

## **LEAD-FREE AND ANTIMONY-FREE TIN SOLDER RELIABLE AT HIGH TEMPERATURES**

The present invention relates generally to the field of metallurgy and to an alloy and, in particular, a lead-free  
5 and antimony-free solder alloy. The alloy is particularly, though not exclusively, suitable for use in electronic soldering applications such as wave soldering, surface mounting technology, hot air leveling and ball grid arrays, land grid arrays, bottom terminated packages, LEDs and chip  
10 scale packages.

Wave soldering (or flow soldering) is a widely used method of mass soldering electronic assemblies. It may be used, for example, for through-hole circuit boards, where the  
15 board is passed over a wave of molten solder, which laps against the bottom of the board to wet the metal surfaces to be joined.

Another soldering technique involves printing of the solder  
20 paste on the soldering pads on the printed circuit boards followed by placement and sending the whole assembly through a reflow oven. During the reflow process, the solder melts and wets the soldering surfaces on the boards as well as the components.

25 Another soldering process involves immersing printed wiring boards into molten solder in order to coat the copper terminations with a solderable protective layer. This process is known as hot-air leveling.

30 A ball grid array joint or chip scale package is assembled typically with spheres of solder between two substrates.

Arrays of these joints are used to mount chips on circuit boards.

5 There are a number of requirements for a solder alloy to be  
suitable for use in wave soldering, hot-air leveling  
processes and ball grid arrays. First, the alloy must  
exhibit good wetting characteristics in relation to a  
variety of substrate materials such as copper, nickel,  
nickel phosphorus ("electroless nickel"). Such substrates  
10 may be coated to improve wetting, for example by using tin  
alloys, gold or organic coatings (OSP). Good wetting also  
enhances the ability of the molten solder to flow into a  
capillary gap, and to climb up the walls of a through-plated  
hole in a printed wiring board, to thereby achieve good hole  
15 filling.

Solder alloys tend to dissolve the substrate and to form an  
intermetallic compound at the interface with the substrate.  
For example, tin in the solder alloy may react with the  
20 substrate at the interface to form an intermetallic compound  
(IMC) layer. If the substrate is copper, then a layer of  
 $\text{Cu}_6\text{Sn}_5$  may be formed. Such a layer typically has a  
thickness of from a fraction of a micron to a few microns.  
At the interface between this layer and the copper substrate  
25 an IMC of  $\text{Cu}_3\text{Sn}$  may be present. The interface intermetallic  
layers will tend to grow during aging, particularly where  
the service is at higher temperatures, and the thicker  
intermetallic layers, together with any voids that may have  
developed may further contribute to premature fracture of a  
30 stressed joint.

Other important factors are: (i) the presence of  
intermetallics in the alloy itself, which results in

improved mechanical properties; (ii) oxidation resistance, which is important in solder spheres where deterioration during storage or during repeated reflows may cause the soldering performance to become less than ideal; (iii)

5   drossing rate; and (iv) alloy stability. These latter considerations are important for applications where the alloy is held in a tank or bath for long periods of time or where the formed solder joints are subjected to high operating temperatures for long periods of time.

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For environmental and health reasons, there is an increasing demand for lead-free and antimony-free replacements for lead- and antimony- containing conventional alloys. Many conventional solder alloys are based around the tin-copper  
15   eutectic composition, Sn-0.7 wt.% Cu. For example, the tin-silver-copper system has been embraced by the electronics industry as a lead-free alternative for soldering materials. One particular alloy, the eutectic alloy SnAg3.0Cu0.5, exhibits a superior fatigue life compared to a Sn-Pb solder  
20   material while maintaining a relatively low melting point of about 217 to 219°C.

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In some fields, such as automotive, high power electronics and energy, including LED lighting, for example, it is desirable for solder alloys to operate at higher  
temperatures, for example 150°C or higher. The SnAg3.0Cu0.5 alloy does not perform well at such temperatures.

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The present invention aims to solve at least some of the problems associated with the prior art or to provide a commercially acceptable alternative.

Accordingly, in a first aspect, the present invention provides a lead-free, antimony-free solder alloy comprising:

(a) 10 wt.% or less of silver

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(b) 10 wt.% or less of bismuth

(c) 3 wt.% or less of copper

10 (d) at least one of the following elements

up to 1 wt.% of nickel

up to 1 wt.% of titanium

up to 1 wt.% of cobalt

15 up to 3.5 wt.% of indium

up to 1 wt.% of zinc

up to 1 wt.% of arsenic

(e) optionally one or more of the following elements

20

0 to 1 wt.% of manganese

0 to 1 wt. % of chromium

0 to 1 wt.% of germanium

0 to 1 wt.% of iron

25 0 to 1 wt.% of aluminum

0 to 1 wt.% of phosphorus

0 to 1 wt.% of gold

0 to 1 wt.% of gallium

0 to 1 wt.% of tellurium

30 0 to 1 wt.% of selenium

0 to 1 wt.% of calcium

0 to 1 wt.% of vanadium

0 to 1 wt.% of molybdenum

0 to 1 wt.% of platinum  
0 to 1 wt.% of magnesium  
0 to 1 wt.% of rare earths

- 5 (f) the balance tin, together with any unavoidable impurities.

The present invention will now be further described. In the following passages different aspects of the invention are  
10 defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being  
15 preferred or advantageous.

