Heat resistance of Sn-9Zn solder/Cu interface with or without coating

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The potential of the newly developed Sn–9Zn solder paste as a lead-free solder, especially focusing on the stability at high temperature, was examined. The initial interface strength between Sn–9Zn and Cu, about 50 MPa by the tensile test, is higher than other interfaces such as Sn–37Pb/Cu. While the Sn–9Zn/Cu interface maintains the high strength level after heat exposure at 125 °C, the heat exposure at 150 °C degrades strength seriously. The degradation at 150 °C is caused by dissipation and by disruption of the Cu–Zn reaction layer at the interface. Where the Cu–Zn layer is eroded to form a whole, Sn directly reacts with a Cu substrate to form a thick Sn–Cu reaction region. Such an interfacial morphology change causes the serious degradation. With the Ni/Pd/Au coating on a Cu substrate, the interface becomes much stronger than the direct interface. Even after heat exposure at 150 °C, strength degradation is not so significant. Zn segregates into the coating layer. During high-temperature exposure, Ni and Pd diffuse each other. Zn also diffuses into the coating layer to form compounds, and as a result, a depleted zone of Zn is formed in the solder close to the interface.

I. INTRODUCTION

In recent years, much effort has been paid for developing lead-free soldering technologies in electronics packaging industries. Among various candidates as a lead-free solder, Sn–Zn alloys have been expected to be one of the best alternative choices for a Sn–Pb eutectic solder because of its melting temperature close to that of a Sn–Pb eutectic alloy, i.e., 198 °C for the Sn–8.8 wt% Zn eutectic composition. Many electronics devices as well as plastic connectors cannot resist the high soldering temperature required for the other alternative solders such as a Sn–Ag eutectic alloy, Sn–Ag–Bi alloys, and a Sn–Cu eutectic alloy. This benefit will enable us to use the present production lines and the present electronic components without any modification. In addition, Sn– Zn alloys or the addition of Zn into other Sn base alloys have been known to provide a mechanical integrity to electronics packaging.^{1,2} The other great benefit for the Sn–Zn alloy system is in its economy. Zn is known to be one of the inexpensive metals, especially compared with Ag. This fact can suppress the price increase in adopting lead-free soldering.

In the previous work done by one of the present authors,³ the basic microstructure of Sn–Zn binary alloys and their interfaces with Cu after soldering have been examined and several important microstructural features became clear. Zn distributes in a Sn matrix as platelets. Three reaction layers are formed at the Sn–Zn/Cu interface, the thick γ –Cu₅Zn₈ adjacent to the solder, the thin β' –CuZn in the middle, and the other thinnest layer adjacent to Cu. Those layers do not contain any Sn. However, the Sn–Zn alloy is known to have a serious drawback on oxidation.^{3–5} Because of poor oxidation resistance of Sn–Zn alloys, an inert soldering process such as N₂ flow furnaces must be used for the production. The poor oxidation resistance is recognized as the fatal factor for the Sn–Zn alloy system to be the lead-free standard

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884 JOURNALS

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alloy. In addition, because of poor oxidation resistance of Sn–Zn alloys, only a limited number of works have been focused on the Sn–Zn alloy system. Recently, some of the present authors have developed a new Sn–Zn solder paste with which an air atmosphere reflow process can be applied for surface mount technology (SMT).⁶ This new solder paste is expected to break through in promoting the lead-free soldering technology. Then the aim of the present work is to examine the heat resistance of the Sn–Zn/Cu interface with or without coating on a Cu substrate.

II. EXPERIMENTAL PROCEDURE

A. Materials and soldering

The new Sn–9 wt% Zn alloy paste was supplied by Senju Metal Industry Co. Ltd., Saitama, Japan. Other alloys such as Sn–3.5 wt% Ag, Sn–37 wt% Pb eutectic alloys, and Sn–2 wt% Ag–7.5 wt% Bi–0.5 wt% Cu (Alloy-H) were also prepared for comparison in the same process mentioned in the previous paper.³

Cu used was 99.99 wt% pure and was a 15-mmdiameter rod. The rod was cut into 15-mm-long short columns, and one of their ends becomes a face to be soldered. The short columns were used for tensile test after soldering. The soldering face was polished to an optical flatness. Some of the Cu columns were electroless plated with a Ni/Pd/Au coating layer. The average thickness of each sub layer was 0.6 μ m/Ni, 0.1 μ m/Pd, and 0.06 μ m/Au.

