Journal of Science & Technology 146 (2020) 049-053

Contact Angle of Sn-8Zn-3Bi Lead-free Solder Alloy on Copper Substrate

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Received: September 30, 2020; Accepted: November 12, 2020

Abstract

The wettability of Sn-8Zn-3Bi lead free solder alloy on the copper substrate was evaluated via measuring the contact angle of the solder and the substrate. The measured contact angle was then compared to the contact angle of the traditional and widely used eutectic Sn-37Pb solder alloy. Experiments to study the effect of temperature, flux, and surface roughness of the substrate on the contact angle were also carried out. The results show that the contact angle of Sn-8Zn-3Bi on copper substrate decreased as temperature increases. The minimum value of the contact angle obtained was approximately 23° for Sn-8Zn-3Bi. At the same experimental conditions, contact angle of Sn-8Zn-3Bi is higher than that of Sn-37Pb. When three types of fluxes were used, at 230°C, contact angle of Sn-8Zn-3Bi has the smallest value with the MHS37 flux, 25°, and it has the largest value with the zinc chloride flux, 47°. The surface roughness of the substrate has little influence on contact angle of Sn-8Zn-3Bi on copperand the contact angle has changed a few degrees as the roughness changed.

Keywords: wettability, contact angle, solder alloy

1. Introduction

In decades of years, tin-lead (Sn-Pb) has been the most common solder alloy used in electronic devices, especially the eutectic Sn-37Pb alloy and the near eutectic Sn-40Pb alloy. The advantages for lead-containing tin-alloys as solder and solderable coating are for example low melting point, good mechanical properties, low price and high availability [1]. However, there are legal, environmental and technological factors that are pressing for alternative soldering materials and processing approaches due to the toxicity of Pb. Alternative lead-free solder alloys based on Sn-Zn [2], Sn-Zn-Ag [3, 4] Sn-Ag [5-7] Sn-Ag-Cu [8-10] has replaced Sn-Pb in most of the application.

Eutectic Sn-Zn lead free solder alloy, that have melting points close to that of the Sn-37Pb solder, have been used as one alternative because they possess the advantages of high strength, good creep resistance, and high thermal fatigue resistance [11]. However, the Sn-Zn system solders show poor wetting during soldering to electrodes [12], poor oxidation resistance in reflow soldering and may cause soldering failures, such as poor wetting and non-wetting [13]. By adding Bi into Sn-Zn solders, the melting point can be decreased, and the greater the amount of Bi rendered, the lower the melting point. Bismuth also helps improve the wettability and corrosion performance of Sn-Zn solders [11].

The wettability of the solder alloy on the substrate is crucial to ensuring the strength of a joint for a particular application. The extent of wetting is indicated by the contact angle which can be calculated by the equation (Young-Dupre equation):

$$Cos\theta = \frac{\gamma_{SF} - \gamma_{LS}}{\gamma_{LF}} \tag{1}$$

where θ is the contact angle, γ_{LF} is the surface tension between the liquid and the flux, the interfacial tension γ_{LS} is the force between the liquid solder and the base metal, and γ_{SF} is the interfacial tension between the solid base metal and the flux.

The lower value of contact angle, the better wetting between solder alloy and substrate and thus, ensuring the strength of the solder joint. Contact angle is more specifically related to the particular materials combination under investigation.

Contact angle of solder alloy on the substrate is affected by a variety of factors, including surface roughness [14], time, flux used [15] and effectiveness of the flux [1], and temperature of measurement [16]. Contact angle of solder alloys, primarily on copper substrates, using a variety of fluxes, has been investigated by numerous researchers [1]. The data on

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contact angles of lead-free solder alloys is quite disparate, therefore a meaningful comparison of the alloy's performances is difficult. It is because of the fact that the measuring temperature, preparation of the Cu substrates, fluxes used, and other experimental variables vary with each investigator. So far, there isn't any established standard procedure for measuring the contact angles of lead-free solder alloys.

