Pb-Free Plating for Electronic Components

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ABSTRACT The authors have developed Pb-free tin alloy plating materials. Preliminary screen tests showed that several alloy candidates had some shortcomings. Sn-Ag plating had high costs, Sn-Bi plating had shortcomings in both thermal stability and workability, and Sn-Zn plating in wettability and jointing capability.

In the Sn-Bi plating, thermal stability and workability have been improved by adopting a double-layer plating, i.e., an Sn-Bi surface layer/Sn undercoat layer. The double-layer plating reduces the total amount of Bi and hence reduces pollution of the soldering material. Also reflow-process improves the environmental resistivity of the plating.

1. INTRODUCTION

Recently, a lot of environmental issues such as fluorocarbon, ethane, dioxin, acid rain, carbon dioxide and lead have been discussed. Various regulations are being proposed and some are now being executed. Among them, lead (Pb) regulation is discussed a lot and there are plans for strong controls. Lead has long been suggested to be harmful to the human nervous system. It is known that lead causes cancer, retardation in infants, genital functional disorder and high blood pressure, and as a result there are increasing regulations against Pb-ion elution from lead-containing products.

Regulations to stop or limit the use of lead in electronic components are also being requested. The uses of lead in these components include Sn-Pb alloys for soldering. The substitution materials of the Sn-Pb alloy have been widely researched by many manufacturers. They are tin-based multi-element alloys including Ag, Bi, Cu, In or Zn, etc. Another application that uses Pb is solder plating as a surface treatment method. Therefore, in order to protect human beings against its harmful effects, it is necessary not to use lead in these applications (Pb-free).

As a Pb-free plating process, Cu-alloy leadframes for semiconductors with Pd-plating have been developed and are now being used.[1)] Because of its high cost and cost fluctuations due to the use of a noble metal, the Pd-plating is available only for small, limited applications, and not for general use as an alternative to Pb-plating.

Pb-free plating materials under development are tin-based alloys, such as Sn-Ag, Sn-Bi and Sn-Zn. Each material has both good qualities and bad qualities. For example, the bath of Sn-Ag plating is unstable and the cost is high. Sn-Bi plating is less ductile and its workability is not very good. Sn-Zn plating does not have good wettability in practical use.

This paper reports on the development of the Pb-free plating that improves the shortcomings of tin-alloy plating by thoroughly investigating its properties.

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2. PRELIMINARY SCREENING OF Pb-FREE PLATING

2.1 Introduction

We selected three tin alloys for screening tests from various tin alloys available: Sn-Ag, Sn-Zn and Sn-Zn, based on the viewpoints such that the alloy is usable for electroplating of electronic components, its plating bath is basically established, and the alloy has a low melting temperature. In order to confirm their electroplating properties, we examined their diffusion rates, wettability, solder joint strength and whisker generation against Cu substrates by heating them.

2.2 Test Samples

Substrates of test samples were tough pitch copper coils (C1100) of 0.4 mm thickness. We prepared three tin alloy samples with the following compositions: Sn-3.5% Ag, Sn-5% Bi and Sn-9% Zn. Reference samples of Sn-10%Pb, Sn and Pd electroplating were also prepared. Electroplating was carried out after electrolytic cleansing and pickling. The thickness of each Sn-alloy plating was 10 μm, and the thickness of the Pd-plating was 0.5 μm. A Ni-plating of 1.0 μm thickness was done as a pre-coat for the Pd-plating.

2.3 Evaluation Items

2.3.1 Growth speed of intermetallic compound

The growth speed was measured by the reduction in solder weight after a heat treatment at 155°C for 16 hrs. The thickness of the solder was measured by the constant current anodic dissolution method with an anode current density of 20 mA/cm^2 in a Kokour R-50 bath.

