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Pb-FREE SOLDER ALLOY, AND SOLDER MATERIAL AND SOLDER JOINT
USING SAME

Field of the Invention

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The present invention relates to a Pb-free solder alloy, and a solder material and a solder joint using same.

Background of the Invention

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Recently, the problem of the toxicity of lead (Pb) has invoked a strong movement in regulating the disposal of lead to an environment. Thus, as a bonding material for parts of electronic products, a Pb-free solder has been substituted for a conventional Sn-Pb solder.

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As for characteristic properties of an alloy necessary as a solder material, there are melting temperature, tensile strength, ductility (or elongation property), wettability, bonding strengths of parts joints, and the like.

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A melting temperature of a solder is preferably to be set at approximately 200 °C. If a melting point of the solder is too high, it will exceed heat resistance temperatures of the parts in a reflow soldering, whereby a current soldering method may possibly incur damages on the parts. On the other hand, if a melting point of the solder is too low, the solder becomes most likely melted such that

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the parts may fall down or be peeled off in case when the environmental temperature surrounding the parts becomes high.

As a solder for a reflow soldering, in which a lead is employed, there is an Sn-37Pb solder alloy, typically.
5 Alternatively, following Pb-free solder alloys have been studied. For example, enumerated are Sn-Ag(-Cu) based, Sn-Cu(-Ni) based, Sn-Ag-Bi-Cu based, Sn-Zn(-Bi,-Al) based, Sn-In-Ag-Bi based solder alloys, and the like.

These are referred to as group I. Out of these, Sn-
10 Ag(-Cu) based, Sn-Cu(-Ni) based, and Sn-Bi-Cu based solder alloys have alloy compositions whose melting points are measured in a range from 210 °C to 230 °C and are used for a flow soldering, a reflow soldering method, or the like. However, the melting points of these alloys are higher than
15 that of a conventional Sn-Pb solder by 30 °C to 40°C. As a result, under a temperature condition of reflow soldering by using these alloys, the melting points thereof may exceed heat resistance temperatures of the parts. It is technically difficult to increase heat resistances of corresponding
20 parts up to a temperature where reflow soldering can be performed by using the aforementioned solder. Meanwhile, Sn-Zn(-Bi,-Al) based and Sn-In-Ag-Bi based solder alloys, and the like (referred to as group II), are employed in a field of PCB (printed circuit board) packaging in which a reflow
25 soldering method is generally adopted. However, group II alloys are highly oxidized in a melting state in the air,

and technically difficult to be applied in the flow soldering method at this point. While a group II alloy has many disadvantages as a solder in comparison with group I, it is advantageous in that its melting point can be adjusted
5 to a temperature region close to that of the conventional Sn-Pb solder. Further, a group II alloy is used by adjusting composition thereof such that melting point thereof falls in the range from approximately 180 °C to 210 °C.

Namely, the Sn-Zn(-Bi,-Al) based solder alloy can be
10 used under the current reflow soldering condition since a melting point is in the range from approximately 190 °C to 200 °C that is close to that of the conventional Sn-37Pb solder alloy, and is advantageous in being of low cost among Pb-free solders. However, it has been considered that
15 wettability to a joint base material of a solder is not good. Further, it has been confirmed that bonding strengths of the parts are significantly deteriorated if the joint to be soldered with a Cu base material is exposed to a high temperature and a high humidity condition, even after the
20 reflow soldering.

Further, it is likely that Zn is eluted from a solder into a flux, possibly incurring problems such as a lowered insulation resistance and a generation of migration, since Zn is employed in solder.

25 A melting point of the Sn-In-Ag-Bi based solder alloy is close to that of an Sn-Pb solder, similarly to the case

for the Sn-Zn based solder. When bonding this alloy system with the Cu base material, a Cu-Zn compound is not formed since Zn is not employed. Accordingly, such a phenomenon does not occur that a bonding strength in a bonding surface with Cu is significantly lowered under the high temperature
5 and high humidity atmosphere.

