reliability and preventing adverse effects on acoustic quality. In order to achieve this object, Patent Document 5 discloses an Sn-Ag-Cu-Sb-Bi-Co-Fe solder alloy containing Sb, Bi, Co, and Fe in the Sn-Ag-Cu solder alloy.

Citation List

Patent Document

[0008] Patent Document 1: Japanese Unexamined Patent Application Publication No. JP 2017-170465 A

Patent Document 2: Japanese Unexamined Patent Application Publication No. JP 2019-058950 A

Patent Document 3: Japanese Patent Publication No.JP 6719443 B

Patent Document 4: Japanese Patent Publication No. JP 6795630 B

Patent Document 5: Japanese Patent Publication No. JP 6889387 B

Summary

Technical Problem

[0009] In paragraph 0008 of Patent Document 1, it is described that a solder alloy having high strength due to the addition of Bi has a disadvantage that stretchability is deteriorated and brittleness is increased. Further, paragraph 0010 of Patent Document 2 discloses that the Bi concentration increases in the vicinity of the interface with the land which is difficult to solidify in the fillet during cooling of the solder alloy. Moreover, in the same paragraph, it is described that the fillet is more difficult to solidify in the vicinity of the interface having a high Bi concentration, and when a contraction force acting perpendicularly on the board is generated, the surface peeling of the fillet from the land is more likely to occur. From these viewpoints, it is preferable that the solder alloys described in Patent Documents 1 and 2 do not contain Bi.

[0010] In addition, the solder alloys described in these documents contain a predetermined amount of Ni as an essential element, so that $(Cu, Ni)_6Sn_5$ is formed in the

the stress application speed in the heat cycle test is caused by the expansion speed and the contraction speed of the solder alloy and the board, the stress application speed is lower than the stress application speed at which stress is instantaneously applied like in drop impact. In an electronic device such as a conventional mobile terminal, dropping is inevitable, and therefore a solder joint capable of withstanding an external stress rapidly applied is required.

[0015] An object of the present disclosure is to provide a solder alloy, a solder ball, a solder paste, and a solder joint that have excellent in thermal conductivity, drop impact resistance, and heat cycle resistance.

Solution to Problem

[0016] The present inventors have investigated the problems of the Sn-Ag-Cu-Sb-Ni solder alloys described in Patent Documents 1 and 2 in detail. Patent Documents 1 and 2 describe that, as a reason for adding Ni, $(Cu,Ni)_6Sn_5$ is formed in a molten solder alloy and dispersed in a base material, so that the crack development in the solder bulk is suppressed. Further, the same documents describe that Ni moves to the vicinity of a joint interface and form fine $(Cu,Ni)_6Sn_5$ during solder bonding, and thus growth of a Cu_3Sn layer at the joint interface is suppressed.

[0017] As described above, it is found that Ni of the Sn-Ag-Cu-Sb-Ni solder alloy contributes to the refinement of the structure of the solder alloy. However, it is considered that since $(Cu,Ni)_6Sn_5$ is dispersed in the base material, the thermal conductivity of the solder joint rather decreases.

[0018] Patent Documents 3 and 4 describe that, as a reason for adding Ni, there is a synergistic effect with Co in addition to the fact that $(Cu,Ni)_6Sn_5$ is formed in a molten solder alloy and dispersed in a base material, similarly to Patent Documents 1 and 2. It is also described that $(Cu,Co)_6Sn_5$ is dispersed in a base material to suppress crack development, and thus it is considered that the thermal conductivity is further reduced in an alloy composition containing Ni and Co at the same time. Since Sn-Ag-Cu-Sb-Bi-Ni

problems when adding only Co and Fe. In general, since all constituent elements of an alloy mutually contribute, it is rare that all the excellent effects are simultaneously exerted only by one element. Therefore, in addition to the contents of Co and Fe, the contents of Ag, Cu, and Sb were also investigated in detail at the same time.