2.3.2 Wettability

The wettability was measured using the Menisco-graph method. The immersion speed was 10 mm/sec, the depth of immersion was 10 mm, and the immersion time was 10 sec. Two solder baths used were: eutectic solder (Sn-36% Pb) of 230°C and Pb-free solder (Sn-7.5% Bi-2.0% Ag-0.5% Cu) of 250°C. The measurement was carried out at two levels: just after plating and after 5000 hrs at room temperature.

2.3.3 Solder joint strength

A copper plated wire of 0.6-mm diameter was jointed to the specimens in a hemisphere-like-shape. The sample was tested with a pull strength tester. The joint strength measurements were carried out at two levels: just after jointing and after heat treatment at 150°C for 1000 hrs. As jointing solders, a eutectic solder (Sn-36% Pb) and a Pb-free solder (Sn-7.5% Bi-2.0% Ag-0.5% Cu) were used. Elements analysis was carried out for some fractured surfaces with fluorescent X-ray and EPMA.

2.3.4 Whisker test

Samples were kept at 50°C for 3000 hrs in a constant temperature oven, and during this period, the appearances of whiskers were checked under an optical microscope(x20) after 100, 200, 500, 1000 and 3000 hrs, respectively.

2.4 Test Results

2.4.1 Growth speed of intermetallic compound

Figure 1 shows the relationship between the eutectic point and the growth speed of intermetallic compound (IMC). The order of the thickness reduction rate before and after heat treatment at 155°C for 16 hrs was as follows: Sn-5% Bi > Sn-10% Pb > Sn-3.5% Ag = Sn-9% Zn > Sn. This order depends on the eutectic point of the alloy rather than on the melting points of layer compositions.

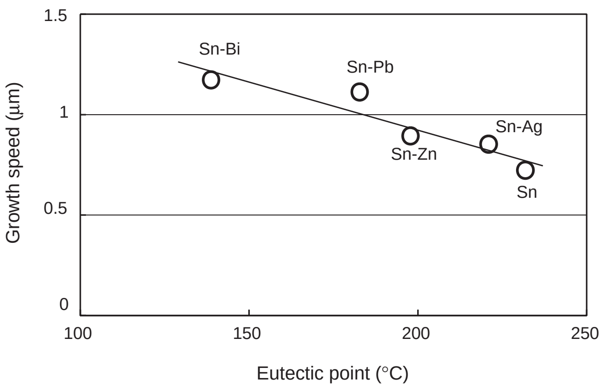


Figure 1 Relationship between eutectic point and intermetallic compound growth speed

2.4.2 Wettability

Figure 2 shows the results of wettability tests. The figure shows that only the Sn-Zn plating after 5000 hrs deteriorated in its wettability due to surface oxidation. The other samples were all good. There was no difference in the wettability by the plating thickness between the eutectic solder of 230°C and the Pb-free solder of 250°C.

2.4.3 Solder joint strength [2)]

Figure 3 shows the results of joint strength tests. The joint strength with the eutectic solder showed approximately the same values except for the Sn-Zn plating both before and after heating in the deterioration test. The joint strength with the Pb-free solder was a little lower than the one with the eutectic solder.

The joint strength between the eutectic solder and Sn-Zn plating is far weaker than the strength of conventional Sn-Pb plating. The elements analysis of the boundary interface showed that Zn was highly condensed at the boundary between Sn and Cu. Therefore, a lot of voids were generated which substantially reduced the joint strength.

The joint strength of Pb-free-solder and Sn-Pb plating after 1000 hrs at 150°C fell sharply. However, the combination of the eutectic solder and the Sn-Bi plating, or the eutectic solder and the Sn-Ag plating did not show degradation in joint strength. Therefore, adopting the Pb-free solder requires careful consideration of the types of solder and plating combinations.