Meanwhile, in case of soldering to an Ag electrode, an Ag-In compound is formed in a bonding surface. It has been confirmed that the compound's phase grows large as time
10 passes and becomes fragile, whereby an interface strength becomes lowered. In addition, it is observed that if a heat cycle is applied in a state where the parts are bonded, a solder of a joint is deformed. A technological development for PCB has been directed to a substrate designing of a
15 narrower pitch, and a more high level packaging technology has been required.

Such a technical trend draws a concern that deformation of the solder may cause short circuits. Further, since the solder contains a large amount of rare and
20 expensive Indium (In), the material cost amounts high and the continuous future supply may not be secured.

Solder alloys having melting points in the range from 180 °C to 210 °C are widely used in a soldering method in which soldering is performed several times (flow soldering
25 after reflow soldering, reflow soldering after reflow soldering, or the like), due to temperature characteristics

thereof. Here, the problematic point is that a place soldered once is peeled off in subsequent soldering processes. Particularly, in a large-scale IC parts or the like, parts leads float from a PCB, together with solder.

5 The reason for such a phenomenon is that on the second soldering or thereafter, a joint solder formed by a former soldering is partially melted and a bonding strength thereof decreases, and, in such a state, the joint is peeled off by a bending of a PCB or deformations of the parts. Namely, in
10 a solder alloy's property, the bigger a difference between a temperature where a solder alloy begins to melt (hereinafter, referred to as a solidus line) and a temperature where the solder alloy completely melts (hereinafter, referred to as a liquidus line), the higher the possibility that the joint is
15 peeled off.

In a conventional art, e.g., Japanese Patent No.2599890 (reference 1), a mechanical strength or a creep resistance is improved by the addition of Zn to an Sn-Ag based solder.

20 At the same time, it is disclosed that a melting point becomes lower by the addition of Zn or In.

However, the Ag concentration described in reference 1 is too high by as much as 1 % in weight or more. For example, in an alloy of a high Ag concentration (1 weight %) such as
25 Sn-6Zn-6In-1Ag, endothermic peak area, whose summit is in the vicinity of a melting point of 200 °C, becomes large, as

can be seen from the measurement results of DSC (differential scanning calorimetry) in Fig. 9. As a result, under a reflow soldering condition same as that of the Sn-Pb solder, it is likely that the solder is not sufficiently melted down. If the solder is not sufficiently melted down, fluidity of the solder is deteriorated, whereby a joint is not fully formed. In that case, voids in the solder remain to thereby lower the bonding strength. Further, in Japanese Patent Laid-Open Publication Heisei No.9-174278 (reference 2), In is added to an alloy of a near Sn-Zn eutectic composition so as to lower a melting temperature and improve wettability to parts metallization. Further, Ag is added so as to make Zn phase needle like solidification microstructures in the Sn-Zn-In alloy into spheroidal solidification microstructures and to finely disperse them. Therefore, the Zn concentration is set at from 6 to 11 % in weight, and the Ag concentration is set at from 0.5 to 3 % in weight.

The conventional Pb-free solder may incur various problems such as poor wettability due to Zn, which is a problem in the Sn-Zn(-Bi,-Al) based solder, and a lowered bonding strength with Cu electrode under the condition of the high temperature and high humidity. Further, using rare metals such as In and Ag becomes a problem in the Sn-In-Ag-Bi based solder alloy.

Summary of the Invention

It is, therefore, an object of the present invention to meet such a condition that a melting temperature characteristic is same as that of an Sn-Pb based solder and to solve the problems of the conventional Sn-Zn(-Bi,-Al) based solder and the Sn-in-Ag-Bi based solder.

Particularly, it is an important object to improve solder joint reliability under the condition of the high temperature and high humidity.

For achieving the objects, a solder alloy in accordance with the present invention is based on an Sn-Zn-In-Ag system having, in weight, $0.3 \% < \text{Zn} < 5.0 \%$, $0.1 \% \leq \text{In} \leq 4.0 \%$, $0.1 \% \leq \text{Ag} \leq 0.4 \%$, and the balance Sn.

