

WETTABILITY STUDIES OF LEAD-FREE SOLDERS

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Abstract

Tin-Lead solder has been the standard joining material for use in electronic, chemical, automotive and other industries until various regulations around the world began to limit the use of lead due to its toxic effects. In this work, some lead-free solder alloys were produced and characterized for possible replacement of Tin-Lead solders. The solder alloys produced are: 91Sn-9Zn, 60Sn-40Zn, 42Sn-58Bi, and 90Sn-10Bi. Tin-lead solder alloy was also produced and subjected to the same wettability test with the other alloys under the same conditions for the purpose of comparing results. A characteristic of lead-free solders that greatly affects its solderability is its ability to wet the materials it joins. Based on this, a wettability test using copper grid was conducted on the solder alloys produced. The result shows that wetting time varied from 4 seconds to 5 seconds for the lead-free solders while it was 4.7 seconds for the Tin-Lead solder. Also wetting area ranged from 5.8% to 8.9% for the lead-free alloys and 8.3% for the lead containing solder. The respective contact angles in degrees for the lead-free solders varied from 58° - 73° , while that for the lead solder was 57° .

Keywords: wettability, solder, lead, alloy, tin

1. Introduction

Tin-lead solder has been the standard material used in electronic, chemical, automotive and other industries due to its low cost and unique material properties like low melting point, availability etc. However, the toxicity of lead during industrial production of components and the ecological damage caused by lead containing compounds has made the use of lead in solders undesirable.

Different laws by different agencies and countries have been enacted to prohibit the use of lead in some industrial applications. Lead-bearing solders are no longer used in the fabrication of foodprocessing equipment and the use of lead pipes for drinking water is now discouraged due to the possibility of lead poisoning from drinking water [1]. Curtailment of the use of lead in different products in the United States began years ago

with the barn of lead in products such as paint and gasoline [2]. Companies in other countries (for instance, many in the Japanese electronics industries) began to introduce some lead-free products years ago and achieved significant commercial success [2].

Recent research has shown that there is no safe level of lead. Any little amount is very harmful, because lead does not break down in the body, but builds up with time. The higher the lead content, the greater the possibility of causing cancer. Lead as a neurotoxin causes learning disabilities, language and behavioural problems [3]. Pregnant women and young children are particularly vulnerable to lead exposure because lead easily diffuses to the brain via the placenta and interferes with normal development. No matter how useful lead containing products may be, you may be getting harmful results later [3].

Solder joints in electronic, electrical, and automotive applications are getting smaller, yet they are expected to carry stronger mechanical, electrical and thermal burdens with better efficiency. This high expectation has led to the development of some lead-free solders with unique properties like non-toxicity, high ductility, high impact strength etc. for improved device performance and reliability. Hence the following lead-free solders have already been produced: 81Sn–9Zn–10In, 68Sn–32Cd and 86Sn–9Zn–5In These alloys have good melting points of 178°C, 177°C and 188°C respectively which is close to that of eutectic tin-lead solder that has a melting point of 183°C [1].

A frequently overlooked property of solders is wettability. Wettability is defined as the tendency for a liquid metal to spread on a solid surface [1]. It describes the solders ability to form the actual joint on a circuit board. Joint formation includes fillet development between vertical and horizontal surfaces and capillary flow by the solder required to fill holes or gaps. A laboratory assessment of solder wettability can be used to predict alloy performance for process development in the subsequent prototype manufacturing efforts [1].

The wetting property of a material (solder) on a base metal (substrate) is categorized by two aspects; namely: the degree of wetting and the speed of wetting. The degree of wetting refers to how far the alloy spreads and is an equilibrium situation controlled by the laws of thermodynamics of surfaces where the surface and interfacial tensions of the liquid and solid are involved. The speed of wetting refers to the rate (i.e. how fast) the solder wets and spreads. However, this is controlled by a combination of several factors namely: the thermal demand of the system; the use of flux; and the chemical reactions occurring at the interfaces [4]. This study therefore aims at conducting the wettability tests of all the solders produced in order to predict their solderability for possible replacement of Tin-Lead alloys used in soldering operations.

Table 1: Impurity Composition of Tin.