The alloys described herein exhibit improved high-temperature reliability and are capable of withstanding operational temperatures of typically at least 150°C. The  
20 alloys exhibit improved mechanical properties and high-temperature creep resistance compared to the conventional SnAg3.0Cu0.5 alloy.

The alloys are lead-free and antimony-free meaning that no  
25 lead or antimony is added intentionally. Thus, the lead and antimony contents are zero or at no more than accidental impurity levels.

The alloy composition comprises 10 wt.% or less of silver,  
30 for example from 1 to 10 wt.%. Preferably, the alloy comprises from 2.5 to 5 wt. % silver, more preferably from 3 to 5 wt.% silver, even more preferably from 3 to 4.5 wt.% silver, and most preferably from 3.5 to 4 wt.% silver. The

presence of silver in the specified amount may serve to improve mechanical properties, for example strength, through the formation of intermetallic compounds. In addition, the presence of silver may act to decrease copper dissolution  
5 and improve wetting and spread.

The alloy composition comprises 10 wt.% or less of bismuth, for example from 1 to 10 wt.%. Preferably, the alloy comprises from 2 to 6 wt.% bismuth, more preferably from 2.5  
10 to 5 wt.% bismuth, even more preferably from 2.7 to 4.5 wt.% bismuth, and most preferably from 2.8 to 4 wt.% bismuth. The presence of bismuth in the specified amount may serve to improve mechanical properties through solid solution strengthening. Bismuth may also act to improve creep  
15 resistance. Bismuth may also improve wetting and spread.

The alloy composition comprises 3 wt.% or less of copper, for example from 0.1 to 3 wt.%. Preferably, the alloy comprises from 0.3 to 2 wt.% copper, more preferably from  
20 0.4 to 1 wt.% copper, even more preferably from 0.5 to 0.9 wt.% copper, and most preferably from 0.6 to 0.8 wt.% copper. The presence of copper in the specified amount may serve to improve mechanical properties, for example strength, through the formation of intermetallic compounds.  
25 In addition, the presence of copper reduces copper dissolution and may also improve creep resistance.

The alloy composition optionally comprises 0 to 1 wt.% of nickel, for example from 0.01 to 1 wt.%. If nickel is  
30 present, the alloy preferably comprises from 0.03 to 0.6 wt.% nickel, more preferably from 0.05 to 0.5 wt.% nickel, even more preferably from 0.07 to 0.4 wt.% nickel, and most preferably from 0.1 to 0.3 wt.% nickel. The presence of

nickel in the specified amount may serve to improve mechanical properties through the formation of intermetallic compounds with tin, which can result in precipitation strengthening. In addition, the presence of nickel may act  
5 to reduce the copper dissolution rate. Nickel may also increase drop shock resistance by decreasing IMC growth at the substrate/solder interface.

The alloy composition optionally comprises 0 to 1 wt.% of  
10 titanium, for example from 0.005 to 1 wt.%. If titanium is present, the alloy preferably comprises from 0.005 to 0.5 wt.% titanium, more preferably from 0.007 to 0.1 wt.% titanium, even more preferably from 0.008 to 0.06 wt.% titanium, and most preferably 0.01 to 0.05 wt.% titanium.  
15 The presence of titanium in the specified amount may serve to improve strength and interfacial reactions. Titanium may also improve drop shock performance.

The alloy composition optionally comprises 0 to 1 wt.% of  
20 cobalt, for example from 0.01 to 1 wt.%. If cobalt is present, the alloy preferably comprises from 0.01 to 0.6 wt.% cobalt, more preferably from 0.02 to 0.5 wt.% cobalt, even more preferably from 0.03 to 0.4 wt.% cobalt, and most preferably 0.04 to 0.3 wt.% cobalt. The presence of cobalt  
25 may act to lower the copper dissolution rate. Cobalt may also slow the rate of IMC formation at the substrate / solder interface, and increase drop-shock resistance.

The alloy composition optionally comprises 0 to 3.5 wt.% of  
30 indium, for example from 0.01 to 3.5 wt.%. If indium is present, the alloy preferably comprises from 0.05 to 3.5 wt.% indium, more preferably from 0.1 to 3.5 wt.% indium.

The presence of indium may act to improve mechanical properties through solid solution strengthening.

5 The alloy composition optionally comprises 0 to 1 wt.% of zinc, for example from 0.01 to 1 wt.%. If zinc is present, the alloy preferably comprises from 0.03 to 0.6 wt.% zinc, more preferably from 0.05 to 0.5 wt.% zinc, even more preferably from 0.07 to 0.4 wt.% zinc, and most preferably 0.1 to 0.3 wt.% zinc. The presence of zinc may act to  
10 improve mechanical properties through solid solution strengthening. Zinc may also act to slow IMC growth and reduce void formation.

15 The alloy composition optionally comprises 0 to 1 wt.% of arsenic, for example from 0.01 to 1 wt.%. If arsenic is present, the alloy preferably comprises from 0.03 to 0.6 wt.% arsenic, more preferably from 0.05 to 0.5 wt.% arsenic, even more preferably from 0.07 to 0.4 wt.% arsenic, and most preferably 0.1 to 0.3 wt.% arsenic. The presence of arsenic  
20 may act to improve mechanical properties through particle dispersion.

