

HIGH STRENGTH LEAD-FREE SOLDER MATERIALS**Field of the Invention**

The present invention relates to tin-based, lead-free solder alloys that have broad-based applications because of a low liquidus temperature and high strength. They are useful as metal joining materials, particularly for interconnections in electronics and microelectronics circuitry applications. Importantly, the compounds of the present invention replace toxic, lead-containing solders and thereby improve worker safety and allow for environmentally-friendly manufacturing processes to be performed. Furthermore, the materials of the present invention provide improved strength to meet the increased demands on the level of performance of the interconnecting material required in future microchip circuitry.

Description of the Art

Lead-containing solder alloys have been successfully used in electronics packaging as interconnecting materials for decades, connecting components electrically, thermally, and mechanically. For electronic printed circuitry, near-eutectic Sn-Pb solders have been chosen due to their good manufacturability and wetting behavior on typical substrates. However, due to the increased density of circuitry and power dissipation, stronger solders are currently required. In addition, the legislative mandate to eliminate or tax the use of lead because of environmental/health concerns is another powerful driving force to develop lead-free alloys.

In order to replace lead in solders, the new alloys must possess phase transition temperatures (liquidus and solidus temperatures) that are comparable to lead-containing solders. In addition, lead-free solders must have suitable physical characteristics, including acceptable electrical and thermal conductivities and thermal expansion coefficients. Furthermore, the lead-free solders must be metallurgically compatible with the substrates of components and boards, and must have acceptable mechanical properties and environmental shelf stability.

Some lead-free solder alloy compositions are known (see textbook: Jennie S. Hwang, *Modern Solder Technology for Competitive Electronics Manufacturing*, Mc-Graw Hill, New York, 1996, pp. 483-508), however, these compositions are deficient due to inferior strengths, incompatible physical properties, or inadequate natural resources of major constitutional elements. One particular known lead-free solder composition is comprised of Sn-Zn-In alloys that may also contain Cu (U.S. Patent No. 5,538,686), however, the combined solid solution and dispersion strengthening in this compound is inadequate.

Summary of the Invention

Accordingly, it is a primary object of this invention to provide a new and improved solder composition.

It is an advantage of this invention to provide a new and improved solder composition that is free of lead, providing the associated safety and avoiding significant environmental problems.

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An additional advantage of the present invention is that the solder composition has physical attributes equivalent or superior to traditional lead containing solders.

Additional objects and advantages of the invention will be set forth in part in the description which follows and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

To achieve the foregoing objects and in accordance with the purpose of the invention, as embodied and broadly described herein, the solder composition of this invention is comprised of a lead-free alloy including tin, copper and gallium. In addition, the alloy may further include indium, zinc, selenium and/or tellurium. Preferably, tin will comprise at least about 75 weight percent of the alloy composition. Preferably, the copper will comprise between 0.1 and 9.5 weight percent and gallium between 0.01 and 5.0 weight percent of the alloy. More preferably, the tin will comprise at least 85 weight percent of the alloy. More preferably, copper will comprise between 0.3 and 4.5 weight percent and gallium between 0.05 and 1.0 weight percent of the alloy composition.

In an additional preferred form of the invention, the solder will be comprised of between 0 and 6 percent by weight indium; between 0 and 9 weight percent zinc; and either selenium or tellurium in an amount between 0 and 1.0 weight percent. In a particularly preferred embodiment, indium is present in the alloy composition between 0.1 and 10.0

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weight percent. In an additional preferred embodiment by the invention, at least indium and zinc (between 1.0 and 19.0 weight percent) are present in the alloy composition.

In an alternative embodiment of the invention, the lead-free solder alloy composition is comprised of tin, copper or silver, and indium and may optionally contain either selenium or tellurium. In addition, the composition may optionally contain zinc, gallium or bismuth. Preferably, the composition will contain at least 75 weight percent Sn, between .1 and 9.5 weight percent Cu and/or .1 and .8 weight percent Ag, and between .1 and 10.0 weight percent In.