Solder sheets and Cu columns were ultrasonically cleaned in ethanol before soldering. Soldering was carried out in air at 250 °C for 5 min. For a tensile specimen, two Cu columns were soldered together with the solder paste or with the solder sheets in between them. The length of the joint becomes about 30 mm by this treatment.

B. Evaluations

Tensile specimens, which were rectangular plates 4 mm wide \times 1 mm thick \times 30 mm long, were cut from the joint. Tensile strength vertical to a soldering interface was measured at a crosshead speed of 0.5 mm/min at room temperature. The influence of high temperature exposure on joint strength was evaluated. The joints were heat-treated at 125 and 150 °C for 100 h in air, which have been recognized as the typical highest temperatures for the electronic circuits of consumer electronics and for vehicles engines. After the exposure, tensile strength was also evaluated in the same manner mentioned above. For each piece of data, more than two samples were tested.

Wettability of solders on a Cu plate was evaluated by the spreading area of solders in air followed by the JIS Z3 197 standard. The number of samples was 6 for each piece of data. Interface microstructure before and after heat exposure was observed by optical microscopy (OM), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA).

III. RESULTS AND DISCUSSION

A. Wetting of new Sn–Zn paste and strength of solders/Cu interface and their changes after high-temperature exposure

The applicability of an air reflow process is the most advanced feature of the present solder paste. Figure 1 shows the comparison of wetting properties for Sn–9Zn and Sn–8Zn–3Bi alloys with various lead-free and leadbearing solders in air. Even though all lead-free solders in the figure have wettability worse than the Sn–Pb eutectic solder, the present Sn–Zn with or without Bi exhibited good wettability almost equivalent to Sn–Ag and Sn–Cu eutectic solders, which have been recognized as the two of the best choices as lead-free solders. The addition of Bi into Sn–Zn seems to improve wettability slightly. In fact, the several reflow trials in air showed the excellent solderability of this alloy as shown in the photograph inserted in Fig. 1. A quadra flat package (QFP) is connected on a circuit board without any serious misconnection.

Figure 2 summarizes the tensile strength of the Cu joints soldered with various solders with or without heattreatment at 125 and 150 °C. It is noteworthy that the joint soldered by the present Sn–9Zn solder paste has quite high strength just after soldering. The strength exceeds about 50 MPa, which is far beyond the strength obtained by a Sn–9Zn solder in the previous work,³ i.e., 25 MPa for the joint soldered in vacuum. Such low strength in the previous work was primarily attributed to poor wetting between Sn–Zn and Cu even in vacuum. Many defects were found at the interface. In contrast, the excellent strength obtained by the present solder paste is achieved by the improvement of wetting property by modifying the flux in the paste.



FIG. 1. Spreading of various solders on Cu with a photograph of air reflow QFP on a printed circuit board with Zn–8Bi–3Bi paste.

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FIG. 2. Summary of tensile strength of Cu joints soldered with various solders with or without heat exposure.

The heat exposure at 125 °C does not influence the strength so much. The heat exposure at 150 °C, however, shows apparent degradation of the joint. The strength after the heat exposure is about 20% of the initial one while all of the other joints maintained about 50–60%. Thus the degradation of the Sn–9Zn/Cu joint is the exceptional case. In constrast to the Sn–9Zn/Cu interface, the Sn–9Zn/Cu coated with the Ni/Pd/Au layer exhibited quite high initial strength and, furthermore, the strength degradation after the heat treatment at 150 °C was not so serious as that for the Sn–9Zn/Cu joint without coating. The strength after the heat treatment is still higher than the initial strengths of all other joints.