The alloy may optionally also contain one or more of 0.005 to 1 wt.% of manganese, 0.005 to 1 wt. % of chromium, 0.005  
25 to 1 wt.% of germanium, 0.005 to 1 wt.% of iron, 0.005 to 1 wt.% of aluminum, 0.005 to 1 wt.% of phosphor, 0.005 to 1 wt.% of gold, 0.005 to 1 wt.% of gallium, 0.005 to 1 wt.% of tellurium, 0.005 to 1 wt.% of selenium, 0.005 to 1 wt.% of calcium, 0.005 to 1 wt.% of vanadium, 0.005 to 1 wt.% of  
30 molybdenum, 0.005 to 1 wt.% of platinum, 0.005 to 1 wt.% of magnesium and/or 0.005 to 1 wt.% of rare earth element(s).

Rare earths may act to improve spread and wettability. Cerium has been found to be particularly effective in this regard. Aluminium, calcium, gallium, germanium, magnesium, phosphorus and vanadium may act as deoxidizers and may also  
5 improve wettability and solder joint strength. Other elemental additions, such as gold, chromium, iron, manganese, molybdenum, platinum, selenium and tellurium may act to improve strength and interfacial reactions.

- 10 The term rare earth element as used herein refers to one or more elements selected from Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

- The alloy will typically comprise at least 88 wt.% tin, more  
15 typically at least 90 wt.% tin, still more typically at least 91 wt.% tin.

- In a further aspect, there is provided an alloy comprising from 3 to 5 wt.% silver, from 2 to 5 wt.% bismuth, from 0.3  
20 to 1.5 wt.% copper, from 0.05 to 0.4 wt.% nickel, optionally 0.008 to 0.06 wt.% titanium, optionally 0.005 to 0.2 of a rare earth element (preferably cerium), optionally 3 to 4 wt.% of indium, optionally up to 1 wt.% germanium, optionally up to 1 wt.% manganese, optionally 0.01 to 0.1  
25 wt.% cobalt, and the balance tin together with unavoidable impurities.

- In one embodiment, there is provided an alloy comprising 3 to 4.5 wt.% silver, 3 to 4.5 wt.% bismuth, 0.5 to 1.5 wt.%  
30 copper, 0.05 to 0.25 wt.% nickel, and the balance tin together with unavoidable impurities. Such an alloy has a melting range of from 207.2 to 215.9°C, which is lower than the near eutectic temperature of the conventional

SnAg3.0Cu0.5 alloy. Such an alloy has a hardness that is about twice the magnitude of the hardness of SnAg3.0Cu0.5. In one specific example of this embodiment, the alloy comprises approximately 3.63 wt.% silver, 3.92 wt.% bismuth, 5 0.76 wt.% copper, 0.18 wt.% nickel, and the balance tin together with unavoidable impurities.

In another embodiment, there is provided an alloy comprising 3 to 4.5 wt.% silver, 3 to 4.5 wt.% bismuth, 0.5 to 1.5 wt.% 10 copper, 0.05 to 0.25 wt.% nickel, 0.005 to 0.05 wt.% of a rare earth element, for example cerium, and the balance tin together with unavoidable impurities. Such an alloy has a melting range of from 208.8 to 219.4°C and a hardness that is about twice the magnitude of the hardness of 15 SnAg3.0Cu0.5. In one specific example of this embodiment, the alloy comprises approximately 3.81 wt.% silver, 3.94 wt.% bismuth, 0.8 wt.% copper, 0.25 wt.% nickel, 0.04 wt.% cerium, and the balance tin together with unavoidable impurities.

20 In another embodiment, there is provided an alloy comprising 3 to 4.5 wt.% silver, 2 to 4 wt.% bismuth, 0.5 to 1.5 wt.% copper, 0.05 to 0.25 wt.% nickel, 0.005 to 0.05 wt.% titanium, and the balance tin together with unavoidable 25 impurities. Such an alloy has a melting range of from 210.4 to 215.9°C and a hardness that is about twice the magnitude of the hardness of SnAg3.0Cu0.5. In one specific example of this embodiment, the alloy comprises approximately 3.8 wt.% silver, 2.98 wt.% bismuth, 0.7 wt.% copper, 0.1 wt.% nickel, 30 0.01 wt.% titanium, and the balance tin together with unavoidable impurities.

In another embodiment, there is provided an alloy comprising 3 to 4.5 wt.% silver, 3 to 5 wt.% bismuth, 0.4 to 1.5 wt.% copper, 0.1 to 0.3 wt.% nickel, 0.01 to 0.2 wt.% of a rare earth element(s) (preferably cerium), and the balance tin together with unavoidable impurities. Such an alloy has a melting range of from 209.0 to 220.4°C. In one specific example of this embodiment, the alloy comprises approximately 3.85 wt.% silver, 3.93 wt.% bismuth, 0.68 wt.% copper, 0.22 wt.% nickel, 0.08 wt.% cerium, and the balance tin together with unavoidable impurities.

In another embodiment, there is provided an alloy comprising 3 to 4.5 wt.% silver, 3 to 5 wt.% bismuth, 0.3 to 1.2 wt.% copper, 0.05 to 0.3 wt.% nickel, 0.01 to 0.1 wt.% of titanium, and the balance tin together with unavoidable impurities. Such an alloy has a melting range of from 209.3 to 220.6°C. In one specific example of this embodiment, the alloy comprises approximately 3.86 wt.% silver, 3.99 wt.% bismuth, 0.63 wt.% copper, 0.16 wt.% nickel, 0.043 wt.% titanium, and the balance tin together with unavoidable impurities.