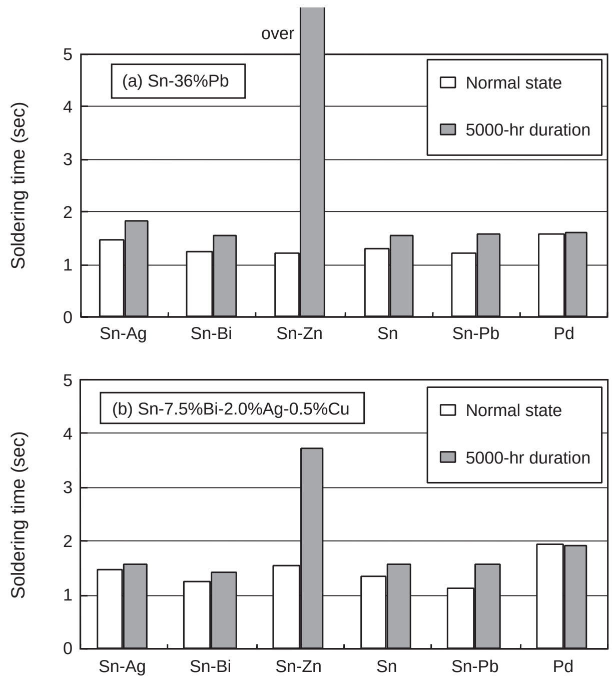


Figure 2 Wettability of Sn-Pb solder (a) and Pb-free solder (b)

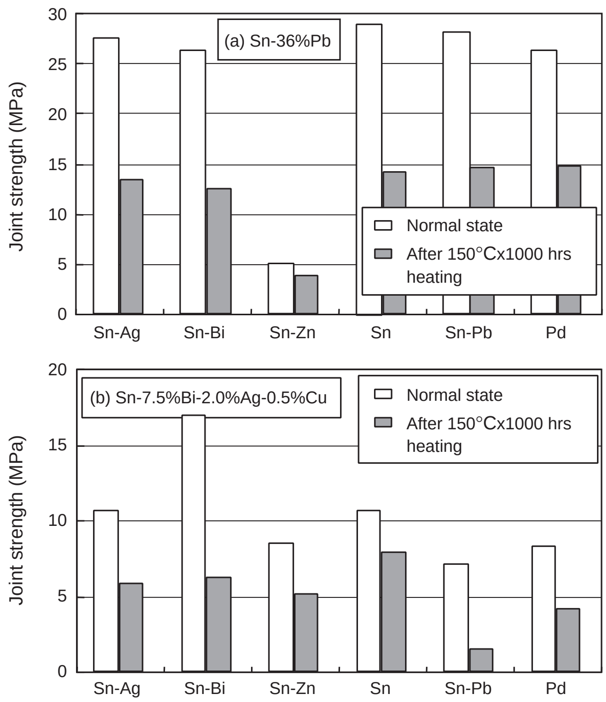


Figure 3 Solder joint strength of Sn-Pb solder (a) and Pb-free solder (b)

2.4.4 Whisker test

The generation of whiskers was found within 100 hrs in the Sn plating. Rugged projections on the surface were found after 500 hrs in the Sn-Zn plating, and whisker generation after 1000 hrs was also found. On the contrary, no whisker was found in the Sn-Ag, Sn-Bi or Sn-Pb plating after 3000 hrs.

2.5 Summary of Screening (Table 1)

Among the three combinations, Sn-Ag, Sn-Bi and Sn-Zn plating, two types (Sn-Ag, and Sn-Bi plating) turned out to be promising. From a practical viewpoint, the Sn-Ag plating is expensive due to not only the expensive material cost, but also the need for a large quantity of a chelating agent in the plating bath to compensate for the large gap in the precipitation potential between Sn and Ag. Thus, waste treatment costs increase.

Sn-Bi plating requires improvement in thermal stability and workability. In order to improve the thermal stability, consideration of the layer composition, such as with or without an undercoat, is essential. Thus we studied the optimization of the layer composition of Sn-Bi plating to improve its thermal stability and workability.

3. IMPROVEMENT OF Sn-Bi PLATING PROPERTIES

3.1 Introduction

We examined two methods to find an optimum layer composition. One is the optimization of the Sn-Bi composition. A lower concentration of Bi improves the workability and thermal stability of the layer. The other is a double-layer plating with Sn-undercoat plating. This process can improve thermal stability due to the Sn undercoat layer, or improve workability by a reduction in the Bi concentration of the total layer due to the double plating.