Brief Description of the Drawings

The above and other objects and features of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:

Fig. 1 is a graph for showing peel strengths of solder joints of solders in accordance with Example 1 of the present invention, as a function of exposure time;

Figs. 2A to 2E show DSC measurement results of solder alloys as a function of temperature, in case when Zn is

added to Sn-3In-0.3Ag of Example 1 of the present invention while varying the Zn concentration in the range from 2 to 6 weight %;

5 Figs. 3A to 3C describe typical views of structures, in case when a small amount of Ag is added to Sn-4Zn-3In of Example 2 of the present invention;

Fig. 4 illustrates a graph for showing electrochemical corrosion potentials as a function of time, in case when a small amount of Ag is added to Sn-4Zn-3In of Example 3 of
10 the present invention;

Figs. 5A to 5E explain variations of melting temperatures as a function of Ag concentration, when a small amount of Ag is added to Sn-4Zn-3In of Example 1 of the present invention;

15 Fig. 6 offers a graph for showing variations of mechanical properties of solder alloys as a function of In concentration, in case when In is added to Sn-4Zn-0.3Ag of Example 6 of the present invention in a range from 0 to 10 weight %;

20 Fig. 7 sets forth to a graph for showing variations of mechanical properties of solder alloys in accordance with Example 8 of the present invention, as a function of exposure time;

Fig. 8 presents a graph for showing variations of
25 mechanical properties of another solder alloys in Example 8 of the present invention, as a function of exposure time;

and

Fig. 9 depicts a DSC measurement result of a conventional Sn-6Zn-6In-1Ag alloy.

5 Detailed Description of the Preferred Embodiments

Hereinafter, preferred embodiments of the present invention will be described in detail with reference to accompanying drawings.

10 In accordance with the present invention, a solder alloy is an Sn-Zn-In-Ag solder containing a small amount of Ag for preventing a bonding interface strength from being lowered when a joint of a Cu base material with a solder is exposed to the high temperature and high humidity atmosphere,
15 based on an Sn-Zn-In based solder having a melting point of 210 °C or less.

In aspects of the melting temperature and bonding reliability, it is preferable that the concentration of each element in such a solder alloy is as follows, in weight:

20 3.0 % < Zn < 5.0 %;
0.1 % ≤ In < 20.0 %; and
0.1 % ≤ Ag ≤ 0.4 %.

Hereinafter, the composition range will be explained.

25 The Zn concentration is from about 3.0 % to 5.0 % in weight. When the Zn concentration is less than 3.0 % in

weight, a melting point of the solder cannot be lowered to about 200 °C. Further, if the Zn concentration is less than 3.0 % in weight, a difference between a solidus temperature and a liquidus temperature becomes large even though the In concentration is increased. As a result, in multiple soldering processes, it is likely that the parts joints are peeled off.

On the other hand, when the Zn contention is more than 5.0 % in weight, a bonding interface strength with a Cu film is lowered under the condition of the high temperature and high humidity. Further, if the Zn concentration increases, wettability of the solder becomes deteriorated, resulting in oxidation of the solder and a lowered electrical insulation of the joint.

The In concentration is from 0.1 to about 20.0 % in weight. When the concentration is less than about 0.1 % in weight, a melting point cannot be expected to be lowered. If the In concentration is more than 20.0 % in weight, a solidus temperature in the solder melting point becomes too low. In case of the Sn-20In, a solidus temperature is 153 °C. If the solidus temperature decreases, the solder is melted and peeled off when being exposed to a high temperature environment.

Further, the same failure may possibly be caused due to heat generation by using equipment. Still further, since the solidus temperature (153 °C) and the liquidus

temperature (199 °C) of the Sn-20In are separated from each other too far, such a phenomenon may occur that the solder is peeled off in the second soldering process or thereafter.