Constituents	Composition (%)
Arsenic (As)	0.0001
Bismuth (Bi)	0.002
Copper (Cu)	0.02
Antimony (Sb)	0.02
Iron (Fe)	0.01
Acid insoluble matter	0.05
Calcium (Ca)	0.002
Lead (Pb)	0.02
Magnesium (Mg)	0.002
Potassium (K)	0.002
Sodium (Na)	0.002

2. Materials and Methods

2.1. Materials

The metals used for the production of the above alloys are granulated Tin, Zinc, Bismuth, Indium and Lead. Tin being the parent metal in all the alloys has a purity of 99% with traces of impurities as shown in Table 1

Some of the materials used for this research work included the following: electric furnace for melting the metals for alloy formation; moulds; weighing balances; digital camera; copper plate; stop watch; tape rule; pencil.

2.2. Methods

91Sn-9Zn, 60Sn-40Zn, 42Sn-58Bi, 90Sn-10Bi and 63Sn-37Pb solder alloys were produced by charging proportionate amounts of respective alloying elements (as determined from charge calculations) into a crucible furnace which was heated until the materials melted starting with the metal of higher melting temperature. The molten alloy was stirred to achieve a homogeneous molten phase and thereafter poured into an air dried mould. The alloys were removed after solidification and cooling; and the wettability tests were conducted as follows:

2.2.1. Wetting rate of solder alloys

The wettability of any solder depends on the following factors: Surface tension, Surface neatness, and Surface roughness. It was reported that random surface scratches may increase the rate of spread of some liquids by as much as 50% [5]. Hence, Grids were made on a $(50 \times 45 \times 6)$ mm

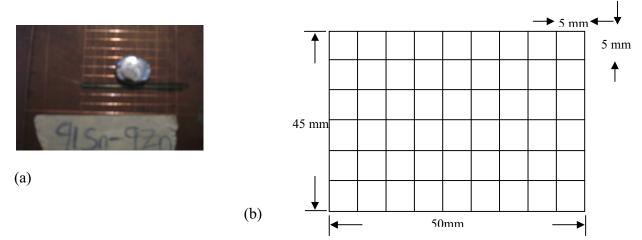


Figure 1: (a) Copper grids with molten solder. (b) Copper grids for wettability analysis.

copper plate to form small squares of (5×5) mm; the total number of squares formed was 90. Ten grams of each alloy was melted and poured on the copper grids; it was allowed to spread and solidify. The wetting rate was determined in percentage as follows:

$$\% squares covered = \frac{number of squares covered}{total number of squares} \times \frac{100}{1}$$
(1)

2.2.2. Wetting time

The wetting time is the time it will take for the molten solder to solidify. Ten grams of each alloy was measured, melted and poured on the copper plate and allowed to solidify. The time for solidification was noted using a stop watch.

2.2.3. Contact angle

Contact angle depends on all three phases in contact and can give information only on the relative strength of the attractions between solid and liquid on one hand and solid and gas on the other hand. The greater the attraction between the solid and the liquid compared with the attraction between the solid and gas, the smaller the contact angle and smaller contact angles depict better wetting. The contact angle was determined by drawing tangent to the drop profile at the point of three-phase contact on the drop profile photograph [5, 6].

The tensions at the three phase contact point are indicated such that: LV is the liquid/vapour point, SL is the solid/liquid point and SV is the

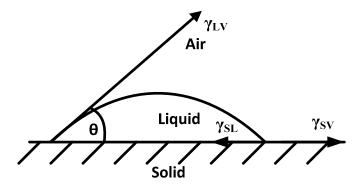


Figure 2: A drop on a horizontal plane. θ is the Contact angle.

solid/vapour point. The Young Equation relating these tensions to the equilibrium contact angle, , may be written as:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \tag{2}$$

Where: γ_{LV} is the surface tension in equilibrium with the vapour V. γ_{SV} is the surface free energy of the solid in equilibrium with the vapour, V. γ_{SL} is the interfacial tension between the solid and the liquid.

3. Results and Discussions

Tin-lead was used as the standard solder to compare with other solders due to its unique properties and industrial applications; it's wetting rate = 8.3% Tin-Bismuth (42Sn-58Bi) also has a wetting rate of 8.3%; the alloy of tin and zinc (91Sn-9Zn) showed a wetting rate of 8.1%

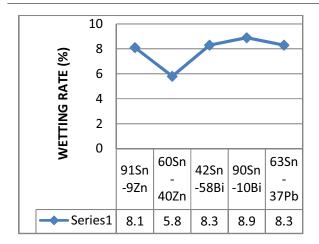


Figure 3: Wetting rate of the alloys.

which is very close to that of the eutectic tinlead solder. Another alloy of tin-bismuth (90Sn– 10Bi) also shows a better wetting rate of 8.9%. Hence it can be concluded from this result that apart from the alloy of tin and zinc (60Sn–40Zn) which showed a lower wetting rate of 5.8%, other lead-free solder alloys investigated can satisfactorily replace the lead bearing solder as far as their wetting power is concerned.