Here, we examined 6 levels of double-layer thickness including a single layer, and 4 levels of Sn-Bi compositions, totaling 24 samples to evaluate Sn-Bi plating properties.

3.2 Test Samples

Tough pitch copper strips of 0.4 mm (C1100) were used as a substrate. The plating processes are; electrolytic cleansing, pickling, undercoat Sn plating, Sn-Bi plating, neutralization and drying, respectively. The thickness of the Sn-Bi plating is 5 levels of 0.2, 0.5, 1, 2 and 5 µm, and the balance is Sn plating, totaling 10 µm. An Sn-Bi single-layer plating was prepared as a reference. Four types of plating baths with different metal concentrations were prepared for the Sn-Bi layer composition.

3.3 Evaluation Items

3.3.1 Layer thickness and composition

The thickness was measured by the constant current anodic dissolution method. The composition was measured with a fluorescent X-ray micro thickness tester.

3.3.2 Growth speed of intermetallic compound

The diffusion speed was evaluated by the reduction in solder thickness before and after heat treatment for 72 hrs. The heating temperature was at two levels, 130°C which is lower than the eutectic point of Sn-Bi (139°C), and 170°C which is higher than the eutectic point.

Table 1 Screening test results of Pb-free plating

Type of plating	Growth speed of IMC	Wettability	Joint strength	Anti-whisker	Workability	Cost
Sn-Ag	○	○	○	○	○	×
Sn-Bi	×	○	○	○	×	△
Sn-Zn	○	×	×	△	○	△
Sn	○	△	○	×	○	◎
Sn-Pb	△	◎	○	○	○	◎
Pd/Ni	◎	○	△	◎	△	×

Evaluation : (Good) ◎ > ○ > △ > ×(No good)

3.3.3 Bendability

The outer portion which was 90 degrees V-bent in 0 mmR was observed under a scanning electron microscope (x300). Evaluations were made of cracking and substrate exposure.

3.3.4 Wettability

A load test for wettability was carried out by the Meniscograph method. Soldering conditions were the same as in the clause 2.3.2. The flux used was Rosin 25%/IPA. Measurements were implemented before and after heat treatment at 170°C for 72 hrs.

Table 2 Composition of Sn-Bi single-layer plating

	No.1	No.2	No.3	No.4
Bi concentration (wt%)	1.7	4.3	8.6	14.3

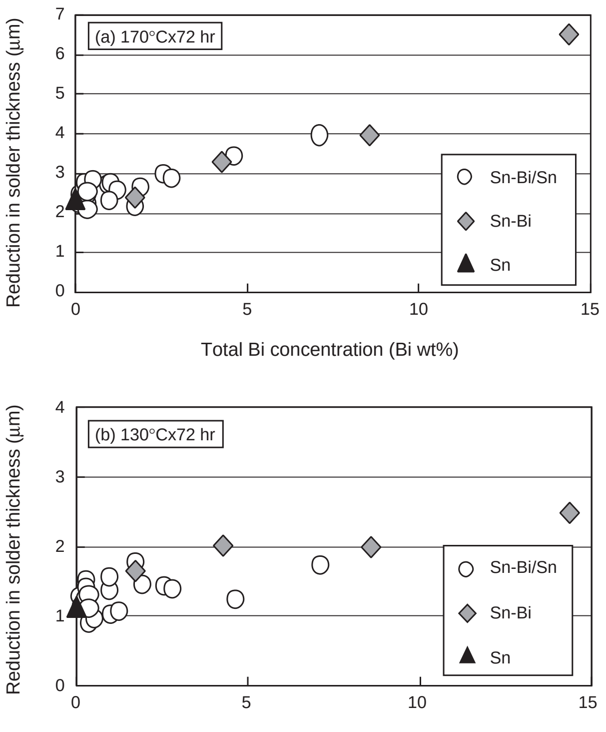


Figure 4 Growth speed of intermetallic compound at 170°Cx72 hr (a) and 130°Cx72 hr (b)