In a further alternative embodiment of the invention, the lead-free alloy composition is comprised of tin, silver, bismuth, either selenium or tellurium, and may optionally contain gallium. Preferably, the composition will include at least 75 weight percent Sn, between 0.5 and 6.5 weight percent Ag, between 0.5 and 8.0 weight percent Bi, and between 0.1 and 5.0 weight percent of Se and/or Te.

Detailed Description of the Invention

Lead-free solder alloys containing Sn (at least 75.0 and preferably 85.0 wt. %), Cu (between 0.3 and 4.5 wt. %) and Ga (between 0.05 and 1.0 wt. %) have tensile properties (according to ASTM B8-96) exceeding 40 MPa, preferably 45 MPa and more preferably 50 MPa. For a variety of purposes such as further increasing the strength or decreasing the liquidus temperature, the alloys may also contain one or more of the following elements: In (not more than 6.0 wt. %), Zn (not more than 9.0 wt. %), either Se or Te (not more than

1.0 wt. %). More particularly, each of the inventive solder alloys described herein provides these tensile properties. Moreover, lead-free solder alloys, of this invention, have tensile properties exceeding those of traditional 60 Sn/40Pb (weight percent) alloys. For a variety of purposes, such as further increasing the strengths, the alloys may also contain Sr, Te, or Zn.

Lead-free solder alloys containing Sn (at least 85.0 wt. %), Cu (between 0.3 and 4.5 wt. %), Ga (between 0.05 and 1.0 wt. %), In (between 1.0 and 6.0 wt. %), and Zn (between 8.0 and 9.0 wt. %) have tensile properties significantly exceeding those of traditional 60Sn-40Pb (wt. %) alloys. For purposes such as further increasing the strength, the alloys may also contain up to 1.0 wt. % of either Se or Te.

Lead-free solder alloys containing Sn (at least 90.0 wt. %), Cu (between 2.0 and 5.0 wt. %), and In (between 1.0 and 6.0 wt. %) have tensile properties exceeding those of traditional 60Sn-40Pb (wt. %) alloys. For purposes such as further increasing the strength, the alloys may also contain up to 1.0 wt. % of either Se or Te.

Lead-free solder alloys containing Sn (at least 85.0 wt. %), Ag (between 0.1 and 0.8 wt. %), and In (between 1.0 and 6.0 wt. %) have tensile properties significantly exceeding those of traditional 60Sn-40Pb (wt. %) alloys. For a variety of purposes such as further increasing the strength or decreasing the liquids temperature, the alloys may also contain one or more of the following elements: Zn (not more than 9.0 wt. %), Ga (not more than 1.0 wt. %), either Se or Te (not more than 1.0 wt. %).

Lead-free solder alloys containing Sn (at least 85.0 wt. %), Ag (between 1.5 and 4.5 wt. %), Bi (between 1.0 and 8.0 wt. %), and either Se or Te (between 0.05 and 1.0 wt. %) have tensile properties significantly exceeding those of traditional 60Sn-40Pb (wt. %) alloys. For a variety of purposes such as further increasing the strength or decreasing the liquidus temperature, the alloys may also contain up to 1.0 wt. % Ga.

Lead-free solder alloys containing Sn (at least 85.0 wt. %), Ag (between 1.5 and 4.5 wt. %), In (between 1.0 and 6.0 wt. %), Bi (between 1.0 and 8.0 wt. %), and either Se or Te (between 0.05 and 1.0 wt. %) have tensile properties significantly exceeding those of traditional 60Sn-40Pb (wt. %) alloys. For a variety of purposes such as further increasing the strength or decreasing the liquidus temperature, the alloys may also contain up to 1.0% Ga.

Lead-free solder alloys containing Sn (at least 85.0 wt. %), Ag (between 1.5 and 4.5 wt. %), In (between 1.0 and 6.0 wt. %), Bi (between 1.0 and 8.0 wt. %), and Ga (between 0.05 and 1.0 wt. %) have tensile properties significantly exceeding those of traditional 60Sn-40Pb (wt. %) alloys.

Examples

The following examples are provided to help demonstrate the invention but are not intended to limit the scope thereof.