[0022] Conventionally, as described above, considering the structure of the solder alloy, there is a contradictory relationship between refinement of the alloy structure and suppression of spalling. For this reason, it has been considered that it is difficult to provide a solder alloy that simultaneously satisfies three types of effects for thermal conductivity, drop impact resistance, and heat cycle resistance. In particular, in a solder alloy containing many kinds of elements to be added to Sn, since various compounds are formed and thus the thermal conductivity is low, there has been little study on the thermal conductivity heretofore. However, as a result of detailed studies, the present inventors have found that the thermal conductivity, the drop impact resistance, and the heat cycle resistance are simultaneously improved only when the contents of Ag, Cu, Sb, Co, and Fe are each within a predetermined range, and thus the present invention has been completed.

The present examples obtained from these findings are as follows.

[0023] (0) A solder alloy consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.10 to 1.00%, Sb: 1.0 to 7.0%, Co: 0.001 to 0.030%, Fe: 0.005 to 0.050%, with the balance being Sn.

(1) A solder alloy having an alloy composition consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.10 to 1.00%, Sb: 1.0 to 7.0%, Co: 0.001 to 0.030%, Fe: 0.005 to 0.050%, with the balance being Sn.

[0024] (2) The solder alloy according to (1) above, further comprising, by mass%, at least one of P, Ge, Ga, and Mn: 0.1% or less in total.

[0025] (3) The solder alloy according to (1) or (2) above, further comprising, by mass%, In: 6.0% or less.

[0026] (4) The solder alloy according to (1) or (2) above, wherein the alloy composition contains In: 0 to 4.0% and satisfies the following Relations (1) and (2):

$$0.040 \leqq Ag \times Cu \times Sb \times Co \leqq 0.075 \quad (1)$$

$1.6 \leqq Ag \times Cu \times Sb \times Co/Fe \leqq 5.7$ (2)

wherein Ag, Cu, Sb, Co, and Fe represent the content (mass%) of the alloy composition in the Relations (1) and (2).

[0027] (5) A solder ball comprising the solder alloy according to (1) or (2) above.

[0028] (6) A solder ball comprising the solder alloy according to (3) above.

[0029] (7) A solder paste comprising a solder powder comprising the solder alloy according to (1) or (2) above.

[0030] (8) A solder paste comprising a solder powder comprising the solder alloy according to (3) above.

[0031] (9) A solder joint comprising the solder alloy according to (1) or (2) above.

[0032] (10) A solder joint comprising the solder alloy according to claim (3).

[0032a] In an aspect of the present disclosure, there is provided a solder alloy having an alloy composition consisting of, by mass%, Ag: 1.0 to 4.0%, Cu: 0.10 to 1.00%, Sb: 1.0 to 7.0%, Co: 0.001 to 0.030%, Fe: 0.005 to 0.050%, with the balance being Sn.

[0032b] In another aspect of the present disclosure, there is provided a solder ball consisting of the solder alloy as disclosed herein.

[0032c] In a further aspect of the present disclosure, there is provided a solder paste comprising a solder powder consisting of the solder alloy as disclosed herein.

[0032d] In another aspect of the present disclosure, there is provided a solder joint comprising the solder alloy as disclosed herein.

Brief Description of Drawings

[0033] FIG. 1 is a cross-sectional SEM photograph of a solder joint, FIG. 1(a) is a cross-sectional SEM photograph of a solder joint using a solder alloy of Comparative Example 18, and FIG. 1(b) is a cross-sectional SEM photograph of a solder joint using a solder alloy of Example 16.

FIG. 2 is a cross-sectional SEM photograph of a solder joint, FIG. 2(a) is a cross-sectional SEM photograph of a solder joint using a solder alloy of Comparative Example

18, FIG. 2(b) is a photograph showing a result of cross-sectional mapping analysis in the solder joint using the solder alloy of Comparative Example 18, and FIG. 2(c) is a cross-sectional SEM photograph of a solder joint using a solder alloy of Example 16.

Description of Embodiments

[0034] The present invention will be described in more detail below. In this description, "%" relating to the solder alloy composition refers to "mass%" unless otherwise specified.