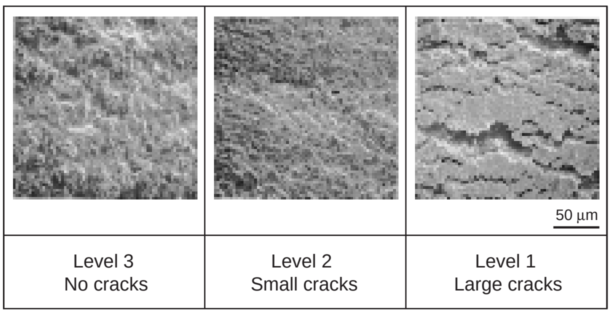


Photo 1 Bendability rating samples

3.4 Test Results

3.4.1 Solder composition

Table 2 shows the composition of the Sn-Bi single-layer plating. As for the average composition of the double-layer plating, it was confirmed that the ratio was almost proportional to the deposited layer thickness.

3.4.2 Growth speed of intermetallic compound

Figure 4 shows the results of the measurement of growth speed of intermetallic compound. Under the thermal treatment of 170°C for 72 hrs, beyond the eutectic point of Sn-Bi (139°C), the diffusion rates of the intermetallic compound were the same as those of Sn-plating within 2% in the total Bi concentration and increased with Bi concentration beyond that point (2%). In the case of a material, which is subjected to thermal hysteresis beyond the eutectic point, the total Bi concentration governs the diffusion rate; and the concentration should, therefore, be less than 2%, as the diffusion rates between the single and double-layer plating are the same.

Under the thermal treatment of 130°C for 72 hrs, lower than the eutectic point, while the diffusion rate in single plating increases with Bi concentration, that in the case of double-layer plating remains at the same level as for the Sn-plating. Consequently, thermal property improvement in the double-layer plating has been confirmed.

3.4.3 Bendability

We observed the bent portion of the specimens to evaluate the bendability of the specimens in four levels. Photo 1 shows the evaluation standards, and Figure 5 shows the evaluation results. They clearly revealed the difference between the single-layer and double-layer plating. In the case of the single-layer plating, there are large cracks (level 1) at the lower Bi concentration of 1.7%, and in the case of the double-layer plating, there are no cracks (level 3) at the combination of Sn-8.6% Bi 2 μm surface layer/Sn 8 μm undercoat.

The lower Bi concentration of 1.7% still yielded cracks in the single-layer plating because this layer is less ductile than the Sn-layer. While in the double-layer plating, the Sn undercoat prevented substrate exposure, even when the surface layer of Sn-Bi was sheared.

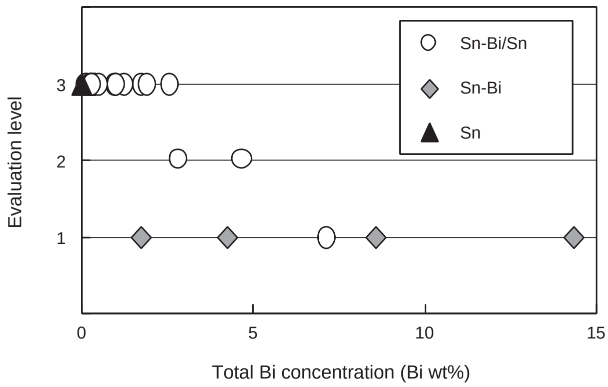


Figure 5 Bendability

3.4.4 Wettability

Figure 6 shows the results of the wettability test. At room temperature and after the heat treatment under 170°C for 72 hrs, the higher Bi concentration in the Sn-Bi surface layer showed better wettability. The layer of Sn-14.3% Bi 10 μm, however, showed substantially reduced wettability after the heat treatment of 170°C for 72 hrs because of increased diffusion of the layer into the substrate. Good wettability is obtained by raising the Bi concentration of the surface layer to the extent that diffusion into the substrate does not occur.