5 The Ag concentration is between 0.1 % and 0.4 % in weight. If the concentration is less than about 0.1 % in weight, an effect that prevents a bonding strength from being lowered cannot be obtained when exposing to an environment of high temperature and high humidity after soldering.

10 If the Ag concentration exceeds 0.4 % in weight, the solder tends to melt at a higher temperature in a melting point temperature area of the solder, so that fluidity of a molten solder becomes poor in the reflow soldering process.

15 Further, it is more preferable that the composition range is as follows below, in weight:

0.3 % < Zn < 5.0 %;

0.1 % ≤ In ≤ 4.0 %; and

0.1 % ≤ Ag ≤ 0.4 %.

20 If the In concentration in the solder alloy increases, ductility of the solder alloy becomes deteriorated. Further, if the In concentration is 4 % in weight and less, elongation of 30 % or greater can be assured. Therefore, a stress can be relieved since the solder is deformed when a
25 stress due to heat-shock or the like is on. In contrast, if the solder does not have ductility, crack may possibly be

developed in the solder joint in case where a PCB or parts are expanded or shrunk.

Meanwhile, 'high temperature and high humidity' of the present invention means a circumstance of 85 °C and 85 %RH
5 (relative humidity).

EXAMPLES

Example 1

10 In Example 1, a peel strength of a joint having, in weight, 3 %In and 0-6 %Zn (the remaining portion was Sn) was measured, with respect to a variation of a bonding strength when exposed to an environment of the high temperature and high humidity.

15 First, a solder alloy, which was mixed to have a predetermined composition, of about 1 kg was held at 230 °C. And then, QFP (Quad Flat Package) parts of 0.65 mm in pitch and 100 pins are fixed to a Cu-attached glass epoxy PCB by using an adhesive. This specimen was applied to a flux, and
20 then, subjected to soldering by dipping into the solder. A soldered article was washed with acetone by using a microwave washing machine, so that residuals of the flux were removed. A soldered PCB specimen after being washed was put into a hygro-thermostat (constant temperature and
25 humidity oven) kept at 85 °C and 85 %RH, and then, a peeling strength of a lead bonding strength was measured for every

250 hours.

Fig. 1 shows a variation of a lead bonding strength, in case when soldering QFP parts with a solder having, in weight, 3 %In, 0-6 %Zn, and the balance Sn. Here, 0-6 %Zn means that the Zn concentration is in the range from 0 to 6 % in weight. Further, it can be noted that as the Zn concentration increases, a bonding strength when being exposed to a condition of high temperature and high humidity significantly declines. Further, in case where the Zn concentration is 6 % in weight, a bonding strength at exposure time of 500 hours becomes 1 kgf or less.

Namely, as the Zn concentration in the solder increases, bonding strengths of the parts tend to decrease under an environment of the high temperature and high humidity. Zn phases in the solder diffuse into a bonding surface and react with a Cu base material under the high temperature and high humidity atmosphere, to thereby form and grow a Cu-Zn compound layer. In the course of the process, Zn oxidizes due to an effect of high humidity, whereby a bonding strength in an interface of the Cu-Zn compound layer of the bonding surface with the solder is significantly lowered. As can be seen from Fig. 1, it is preferable that the Zn concentration is less than about 5 % in weight.

Meanwhile, Figs. 2A to 2E describe DSC measurement results of solders, each having, in weight, 3 %In, 2-6 %Zn,

0.3 %Ag, and the balance Sn. If the Zn concentration is less than 3 % in weight, a melting point of a metal exceeds 210 °C. Therefore, it is preferable that the Zn concentration is greater than about 3 % in weight.

5 Further, if the Zn concentration is greater than 5 % in weight, a bonding strength under the high temperature and high humidity is gradually lowered. Thus, it is preferable that the Zn concentration is less than about 5 % in weight.