As stated earlier on, small contact angle indicates strong wetting power. From Fig. 4, the contact angle of the lead solder (63Sn-37Pb) is 57°, while the contact angles of the solders: 60Sn-40Zn and 42Sn-58Bi are 58° and 65°, respectively. These solders have contact angle close to that of the conventional lead solder. Hence they are good candidate materials for the replacement of tin-lead solders. Contact angles of 68° and 73° were observed for the 91Sn-9Zn and 90Sn-10Bi solders. These values are higher than that of 63Sn-37Pb solder. However, that does not disqualify them from being candidate materials for the replacement of tin-lead solder, since it has been shown that liquidsolid (i.e. soldersubstrate) attraction can still be very STRONG even if the contact angle is large. This can be confirmed from the previous result of the wetting rate, where the same alloy of tin and bismuth (90Sn-10Bi) depicted the highest wetting rate of 8.9%.

Fig.5 shows the wetting time of tin-lead solder to be 4.7sec. The 90Sn-10Bi composition wets the substrates at 4.8sec. which is very close to that of lead solder. The alloy of 60Sn-40Zn

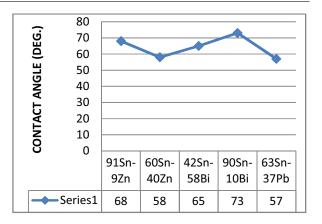


Figure 4: Contact angle of the alloys.

even wets faster than that of lead solder at 4.0sec. 91Sn-9Zn took a little longer to wet the copper substrate at 6.9sec. All these solders are qualified to replace the tin-lead solder. The only alloy with a high wetting time is the alloy of tin and bismuth (42Sn-58Bi) which wets at 50.1sec. This is due to the low thermal conductivity of Bismuth which is about 0.0200 cal/sqcm/cm/°C/sec; hence the more quantity of Bismuth in an alloy the slower will be the rate of solidification of that alloy. However, it is good to note that no time of wetting is too high or too low, it all depends on the area of application. Large gaps and joints require solders with longer time of wetting, so that the molten alloy can flow into all the necessary parts of the joints before it solidifies. In like manner, joints with small gaps will require solders with short time of wetting [1]. This implies that each of the alloy's wetting time is acceptable, depending on the area of application. Hence, any of the lead-free solders can be used in place of leadbearing solders.

4. Conclusion

The following conclusions can be drawn from the study:

- 1. The wetting rate of 58Sn-42In is 8.6%, and that of 90Sn-10Bi is 8.9%; while that of lead solder is 8.3%. Hence 58Sn-42In and 90Sn-10Bi alloys possess higher ability to wet their substrates than the lead solder.
- 2. The wetting time of the lead-free solders were as follows: 91Sn-9Zn, 6.9sec.; 60Sn-40Zn, 4.0sec.; 90Sn-10Bi, 4.8sec.; while that

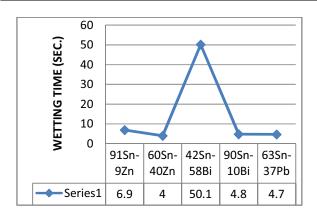


Figure 5: Wetting time of the alloys.

of lead solder (63Sn–37Pb) was 4.7sec. Thus, the wetting time of each solder is moderately good compared to that of lead solders. The alloy, 42Sn–58Bi with high wetting time of 50.1sec can be used on substrates with large gaps and joints which require more time for the gaps to be filled.

3. Since low value of contact angle is often associated with maximum rate of spread, the respective contact angles in degrees of the lead-free solders (68°, 58°, 65°, and 73°), compared to that of lead solder (57°) reveal that the lead-free solders have strong wetting power.

Comparing the wetting times, the wetting area values, and contact angles of the lead-free solders with those of the popular tin-lead solder, it is evident that the lead-free solders are possible substitutes for the tin-lead solder.

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