[0035] 1. Solder Alloy

(1) Ag: 1.0 to 4.0%

Ag forms a network of Ag_3Sn, and contributes to improvement of heat cycle resistance and drop impact resistance. Ag also contributes to improvement of wettability of the molten solder. When the Ag content is less than 1.0%, the precipitation amount of Ag_3Sn is small, so that heat cycle resistance is deteriorated. In terms of the lower limit, the Ag content is 1.0% or more, preferably 2.0% or more, more preferably 3.0% or more, and further preferably 3.2% or more. On the other hand, when the Ag content is more than 4.0%, coarse primary crystals of Ag_3Sn are crystallized, and the drop impact resistance is deteriorated. Also, thermal conductivity may be deteriorated. In terms of the upper limit, the Ag content is 4.0% or less, preferably 3.8% or less, and more preferably 3.5% or less.

[0036] (2) Cu: 0.10 to 1.00%

Cu forms a compound with Sn in the solder bulk and in the vicinity of the joint interface. Therefore, addition of Cu improves thermal conductivity, heat cycle resistance, and drop impact resistance. Further, wettability of the molten solder is also improved. When the Cu content is less than 0.10%, the amount of Cu_6Sn_5, etc., deposited is small, so that the drop impact resistance is deteriorated. Also, heat cycle resistance may be deteriorated. In terms of the lower limit, the Cu content is 0.10% or more, preferably 0.30% or more, and more preferably 0.50% or more. On the other hand, when the Cu content more than 1.00%, the intermetallic compound formed at the joint interface is spalled, so that the thermal conductivity is deteriorated. Drop impact resistance may be deteriorated. Further, the liquidus-line temperature rises. In terms of the upper limit, the Cu content is 1.00% or less, preferably 0.80% or less, and more preferably 0.70% or less.

[0037] (3) Sb: 1.0 to 7.0%

Sb dissolves in Sn and also precipitates an SnSb compound, thus contributing to improvement of heat cycle resistance. When the Sb content is less than 1.0%, the precipitation amount of the SnSb compound is small, and the heat cycle resistance is not improved. In terms of the lower limit, the Sb content is 1.0% or more, preferably 2.0%

or more, and more preferably 3.0% or more. On the other hand, when the Sb content more than 7.0%, due to an excessively high precipitation amount of SnSb, the thermal conductivity decreases. In terms of the upper limit, the Sb content is 7.0% or less, preferably 6.0% or less, more preferably 5.0% or less, and further preferably 4.0% or less.

[0038] (4) Co: 0.001 to 0.030%

Co makes the Sn crystal grains finer and contributes to improvement in drop impact resistance and heat cycle resistance. When the Co content is less than 0.001%, Sn crystal grains do not become fine, and heat cycle resistance is not improved. Further, the liquidus-line temperature rises. In terms of the lower limit, the Co content is 0.001% or more, more preferably 0.003% or more, and further preferably 0.006% or more. On the other hand, when the Co content more than 0.030%, the amount of the compound becomes too large, a coarser compound is generated, the structure is deteriorated, and the drop impact resistance is deteriorated. In terms of the upper limit, the Co content is 0.030% or less, preferably 0.010% or less, and more preferably 0.008% or less.

[0039] (5) Fe: 0.005 to 0.050%

Fe makes the intermetallic compound precipitated at the joint interface fine to some extent, and also suppresses spalling of the intermetallic compound into the solder bulk. Therefore, the addition of Fe improves the thermal conductivity and the drop impact resistance. When the Fe content is less than 0.005%, the intermetallic compound precipitated at the joint interface cannot be made fine, and the drop impact resistance is deteriorated. In addition, since spalling of the intermetallic compound is not suppressed, the thermal conductivity is not improved. In terms of the lower limit, the Fe content is 0.005% or more, preferably 0.010% or more, and more preferably 0.020% or more. On the other hand, when the Fe content is more than 0.050%, the intermetallic compound does not become fine, and the drop impact resistance decreases. Further, the liquidus-line temperature rises. In terms of the upper limit, the Fe content is 0.050% or less, preferably 0.040% or less, and more preferably 0.025% or less.

[0040] (6) In: 6.0% or less

In is an optional element that may be contained within a range in which the above-described effect in the solder alloy according to the present invention is not impaired. In terms of the upper limit, the In content is preferably 6.0% or less, and more preferably 5.0% or less. A lower limit is not particularly limited, but is preferably more than 0%, more preferably 0.1% or more, and further preferably 0.5% or more.

