Investigations on microhardness of Sn–Zn based lead-free solder alloys as replacement of Sn–Pb solder

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Abstract

The microhardness of the Sn–Zn based solder pastes have been compared with the Sn–Pb solder paste. Two types of solder such as Sn–9Zn and Sn–8Zn–3Bi have been investigated along with Sn–37Pb solder for reference. The variation of microhardness with reflow temperature from 220 to 250 °C shows two different characteristics for eutectic and non-eutectic solder pastes. Hardness of Sn–37Pb and Sn–9Zn (eutectic) decreases with increasing reflow temperature while the microhardness of Sn–8Zn–3Bi (non-eutectic) increases with the increasing reflow temperature. Microstructural characterization at 220 and 250 °C shows grain coarsening in Sn–37Pb and Sn–9Zn solders, which cause the hardness to drop a little. For Sn–8Zn–3Bi, with increasing temperature the amount of hard Bi segregation increases which is the main cause of the rise in hardness. SEM images show the formation of Pb rich islands in Sn–37Pb, formation of Zn rod from spheroids in Sn–9Zn and precipitation of Bi rich phase in Sn–8Zn–3Bi are the important features that contribute to the different hardness nature. Again the effect of cooling rate on hardness was also studied and compared among these three solder pastes. The result shows that the Sn–9Zn is the most sensitive to cooling rate. With the change in cooling rate, the hardness increase in Sn–9Zn is greater (58% after water cooling) than in Sn–37Pb (30%) and Sn–8Zn–3Bi (33%). The hardness profile along the distance from the centre shows that the hardness gradient is also found highest on Sn–9Zn solder paste whereas similar trendlines were found in Sn–37Pb and Sn–8Zn–3Bi solder. SEM images of air- and water-cooled microstructures show preferential Zn formed at the edge in Sn–9Zn solder while Pb rich islands at the centre (for Sn–37Pb) and precipitation of Bi at the edge (for Sn–8Zn–3Bi) was found along with grain refinement.

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1. Introduction

Lead-containing solders, particularly tin–lead solders, have been widely used as low temperature joining alloys for some time because of their good combination of process attributes, properties and cost. However, concerns about lead toxicity have resulted in the ban of lead-containing solders for use in water piping, food and beverage cans, and automobile bodies. In the electronics industry, the main concern regarding lead-containing solders arises from the ultimate disposal of solder-containing devices in landfills when the recycling of electronics components is not properly practiced.

The restriction of lead use in industry has been strongly promoted to protect the environment. European Union has already banned the lead containing electronic product manufacturing from 1 July 2006. Lead-bearing solders, which have been widely used in electronics and automobile products, have been one of the main targets for replacement with non-toxic substances. Therefore, establishing a lead-free solder has become a critical issue. In fact, many studies of new solders have been reported in the last decade [1]. New solders must fulfill several requirements both from economic and physical/chemical points of view. For example, the melting temperature must be in the same range as that for conventional solders, strength and integrity must be similar or superior to conventional solders, supply must be adequate for the required uses, and prices must be com-
petitive. The properties of Sn–Ag solders and their interface microstructures with Cu have already been reported [2–5], but these alloys have somewhat higher melting temperatures, 216–221°C, than that for the Sn–Pb eutectic alloy, which may require the modification of existing production plants. In addition, increasing soldering temperature may cause the serious problem of damaging electronics components.