In another embodiment, there is provided an alloy comprising 3 to 4.5 wt.% silver, 3 to 5 wt.% bismuth, 0.3 to 1.2 wt.% copper, 0.05 to 0.3 wt.% nickel, 0.01 to 0.1 wt.% of cobalt, and the balance tin together with unavoidable impurities. Such an alloy has a melting range of from 209.1 to 216.1°C. In one specific example of this embodiment, the alloy comprises approximately 3.82 wt.% silver, 3.96 wt.% bismuth, 0.6 wt.% copper, 0.16 wt.% nickel, 0.042 wt.% cobalt, and the balance tin together with unavoidable impurities.

In another embodiment, there is provided an alloy comprising 3 to 4.5 wt.% silver, 2 to 4 wt.% bismuth, 0.3 to 1.2 wt.% copper, 0.05 to 0.25 wt.% nickel, 0.001 to 0.01 wt.% of manganese, and the balance tin together with unavoidable  
5 impurities. Such an alloy has a melting range of from 209.2 to 216.8°C. In one specific example of this embodiment, the alloy comprises approximately 3.9 wt.% silver, 3 wt.% bismuth, 0.6 wt.% copper, 0.12 wt.% nickel, 0.006 wt.% Mn, and the balance tin together with unavoidable impurities.

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In another embodiment, there is provided an alloy comprising 3 to 4.5 wt.% silver, 2 to 4 wt.% bismuth, 0.3 to 1.2wt.% copper, 0.05 to 0.3 wt.% nickel, 0.001 to 0.01 wt.% of germanium, and the balance tin together with unavoidable  
15 impurities. Such an alloy has a melting range of from 208.2 to 218.6°C. In one specific example of this embodiment, the alloy comprises approximately 3.85 wt.% silver, 3.93 wt.% bismuth, 0.63 wt.% copper, 0.15 wt.% nickel, 0.006 wt.% germanium, and the balance tin together with unavoidable  
20 impurities.

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In another embodiment, there is provided an alloy comprising 4 to 5 wt.% silver, 3 to 5 wt.% bismuth, 0.3 to 1.2 wt.% copper, 0.05 to 0.3 wt.% nickel, 3 to 4 wt.% of indium, and  
25 the balance tin together with unavoidable impurities. Such an alloy has a melting range of from 195.6 to 210.7°C. In one specific example of this embodiment, the alloy comprises approximately 4.24 wt.% silver, 3.99 wt.% bismuth, 0.63 wt.% copper, 0.18 wt.% nickel, 3.22 wt.% indium, and the balance  
30 tin together with unavoidable impurities.

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In another embodiment, there is provided an alloy comprising 3.5 to 5 wt.% silver, 2 to 5 wt.% bismuth, 0.4 to 1.3 wt.%

copper, 0.05 to 0.3 wt.% nickel, 0.01 to 0.1 wt.% of cerium, and the balance tin together with unavoidable impurities.

Such an alloy has a melting range of from 209.8 to 217.0°C.

In one specific example of this embodiment, the alloy

5 comprises approximately 3.91 wt.% silver, 2.9 wt.% bismuth, 0.72 wt.% copper, 0.2 wt.% nickel, 0.04 wt.% cerium, and the balance tin together with unavoidable impurities.

In another embodiment, there is provided an alloy comprising

10 3.5 to 5 wt.% silver, 2 to 5 wt.% bismuth, 0.3 to 1.2 wt.% copper, 0.05 to 0.3 wt.% nickel, 0.01 to 0.08 wt.%

lanthanum, and the balance tin together with unavoidable impurities. Such an alloy has a melting range of from

210.96 to 220.8°C. In one specific example of this

15 embodiment, the alloy comprises approximately 3.87 wt.% silver, 3.02 wt.% bismuth, 0.61 wt.% copper, 0.14 wt.% nickel, 0.038% lanthanum, and the balance tin together with unavoidable impurities.

20 In another embodiment, there is provided an alloy comprising 3.5 to 5 wt.% silver, 3 to 5 wt.% bismuth, 0.3 to 1.2 wt.% copper, 0.05 to 0.3 wt.% nickel, 0.01 to 0.08 wt.%

neodymium, and the balance tin together with unavoidable impurities. Such an alloy has a melting range of from 207.8

25 to 219.5°C. In one specific example of this embodiment, the alloy comprises approximately 3.86% silver, 3.99% bismuth, 0.64% copper, 0.14% nickel, 0.044% neodymium, and the balance tin together with unavoidable impurities.

30 In another embodiment, there is provided an alloy comprising 3.5 to 5 wt.% silver, 3 to 5 wt.% bismuth, 0.3 to 1.2 wt.% copper, 0.05 to 0.3 wt.% nickel, 0.01 to 0.08 wt.% cobalt, and the balance tin together with unavoidable impurities.

Such an alloy has a melting range of from 209 to 217°C. In one specific example of this embodiment, the alloy comprises approximately 3.94% silver, 3.92% bismuth, 0.7% copper, 0.12% nickel, 0.023% cobalt, and the balance tin together  
5 with unavoidable impurities.

