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(54) **TIN-SILVER SOLDERING ALLOY**

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(57) **ABSTRACT**

A tin—silver soldering alloy comprising 3 to 4% by weight of silver, 5 to 10% by weight of bismuth, 0 to 5% by weight of indium, and 0.1 to 1.5% by weight of zinc, with the balance being tin.

pulling direction

Cu

250°C

molten solder
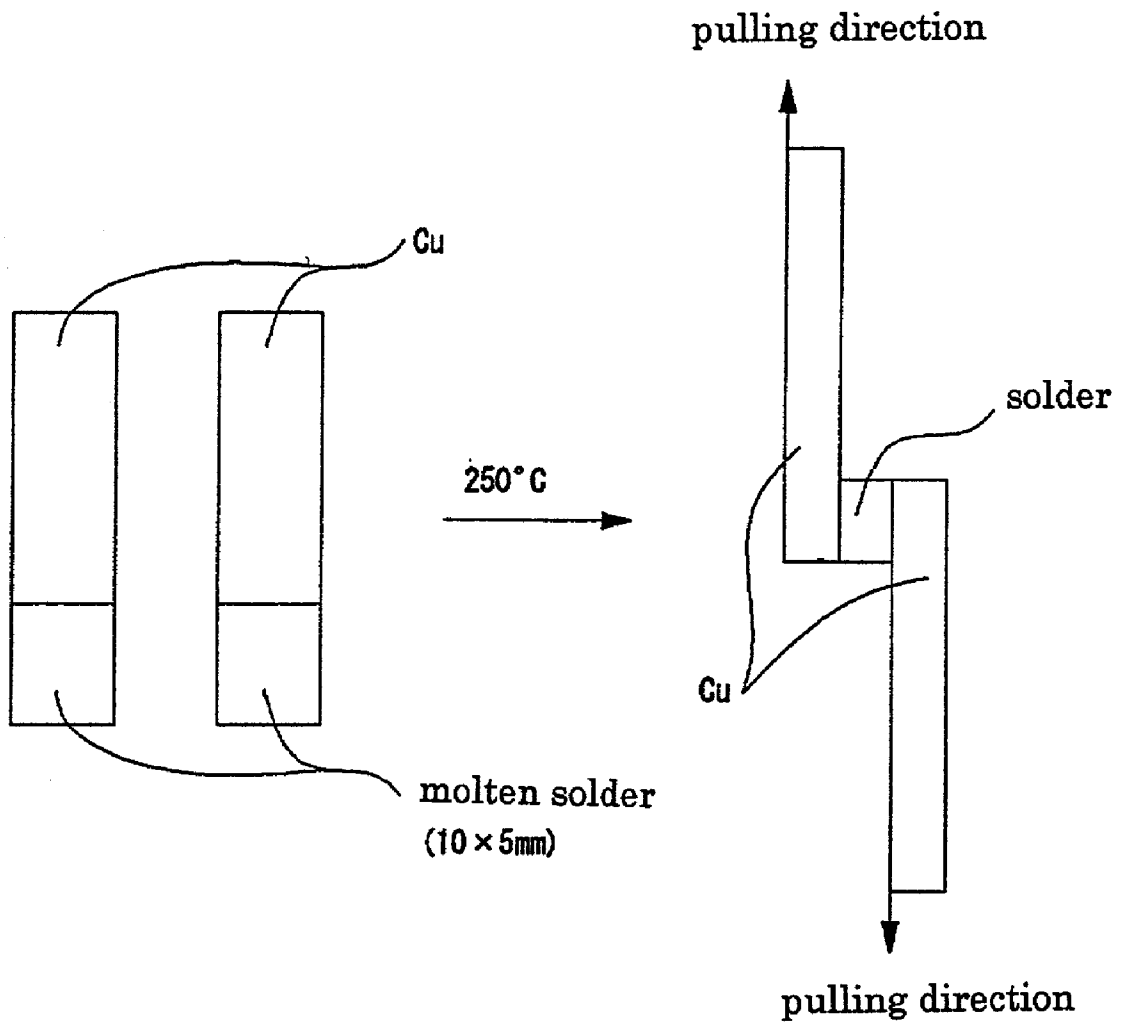(10 × 5mm)

