

A REVIEW OF SOLDER EVOLUTION IN ELECTRONIC APPLICATION

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Abstract- This paper discusses the evolution of lead-free solder alloy from lead solder. The development of lead free solder is due to the high toxicity of lead solder, Sn-Pb which would bring a lot of negative effect on the environment and human health.

Keywords: solder; lead-free solder; phase diagram; sn-pb

1 Solder Evolution

1.1 Solder

Soldering is a metallurgical joining method using solder with a melting point of below 315°C as filler [1]. Also, soldering can be explained as any of various alloys fused and applied to the joint between metal objects to unite them without heating the objects to the melting point [55]. In year 1921, Ernst Sachs (founder of ERSA) was the first man who invented the first electric and mass-produces soldering iron for industry [2].

1.2 Lead Solder, Sn-Pb

Callister [7] states that solders are metal alloys that are used to bond or join two or more components (usually other metal alloys). They are used extensively in the electronics industry to physically hold assemblies together [7]. Furthermore, they must allow expansion and contraction of the various components, must transmit electrical signals, and also dissipate any heat that is generated [7]. The bonding action is accomplished by melting solder material, allowing it to flow among and make contact with the components to be joined; which do not melt [7]. Finally, upon solidification, a physical bond with all of these components is formed [7].

As shown in Figure 1, Sn-Pb has low eutectic temperature of 183°C[7]. Great strength and good ductility makes it can endure thermal

cycling [7]. Pb is an adequate solubility but it combines rapidly with Sn [7]. In board level packaging the solder used is primarily 63Sn-37Pb, a eutectic composition, or 60Sn-40Pb, a near eutectic composition [3].

Since Sn-Pb is used as primary components of eutectic solders, Pb provides many technical advantages, which includes the following Sn-Pb solders:

Pb reduces the surface tension of pure tin, which is 550N/m at 232°C, and the lower surface tension of 63Sn-37Pb solder (470mN/m at 280°C) facilitates wetting [9].

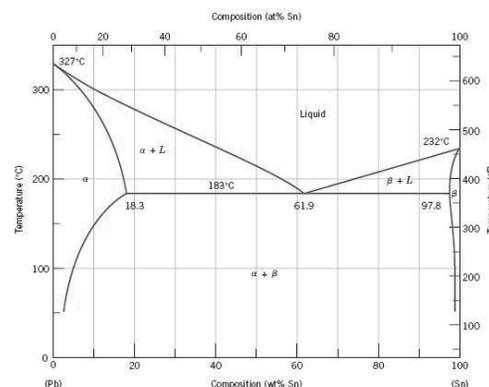


Figure 1. Sn-Pb Phase Diagram [8]

1. As an impurity in tin, even at levels as low as 0.1wt%, Pb prevents the transformation of white or beta (β) tin to alpha (α) tin upon cooling past 13°C. The transformation, if it occurs, results in a 26% increase in volume



- and causes loss of structural integrity to the tin [10].
2. Pb serves as a solvent metal, enabling the other joint constituents such as Sn and Cu to form intermetallic bonds rapidly by diffusing in the liquid state [3].
 3. Sn-Pb is inexpensive. Also, for soldering, it needs simple equipment which is soldering iron and torch. Moreover, having low skilled operator is enough to soldering [11].

A good understanding of the behaviour of Sn-Pb solders has enabled current board level technology to assemble and create small geometry solder joints, approaching 75µm in size, in high volume, and at a competitive cost [3].

Metallic lead and its alloys have been used for productions without concerning the risk and consequences. Before, lead is used to make plates, bowls, drinking glasses and many more [1].

In recent times, health and environment matter have been taken seriously. The first serious concern started with the lead-containing pigments used in paint [1]. Electronic and electrical waste devices may wind up in the refuse heap. Therefore, lead may spread into the air particle and may be affected to the environment, such as, air pollution [16]. Next, effect of lead to human can be listed as below:

1. Harm to foetus including brain damage or death [13].
2. High blood pressure [13].
3. Digestive issues [13].
4. Nerve disorders [13].
5. Muscle and joint pain [13].

Due to the negativities of lead to human and environment, a legislation of lead usage has been enacted.

1.3 Legislation of Lead Solder

The European Commission of environment and waste had perform a consultation on the adaptation of scientific and technical progress under Directive 2002/95/EC of the European Parliament and of the Council on the restriction of the use of certain hazardous substances in electrical and electronic equipment [14].

