like the electrochemical characterization of the lead-free solders. Therefore, lead-free solder electrochemical corrosion aspects have been taken up in this investigation. In this present study, binary lead-free solder alloys will be synthesized in a vacuum induction furnace with varying compositions of one component in the ternary alloys. This is done to study the effect of that element on the various properties of the alloys. The developed binary and ternary solder alloys will be subjected to corrosion analysis by non-electrochemical (weight loss) and electrochemical methods (potentiodynamic and electrochemical impedance spectroscopy). Advanced characterization instruments such as X-Ray

Diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDS or EDX), and X-ray photoelectron spectroscopy (XPS) will be used to analyse corroded and non-Corroded solder alloys thoroughly. This will help in predicting the corrosion mechanism for that alloy. At last, it is expected to predict the suitable alloy or alloys for the lead-free solder application based on the corrosion measurements.

2.16 Objective

The literature survey and scope of this studies, it is aimed to achieve the following objectives

❖ The synthesis of binary and ternary lead-free solder alloys like Sn-Zn, Sn-Cu, Sn-Cu-In, Sn-Cu-Al, and Sn-Cu-Zn with varying concentrations of one of the components in the ternary alloys.

❖ The microstructure and composition analysis of lead-free solder alloys using a scanning electron microscope (SEM) with Energy-dispersive X-ray spectroscopy (EDS or EDX) need to be done before the corrosion investigation to observe the phase evolution of the alloys.

❖ Non-electrochemical corrosion studies are aimed to be carried out in the simulated marine medium to find the corrosion rate by weight loss or immersion method.

❖ Electrochemical corrosion behaviour analysis by Potentiodynamic polarization will be carried out to assess the corrosion rate in the simulated marine atmosphere.

❖ The electrochemical impedance spectroscopy (EIS) technique will be used to find the kinetics of the corrosion process of these alloys.

❖ After the corrosion investigations are over, the sample will be subjected to surface characterization of the corrosion product by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to observe the surface morphology.

❖ The prediction of the corrosion mechanism will be made based on the surface characterization.