solder

Cu

pulling direction
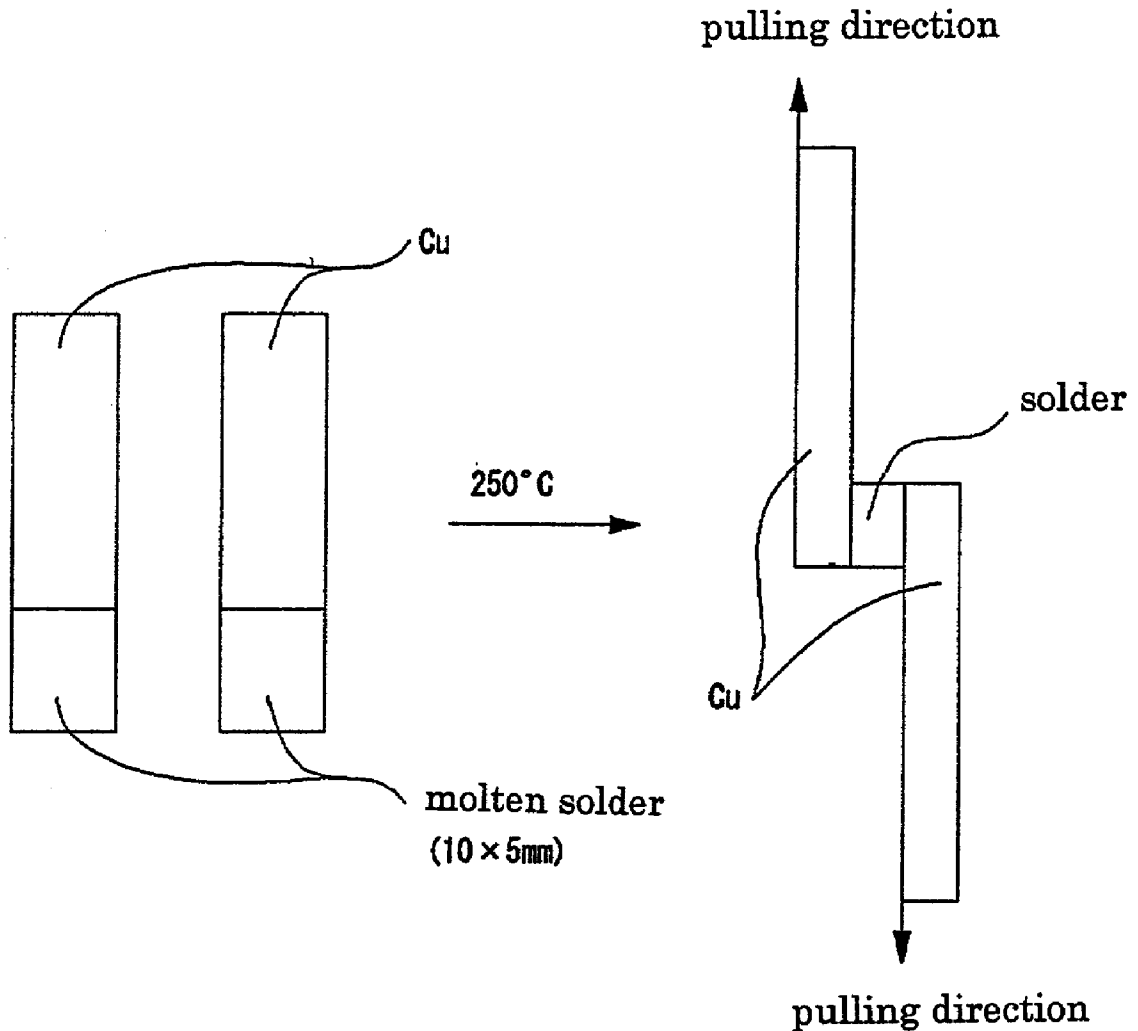
Fig. 1

TIN-SILVER SOLDERING ALLOY

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a tin—silver soldering alloy and, more particularly, to a tin—silver soldering alloy having satisfactory elongation characteristics to secure high joint reliability.