Article 4(1) of Directive 2002/95/EC [15] on the restriction of the use of certain hazardous substances in electrical and electronic equipment provides 'that from 1 July 2006, new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium, hexavalent chromium, PBB or PBDE' [15]. In other words, all of the electrical and electronic production devices must be in lead-free condition. The annex to the Directive lists a limited number of applications of lead, mercury, cadmium and hexavalent chromium, which are exempted from the requirements of Article 4(1) [15]. Furthermore, there are certain countries such as Japan, Korean, United States and Europe that had already banned lead, especially in the solder.

In Japan, the legislations of RoHS and WEEE were not implemented [17]. On the other hand, the Japanese are controlling the use of the hazardous substances in their manufacturing processes. Dated 12th December 2006, the South Korean Government [18] enacted a law entitled The Act for Resource Recycling of Electrical/Electronic Products and Automobiles or in other words, the Korea RoHS. This law is similar to the EU directives which banning the usage of hazardous material in manufacturing process [18]. China RoHS [19] or formally named, Administration of The Control and Electronic Information Products, is going for the same objective, that is to exclude Pb in electrical and electronic devices for soldering. However, China is doing so by different approach in compare with the EU [19].

Also, Safe Drinking Water Act Amendments (SDWA, 1986) had implemented to have lead-free pipes, fixtures, fitting and solder in public water system [21].

1.4 Lead-free Solder

Lead-free solder is solder that contains less than 0.2% lead [22]. Lead-free solder has different properties and appearance than lead-based solder [22]. Lead-free solder is dull and grainy, and requires hotter soldering temperatures [22]. Currently, the used of lead-free solder alloy of Sn-Ag-Cu (SAC) is the most popular solder composition to replace lead solder

[36, 56, 57]. Allowable lead content in solder can be tabulated in the Table 1 below [20].

Table 1. Allowable Lead Content in Solder [20]

Allowable Lead Content in Solder (%max)			
Solder Bar/Wire/Paste			
IPC J-STD-006	ISO 9453	JIS-Z-3282	High-Purity Tin 99.99%
0.2% (Common) 0.1% (Variation E)	0.1%	0.1%	0.002% (20ppm)
Solder Anodes for Electroplating			
American/European Customers		Japanese Customers	
550ppm		1000ppm	

1.4.1 Requirement of Lead-free Solders

Due to the restrictive usage of lead solders which have stimulated development efforts of lead-free solders without risky components. The wettability of a new lead free solder should be better or equivalent to Sn-Pb alloys [23].

According to S.K. Kang (2001) [24], there are several requirements for new lead free solder alloy in order to replace the lead solder Sn-Pb.

One of the requirements for new lead free solder is can be used with water-soluble or no-clean flux [58]. Furthermore, the low melting temperature of new lead free solder can reduce the degree of thermal stresses experiment during soldering. In addition, the new solder must also be able to produce strong joints that can resist thermal fatigue over the projected operating life of the soldered assembly and meet other reliability requirements such as adequate corrosion, oxidation, or electro-migration resistance.

Further, the material price of the new solder should not be high as the expensive assembly cost. In 1997, the National Centre for Manufacturing Science (NCMS) Pb-Free Solder Project had completed the pass-fail criteria for candidate alloys as shown in Table 2 [25-28]:

Table 2. Pass-Fail Criteria for Candidate Alloys [25-28]

Criteria	Definition	Notes
Liquids Temperature < 225 °C	Temperature at which solder alloy is completely molten.	To avoid component thermal damage.
Pasty Range < 30°C	The difference of temperature between solidus and liquidus temperatures; the alloy is part of solid and past of liquid in this temperature range.	To prevent rupture during wave soldering.
Thermo-Mechanical Fatigue: Some percentage, usually > 50%	Cycles-to-failure for a given percent failed of a test population refer to a specific solder-joint and board configuration.	Compared to eutectic Sn-Pb.

Continuation of Table 2

Criteria	Definition
Wettability: Equivalent to Eutectic Sn/Pb which is $F_{max} > 300\mu N$, $t_0 < 0.6s$, $t_{2/3} < 1s$	A wetting balance test assesses the force can be resulted when a copper wire is immersed in and wetted by a molten solder bath. A large force indicates good wetting, as does a short time to achieve a wetting force of zero and a value of two-thirds of the maximum wetting force.
Area of Coverage > 95% coverage	The coverage of the solder on Cu substrate been assesses after a

	typical dip test.
Drossing: Qualitative Scale	The amount of oxide formed in air on the surface of molten solder been assesses after a fixed time at the soldering temperature.