Sn–Zn alloys have been expected to be one of the best alternative choices for a Sn–Pb eutectic solder because their melting temperatures are close to that of a Sn–Pb eutectic alloy, i.e., 198°C for the Sn–9 wt.% Zn eutectic composition according to the Sn–Zn phase diagram shown in Fig. 1. This benefit will enable us to use existing production lines and electronics components without any modification. In

Fig. 1. Equilibrium phase diagram of three different systems: (a) Sn–Pb; (b) Sn–Zn; (c) Sn–Zn–Bi system.
addition, Sn–Zn alloys or the addition of Zn into other Sn base alloys have been known to provide mechanical integrity to electronics packaging [6,7]. The other great benefit for the Sn–Zn alloy system is its price. Zn (US$1.08 kg\(^{-1}\)) is known to be one of the inexpensive metals, especially compared with Ag (US$153.2 kg\(^{-1}\)). This means that the price increase associated with adopting lead-free soldering can be suppressed. Other than the eutectic Sn–Zn, small addition of Bismuth will be advantageous to reduce the solidus melting point (solidus line is at 189\(^\circ\)C for Sn–8Zn–3Bi shown in Sn–8Zn–(0–8)Bi system) a bit from the eutectic Sn–Zn solder. According to researches, it is known that the tensile strength and the creep resistance of eutectic Sn–Bi solder is higher than that of eutectic Sn–Pb [8], so it is expected that the addition of some Bi element will have good effect on the mechanical properties of Sn–9Zn [9].

Microhardness measurement technique is a very sensitive technique to detect structure changes of different soft solders at different temperatures. Usually micro hardness testing is a non-destructive testing but it leaves a small pit in the structure. Micro hardness testing can be the easiest way to determine the mechanical properties of the different phases of the structure [10]. The rule of thumb is the higher the hardness the higher is the mechanical strength. For soldering technology it is very important to study the microhardness of the structure because in soldering many soft and hard phases form, which are hard and brittle, and induce some hardness in the structure. Micro hardness testing can be the easiest way to determine the mechanical properties of the different phases of the structure [10]. The rule of thumb is the higher the hardness the higher is the mechanical strength. For soldering technology it is very important to study the microhardness of the structure because in soldering many soft and hard phases form, which are hard and brittle, and induce some hardness in the structure.

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2. Experimental

Sn–37Pb (KOKI SE48-M05S), Sn–9Zn (Showa Denko JUFFIT-E 9ZSN10M) and Sn–8Zn–3Bi (Showa Denko JUFFIT-E 8Z3B05M2) solder paste were used for our experiment. At first the solder pastes were taken out from the fridge where the temperature was 4\(^\circ\)C to a room temperature for an hour. Then the samples were printed in the alumina substrate (for solder balling). The printing was done by EKRA MAT 530 screen-printing machine. The stencil used was a stainless steel stencil with a thickness of 0.15 mm with nine holes of 6.5 mm diameter with a minimum distance between centres was at least 10 mm. All the batches of samples were reflowed in a reflow oven from 220 to 250\(^\circ\)C. For each batch nine samples were prepared. A typical reflow profile has been shown in Fig. 2. Another two sets of samples were prepared with different cooling rate. Here the samples were heated up to 230\(^\circ\)C and then one set is cooled in water (cooling rate approximately 20\(^\circ\)C/s) and the other in air (cooling rate approximately 2\(^\circ\)C/s). Three samples for each solder paste were prepared for each cooling rate.

Sn–37Pb and Sn–9Zn both are eutectic alloys with primary phases due to non-equilibrium cooling where the hardness profiles will be an interesting study to identify the phase changes. Along with these two eutectic alloys, a comparison of Sn–8Zn–3Bi will give us the opportunity to compare the effect of Bi on the structure. Here Sn–37Pb has been studied as a reference to compare with some new lead-free Sn–Zn based solder alloys.
solder pastes.

Fig. 3. Variation of hardness with reflow temperature for three different solder alloys [Sn–37Pb, Sn–9Zn and Sn–8Zn–3Bi]. An interesting feature has been revealed from this graph that with increasing temperature the microhardness of the eutectic alloys such as Sn–37Pb and Sn–9Zn decreases but the microhardness of the non-eutectic alloy such as Sn–8Zn–3Bi increases. Also it can be stated that with introducing Bi in Sn–Zn system, a complex ternary alloy has formed, microhardness of which depends upon various conditions like microstructure, shape of the phases, presence of hard Bi rich phase in the matrix, grain size, etc. On the other hand, microhardness of the eutectic alloy depends upon the grain size, presence of second phase and the distribution of the second phase in the matrix.