[0002] Eutectic or nearly eutectic Pb—Sn alloys are known as typical soft solders. Zn—Cd alloys having higher strength than eutectic Pb—Sn alloys are also known. These known soldering alloys are problematical due to the harm of lead or the adverse influence of cadmium vapor on workers and unacceptable from the standpoint of recent environmental issues.

[0003] Various Sn—Ag soldering alloys have been proposed as leadless solder free of harmful Pb, Cd, etc. However, because the Sn—Ag alloys have a higher melting point than the currently prevailing Pb—Sn alloys (melting point: 183° C. with an Sn content of 37 wt %), they need an increased soldering temperature, which may involve thermal influences on parts. Therefore, to lower the melting point of Sn—Ag solder has been of great concern.

[0004] The melting point of Sn—Ag solder can be lowered by addition of a third element or third and fourth elements. Indium, bismuth and copper are usually added for their abundance or producibility. For example, an Sn—Ag—Cu solder can have its melting point reduced to about 217° C. at the lowest and requires addition of In and Bi for further reduction. However, use of In is limited from economical considerations. Addition of Bi is effective in lowering the melting point and improving tensile strength but, in turn, reduces elongation at break. Seeing that the elongation characteristics of solder make a great contribution to reliability of solder joints, addition of Bi is considered to reduce the joint reliability. It has also been pointed out that solder having a Bi content of 5% by weight or more undergoes appreciable reduction in strength on some kinds of plating materials of electronic board lands and electrode materials of electronic components. Reduction in joint reliability caused by Bi addition has now come to be a problem to be solved and, on the other hand, there still has been a demand for solder having a melting point around 205° C. for application to electronic components.

[0005] Accordingly, it has been desired to develop Bi-containing solder having a Bi content of 5% by weight or more and yet promising high joint reliability. It seems that high joint reliability of solder will be obtained through stability of the solder structure, slow growth of the reactive layer on the joint interface, satisfactory elongation characteristics of the soldering alloy, and the like.

SUMMARY OF THE INVENTION

[0006] An object of the present invention is to provide a tin—silver soldering alloy having satisfactory elongation characteristics to secure high joint reliability.

[0007] As a result of investigations, the present inventors have found that the interface of a tin—silver soldering alloy having a given bismuth content or a given bismuth/indium content can be modified so as to suppress growth of the reactive layer by adding a specific amount of zinc that diffuses in copper easily. The object of the invention is accomplished based on this finding.

[0008] The present invention provides a tin—silver soldering alloy comprising 3 to 4% by weight of silver, 5 to 10% by weight of bismuth, and 0.1 to 1.5% by weight of zinc, with the balance being tin.

[0009] The present invention also provides a tin—silver soldering alloy comprising 3 to 4% by weight of silver, 5 to 10% by weight of bismuth, 5% by weight or less of indium, and 0.1 to 1.5% by weight of zinc, with the balance being tin.

[0010] The tin—silver soldering alloy according to the present invention exhibits satisfactory elongation characteristics and thereby secures high joint reliability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The present invention will be more particularly described with reference to the accompanying drawings, in which:

[0012] FIG. 1 schematically illustrates the method of measuring joint strength.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] The tin—silver soldering alloy of the present invention has an Ag content of 3 to 4% by weight. While the optimum Ag content is 3.5% by weight, the above range is acceptable from considerations to production yield in solder preparation.

[0014] The Bi content ranges from 5 to 10% by weight. A Bi content lower than 5% results in an increased melting point and reduced tensile strength. A Bi content higher than 10% results in reduced joint reliability.

[0015] Where In is also incorporated, its content is 5% by weight or lower. An In content exceeding 5% is not favorable from the viewpoint of cost performance.

[0016] The tin—silver soldering alloy of the present invention is characterized by having a zinc content of 0.1 to 1.5% by weight. Addition of zinc brings about improved joint reliability. A zinc content less than 0.1% or more than 1.5% fails to produce the effect of improving joint reliability. The tin—silver soldering alloy of the present invention thus exhibits improved joint reliability owing to the specific zinc content.

[0017] The present invention will now be illustrated in greater detail with reference to Examples. In tables 1 and 2, the figures of the alloy compositions indicate the content of the respective following elements in percent by weight.