In this work, contact angle of Sn-8Zn-3Bi lead free solder alloy on copper substrate was measured at different temperatures. The effect of other factors such as surface roughness and flux used were also studied.

2. Experiment

Copper substrate used in this study was commercial copper foil of 0.4 mm in thickness and has a purity of 99.9%. The fluxed used were hydrochloric acid-based (HCl-based) flux, zinc chloride flux and MHS37 flux (rosin-type organic flux). The solder alloys used were commercially available Sn-8Zn-3Bi and Sn-37Pb.

The copper foil was cut into squares of 30 mm on each side. After that, they were polished with abrasive paper (No.1000) and finally polished with 0.05 µm alumina powder. The substrate was then cleaned using alcohol and dried by an air gun.

In the experiments to study the effect of surface roughness, rough copper substrates were also polished by abrasive paper. Five types of abrasive paper 240, 400, 600, 800, and 1000 were used respectively for this experiment. The polishing time with each paper is fixed at 5 minutes on a polishing machine under a load of approx. 1 N. After that, it was clean with alcohol and dried by an air gun. The surface roughness of copper substrates were measured using a SURFTEST SV-400 surface measuring instrument.

For contact angle measurement a drop of flux was applied on the copper foil and a piece of solder alloy (5 mm in diameter and 3 mm in height) was placed on top of the flux (Fig.1a). The system was then heated up and held at the testing temperature for approx. 60 seconds. After cooling, the cross-section of the samples was made, and the contact angle was measured using the image analysis method (Fig.1b).

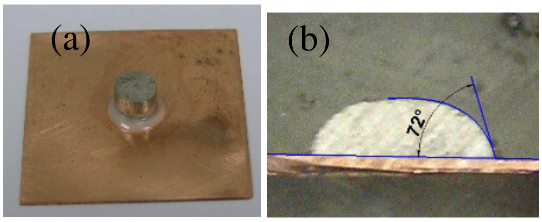

Fig. 1. a) Solder on substrate before melting and b) Cross-sectioned specimen after melting

3. Results and Discussions

3.1 Effect of Temperatures on Contact Angle

The temperature has strongly affected the contact angle of Sn-8Zn-3Bi on copper substrate, it can be proven from the values measured of contact angle which were presented in Fig.2.

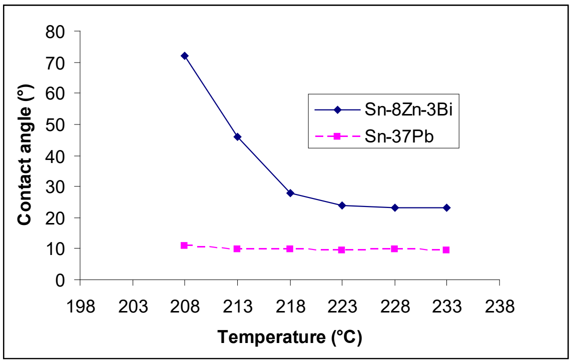

Fig. 2. Contact Angle vs Temperature

As can be seen in Fig.2, contact angle of Sn-8Zn-3Bi decreases with the increasing temperature. At 10°C above the liquidus temperature of the solder alloy, 208°C, the contact angle measured was approximately 72°. When temperature increases, contact angle decreases rapidly, the value of contact angle at 218°C is approximately one-third as that at 208°C. The rate of decreasing is sharp in the first few temperature increases and reaches almost the equilibrium value when the temperature was 223°C, the minimum contact angle obtained was approximately 23°.

For comparison, the same experiment was carried out for the eutectic Sn-37Pb, the obtained results were also included in Fig.2. In the same experimental conditions, contact angles of eutectic Sn-37Pb measured were lower than that of Sn-8Zn-3Bi. The values of contact angle of Sn-37Pb obtained were around 10° and it almost remains constant when temperature varies from 208°C to 233°C.