It will be appreciated that the alloys described herein may contain unavoidable impurities, although, in total, these are unlikely to exceed 1 wt.% of the composition.  
10 Preferably, the alloys contain unavoidable impurities in an amount of not more than 0.5 wt.% of the composition, more preferably not more than 0.3 wt.% of the composition, still more preferably not more than 0.1 wt.% of the composition, still more preferably not more than 0.05 wt.% of the  
15 composition, and most preferably not more than 0.02 wt.% of the composition.

The alloys described herein may consist essentially of the recited elements. It will therefore be appreciated that in  
20 addition to those elements that are mandatory (i.e. Sn, Ag, Bi, Cu and at least one of Ni, Ti, Co, In, Zn and/or As) other non-specified elements may be present in the composition provided that the essential characteristics of the composition are not materially affected by their  
25 presence.

In one embodiment, the alloy exhibits a relatively low melting point, typically from about 195 to about 222°C (more typically about 209 to about 218°C). This is advantageous  
30 because it enables a reflow peak temperature of from about 230 to about 240°C.

In another embodiment, the alloy exhibits a thermal conductivity and/or an electrical conductivity which is/are higher or equivalent to the conventional SnAg3.0Cu0.5 alloy. This is advantageous in energy-related applications such as,  
5 for example, light-emitting diodes (LED), solar and power electronics.

The alloys of the present invention may be in the form of, for example, a bar, a stick, a solid or flux cored wire, a  
10 foil or strip, a film, a preform, or a powder or paste (powder plus flux blend), or solder spheres for use in ball grid array joints, or a pre-formed solder piece or a reflowed or solidified solder joint, or pre-applied on any solderable material such as a copper ribbon for photovoltaic  
15 applications or a printed circuit board of any type.

In another aspect, the present invention provides a method of forming a solder joint comprising:

- (i) providing two or more work pieces to be joined;
- 20 (ii) providing a solder alloy as defined in any of claims 1 to 10; and
- (iii) heating the solder alloy in the vicinity of the work pieces to be joined.

25 In another aspect, the present invention provides the use of an alloy, as herein described, in a soldering method. Such soldering methods include, but are not restricted to, wave soldering, Surface Mount Technology (SMT) soldering, die attach soldering, thermal interface soldering, hand  
30 soldering, laser and RF induction soldering, and rework soldering, lamination, for example.

The present invention will now be described further, by way of few non-limiting examples of these alloys and a summary of their performance, with reference to the following drawings in which:

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Figure 1 shows electron microscope images of the microstructure of Alloy A (a) as cast, and (b) after heat treatment at 150°C. Intermetallics compounds were identified  
10 by SEM-EDS.

Figure 2 shows electron microscope images of the microstructure of Alloy B (a) as cast, and (b) after heat treatment at 150°C. Intermetallics compounds were identified  
15 by SEM-EDS.

Figure 3 shows electron microscope images of the microstructure of Alloy C (a) as cast, and (b) after heat treatment at 150°C. Intermetallics compounds were identified  
20 by SEM-EDS.

Figure 4 shows electron microscope images of the microstructure of Alloy D (a) as cast, and (b) after heat treatment at 150°C. Intermetallics compounds were identified  
25 by SEM-EDS.

Figure 5 shows a comparison of (a) ultimate tensile strength, and (b) yield strength at room temperature for SnAg3.0Cu0.5 and alloys according to the present invention.  
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Figure 6 shows a comparison of (a) ultimate tensile strength, and (b) yield strength at 150°C for SnAg3.0Cu0.5 and alloys according to the present invention.

Figure 7 shows a comparison of (a) creep rupture time and (b) creep elongation at rupture measured at 150°C of for SnAg3.0Cu0.5 and alloys according to the present invention.

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Figure 8 shows zero wetting time of SnAg3.0Cu0.5 and alloys according to the present invention as a measure of their solderability.

10 Figure 9 shows the Weibull distribution curves describing BGA failures during drop shock test.

Figure 10 shows the Weibull distribution curves describing BGA failures during thermal cycling test.

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Figure 11 shows electron microscope images of BGA cross-sections before and after thermal cycling test.

Figure 12 shows shear force of chip resistors components  
20 measured before and after thermal cycling test.

The present invention will now be described further with reference to the following non-limiting examples.

#### 25 Example 1 - Alloy A

Alloy A comprises 3.63 wt% silver, 3.92 wt% bismuth, 0.76 wt% copper, 0.18 wt% nickel, and the balance tin together with unavoidable impurities.

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A cross-section of this alloy, as cast, reveals a microstructure containing  $\text{Bi}_2\text{Sn}$ ,  $\text{Ag}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  (see Figure 1(a)). The  $\text{Ag}_3\text{Sn}$  is dispersed in the tin matrix, but also

appears as needle-shaped precipitates. Other intermetallics Sn-Bi and Sn-Cu precipitates are non-homogeneously distributed in the matrix. After heat treatment at approximately 150°C for about 200 hours, significant  
5 reduction of needle-shape  $\text{Ag}_3\text{Sn}$  is observed, revealing a more homogeneous microstructure. Also, after the heat-treatment, the microstructure shows a more homogeneous distribution of the precipitates in the Sn-matrix and the presence of Ni, Cu-Sn precipitates (see Figure 1(b)).

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Such a microstructure, i.e. a more homogeneous matrix and the presence of finely distributed intermetallics precipitates, suggests that both solid solution and precipitation hardening are responsible for alloy  
15 strengthening and improved mechanical properties. The phenomenon of creep is expected to be reduced by such a microstructure.