EXAMPLES 1 TO 5 AND COMPARATIVE EXAMPLES 1 AND 2

[0018] Raw materials were weighed out to give the compositions shown in Table 1 (the balance was Sn) totally weighing 10 kg. The mixture was put in a graphite crucible and melted at 300° C. in the air in an electric oven. After complete melting, the melt was stirred thoroughly to avoid gravity segregation.

[0019] For testing the tinsilver soldering alloy thus prepared, two copper plates 10 mm wide, 30 mm long and 1 mm

thick were prepared. As shown in **FIG. 1**, the solder was applied to a 5 mm wide and 10 mm long tip area of each copper plate, and the tips were overlap-joined to make a test specimen. The test specimen was pulled in the direction shown in **FIG. 1** on an Instron tensile tester to measure a joint strength. The measurement was made immediately after joining (0 hr) and after 1000 hours each at 100° C., and a deterioration rate (%) was calculated. The results obtained are shown in Table 1.

TABLE 1

| | | Joint Strength (MPa) | | Deterioration |
	Alloy Composition	0 hr	1000 hrs	Rate (%)
Example 1	3Ag—5Bi—0.1Zn	34.37	31.67	8
Example 2	3Ag—5Bi—0.5Zn	32.52	30.43	6
Example 3	3Ag—5Bi—1Zn	32.2	32.02	1
Example 4	3Ag—5Bi—1.5Zn	32.24	31.22	3
Example 5	3.5Ag—3In—6Bi—1Zn	32.23	33.21	−3
Comparative Example 1	3Ag—5Bi	35.82	29.6	17
Comparative Example 2	3.5Ag—3In—6Bi	37.04	29.6	20

[0020] As is apparent from the results in Table 1, incorporation of a given amount of zinc reduces the deterioration rate of joint strength (Examples 1 to 5), whereas the solder containing no zinc (Comparative Examples 1 and 2) undergoes considerable deterioration in strength.

[0021] After the tensile testing, the cut area of the specimen was polished, and the joint interface of the solder was observed under an energy dispersive scanning electron microscope (SEM) to measure the thickness of the reactive layer on the interface at 10 points of the SEM micrograph. The average reactive layer thickness is shown in Table 2.

TABLE 2

| | | Reactive Layer Thickness (μm) | |
	Alloy Composition	0 hr	1000 hrs
Example 1	3Ag—5Bi—0.1Zn	1.6	2.44
Example 2	3Ag—5Bi—0.5Zn	2.03	2.13
Example 3	3Ag—5Bi—1Zn	1.16	1.66
Example 4	3Ag—5Bi—1.5Zn	1.03	1.92
Example 5	3.5Ag—3In—6Bi—1Zn	1.11	1.3
Comparative Example 1	3Ag—5Bi	2.31	2.93
Comparative Example 2	3.5Ag—3In—6Bi	2.57	3.51

[0022] As can be seen from Table 2, the solder formulae of Examples 1 to 5 are generally slow in growth of the interfacial reactive layer as compared with the solder of Comparative Examples 1 and 2.

[0023] Where solder contains no zinc (Comparative Examples 1 and 2), a Cu—Sn reactive layer is usually formed to make a Cu/Cu—Sn reactive layer/solder structure in the joint interface. It was confirmed that existence of zinc in the solder provided a Cu/Cu—Sn reactive layer/Cu—Zn reactive layer/solder structure in the interface. It is considered that the Cu—Zn reactive layer suppresses the growth of the Cu—Sn reactive layer. It is noted that the solder having a zinc content of 1% by weight (Examples 3 and 5), while showing a slight growth of the reactive layer after reflow, stably maintained the initial interfacial structure.

What is claimed is:

1. A tin—silver soldering alloy comprising 3 to 4% by weight of silver, 5 to 10% by weight of bismuth, and 0.1 to 1.5% by weight of zinc, with the balance being tin.

2. A tin—silver soldering alloy comprising 3 to 4% by weight of silver, 5 to 10% by weight of bismuth, 5% by weight or less of indium, and 0.1 to 1.5% by weight of zinc, with the balance being tin.

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