Table 1: EDX results at different spots shown in Figs. 4 and 5.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Pointed in</th>
<th>Chemical composition (at.%)</th>
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<tr>
<td>1</td>
<td>Fig. 4</td>
<td>65.8 – 0.4 – – – –</td>
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<tr>
<td>2</td>
<td>Fig. 4</td>
<td>53.2 – 15.6 – 44.4 – – –</td>
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<td>3</td>
<td>Fig. 4</td>
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<td>4</td>
<td>Fig. 4</td>
<td>18 – 82 – 3.3 – 4.7 –</td>
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<td>5</td>
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<td>18 – 82 – 3.3 – 4.7 –</td>
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<td>6</td>
<td>Fig. 4</td>
<td>– 99.3 – 0.7 – – – –</td>
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<td>7</td>
<td>Fig. 4</td>
<td>25.2 – 7.4 – 67.4 – –</td>
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<tr>
<td>8</td>
<td>Fig. 4</td>
<td>13.4 – 86.6 – – – –</td>
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in Table 1. The EDX spots have been spotted as 1, 2, 3, etc. in different SEM images.

3. Result and discussion

3.1. Effect of reflow temperature and microstructure on micro hardness

The micro hardness of a solder alloy depends on the motion of dislocation and growth and configuration of grains. The processes are more sensitive to the microstructure of the solder than its chemical composition. So the mechanical property such as the microhardness depends especially on the microstructure, processing temperature, the composition, etc. [11].

Fig. 3 shows variation of microhardness with reflow temperature of three different solder alloys [Sn–37Pb, Sn–9Zn and Sn–8Zn–3Bi]. An interesting feature has been revealed from this graph that with increasing temperature the microhardness of the eutectic alloys such as Sn–37Pb and Sn–9Zn decreases but the microhardness of the non-eutectic alloy such as Sn–8Zn–3Bi increases. Also it can be stated that with introducing Bi in Sn–Zn system, a complex ternary alloy has formed, microhardness of which depends upon various conditions like microstructure, shape of the phases, presence of hard Bi rich phase in the matrix, grain size, etc. On the other hand, microhardness of the eutectic alloy depends upon the grain size, presence of second phase and the distribution of the second phase in the matrix.

Fig. 4 shows the SEM images of three different solder alloys at 220 and 250 °C, which clearly describes the distinction in microstructure of each solders as the reflow temperature increases. It is clearly evident that a second phase is absent in the structure at 220 °C for eutectic alloys. For Sn–37Pb solder, only the eutectic mixture of Sn and Pb rich phase has been found. In some locations a Pb rich phase within the eutectic mixture has found to occur in large amount but no distinct Pb rich islands were observed. The matrix is surely βSn which is the primary constituent of this alloy. The microstructure at 250 °C shows large areas of Pb rich islands, which forms due to the higher super heating temperature. At 250 °C the superheating temperature is 67 °C [220 °C – 153 °C], which is 30 °C higher than the superheating at 220 °C [220 °C – 183 °C = 37 °C]. For this reason the structure gets some extra time before solidification to form some of its Pb rich islands within the eutectic matrix. The introduction of this phase surely contributes to the reduction in hardness as it is a softer phase than the eutectic one. Other than this, the grain coarsening is another thing which contributes in the reduction of microhardness. Eutectic microstructure has a very high surface area per unit volume and is therefore very hard for a dislocation line to move within the eutectic structure, which causes the structure to be hard [15.4 VHN] as found at 220 °C. With increasing temperature, the hardness decreases to 12.4 VHN at 250 °C. With a 30 °C higher superheating temperature, all the grains have sufficient energy to combine together and make a coarse grain which is thermodynamically more stable form as the surface area per unit volume decreases. So the grain coarsening effect also has a marked effect on the microhardness of the structure.