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Alloy A has a melting range of 207.2 to 215.9°C; a coefficient of thermal expansion CTE ( $\mu\text{m}/\text{mK}$ ) (30-100°C) of 19.6; and a Vickers Hardness (HV-1) of 31. For comparison purposes, the conventional alloy,  $\text{SnAg}_{3.0}\text{Cu}_{0.5}$ , has a melting range of 216.6 to 219.7°C; a coefficient of thermal expansion CTE ( $\mu\text{m}/\text{mK}$ ) (30-100°C) of 22.4; and a Vickers  
25 Hardness (HV-0.5) of 15.

#### Example 2 - Alloy B

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Alloy B comprises 3.81 wt% silver, 3.94 wt% bismuth, 0.8 wt% copper, 0.25 wt% nickel, 0.04 wt% cerium, and the balance tin together with unavoidable impurities. Alloy B also reveals a microstructure containing  $\text{Bi}_2\text{Sn}$ ,  $\text{Ag}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  (see Figure 2(a)). Similar to Alloy A,  $\text{Ag}_3\text{Sn}$  is dispersed in

the Sn matrix, but also appears as needle-shaped precipitates, and Sn-Cu precipitates are non-homogeneously distributed in the matrix. After a heat-treatment at approximately 150°C for about 200 hours, the eutectic Ag-Sn can clearly be seen and a significant reduction of needle-shaped Ag<sub>3</sub>Sn is also observed, showing a more homogeneous microstructure (see Figure 2(b)). As with Alloy A, Ni, Cu-Sn precipitates are identified in the matrix after the heat-treatment. Such precipitates have been identified by X-ray diffraction analysis as NiSn<sub>2</sub> precipitates.

Alloy B has a melting range of 208.8 to 219.4°C; a coefficient of thermal expansion CTE (µm/mK) (30-100°C) of 22.8; and a Vickers Hardness (HV-1) of 28.

#### Example 3 - Alloy C

Alloy C comprises 3.8 wt% silver, 2.98 wt% bismuth, 0.7 wt% copper, 0.1 wt% nickel, 0.01 wt% titanium, and the balance tin together with unavoidable impurities. The as cast microstructure (Figure 3(a)) consists of large concentration of finer Ag<sub>3</sub>Sn precipitates dispersed along the grain boundaries, which is expected to prevent grain boundary sliding during creep and thus improving creep resistance of the alloy. Significant growth of the precipitates is observed after aging at 150°C for about 200 hours (Figure 3(b)).

Alloy C has a melting range of 210.4 to 215.9°C; a coefficient of thermal expansion CTE (µm/mK) (30-100°C) of 23.8; and a Vickers Hardness (HV-1) of 28.

#### Example 4 - Alloy D

Alloy D comprises 3.85% silver, 3.93% bismuth, 0.68% copper, 0.22% nickel, 0.078% cerium, and the balance tin together with unavoidable impurities. This alloy microstructure  
5 (figure 4(a)) reveals long needle-shaped  $\text{Ag}_3\text{Sn}$  along with  $\text{Cu}_6\text{Sn}_5$  precipitates.

Alloy D has a melting range of 209.0 to 220.4°C; a coefficient of thermal expansion CTE ( $\mu\text{m}/\text{mK}$ ) (30-100°C) of  
10 22; and a Vickers Hardness (HV-1) of 29.

#### Example 5 - Alloy E

Alloy E comprises 3.86% silver, 3.99% bismuth, 0.63% copper,  
15 0.16% nickel, 0.043% titanium, and the balance tin together with unavoidable impurities. It has a melting range of 209.3 to 220.6°C; and Vickers Hardness (HV-1) of 30.

#### Example 6 - Alloy F

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Alloy F comprises 3.82% silver, 3.96% bismuth, 0.6% copper, 0.16% nickel, 0.042% cobalt, and the balance tin together with unavoidable impurities. It has a melting range of 209.1 to 216.1°C; and a coefficient of thermal expansion CTE  
25 ( $\mu\text{m}/\text{mK}$ ) (30-100°C) of 22.4.

#### Example 7 - Alloy G

Alloy G comprises 3.9% silver, 3% bismuth, 0.6% copper,  
30 0.12% nickel, 0.006% manganese, and the balance tin together with unavoidable impurities. It has a melting range of 209.2 to 216.8°C; and a Vickers Hardness (HV-1) of 28.

Example 8 - Alloy H

Alloy H comprises 3.83% silver, 3.93% bismuth, 0.63% copper,  
0.15% nickel, 0.006% germanium, and the balance tin together  
5 with unavoidable impurities. It has a melting range of 208.2  
to 218.6°C; a coefficient of thermal expansion CTE ( $\mu\text{m}/\text{mK}$ )  
(30-100°C) of 21.7; and a Vickers Hardness (HV-1) of 29.

Example 9 - Alloy I

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Alloy I comprises 4.20% silver, 3.99% bismuth, 0.63% copper,  
0.18% nickel, 3.22% indium, and the balance tin together  
with unavoidable impurities. It has a melting range of 195.6  
to 210.7°C.

15

Example 10 - Alloy J

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Alloy J comprises 3.91% silver, 2.9% bismuth, 0.72% copper,  
0.2% nickel, 0.04% cerium, and the balance tin together with  
unavoidable impurities. It has a melting range of 209.8 to  
217.0°C; a coefficient of thermal expansion CTE ( $\mu\text{m}/\text{mK}$ ) (30-  
100°C) of 22.7; and a Vickers Hardness (HV-1) of 27.