B. Interface microstructure of Sn–9Zn/Cu with or without high-temperature exposure

Figure 3(a) shows the interface microstructure between a Cu substrate and the Sn–9Zn solder. Inside a Sn matrix, Zn distributes as thin platelets. In the photograph, Zn is etched by a dilute hydrochloric acid. At the interface a thin reaction layer, of thickness about 5 µm, is formed. This reaction layer contains only Cu and Zn without Sn as shown in Fig. 4. As already reported in the previous work,³ this reaction layer is composed of three sublayers. From the Sn-Zn solder side, they are γ -Cu₅Zn₈/ β '-CuZn/a thin unknown Cu-Zn phase. The other feature of this interface is in its morphology. In comparison with the interfaces of Cu/other solders, the Cu/Sn-Zn solder interface exhibits rather flat layer structure. Many Sn alloys form quite irregular reaction products growing into solder.⁵ A thick and rough interface, which is the Sn solders/Cu₆Sn₅ layer one, is always



(a)





FIG. 3. SEM photographs of Sn–9Zn/Cu interfaces: (a) the initial interface, (b) the interface after heat exposure at 125 $^{\circ}$ C for 100 h.

formed between Sn alloys and Cu. By the same soldering condition in the present work, a Cu_6Sn_5 layer grows more than 10 μ m thick and forms long peninsula structures into a solder.⁵ Such a peninsula structure weakens interfaces by becoming a fracture origin at a low stress level. The relatively thin and flat interface of the Sn–Zn/Cu system is expected to provide high strength to joints without any severe stress concentration.

The reaction structure does not change so much even after heat exposure at 125 °C for 100 h. Figure 3(b) shows such a typical SEM photograph. The thickness of the reaction layer is almost the same as that just after soldering. In contrast to the interface microstructure, the morphology of Zn distributing in the Sn matrix changed from platelet to rather particulate. In addition, the distributing phase is not etched by a dilute hydrochloric acid. These features indicate that the Zn platelets changed their nature by the heat exposure. By EPMA

886



FIG. 4. EPMA line analysis across the Sn–9Zn/Cu interface just after soldering.

analysis, it is revealed that this phase contains much amount of Cu in addition to Zn. This fact tells the occurrence of Cu diffusion from Cu or from the reaction layer at the interface deeply into the Sn–Zn solder side. Nevertheless, the strength of the soldered joint did not change so much even after the heat exposure at 125 °C, which is believed to be attributed to the fact that the change of the interface microstructure between assoldered and after-heat-exposed joints is not so very significant.

After the heat exposure at 150 °C, this morphology change of Zn in the solder becomes much clearer. Figure 5 shows the SEM micrograph with the corresponding EPMA element mappings of the interface after the heat exposure, and Fig. 6 shows the line analysis of the same interface. By the quantification with EPMA of the particles in the solder alloy, they contain Cu and Zn approximately at the composition of a Cu₅Zn₈ phase. In addition to the morphology change of Zn in the solder, the interface microstructure exhibits a great change after the heat exposure. The Cu-Zn reaction layers do not maintain a flat interface with the solder nor with the Cu. The EPMA element mapping clearly shows that the Cu-Zn reaction layer becomes thinner and partly disappears, where Sn diffuses into the Cu side behind the reaction layer to form a Cu-Sn reaction product, which is confirmed as Cu₅Sn₆ by the EPMA quantitative analysis. As a whole, the reacted region becomes much thicker and much more irregular than the interface without heat ex-



FIG. 5. SEM photograph and EPMA mapping of Sn-9Zn/Cu interface after heat exposure at 150 °C for 100 h.

posure or with heat exposure at 125 °C. This fact gives the reason the Cu/Sn-Zn interface degrades significantly by the heat exposure at 150 °C.

Thus, the Sn-Zn/Cu interface with the Cu-Zn reaction layer is no more stable at 150 °C and the reaction layer decomposes by the diffusion of Cu into the Cu-Zn solder to form Cu₅Zn₈ particulate reaction products. Where the hole is formed in the reaction layer, Sn easily diffuses into the Cu substrate to form the thick Cu₅Sn₆ intermetallic compound. Thus, at high temperature, one has to be careful because the decomposition rate of the reaction layer becomes much faster than supplying Cu from the Cu substrate to maintain the reaction layer at the interface. At 125 °C, however, the decomposition rate of the Cu-Zn reaction layer is not so fast and the thickness of reaction layer does not decrease.