10 Example 2

Example 2 was carried out for observing a structure, in case when a small amount of Ag is added to an Sn-4Zn-3In. Each solder having, in weight, 4 %Zn, 3 %In, 0.1-0.5 %Ag, and the balance Sn of about 0.6 g was melted on a ceramic
15 plate to form a sphere shape, and in that state, cooled in the air. A section of each solder particle was polished and observed by using scanning electron microscope (SEM). The results were described in Figs. 3A to 3C.

As is known from Figs. 3A to 3C, needle like Zn phases
20 decrease as the Ag concentration increases. Further, it can be noted that spheroidal Zn-Ag phases increase in Figs. 3B and 3C. Still further, a fine structure of the solder is confirmed. Zn phases are finely dispersed, so that a connection between the Zn phases disappears. Accordingly,
25 oxidation of Zn, which causes to lower a bonding strength, does not spread towards an inside of the solder, and

lowering of a bonding strength under the condition of the high temperature and high humidity is suppressed.

In case where the Ag concentration is 0.1 % in weight, many needle like Zn phases are observed, as shown in Fig. 3A. However, a spheroidal Zn-Ag layer is certainly confirmed.

Example 3

In Example 3, a variation of an electrochemical corrosion potential would be explained, in case when a small amount of Ag is added to the Sn-4Zn-3In.

Each solder having, in weight, 4 %Zn, 3 %In, 0-0.5 %Ag, and the balance Sn was prepared with a bar shape having a cross section of 5 mm × 5 mm. A surface of the bar-shaped specimen was polished with water resistance polishing paper of 1200 mesh, and then, subjected to buffing by using Al₂O₃ suspension. Subsequently, the specimen was immersed into a 3.5 wt.% NaCl water solution at 25 °C. Further, by using a standard electrode employing a silver electrode, a silver chloride electrode, and a saturated KCl water solution, an electromotive force difference, which is generated between Ag of the standard electrode and the solder specimen, was measured. The result was shown in Fig. 4. Still further, as a reference sample, an electrochemical corrosion potential of the Sn-3In solder not containing Zn was described.

As is known from Fig. 4, oxidation of Zn in the solder becomes difficult as an electromotive force is close to that

of the Sn-3In solder. Namely, by the addition of Ag with 0.1 % in weight or more, such an effect can be obtained that oxidation is prevented from progressing.

5 Example 4

10 In Example 4, an observation result of a bonding surface would be explained when soldering the Sn-4Zn-3In-0.3Ag with a Cu plate. The Sn-4Zn-3In-0.3Ag solder of 0.3 g was placed on the Cu plate and applied to a flux. Then, it was heated on a 230 °C heat plate and soldered. After this specimen was filled into a resin, polished, and evaporated, a section of the bonding surface was observed by using SEM and X-ray micro analyzer (XMA). As a result of the observation using SEM and XMA, a Zn layer and an Ag layer
15 could be observed to be generated in a bonding surface between the solder and the Cu plate. Namely, it can be known that a Zn-Ag phase is formed in the bonding surface between the Cu plate and the bonding surface. If a Zn-Cu compound phase is formed in a bonding surface, oxidation in an
20 interface of the solder with the Zn-Cu compound progresses, so that a bonding strength is lowered. Namely, by preventing the formation of the Zn-Cu compound layer, a bonding strength can be prevented from being lowered.

25 Example 5

 In Example 5, a variation of a melting point would be

explained, in case when a small amount of Ag is added to the Sn-4Zn-3In. Figs. 5A to 5E show measurement results of melting points of solders, each having, in weight, 4 %Zn, 3 %In, 0-0.5 %Ag, and the balance Sn, by using DSC. As can be seen from Figs. 5A to 5E, it could be noted that as the Ag concentration increases, a peak representing a heat absorbing amount in the vicinity of 205 °C to 210 °C becomes large, and a melting amount of the solder increases in this temperature area. If the Ag concentration becomes 0.5 % in weight, an endothermic peak in the vicinity of 205 °C to 210 °C grows as much as substantially same as that in the vicinity of 190 °C. As a result, in case when being employed as a solder, it is difficult to be melted. In other words, the solder is melted at a lower temperature (about 193 °C) first, and melted again at a higher temperature. Further, wettability or fluidity of the solder becomes deteriorated.