Example 1

Casting of a 60Sn-40Pb (wt. %) alloy was conducted by placing an inert container containing the alloying elements in a box furnace and heating the furnace to the anticipated melting temperature. The container was sealed with a lid that provided access to a thermocouple and a tube supplying argon to protect the melt from oxidation. The melt was periodically stirred to improve homogeneity and finally poured into an aluminum mold to provide tensile specimens. Room temperature tensile tests were conducted at a test speed of 1 mm min^{-1} . A 0.2% offset yield strength of 30 MPa and an ultimate tensile strength of 37 MPa were measured. A 95.3Sn-4.0Cu-0.5Ga-0.2Se (wt. %) alloy was prepared and tested in substantially the same manner as described above. A 0.2 % offset yield strength of 42 MPa (exceeding the yield strength of the 60Sn-40Pb (wt. %) alloy by 40%) and an ultimate tensile strength of 49 MPa (exceeding the tensile strength of the 60Sn-40Pb (wt. %) alloy by 32%) were determined.

Example 2

A 91.1Sn-3.9Cu-1.0Ga-4.0In (wt. %) alloy was prepared and tested in substantially the same manner as described in Example 1. A 0.2% offset yield strength and an ultimate tensile strength of both 48 MPa (exceeding the yield strength and the ultimate tensile strength of the 60Sn-40Pb (wt. %) alloy by 60% and 30%, respectively) were determined.

Example 3

An 86.2Sn-0.7Cu-0.5Ga-4.0In-8.6Zn (wt. %) alloy was prepared and tested in substantially the same manner as described in Example 1. A 0.2% offset yield strength of 63 MPa (exceeding the yield strength of the 60Sn-40Pb (wt. %) alloy by 110% and the yield strength of 86.0Sn-5.0In-9.0Zn alloy (55 MPa) by 15%) and an ultimate tensile strength of

73 MPa (exceeding the tensile strength of the 60Sn-40Pb (wt. %) alloy by 97% and the tensile strength of 86.0Sn-5.0In-9.0Zn alloy (62 MPa) by 18%)) were determined.

Example 4

92.8Sn-3.0Cu-4.0In-0.2Se (wt. %) and 91.8Sn-4.0Cu-4.0In-0.2Se (wt. %) alloys were prepared and tested in substantially the same manner as described in Example 1. A 0.2% offset yield strength of 40 and 46 MPa, respectively (exceeding the yield strength of the 60Sn-40Pb (wt. %) alloy by 33 and 53 %), and an ultimate tensile strength of 47 and 48 MPa, respectively (exceeding the tensile strength of the 60Sn-40Pb (wt. %) alloy by 27 and 30 %), were determined.

Example 5

An 86.9Sn-0.5Ag-4.0In-8.6Zn (wt. %) alloy was prepared and tested in substantially the same manner as described in Example 1. A 0.2% offset yield strength of 56 MPa (exceeding the yield strength of the 60Sn-40Pb (wt. %) alloy by 87%) and an ultimate tensile strength of 64 MPa (exceeding the tensile strength of the 60Sn-40Pb (wt. %) alloy by 73 %) were determined.

Example 6

An 89.9Sn-3.1Ag-6.5Bi-0.5Se (wt. %) alloy was prepared and tested in substantially the same manner as described in Example 1. A 0.2% offset yield strength of 60 MPa

(exceeding the yield strength of the 60Sn-40Pb (wt. %) alloy by 100%) and an ultimate tensile strength of 82 MPa (exceeding the tensile strength of the 60Sn-40Pb (wt. %) alloy by 122%) were determined.

Example 7

87.8Sn-3.2Ag-4.0In-4.5Bi-0.5Se (wt. %) and 87.3Sn-3.2Ag-4.0In-4.5Bi-1.0Se (wt. %) alloys were prepared and tested in substantially the same manner as described in Example 1. A 0.2% offset yield strength of 72 and 64 MPa, respectively (exceeding the yield strength of the 60Sn-40Pb (wt. %) alloy by 140 and 113 %), and an ultimate tensile strength of 84 and 77 MPa, respectively (exceeding the tensile strength of the 60Sn-40Pb (wt. %) alloy by 127 and 108 %), were determined.