3.5 Conclusion for Characteristics Improvement of Sn-Bi Plating

In the Sn-Bi single-layer plating, a higher Bi concentration improves wettability but remarkably reduces workability and thermal stability; a lower Bi concentration reduces wettability and does not substantially improve workability.

The double-layer plating is essential for good workability. The lower Bi concentration in total improves thermal stability, too. Improvement in wettability is effectively achieved with a higher Bi concentration in the surface layer; a higher Bi concentration in the Sn-Bi surface layer is particularly effective. Also environmental resistivity is improved by the Bi condensation from the reflow treatment. Therefore, this treatment is very practical in use.

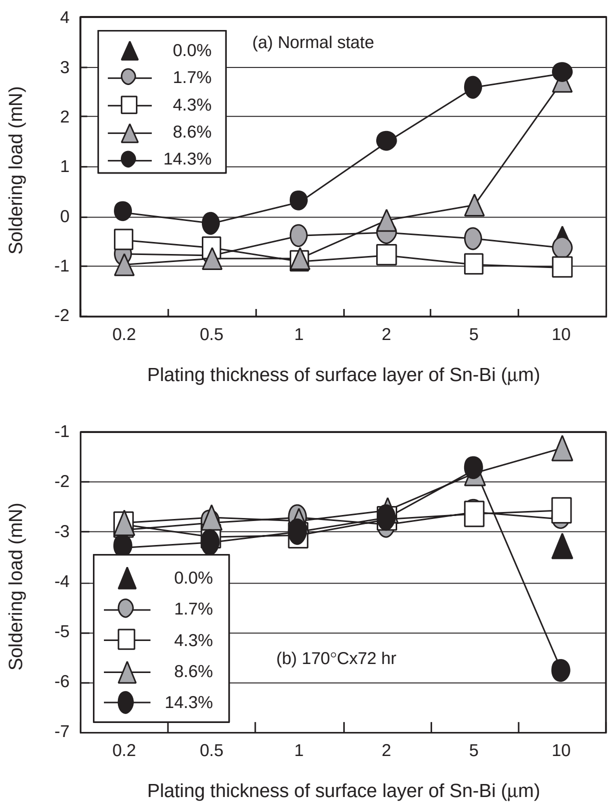


Figure 6 Wettability

4. STUDY FOR COMMERCIALIZATION VIABILITY

4.1 Introduction

Based on the above-mentioned results, we tried to produce and evaluate the Pb-free plating samples in a production line. The samples were double-layer-plated wires with Sn-Bi surface layer/Sn undercoat that generally used for lead wires in electronic components.

4.2 Test Samples

A copper plated wire of 0.57 mmϕ was used as a substrate material. The composition of the layer is an Sn-7% Bi 2 μm surface layer/Sn 8 μm undercoat. The plating was carried out in a pilot line: first, electrolytic cleansing, followed by pickling, Sn plating, Sn-Bi plating, neutralization, hot water rinsing and drying. We also prepared reflowed samples.

We used Sn-Pb wires, Sn plated wires, and Sn-Bi single-layer plated wires as references for the same evaluation items.

4.3 Evaluation

4.3.1 Growth speed of intermetallic compound

Refer to the clause 3.3.2.

4.3.2 Whisker test

We observed whisker generation in samples kept at 50°C for 6 months. The test samples were made to enhance whisker generation by welding aluminum wire; this gives rise to whiskers due to surplus jointing stress.

4.3.3 Oxidation

We evaluated the level of oxidation by the electricity for reduction. The constant current anodic reduction method was implemented using a 0.1 mA/cm^2 cathode current density in a 0.1 N KCl solution. There were three samples: just after plated, after a heat treatment of 170°C for 72 hrs, and after a pressure cooker test of 105°C, 100% RH for 16 hrs.