From the aforementioned measurement results, by an addition of Ag with 0.1 % in weight or more, an electrochemical corrosion potential is improved. On the other hand, if Ag is added more than 0.5 % in weight, as described by DSC measurement of the alloy, higher temperature peaks increase. Accordingly, the solder is difficult to be melted, so that wettability or fluidity characteristic thereof becomes deteriorated.

Further, if Ag is added to the solder containing Zn, needle like Zn phases decrease and spheroidal Zn-Ag phases

increase. As a result, a fine structure of the solder can be confirmed by a structure observation. While needle like Zn phases are observed in case where the Ag concentration is 0.1 % in weight, an effect of improving an electrochemical corrosion potential can be obtained even in that case, as mentioned above.

Further, by the addition of Ag, the Zn-Ag compound phase is formed in a bonding surface when soldering on a Cu, to thereby serve as a barrier layer for suppressing a reaction between Cu and Zn. As a result, formation of the Zn-Cu compound layer, which tends to be easily oxidized, can be suppressed, so that oxidation in the bonding surface is suppressed to thereby prevent the bonding strength from being lowered.

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Example 6

Each solder having, in weight, 4 %Zn, 0-10 %In, 0.3 %Ag, and the balance Sn was molded to a plate shape at a temperature higher than a solder liquidus temperature by 50 °C, and a tensile specimen was prepared.

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The specimen was JIS4 specimen. The tensile test was performed at a tensile rate of 5.0 mm/min.

The result was described in Fig. 6. As is evident from Fig. 6, elongation of 30 % or greater is held in the range from 0 to 4 % In, in weight.

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Example 7

Preferably, a Pb-free solder material formed of a solder alloy and a flux is utilized in a wire solder and a cream solder. Here, the solder alloy is based on the Sn-Zn-In-Ag system having, in weight:

3.0 % < Zn < 5.0 %;

0.1 % ≤ In ≤ 4.0 %;

0.1 % ≤ Ag ≤ 0.4 %; and

the balance Sn.

Further, as the flux, a known flux may be used.

Example 8

In Example 8, a solder bonding strength would be explained by using a solder alloy, which has at least one element selected from a group consisting of Ni, Ti, Mg, Al, and Co, based on the Sn-Zn-In-Ag system having, in weight:

3.0 % < Zn < 5.0 %;

0.1 % ≤ In ≤ 4.0 %; and

0.1 % ≤ Ag ≤ 0.4 %.

Here, a total concentration of at least one element is in the range from 0.001 % to 0.05 % in weight and the remainder is Sn.

The high temperature and high humidity test was carried out on the following samples. Fig. 7 exhibits variations of bonding strengths thereof. Bonding strength was measured by the same method as in Example 1. The samples

were prepared by using solder alloys, each having one of the
aforementioned elements and performing a reflow soldering on
a Cu film.

5 In Fig. 7, F represents a standard Pb-free solder
alloy of the present invention. Further, A, B, C, D, and E
have the same composition with F other than Sn, and contain
0.004 %Ti, 0.01 %Ni, 0.01 %Mg, 0.05 %Al, and 0.05 %Co, in
weight, respectively. And, the remaining portion thereof is
Sn. Comparing bonding strengths after being exposed for 1000
10 hours under the condition of the high temperature and high
humidity, the samples A, B, C, and E are found to be
superior to the standard F. Further, it can be noted that
the sample D maintains a bonding strength at least equal to
or greater than F.

15 Fig. 8 shows variations of bonding strengths under the
high temperature and high humidity on three solder joint
compositions: Sn-8Znn-3Bi, Sn-4Zn-3In-0.3Ag, and Sn-4Zn-3In-
0.3Ag-0.003Ti. Further, the solder joints are formed by the
same manner as in Example 1. As can be seen from Fig. 8, the
20 addition of Ti is clearly demonstrated to be effective after
1500 hours.