1.4.2 Pb-free Solder Alloy Compositions

A great number of Pb-free solder alloys have been introduced and summarized. The solder alloys are binary, ternary and some are even quaternary alloys. A total of 69 alloys were identified from the literature [3].

It can be observed that a very large number of these solder alloys are based on Sn being the primary or major element. Followed by In and Bi are also the major constituents.

Some of the Pb-free solder alloys compositions to replace Sn-Pb are Sn-Zn, Sn-Zn-Bi, Sn-Ag, Sn-Ag-Cu and many more [3]. The eutectic temperature of the mentioned solder alloys compositions are tabulated as in Table 3 [3].

Table 3. Eutectic Temperature of Certain Solder Alloy Compositions

Eutectic Composition	Eutectic Temperature (°C)	Reference
Sn-Zn	198	[60]
Sn-Zn-Bi	127	[59]
Sn-Ag	221	[60]
Sn-Ag-Cu	217	[3]

The pros and cons of the above eutectic compositions are to be discussed in Table 4 and Table 5 below:

Table 4. The Advantages of Sn-Zn, Sn-Zn-Bi, Sn-Ag and Sn-Ag-Cu

Compositions	Advantages
Sn-Zn	1. Lowest melting temperature in compare with Sn-Ag-Cu which gives the

	difference of 18°C [29]. 2. Capable of enduring higher melting temperature [29]. 3. Low cost metal and good mechanical property of Zn [29].
Sn-Zn-Bi	1. Improve soldering property in electronic packaging by lowering melting temperature [30]. 2. Additional of Bi to Sn-Zn can improve the wettability by lowering the melting temperature to 127°C [31].
Sn-Ag	1. Higher strength, superior resistance to creep and thermal fatigue compared with eutectic Sn-Pb solder [34]. 2. Cost effectiveness compared with other lead-free solder alternatives [34].

Compositions	Advantages
Sn-Ag-Cu	1. Relatively low melting temperature compared with Sn-Ag eutectic alloy. 2. Superior mechanical properties. 3. Relatively good solderability.

Table 5. The Disadvantages of Sn-Zn, Sn-Zn-Bi, Sn-Ag and Sn-Ag-Cu

Compositions	Disadvantages
Sn-Zn	<ol style="list-style-type: none"> 1. Susceptible oxidation [30]. 2. Poor wettability [30]. 3. Poor compatibility with a Cu substrate under high temperature conditions [30]. 4. Prone to corrosion [30].
Sn-Zn-Bi	<ol style="list-style-type: none"> 1. Bi is brittle in nature [30]. 2. Bi has a strong tendency to segregation [30].
Sn-Ag	<ol style="list-style-type: none"> 1. Sn-Ag solder microstructure is unstable at high temperature [32]. 2. Microstructural evolution can cause solder joint failure [32]. 3. High melting point [33]. 4. Poor wettability compared with the eutectic Sn-Pb solders [33].
Sn-Ag-Cu	<ol style="list-style-type: none"> 1. Exhibits a number of properties in common with Sn-Pb and Sn-Ag [35].

2 Wettability

Wetting refers to the capacity of molten solder to react with a substrate, at the interface of solder and substrate, to form a certain amount of intermetallic compound that acts as an adhesion layer to join the solder and the substrate [37]. The reaction between the solder and substrate is important as it may affect the micro-structure and eventually the mechanical strength of the solder joint [37]. The extent of wetting is

measured by the spreading area and the contact angle that is formed at the juncture of a solid and a liquid in a particular environment [38]. The Young equation has been used to determine contact angles and the balance of surface tension at the juncture [38].

2.1 Young Equation

Young Equation [3] can be explained graphically as Figure 2 below.

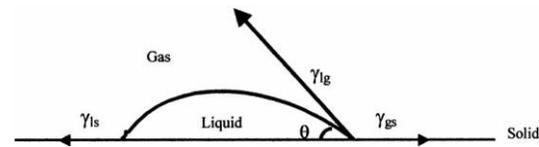


Figure 2. Diagram of Wetting Angle [3]

The extent of wetting is measured by the contact angle that is formed at the juncture of a solid and liquid in a particular environment, as shown in Figure 2. In general, if the wetting or contact angle lies between 0 and 90° the system is said to wet, and if the wetting angle is between 90° and 180°, the system is considered to be non-wetting [3]. The contact angle (θ) is determined from the balance of surface tensions at the juncture, according to the Young – Dupreequation (1):

$$\gamma_{gs} = \gamma_{ls} + \gamma_{gl} \cos \theta \quad (1)$$

Where γ_{gs} is the surface tension of the solid in the particular environment, γ_{ls} is the interfacial energy (surface tension) between the solid and the liquid, and γ_{gl} is the surface tension of the liquid in the same environment [63].