For Sn–9Zn eutectic alloy similar feature described above have been observed. Grain coarsening has clearly been occurred as the structure moves from 220 to 250 °C. Also the introduction of second phase has been done which is shown in Fig. 4. Another important feature has been revealed in the structure that is the change in shape of the second phase. The normal microstructure of Sn–Zn eutectic is that Zn distributes in Sn matrix as platelets [12]. In Fig. 4 and also in Fig. 5 [magnified image] shows that at 220 °C, some of the Zn rich phase, other than the Zn platelets, were of a small circular shape (confirmed by EDX, Table 1 – spot 9) and dispersed all over in the matrix. Together with small gain size of the eutectic mixture, this dispersed spheroids cause the hardness to be high at 220 °C as they hinder the movement of the dislocation lines. With increasing reflow temperature is dispersed Zn phase starts to combine together to form a rod like shape. As the number of spheroids decreased in the matrix at 250 °C the dislocation line can easily move across the struc-
Fig. 4. Phase changing of three different solders at two different temperatures.

Structure, making it a much softer structure. Similarly the grain size of the eutectic mixture also increases due to the higher superheating temperature. A similar explanation for Sn–37Pb has already been given above. So the grain coarsening, introduction of second phase [Zn] and also the accumulation of the dispersed Zn spheroids into a rod cause the structure to become less hard at 250°C (17.3 VHN) than that at 220°C (19.3 VHN). For Sn–9Zn the hardness is greater than that of Sn–37Pb. This means that the mechanical properties of Sn–9Zn will be superior to that of Sn–37Pb solders [13].

Sn8Zn3Bi is found to be the hardest structure (28 VHN at 250°C) among all the three solders examined and its hardness increases with increasing temperature unlike the other two solders. At 220°C the microstructure is Zn rich phase (platelets) with βSn, with some bismuth dissolved in Sn (EDX analysis) [9]. The matrix is mainly a Sn rich phase in which Zn needles and platelets are dispersed randomly. The hardness of such structure is about 23 VHN. With increasing temperature small Bi rich regions form within Sn rich phase. EDX analysis confirmed those white regions as the Bi rich phase (Table 1 – spot 8). This secondary precipitation is due to the fact that the solubility of Bi in Sn decreases significantly as the temperature is lowered below the eutectic points [11]. For a reflow temperature at 250°C, the Bi rich
Fig. 5. Sn–9Zn solder at 220 °C showing the Zn spheroids dispersed in the Zn matrix.

phase has a much longer time to be formed than that at 220 °C. Again at high temperature a larger amount of Bi can into the solution of Sn and Zn. Also with larger grain size at higher temperature this phase becomes so distinct that below the eutectic temperature it starts to segregate from the Sn and Zn rich phase. The Sn and Zn rich phase becomes increasingly supersaturated with Bi. The supersaturation is relieved by the precipitation of Bi rich phases within the Sn rich phases. This segregation of Bi with increasing the temperature causes the structure to be hard and in Fig. 3, a rise in microhardness at 230 °C is clearly observed. At 250 °C almost 20% increase in microhardness has been recorded which is a crucial point for the controlled use of Bi in solder alloy. With increasing

Fig. 6. Hardness variation with different cooling rates.

Fig. 7. Hardness profile of different solder pastes after cooled in air (approximately 2 °C/s).

Fig. 8. Hardness profile of different solder pastes after cooled in water (approximately 20 °C/s).
Bi (>3%) the structure tends to be very hard and brittle as a high amount of segregation of Bi is allowed.