Example 11 - Alloy K

25

Alloy K comprises 3.87% silver, 3.02% bismuth, 0.61% copper,  
0.14% nickel, 0.038% lanthanum, and the balance tin together  
with unavoidable impurities. It has a melting range of  
210.96 to 220.8°C; and a Vickers Hardness (HV-1) of 29.

30

Example 12 - Alloy L

Alloy L comprises 3.86% silver, 3.99% bismuth, 0.64% copper, 0.14% nickel, 0.044% neodymium, and the balance tin together with unavoidable impurities. It has a melting range of 207.8 to 219.5°C; and a Vickers Hardness (HV-1) of 29.

5

Example 13 - Alloy M

Alloy M comprises 3.94% silver, 3.92% bismuth, 0.7% copper, 0.12% nickel, 0.023% cobalt, and the balance tin together  
10 with unavoidable impurities. It has a melting range of 209 to 217°C; and a coefficient of thermal expansion CTE ( $\mu\text{m}/\text{mK}$ ) (30-100°C) of 22.6.

Table 1 shows the solidus and liquidus temperatures of  
15 SnAg3.0Cu0.5 and Alloys A - M. Solidus temperatures are lower than the near eutectic temperature of the conventional SnAg3.0Cu0.5 alloy for all Alloys A - M. Liquidus temperatures of Alloys A - M and conventional SnAg3.0Cu0.5 alloy are nearly the same.

20

| <b>Alloys</b> | <b>Solidus Temperature<br/>(°C)</b> | <b>Liquidus<br/>Temperature (°C)</b> |
|---------------|-------------------------------------|--------------------------------------|
| SnAg3.0Cu0.5  | 216.6                               | 219.7                                |
| A             | 207.2                               | 215.9                                |
| B             | 208.8                               | 219.4                                |
| C             | 210.4                               | 215.9                                |
| D             | 209.0                               | 220.4                                |
| E             | 209.3                               | 220.6                                |
| F             | 209.1                               | 216.1                                |
| G             | 209.2                               | 216.8                                |
| H             | 208.2                               | 218.6                                |
| I             | 195.6                               | 210.7                                |

|   |       |       |
|---|-------|-------|
| J | 209.8 | 217.0 |
| K | 211.0 | 220.8 |
| L | 207.8 | 219.5 |
| M | 209.0 | 217.0 |

**Table 1 - Solidus Temperatures and Liquidus Temperatures of SnAg3.0Cu0.5 and Alloys A - M.**

5 Figure 5 shows a comparison of (a) ultimate tensile strength, and (b) yield strength at room temperature for SnAg3.0Cu0.5 and alloys according to the present invention (see ASTM E8/E8M-09 for test methods of tensile measurements). The tensile properties at room temperature  
10 show a significant improvement. In particular, the ultimate tensile strengths at room temperature for Alloys A, B, C, D, E, F, I, J, K and L are between 60% and 110% higher than that of SnAg3.0Cu0.5. The yield strength shows similar increase in strength of these alloys, showing between 40%  
15 and 81% improvement over SnAg3.0Cu0.5.

Figure 6 shows a comparison of (a) ultimate tensile strength, and (b) yield strength at 150°C for SnAg3.0Cu0.5 and alloys according to the present invention (see ASTM  
20 E8/E8M-09 for test methods of tensile measurements). The ultimate tensile strength and yield strength decrease at 150°C. However, the superior properties of Alloys A, B and C over SnAg3.0Cu0.5 remain. Both properties show about 30 to 43% improvement when compared to SnAg3.0Cu0.5.

25

Testing of the creep properties evaluates the change in deformation (elastic and plastic) over a relatively long time. In the case of high temperature creep, the phenomena

of microstructure strengthening alternates with the stress relief caused due to microstructure annealing.

Figure 7 shows a comparison of (a) creep rupture time and (b) creep elongation at rupture measured at 150°C of SnAg3.0Cu0.5 and alloys according to the present invention (see ASTM E139 for test methods of creep measurements). The alloys of the present invention have significantly higher creep strength, which is given by the creep rupture time and creep total plastic strain, than SnAg3.0Cu0.5. For example, the creep strength at 150°C of Alloy C is 141% higher than of SnAg3.0Cu0.5. Similar trend was observed for the creep elongation at rupture, which for Alloy C is 76% than SnAg3.0Cu0.5.

Figure 8 shows zero wetting time of SnAg3.0Cu0.5 and new alloys as a measure of their solderability and wettability (see JIS Z 3198-4 for test method of wetting balance measurements). Wetting properties of alloys according to the present invention are comparable to conventional SnAg3.0Cu0.5 alloy.

Intermetallics formation due to alloying addition in the alloys according to the present invention resulted in additional strength of the bulk alloy and the solder joint. So far, this has been exemplified here through tensile, hardness and creep measurements. Next, drop shock and thermal cycling performance of the alloys according to the present invention are compared to standard SnAg3.0Cu0.5.

Figure 9 shows the Weibull distribution curves describing BGA failures during drop shock test (see JESD22-B111 for test method of drop shock testing). Alloys A, B and C have

about 37%, 23% and 44% drop shock improvement of their characteristic life (i.e., at 63% failures level) over SnAg3.0Cu0.5.