The most basic characterization of wetting is given by considering the thermodynamics of the wetting forces [3]. In terms of free energy, good wetting will occur if there is a net lowering of the total free energy, i.e. the surface energy of the solder is lowered by it forming an interface that is at a lower surface interfacial energy [3].

3 Materials Used in Electronics Application

3.1 Copper (Cu) as a Substrate

Cu is an element that is most widely used as a substrate in electronics applications [39, 40].

Cu is a ductile metal having high thermal and electrical conductivity [41].

In addition, Cu can be classified as superior corrosion resistance [36], striking colour [41], excellent practical [41] and good mechanical properties [36]. Therefore, Cu can transform into so many shapes and sizes [41]. Moreover, Cu is a great element that can produce electricity [41]. Thus, in electronics application, Cu is a popular element to use as a substrate in soldering.

According to Kuneman and Dickson [42], a thin, direct bond copper ceramic substrate of high strength and good thermal conductivity and suitable for high temperature thick film processing is described. It comprises two outer layers of alumina of equal thickness and matching dimensions for bending stress equalization, and an inner copper core, itself formed of three component layers, bonded by a copper oxygen eutectic between the layers of alumina [42]. The thickness of the copper core is held between one-tenth and one-third the thickness of the substrate [42]. The laminated structure, which permits recycling for high temperature thick film processing, sustains stresses at working temperatures, strengthening the substrate, and provides high thermal conductivity for heat management in a high density environment [42].

Jiang et al. [45] have conducted a study upon hetero-epitaxy of diamond films on non-diamond substrates because it has been the subject of intensive research because of its potential impact on the electronic industry. Cu is chosen in this research to be the ideal candidates for hetero-epitaxial growth of diamond [45]. This is because that the (111) oriented diamond films on Cu have been successfully achieved [45-47]. It is interpreted that Cu has cubic crystal structures, and its calculated lattice mismatches with diamond are less than 10%, and furthermore, Cu produce no carbide. These particular properties are thought to make Cu as an excellent candidate for the hetero-epitaxial growth of diamond [45, 46, 48].

Also, the self-alignment of advanced packages (μ BGA) on both non-pinhole and pinhole Cu pads has been discussed by Hung and

members [49]. It is found that a slight reduction of self-alignment of the packages using pinhole pads happens [49]. Rutherford backscattering spectrometer (RBS) results propose that this reduction should not be attributed to the oxide formation of the surface or interface layer in the Cu pads [49]. The solder wetting experiments show that slow spreading of molten solder on pinhole pads may result in a reduction of effective board pad surface area that can be wetted [49]. This will reduce the restoring force of the solder joints, and thus causing a less good self-alignment of the packages using pinhole pads [49]. In the interest of manufacturing high reliable and good performance electronics products using advanced packages, it is necessary to understand which mechanisms of oxidation are factors to limit the wettability and how it affects and relates to the self-alignment of the packages [49].

Furthermore, Sharif and Chan [50] conducted a study on the consumption rate of Cu as a substrate with Sn-Pb and Sn-Ag solders. Cu is widely used in the under bump metallurgy and substrate metallization for flip-chip and BGA application [50]. At the liquid solder/Cu substrate interface, the formation and growth of intermetallic compounds occur by the dissolution of Cu into the molten solder [50]. A fast dissolution of the substrate occurred in the beginning for the molten solder/solid Cu reaction couple [50]. However, the dissolution in Sn-Ag is much higher than that in Sn-Pb solder [50]. As a result, the energy of 54 and 116kJ/mol is obtained for the dissolution reaction in Sn-Ag and Sn-Pb solder, respectively [50].

A Cu-based substrate has been made by electrodepositing a Ni layer on top of cube-textured Cu tape obtained by an alternating mechanical/thermal treatment [51]. In accordance with Yu and members [51], it could be found that the volume fraction of the cube texture component of Cu tapes increased with the annealing temperatures for an optimized rolling process. When the annealing temperature is at 800 °C, the sharpness of cube texture is best. In order to fabricate Lanthanum Zirconium Oxide (LZO) films on the Cu-based substrate, a Ni layer was added on top of the Cu tape by electroplating [51]. The thickness of Ni layer not



only affects the texture sharpness of the substrate, but also affects its thermal stability of texture [51]. A thickness of 15 μ m was efficient to protect the Cu tapes [51]. Fabricating well bi-axially textured LZO film on this bi-metallic substrate proves that this new Cu-based substrate is a good choice for coated conductor [51].