3.2. Effect of cooling rate on microhardness

The cooling rate has a marked effect on microstructure and hence on microhardness. Fig. 6 shows a typical bar chart of varying cooling rate and its effect on the microhardness of the three different solder pastes. Here the average hardness of these three solder pastes cooled in a furnace, air and water from 230 °C has been shown. The main feature of this graph is with increasing the cooling rate, the microhardness increases. The general view of a faster cooling rate is that it will lead to a fine-grained microstructure. With a large number of fine-grained structures, the surface area per unit volume increases. Therefore it will be difficult for dislocation lines to pass through and hence the structure becomes much harder. From Fig. 6, it is quite evident that Sn–9Zn is the most sensitive to cooling rate among all the solder pastes. The hardness increase is almost 18% and 58% in the air-cooled and water-cooled structure, respectively. Sn–37Pb (15% and 30%) and Sn–8Zn–3Bi (12% and 33%) are much less sensi-
Fig. 10. SEM images of three different solder pastes cooled in water (20°C/s) showing difference between the centre and the edge microstructure.

Fig. 10. SEM images of three different solder pastes cooled in water (20°C/s) showing difference between the centre and the edge microstructure.
hardness drops rapidly and the structure clearly shows a variation in microstructure. Another quite evident characteristic is that grain refinement has occurred extensively in the water-cooled structure. With the same magnification SEM image of the air-cooled structure shows larger grains than the water-cooled structure. The water-cooled structure shows almost an equiaxed grain size.

Other than Sn–9Zn, Sn–37Pb and Sn–8Zn–3Bi show a similar gradient between the edge and the centre (Figs. 8 and 9). In Sn–37Pb some difference between the edge and the centre has been found due to the formations of Pb rich islands in the eutectic matrix. As the centre is cooled slower than the edge the Pb rich phase had some time to nucleate at the centre. But as the edges were cooled very fast there is no time for Pb to nucleate near the edge. Again in Sn–8Zn–3Bi, other than grain refinement, precipitation of the hard Bi rich phase occurs at the edge region, where the cooling rate is much faster. This preferential precipitation of the Bi rich phase makes the...
edges harder. A similar behaviour was found both in the air-cooled and water-cooled structure. Also grain refinement has occurred in both Sn–37Pb and Sn–8Zn–3Bi as in Sn–9Zn. In Sn–37Pb, due to faster cooling in water, the Pb rich islands which were present in the air-cooled structure are now absent. This makes the average hardness to be increased in the water-cooled structure. Also in Sn–8Zn–3Bi, the precipitation of Bi is higher in the water-cooled structure than in the air-cooled structure, which makes the structure harder.

4. Conclusions

In this paper the microhardness of Sn–37Pb, Sn–9Zn and Sn–8Zn–3Bi has been investigated and compared. We have tried to establish the microstructure–microhardness relationship. Also the effect of cooling rate on the microhardness was examined in order to obtain a sensitive solder paste in terms of hardness gradient. It is found that with increasing reflow temperature the hardness of Sn–9Zn and Sn–37Pb decreases due to the fact that larger grains were formed at higher temperature; especially Sn–9Zn shows a gradual decrease in hardness with increasing temperature. In contrast, the microhardness of Sn–8Zn–3Bi increases with increasing temperature due to segregation of a hard Bi rich phase in the structure. More Bi can dissolve in Sn and Zn at 250 °C than at 220 °C, so when it is cooled to below the solidification temperature higher amount of Bi precipitates which make the hardness to rise from 22.7 to 28 VHN. EDX analysis confirmed the existence of a Bi rich phase in the structure. The cooling rate has a marked effect on Sn–9Zn solder paste as the hardness increases almost by 18% and 58% after air and water cooling whereas the other two show a 30–33% increase in hardness after water cooling. Also the hardness profiles along the distance from the centre support the sensitive behaviour of the Sn–9Zn solder paste. Almost 22% and 34% hardness increase were reported at the edge and in the water-cooled structure. So if a slow cooling rate is maintained, then Sn–9Zn can replace the Sn–37Pb as it has higher hardness, but with increasing cooling rate it becomes more susceptible to the cooling rate, whereas Sn–8Zn–3Bi is found to be much harder which may induce some brittleness in the structure.

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