5 Figure 10 shows the Weibull distribution curves describing BGA failures during thermal cycling test. Thermal cycle profile used was -40°C to +150°C with 30 minutes dwell time at each temperature (see IPC-9701 for test method of thermal cycling measurements). This test was carried out for a  
10 total of 2000 cycles to evaluate thermal-mechanical fatigue resistance of the new alloys. The reference alloy is represented by a circle, alloy A by a square and alloy C by a diamond symbol. Before the completion of 2000 cycles, 100% of SnAg3.0Cu0.5 BGA and solder paste assemblies has failed.  
15 However, 32% and 40%, respectively, of Alloy A and C BGA and solder paste assemblies have survived the thermal cycling test. Overall, a considerable improvement over SnAg3.0Cu0.5 of the characteristic life (i.e., at 63% failures level) was observed for Alloy C.

20

Figure 11 shows electron microscope images of BGA cross-sections before and after thermal cycling test. Crack initiation in SnAg3.0Cu0.5 was observed after 500 thermal cycles. For the Alloys A and C cracks were observed only  
25 after 1000 thermal cycles. After 1500 cycles, extensive cracks were observed in component using SnAg3.0Cu0.5 BGA and solder paste assembly.

Figure 12 shows shear force of chip resistors components  
30 measured before and after thermal cycling test (see JIS Z3198-7 for test methods of shear force measurements). After 1000 thermal cycles, the force necessary to shear a 1206 chip resistor bonded to the PCB using Alloy A or C is 70%

higher than using SnAg3.0Cu0.5 alloy. These results corroborate the superior thermal cycling performance of the new alloys.

- 5 Accordingly, the alloy compositions exhibit improved room-temperature and also elevated temperature mechanical properties compared to the conventional alloy, SnAg3.0Cu0.5. These alloy compositions have also demonstrated solderability and wettability comparable to SnAg3.0Cu0.5.
- 10 Additionally, these alloy compositions have shown improved drop shock resistance and superior thermal-mechanical reliability compared to conventional SnAg3.0Cu0.5 alloy.

- The foregoing detailed description has been provided by way
- 15 of explanation and illustration, and is not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments illustrated herein will be apparent to one of ordinary skill in the art, and remain within the scope of the appended claims and their
- 20 equivalents.

**CLAIMS**

1. A lead-free, antimony-free solder alloy comprising:

1 to 10 wt.% of silver  
1 to 10 wt.% of bismuth  
0.1 to 3 wt.% of copper  
0.01 to 1 wt.% of nickel  
0.005 to 1 wt.% of germanium

optionally one or more of the following elements

up to 3.5 wt. % of indium  
up to 1 wt. % of zinc  
0 to 1 wt. % of chromium  
0 to 1 wt.% of iron  
0 to 1 wt.% of aluminum  
0 to 1 wt.% of phosphorus  
0 to 1 wt.% of gold  
0 to 1 wt.% of gallium  
0 to 1 wt.% of tellurium  
0 to 1 wt.% of selenium  
0 to 1 wt.% of calcium  
0 to 1 wt.% of vanadium  
0 to 1 wt.% of molybdenum  
0 to 1 wt.% of platinum  
0 to 1 wt.% of magnesium  
0 to 1 wt.% of rare earths

the balance tin, together with any unavoidable impurities.

2. The solder alloy according to claim 1, wherein the alloy comprises:
  - from 2.5 to 5 wt.% of silver;
  - from 2 to 6 wt.% of bismuth;
  - from 0.1 to 3 wt.% of copper;
  - from 0.03 to 0.6 wt.% of nickel;
  - from 0.005 to 1.0 wt.% germanium,
  - the balance tin, along with any unavoidable impurities.
3. The solder alloy according to claim 1, wherein the alloy comprises:
  - from 3.0 to 5 wt.% of silver;
  - from 2.5 to 5 wt.% of bismuth;
  - from 0.3 to 2.0 wt.% of copper;
  - from 0.05 to 0.5 wt.% of nickel;
  - from 0.005 to 1.0 wt.% germanium,
  - the balance tin, along with any unavoidable impurities.
4. The solder alloy according to claim 1, wherein the alloy can withstand operational temperatures of at least 150 °C.
5. The solder alloy according to claim 1, wherein the alloy exhibits improved mechanical properties compared to SnAg3.0Cu0.5 alloy.
6. The solder alloy as claimed in claim 1 or 2 in the form of a bar, a stick, a solid or flux cored wire, a foil or strip, or a powder or paste (powder plus flux blend), or solder spheres for use in ball grid array joints or chip scale packages, or other

pre-formed solder pieces, with or without a flux core or a flux coating.

7. A soldered joint comprising an alloy as defined in claim 1 or 2.

8. A method of forming a solder joint comprising:

(i) providing two or more work pieces to be joined;

(ii) providing a solder alloy as defined in claim 1 or 2;

and

(iii) heating the solder alloy in the vicinity of the work pieces to be joined.

9. Use of an alloy composition as defined in claim 1 or 2 in a soldering method such as wave soldering, Surface Mount Technology (SMT) soldering, die attach soldering, thermal interface soldering, hand soldering, laser and RF induction soldering, and rework soldering, lamination.

10. The solder alloy according to claim 2, wherein the alloy comprises 0.005 to 0.05 wt.% germanium.