[0041] (7) At least one of P, Ge, Ga, and Mn: 0.1% or less in total.

P, Ge, Ga, and Mn are optional elements that may be contained as an oxidation suppression effect of the solder alloy. These elements are preferably 0.1% or less in total. A lower limit is not particularly limited, but may be 0.001% or more in total. In addition, the content of each of these elements is more preferably 0.001 to 0.1%, and further preferably 0.001 to 0.050%.

[0042] (8) Balance: Sn

The balance of the solder alloy according to the present invention is Sn. In addition to the above-described elements, unavoidable impurity may be contained. Even when unavoidable impurity is contained, it does not affect the above-described effects.

Note that, in the solder alloy according to the present invention, it is better not to contain Ni and Bi. Since Ni makes the alloy structure finer than necessary, the intermetallic compound is spalled from the joint interface into the solder bulk, and the thermal conductivity decreases. Since Bi forms a concentrated layer in the solder alloy, drop impact resistance decreases and further, lift-off is caused.

[0043] (9) Relations (1) and (2)

$$0.040 \leqq Ag \times Cu \times Sb \times Co \leqq 0.075 \quad (1)$$

$$1.6 \leqq Ag \times Cu \times Sb \times Co/Fe \leqq 5.7 \quad (2)$$

Ag, Cu, Sb, Co, and Fe in the Relations (1) and (2) each represent the contents (mass%) thereof in the alloy composition.

The Relation (1) is a relation concerning an element having an effect of improving heat cycle resistance. In the Relation (1), the contents of Ag, Cu, and Sb are larger than Co, but Co greatly contributes to improvement of heat cycle resistance even if the content

is small. Therefore, although the ratio of the Co content is about 1/10 to 1/10000 times as large as the contents of Ag, Cu, and Sb, it is considered that the degree of contribution to the characteristics of the solder alloy is about the same. Therefore, in order to further improve the heat cycle resistance characteristics in the present invention, it is not meaningful to calculate the total amount of the constituent elements of Relation (1), and it is preferable that the content is balanced.

In the calculation of the Relations (1) and (2), numerical values expressed in the actual measured values of the alloy composition shown in the following Tables 1 and 2 are directly used. That is, in the calculation of the Relations (1) and (2), all digits less than the number of significant digits in the actual measured values shown in the following Tables 1 and 2 are treated as 0. For example, when the Co content is “0.008” mass% as an actual measured value, the Co content used for the calculation of the Relations (1) and (2) does not have a range of 0.0075 to 0.0084%, but is handled as “0.008000…”. The Relation (1) is calculated up to the third decimal place, and the Relation (2) is calculated up to the first decimal place.

Note that when the Relations (1) and (2) are calculated from the alloy compositions specifically disclosed in the patent documents and other documents described in the present specification, the Relations (1) and (2) are also handled in the same manner.

[0044] The Relation (2) is a relation concerning a ratio between an element contributing to improvement of drop impact resistance and an element contributing to improvement of thermal conductivity. The Relation (2) also contains Ag, Cu, and Sb which are relatively high contents and Co and Fe which are relatively low contents, similarly to the Relation (1). However, even though the Co content is relatively low, Co contributes to the refinement of the alloy structure, so that it can greatly contribute to the drop impact resistance. Although Fe is about the same as the range of the Co content, Fe contributes to the refinement of the alloy structure than Co and also contributes to suppression of spalling. In addition, Fe is an element that can actively improve the thermal conductivity among

elements constituting the solder alloy according to the present invention. In order to be able to exhibit all of thermal conductivity, heat cycle resistance, and drop impact resistance at a higher level, it is desirable to satisfy the Relation (2) in which thermal conductivity and heat cycle resistance are considered, in addition to the Relation (1).

[0045] Further, when In is contained, it is desirable that In contents are 4.0% or less in addition to satisfying the Relations (1) and (2). Even if the In content is 0% in the alloy composition, the above effect is exhibited when the Relations (1) and (2) are satisfied. Since In may form a compound with Sn, when the In content is 4.0% or less, a decrease in thermal conductivity due to the formed compound is suppressed, and the effect when the Relations (1) and (2) are satisfied is more easily exhibited.