4.3.4 Wettability

We evaluated the samples with the Menisco-graph method. The test was implemented at 2 mm/sec immersion rate, 2 mm immersion depth and 10 sec immersion time using a 230°C eutectic solder bath (Sn-36% Pb). There were three tested samples: just after plated, after a heat treatment of 170°C for 72 hrs, and after a pressure cooker test of 105°C, 100% RH for 16 hrs.

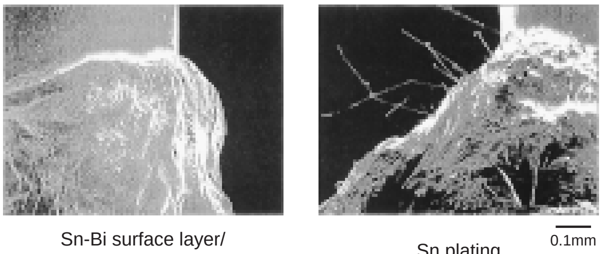
4.3.5 Workability

We observed the appearance of twisted samples after 170°C for 72 hrs heat treatment. The 40 mm long specimens were twisted 20 times forward and 5 times backward, followed by scanning electron microscopic observation.

Table 3 Evaluation test results of Sn-Bi/Sn plated wire

Surface treatment	Growth speed of IMC (μm)	Electricity for reduction (mC/cm^2)			Solder wetting hours (sec)		
		Normal state	Heating	Pressure cooker test	Normal state	Heating	Pressure cooker test
Reflow	2.2	1.7	8.4	12.6	0.9	2.6	1.6
Plating	2.2	1.6	12.0	16.2	1.1	3.5	2.3

Plating composition of samples: Sn-7% Bi 2 μm / Sn 10 μm



Sn-Bi surface layer/
Sn undercoat plating

Sn plating

Photo 2 Observation of whisker

4.4 Test Results (Table 3)

4.4.1 Growth speed of intermetallic compound

We found the growth speed of intermetallic compound of the Sn-Bi/Sn undercoat plating into the wire to be 2.2 μm in specific depth, the same with the preliminary test, and did not find any difference between non reflowed and reflowed samples.

4.4.2 Whisker test

Photo 2 shows the appearance of the sample after six months, revealing no sign of whisker generation in the Sn-Bi surface layer/Sn undercoat plated wire, while a lot of whiskers were observed in the reference samples of the Sn plated wire. Therefore, Sn-Bi surface plating is approved for suppressing whisker generation.

4.4.3 Oxidation

Improvements against oxidization of both heat-treated and pressure cooker tested samples were achieved through the reflow process. The reflow treatment is useful to prevent oxidation of a layer surface.

4.4.4 Wettability

The effect of reflow treatment on wettability was observed and is shown in Table 3. The improvement in wettability resulted due to the improvement in anti-oxidization from the reflow treatment.

4.4.5 Workability

The double-layer plating showed no stripping; on the contrary, large cracks were generated, and layer stripping occurred in the Sn single-layer plating.

4.5 Summary of Commercial Applications

We have developed a satisfactory alternative for the Sn-Pb plating. This method is hard to yield whiskers giving good thermal stability and workability. Furthermore, we found that the reflow treatment improved the anti-oxidation property and wettability.

5. CONCLUSION

In this report, a Pb-free plating was introduced: i.e., an Sn-Bi surface layer/Sn undercoat double-layer plating proved to be very useful. This method requires no noble metals. In particular, it is useful today when Pb-containing joints are still being used in the electronic component market.

The double-layer plating allows the total amount of Bi to be reduced compared to the single-layer plating, resulting in the reduction of pollution in the solder.

Selection between the Pd plating or Sn-Bi plating depends on the actual application and the results expected. The Pd plating is likely to be preferable for higher temperature use, shorter lead-time and high-reliability connections, and the Sn-Bi/Sn undercoat plating is useful for low-cost applications. The Sn-Bi/Sn undercoat plating as a substitute for the Sn-Pb plating offers, in addition to lower material costs, a benefit that conventional equipment can be used with only a small remodeling cost.

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