As the temperature is increased, the contact angle is expected to decrease [1,17]. The result obtained from Sn-8Zn-3Bi does support this expectation. However, there are some solder alloys which do not support this expectation. The contact angle of Sn-10Bi-0.8Cu solder alloy on copper substrate reported by Loomans [16] reduced as temperature increases. With the same flux, Kester #197, the contact angle of Sn-10Bi-0.8Cu was 32° at 250 °C, meanwhile, it was 42° at 340°C. Also reported by Loomans, the contact angle of Sn-10Bi-5Sb solder alloy was 39° at 250°C and increased to 48° at 340°C. However, the data reported by Loomans just available at two temperatures, and 340°C is a very high temperature, 123°C above the liquidus temperature of

Sn-10Bi-0.8Cu and 108°C above the liquidus temperature of Sn-10Bi-5Sb. Thus, too high temperature may have different types of effect on contact angle.

Generally, the reflow temperature of solder alloys (or the temperature of wave soldering) depends on its melting temperature. In this case, the liquidus temperature of Sn-8Zn-3Bi was 198°C, 15°C higher than that of Sn-37Pb. Therefore, a comparison at the same different temperature $t_d = t_{ex} - t_m$ (t_{ex} is the experimental temperature and t_m is the melting temperature of the solder alloy) is needed. For this reason, experiments at the same different temperature were carried out with Sn-37Pb solder, obtained results are shown in Fig. 3.

At t_d = 10 °C, the contact angle of Sn-8Zn-3Bi is significantly higher than that of Sn-37Pb, 72° in Sn-8Zn-3Bi and 18° in Sn-37Pb, respectively. The difference reduces as temperature increases. At t_d = 25°C, contact angle of Sn-8Zn-3Bi is around twice that in Sn-37Pb.

Even though the contact angle of Sn-8Zn-3Bi was significantly higher than that of Sn-37Pb, 23° compare to 10° of Sn-37Pb, the value of 23° of contact angle still indicates that Sn-8Zn-3Bi has very good wettability on Cu substrate.

3.2 Effect of Fluxes on Contact Angle

Effect of fluxes on contact angle experiments was carried out with three different fluxes and the obtained results are shown in Fig.4.

At the same temperature of 230 °C, the contact angle obtained using MHS37 flux was the lowest value of contact angles measured among three different fluxes, the angle measured was approximately 24°. With HCl-based flux and zinc chloride flux, contact angles measured are quite similar in value, 42° – 45°. The results shown in Fig. 4 depicted that for Sn-8Zn-3Bi solder, MHS37 flux is better than HCl-based flux. However, when the experiment was performed with HCl-based flux, the flux was rapidly evaporated. The lack of flux due to flux evaporation may influence the spreading of solder resulted in a change in contact angle.

The flux has two major functions: (1) to provide a tarnish-free surface and keep the surface in a clean state and (2) to influence the surface tension equilibrium in the direction of solder spreading by decreasing the contact angle [18]. The second function of flux indicates the effect of flux on the degree of wetting which is measured by the contact angle. As can be seen in the equation (1.1), the flux takes effect on two values, γ_{LF} and γ_{SF}.