Further, in the comparative Sn-8Zn-3Bi, a bonding
strength becomes less than 1 kgf after 250 hours. Other
elements such as Ni, Mg, Al, and Co provide the same effects
25 as Ti.

Example 9

A Pb-free solder material formed of a solder alloy and a flux of Example 9 is utilized in a wire solder and a cream solder. Here, the solder alloy has at least one element
5 selected from the group consisting of Ni, Ti, Mg, Al and Co, based on the Sn-Zn-In-Ag having, in weight:

$3.0 \% < \text{Zn} < 5.0 \%$;

$0.1 \% \leq \text{In} \leq 4.0 \%$; and

$0.1 \% \leq \text{Ag} \leq 0.4 \%$.

10 Here, a total concentration of at least one element is in the range from about 0.001 % to about 0.05 % in weight and the remainder is Sn.

Further, as the flux, a known flux may be used.

As mentioned above, in accordance with the present
15 invention, the Zn concentration is in the range from about 3 to 5 % in weight, so that solder joint reliability can be improved under the high temperature and high humidity atmosphere. Further, a solder alloy of the present invention may be a bar solder (molten solder), and a Pb-free solder
20 alloy suitable for a diffusion bonding. Still further, the present invention may include a solder joint of electrical and electronic equipment using the solder alloy of the present invention.

A Pb-free solder using a solder alloy in accordance
25 with the present invention has a melting temperature substantially equal to that of a conventional Sn-Pb solder.

Therefore, the current Sn-Pb soldering method and the current parts or production equipment can be employed as it is. Further, a Pb-free solder material having a solder characteristic with excellent bonding strengths of the parts
5 can be provided.

Further, since a difference between a solidus temperature and a liquidus temperature is small, floating of the parts leads can be suppressed, even in case where packaging processes are performed many times over. Still
10 further, when the joint is exposed to the high temperature and high humidity atmosphere, the bonding strength can be prevented from being lowered.

While the invention has been shown and described with respect to the preferred embodiments, it will be understood
15 by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention as defined in the following claims.

What is claimed is:

1. A solder alloy based on an Sn-Zn-In-Ag system, the solder alloy comprising, in weight:

5 3.0 % < Zn < 5.0 %;
 0.1 % ≤ In ≤ 4.0 %;
 0.1 % ≤ Ag ≤ 0.4 %; and
 the balance Sn.

10 2. A Pb-free solder material comprising a solder alloy and a flux, wherein the solder alloy is based on an Sn-Zn-In-Ag system having, in weight:

 3.0 % < Zn < 5.0 %;
 0.1 % ≤ In ≤ 4.0 %;
15 0.1 % ≤ Ag ≤ 0.4 %; and
 the balance Sn.

3. A solder alloy based on an Sn-Zn-In-Ag system and having at least one element selected from the group
20 consisting of Ni, Ti, Mg, Al, and Co, the solder alloy comprising, in weight:

 3.0 % < Zn < 5.0 %;
 0.1 % ≤ In ≤ 4.0 %; and
 0.1 % ≤ Ag ≤ 0.4 %,
25 wherein a total concentration of said at least one element is in the range from about 0.001 % to about 0.05 %

in weight, and the remaining portion thereof is Sn.

4. A Pb-free solder material comprising a solder alloy
and a flux, wherein the solder alloy has at least one
5 element selected from a group consisting of Ni, Ti, Mg, Al,
and Co, based on an Sn-Zn-In-Ag based solder alloy having:

3.0 % < Zn < 5.0 %;

0.1 % ≤ In ≤ 4.0 %; and

0.1 % ≤ Ag ≤ 0.4 %,

10 wherein a total concentration of said at least one
element is in the range from about 0.001 to about 0.05 % in
weight and the remaining portion thereof is Sn.

5. A solder joint of electrical and electronic equipment
15 comprising the solder alloy of claim 1.

6. A solder joint of electrical and electronic equipment
comprising the solder alloy of claim 3.