[0046] As described above, in the alloy, all the constituent elements do not function individually, but all the constituent elements form one object as a whole. Therefore, it is rare that all the excellent effects are simultaneously exerted only by one element. Therefore, as described above, in order to exhibit more excellent characteristics within the range of the optimum content of each constituent element, it is necessary to investigate the constituent elements as a whole. In the solder alloy according to the present invention, in order to simultaneously satisfy all requirements of the heat cycle resistance, the thermal conductivity, and the drop impact resistance at a higher level, the In content is preferably 4.0% or less, and the Relations (1) and (2) are preferably satisfied.

[0047] In terms of the lower limit, the Relation (1) is preferably 0.040 or more, more preferably 0.042 or more, further preferably 0.043 or more, further more preferably 0.046 or more, particularly preferably 0.047 or more, most preferably 0.050 or more, and may be 0.055 or more. In terms of the upper limit, the Relation (1) is preferably 0.075 or less, more preferably 0.070 or less, further preferably 0.069 or less, further more preferably 0.058 or less, and particularly preferably 0.056 or less.

The Relation (1) is preferably 0.042 to 0.070, more preferably 0.043 to 0.069, further preferably 0.046 to 0.058, and particularly preferably 0.047 to 0.056.

[0048] In terms of the lower limit, the Relation (2) is preferably 1.6 or more, more

to evaluate drop impact resistance. In this drop test, a situation in which a crack was developing in the solder joint was confirmed based on whether the electric resistance value increased by 50% from the initial value. In the determination on the crack development, when the electric resistance value did not increase by 50% from the initial value after dropping 85 times or more, it was judged as “Excellent”, when the number of drops when the electric resistance value exceeded 50% from the initial value was 80 to 84 times, it was judged as “Good”, and when the number of drops when the electric resistance value exceeded 50% from the initial value was 79 times or less, it was judged as “Poor”.

The evaluation results are shown in Tables 1 and 2.

16. Five samples were prepared for each of the examples and the comparative examples, and an alloy layer and a region of 0 to 20 μm from a surface treatment interface (region illustrated as “target region” in FIG. 1) were observed.

A powder of each of the solder alloys described in Example 16 and Comparative Example 18 was prepared by an atomizing method. The powder of the alloy was mixed with a flux (“GLV” made by Senju Metal Industry Co., Ltd.) containing rosin, a solvent, a thixotropic agent, and an organic acid, etc., to prepare a solder paste. The solder paste containing the alloy powder of the solder paste in an amount of 88 mass% and the flux in an amount of 12 mass% was printed on Cu lands of six layers of printed circuit boards (FR-4, Cu-OSP) with a metal mask of 150μm, and then a chip resistor of 3216 was mounted with a mounter. Then, a test board was produced by performing reflow soldering by melting the solder paste under heating conditions where a maximum temperature was 245℃ and a holding time was 40 seconds.

[0068] After that, the test board was cut out and polished, and the vicinity of a joint interface in a cross section was observed at a magnification of 1000. A total area and an area of the CuSn-based compound were calculated by using image analysis software. As the image analysis software, Scandium was used. By using results of calculation of the respective areas, an area ratio of the CuSn-based compound was calculated according to (area ratio of CuSn-based compound) (%) = (area of CuSn-based compound) × 100 / (area of target region).

[0069] As is clear from FIG. 1(b), in the target region in Example 16, the ratio of the CuSn-based compound was 0%. FIG. 1(a) illustrates an image of Comparative Example 18, and the ratio of the CuSnNi-based compound was 15 to 20% in the target region. Thus, in the example, it was found that no compound spalling occurred. The results of other examples were similar to those of Example 16.

[0070] FIG. 2 is a cross-sectional SEM photograph of a solder joint, FIG. 2(a) is a cross-sectional SEM photograph of a solder joint using a solder alloy of Comparative Example 18, FIG. 2(b) is a photograph showing a result of cross-sectional mapping analysis in the