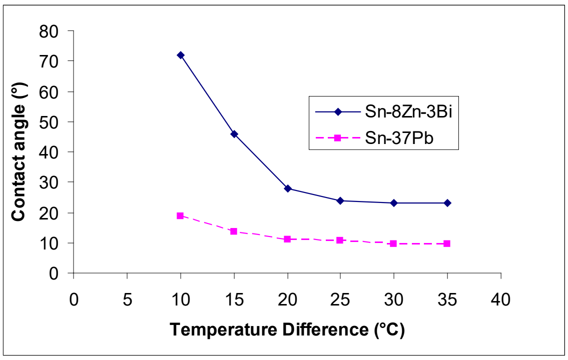

Fig. 3. Contact Angle vs Temperature Difference

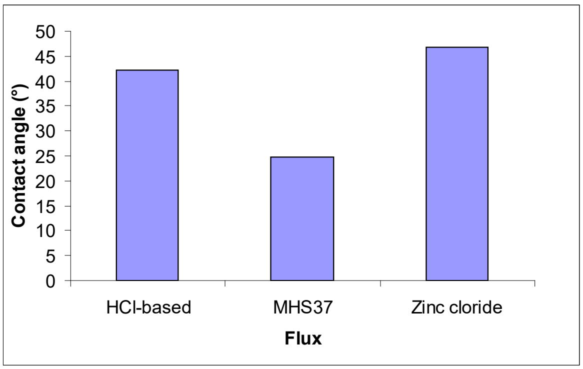

Fig. 4. Contact Angle of Sn-8Zn-3Bi on Cu Substrate at 230 °C

3.3 Effect of Surface Roughness on Contact Angle

The roughness of copper surfaces prepared by using abrasive paper is measured and the results are shown in Table 1.

Table 1. The roughness of Cu substrates

Abrasive paper's No.	Avg. roughness (nm)
240	500
400	340
600	270
800	170
1000	100
Alumina powder (0.5 µm)	60

An early study on the effects of surface roughness on the equilibrium contact angle, θ_0, between wetting liquid and solid substrate was carried out by Wenzel [19]. Wenzel claimed that for surfaces has a wetting angle $\theta_0 < 90°$, smooth surface would have better wettability than the wettability of the rough surface, or contact angle obtained with smooth surface will be smaller than that when rough surface is used. Conversely, he argued that if the smooth surface does not wet well ($\theta_0 < 90°$), the rough surface would have worse wettability or the contact angle will be larger in the rough surface.

However, the results obtained in this present study did not obey Wenzel's findings. The contact angle of Sn-8Zn-3Bi on copper substrate only decreased when surface roughness increased up to around 270 nm, when continues to increase the surface roughness, the contact angle is increased. Meanwhile, with Sn-37Pb, the results show a fully increasing contact angle when surface roughness increases (Fig.5).

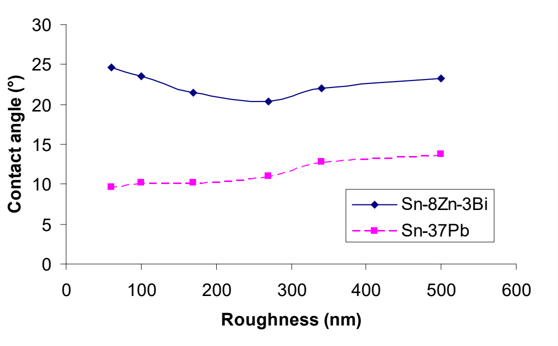

Fig. 5. Contact Angle vs Surface Roughness

Although surface roughness influences contact angle, the variation of contact angle is quite small, Fig.5. The difference between the largest value and the smallest value was just around 4°. It seems that at the range of 60-500 nm, surface roughness has little effect on contact angle.

The effect of surface roughness on contact angle is somewhat complicated and it is not clear. Some researchers found that in some cases the effect of surface roughness on contact angle obeys Wenzel finding, in the other cases, it does not. Lin [14] has studied the effect of surface roughness on contact angle for several solder alloys and found that in some cases the contact angle decreased as surface roughness increases, in the other case it was increased as surface roughness increases. Even in one solder alloy, the difference of methodology to prepare the rough surface also influences contact angle.

4. Conclusion

The contact angle of Sn-8Zn-3Bi on copper substrate decreases as temperature increases. The minimum value of the contact angle obtained was approximately 23° for Sn-8Zn-3Bi. When three types of fluxes were used, at 230 °C, the contact angle of Sn-8Zn-3Bi has the smallest value with the MHS37 flux, 25°, and it has the largest value with the zinc chloride flux, 47°. The surface roughness of the substrate shows little influence on the contact angle of Sn-8Zn-3Bi, the contact angle changes a few degrees as the roughness changed.

Although the contact angles of the Sn-8Zn-3Bi lead-free solder alloy are larger than those of the Sn-37Pb, the alloy still shows good wettability on copper substrate as the contact angle goes under 30° in several conditions. This is an important factor ensuring proper bond and strength of the solder joint. Thus, the Sn-8Zn-3Bi alloy could be used as a replacement for the Sn-37Pb without any concern for wetting characteristics.

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