Wang and team [52], reports on a novel amperometric hydrazine sensor of CuO nanoarray based on a Cu substrate. Copper oxide nanoarray was directly grown on Cu substrates using a one-step facile hydrothermal method and was characterized using scanning electron microscopy and X-ray powder diffraction [52]. The electrochemical study has shown that the CuO nanoarray exhibits higher catalytic effect on the hydrazine than the normal CuO nanoparticles [52]. This may be attributed to the special structure of the nano materials especially the substrate of the electric Cu [52]. And the amperometric response showed that the CuO nanoarray modified glassy carbon electrode has a low detection and a high sensitivity for hydrazine [52].

3.2 Flux and Its Functions

Solder flux, known as its name, is made to assist soldering task [43]. A material for better soldering is needed when doing surface-mount technology (SMT) repairing for the purpose to avoid the soldering point get oxidation so that the repairing parts can stick closely [43]. Mostly, soldering flux contains zinc chloride (ZnCl) and it is normally known as "acid" in the flux [44].

A number of chemical substances such as ZnCl or HCl may be used effectively to remove oxide contamination from a metal [44]. These acidic materials are quite corrosive to the metal itself [53]. For this reason, rosin fluxes have been used extensively which, although less acidic in character, but do not afford as good fluxing action [53]. Thompson et. Al (1958) said certain organic modifying agents have been incorporated into these fluxes to increase acidic content [53]. However, these fluxes often have the undesirable property of producing toxic decomposition products at the soldering temperature [53].

The invention of flux provides a composition which is capable of removing residues of a variety of soldering fluxes with surprising efficiency and convenience [54]. Furthermore, the materials (ZnCl or HCl) used in the composition are relatively environmentally safe as compared to the chloro fluoro carbons [53, 54]. The proportions of materials in the composition are adjustable according to the substrate flux [54]. However, the composition itself, which can, when in use, be mixed with water or not, is of the following components [53]:

1. 25 – 90% terpene and/or terpenol.
2. 1- 10% surfactant.
3. 5 – 65% remainder of a polar aprotic solvent.

Taguchi et al, 1991, state that a water-soluble soldering flux and paste solder using the flux is disclosed. Furthermore, the flux is compromises of fluxing agent, a resinous reaction product of at least one carboxyl-containing compound having eight or less carbon atoms, selected from a group consisting of monocarboxylic acids, poly carboxylic acids and hydroxyl carboxylic acids with tris-(2, 3-epoxypropyl)-iso cyanurate [58].

Organic fluxes are typically based on water-insoluble rosin or water-soluble organic acid [58, 61]. Activated rosin fluxes are used in soldering electrical connections on printed circuit boards [61]. Wave soldering is used for mass production board soldering as by applying the flux, preheating the board, applying the solder, cooling the boards and cleaning it to remove flux residue [61].

In the electronics industry, however, it is desirable to use fluxes of fairly low activity and which are non-corrosive in that they will not result in corrosion of the soldered joint over a period of time even if it becomes damp [62]. Oddy and Wagland (1990) quoted that corrosion is most often caused by corrosive flux residues being left on the substrate. Thus any residue left should be non-corrosive and also there will be preferably as little residue as possible.



Overall, the main functions for soldering flux are as listed below [43]:

- 1) Assist heat conduction.
- 2) Wipe off oxide.
- 3) Reduce the tension on the surface of soldering material.
- 4) Wipe off the greasy dirt on the surface of soldering material.
- 5) Magnify the soldering area.
- 6) Avoid re-oxidize.

The working theory of soldering flux aims at use its functions of active material to wipe of the oxide on the surface of soldering material as well as to reduce the tension on the surface between soldering material and the solder fluid [43]. At the same time, solder flux contributes to move and infiltrate the solder fluid so that lead to successful soldering task [43].

A good solder flux should have the features of active material so that enable to wipe off the oxide [43]. Also, its well heat stability shall ensure the soldering tin will not resolve under high temperature [43].

Therefore, the invention is directed to a method to remove soldering flux residues from assembled or partially assembled circuit boards by contacting the circuit board to be cleaned with the composition of the invention for a time period effective to solubilize or mobilize the flux residue, followed by removal of the cleaning composition [54].

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