C. Interface microstructure of Sn-9Zn/Cu with coating and influence of high-temperature exposure

With the coating of the Ni/Pd/Au layers, Zn does not form any compound with Cu because the coating layer completely protects the Cu substrate from the reaction. Figure 7 shows the interface just after soldering. The interface consists of two distinct layers. Both layers are quite thin. The layer adjacent to the Cu substrate is about 1 µm thick corresponding to the Ni layer, which is shown in the EPMA line analysis in Fig. 8. Zn diffuses to reach the Ni. Because of the low spatial resolution of EPMA analysis, i.e., about a few µm, the second layer

(arbitrary unit) Cu Sn X-ray intensity Zn O 20 30 40 10 0 Distance (μm)

FIG. 6. EPMA line analysis across Sn-9Zn/Cu interface after heat exposure at 150 °C for 100 h.

adjacent to Sn-Zn solder seems to be the reaction layer among Ni, Pd, Au, and Zn. The thickness is about 0.7 to $0.8 \mu m$, which is much thicker than the initial thickness of the Pd and Au coating layers (0.074 and 0.008 µm, respectively). In addition, the feature of having vertical fine cracks in the second layer indicates the brittleness of the reaction layer. Thus, the second layer is the intermetallic compound of these elements. It is noteworthy that



FIG. 7. SEM photograph of Sn-9Zn/Cu interface with Ni/Pd/Au coating on Cu.



FIG. 8. EPMA line analysis across Sn-9Zn/Cu interface with Ni/Pd/ Au coating on Cu just after soldering.

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Sn does not diffuse into the reaction layer with Zn. Because the brittle reaction layer is quite thin less than 1 μ m and is flat, the influence of the interface reaction is not so significant and the strength of the interface is very high as shown in Fig. 2.

After the heat exposure at 125 °C, little change in the interface microstructure was observed, which gives the reason why the joint strength does not decrease at all as shown in Fig. 2. After the heat exposure at 150 °C, macroscopic observation shows the formation of the depleted zones without Zn precipitates close to the interfaces clearly as shown in Fig. 9. The thickness of the zone is about 15 to 20 µm. The distribution morphology of Zn precipitates in the central region, however, does not change from the initial one. Figure 10 shows the enlarged photograph of the interface. There are also two distinct layers. One is dark and about 1-µm thick adjacent to the Cu substrate, and the other is thinner than about 1 µm adjacent to the solder. In comparison with the initial microstructure in Fig. 7, the thicker layer corresponds to the coating layer and the thinner layer is to be the reaction layer. These are confirmed by the EPMA line analysis as shown in Fig. 11. In comparison with the interface of the initial state, each element in the coating sublayers diffuses each other. Ni diffuses into the Pd/Au layer, and Pd diffuses into the Ni layer. In addition, Zn diffuses very deeply into the coating layer, which seems to give the reason for the formation of the Zn-depleted zones close to the interface as shown in Fig. 9.

As shown in Figs. 9 and 10, the Ni layer after heat treatment exhibits a dark contrast as compared with that in Fig. 7. This dark contrast seems to indicate that the layer contains some kind of a light element. The EPMA line analysis clearly shows the rerichment of O in the Ni layer. The origin of O is still in question. O can diffuse especially in Cu and also in Sn. However, there was no O in the Cu substrate nor in the Sn–Zn solder. These facts imply that the Ni coating layer and the interfaces with the



FIG. 9. SEM photograph of soldering region after heat exposure at 150 $^{\circ}\mathrm{C}$ for 100 h.

Cu layer and with the Pd layer, which have some sort of defect such as porosity, can be the diffusion path for O. A slight degradation in strength in Fig. 2, which is still higher than the initial strengths of most of the other joints, is attributed to the oxidation of the Ni layer and also to the growth of the reaction layer.



FIG. 10. Enlarged photograph of the interface in Fig. 9.



FIG. 11. EPMA line analysis across the Sn–9Zn/Cu interface after heat exposure at 150 $^{\circ}$ C for 100 h.

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D. Reaction mechanism at the high-temperature range

By summary of the reaction features at high temperature mentioned in the forgoing sections, the schematics for the reaction mechanism can be shown in Fig. 12. Without coating, Cu diffuses from the substrate and the reaction layer into the solders to form Cu-Zn reaction products, i.e., Cu₅Zn₈, even at 125 °C. Most of the Zn precipitates in the solder form the intermetallic compound with Cu. Such a microstructural change, however, does not cause serious degradation in strength primarily because the interface microstructure does not change so much. However, the Cu-Zn interface reaction layer is not stable at 150 °C and becomes thin. When the whole at the reaction layer is open, Sn directly reacts with the Cu substrate to form a Sn-Cu intermetallic compound growing into the substrate deeply. Such an interfacial microstructural change weakens the interface significantly.

Sn-Zn Cu Sn Cu-Sn reaction product Cu-Zń reaction product Cu Sn-Zn Ni Zn depleted zone Źn Zn-Ni,Pd,Au reaction product O? Pd Au

FIG. 12. Schematic illustration of interfacial morphology change by heat exposure at 150 °C at Sn–9Zn/Cu interface (a) with or (b) without Ni/Pd/Au coating.

In contrast to the direct contact interface between a Sn–Zn alloy and a Cu substrate, the presence of the Ni/Pd/Au coating layer protects the interface from undesirable reaction even at 150 °C. At this temperature range, Ni diffuses into Pd and Au layers and Pd does the same. Zn also diffuses into the coating layer to form reaction products with Ni, Pd, and Au. The Zn diffusion into the interface makes the Zn-depleted zone close to the interface in the solder. O is enriched in the Ni layer after heat exposure. The oxidized Ni seems to be more brittle than the Ni layer. Nevertheless, the total thickness of the coating and the reaction layers is thin enough to maintain the high strength level.

Thus, the direct interface between Cu and Sn–Zn solders will have a temperature limit to be used below 125 °C, which is enough for most of the commercial electronics applications. In addition, the direct interface can provide much greater strength than other types of solders. If one needs very high temperature heat resistance or even a higher strength level, one can adopt the coating with the Ni/Pd/Au layer on a Cu substrate. With this coating, the interface is quite tight and the heat resistance is excellent.

IV. CONCLUSIONS

The present work has been carried out to examine the potentials of the newly developed Sn–9Zn solder paste as a lead-free solder, especially focusing on the stability at high temperature. Several characteristics of this new paste have been obtained as follows:

(1) The initial interface strength between Sn-9Zn and Cu, about 50 MPa by tensile test, is higher than other interfaces such as Sn-37Pb/Cu.

(2) While the Sn–9Zn/Cu interface maintains the high strength level after heat exposure at 125 °C, heat exposure at 150 °C degrades strength seriously.

(3) The degradation at 150 °C is caused by dissipation and by disruption of the Cu–Zn reaction layer at the interface. Where the Cu–Zn layer is eroded to form a whole, Sn directly reacts with a Cu substrate to form a thick Sn–Cu reaction region. Such an interfacial morphology change causes serious degradation.

(4) With the Ni/Pd/Au coating on a Cu substrate, the interface becomes much stronger than the direct interface at the initial state. Even after heat exposure at 150 °C, strength degradation is not so serious.

(5) Zn segregates into the coating layer during hightemperature exposure. Ni and Pd diffuse each other. Zn also diffuses into the coating layer to form compounds, and as a result, a depleted zone of Zn is formed in the solder close to the interface.

Thus, the great potential of the Sn–9Zn alloy paste as a candidate for lead-free soldering has become clear. The greatest advantages of the Sn–9Zn solder are its low soldering temperature equivalent to the current Sn–Pb eutectic solder and its economy. The present solder paste, furthermore, can be used in air atmosphere. For most of the electronics applications, which are used below 100 °C, this solder can be used without any coating on Cu. If one requires much higher temperature stability such as for automobile engine components, the protective coating of a Ni/Pd/Au layer is useful to ensure heat resistance up to 150 °C.

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