Example 8

An 87.5Sn-3.2Ag-4.0In-4.5Bi-0.8Ga (wt. %) alloy was prepared and tested in substantially the same manner as described in Example 1. A 0.2% offset yield strength of 75 MPa (exceeding the yield strength of the 60Sn-40Pb (wt. %) alloy by 150%) and an ultimate tensile strength of 77 MPa (exceeding the tensile strength of the 60Sn-40Pb (wt. %) alloy by 108%) were determined.

Thus it is apparent that there has been provided, in accordance with the invention, a lead-free solder alloy composition that fully satisfies the objects, aims and advantages set forth above. While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such modifications, and variations as fall within the spirit and broad scope of the appended claims.

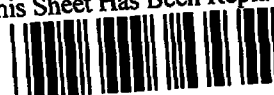
We claim:

1. A lead-free alloy solder composition comprised of Sn, Cu, and Ga.
2. The lead-free alloy composition of claim 1 including at least about 75 weight percent Sn, between about 0.1 and 9.5 weight percent Cu, and between about .01 and 5.0 weight percent Ga.
3. The solder of claim 1, wherein the alloy also includes an element selected from the group consisting of In, Zn, Se and Te or mixtures thereof.
4. The solder to claim 1, wherein the alloy also includes one or more of the following elements: between about 0 and 6.0 weight percent In, between about 0 and 9.0 weight percent Zn, and either Se or Te in an amount of not greater than 1.0 weight percent.
5. A lead-free solder composition comprising an alloy of at least about 75.0 wt % Sn, between about 0.1 and 9.5 wt. % Cu, between about 0.01 and 5.0 wt. % Ga, and between about 0.1 and 10.0 wt. % In.
6. The solder composition of claim 5, wherein the alloy may also include one or more of Se and Te in an amount of between greater than 0 and 5.0 wt. %.

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7. A solder composition, comprised of a lead-free alloy including at least about 75.0 wt. % Sn, between about 0.1 and 9.5 wt. % Cu, between about 0.01 and 5.0 wt. % Ga, between about 0.1 and 10.0 wt. % In, and between about 1.0 and 19.0 wt. % Zn.

8. The solder of claim 7, wherein the alloy may also include between greater than 0 and 5.0 weight percent of either Se or Te.

9. A solder composition, consisting essentially of a lead-free alloy including at least 75.0 wt. % Sn, between about .1 and 9.5 wt. % Cu, and between about .1 and 10.0 wt. % In.

10. A solder composition comprised of a lead-free alloy including, at least about 75.0 weight percent Sn, between about 0.1 and 9.5 weight percent Cu, between about 0.1 and 10.0 weight percent In, and without the inclusion of Ag.

11. The solder of claim 10, wherein the alloy also includes between greater than 0 and 5.0 wt. % of either Se or Te.

12. A solder composition, comprised of a lead-free alloy including at least about 75.0 wt. % Sn, between about 0.1 and 0.8 wt. % Ag, and between about 0.1 and 10.0 wt. % In.

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13. The solder of claim 12, wherein the alloy may also include one or more of the following elements: Zn in an amount of not greater than about 9.0 wt. %, Ga in an amount of not greater than about 1.0 wt. %, either Se or Te in an amount of not greater than about 1.0 wt. %.

14. A solder composition comprised of a lead-free alloy including at least about 75.0 wt. % Sn, between about 0.5 and 6.5 wt. % Ag, between about 0.5 and 8.0 wt. % Bi, and between about 0.01 and 5.0 wt. % of either Se or Te.

15. The solder of claim 14, wherein the alloy also includes from greater than about 0 to about 5.0 wt. % Ga.

16. A solder composition, comprising a lead-free solder alloy containing at least about 75.0 wt. % Sn, between about .5 and 6.5 wt. % Ag, between about .1 and 10.0 wt. % In, between about .5 and 8.0 wt. % Bi, and between about .01 and 5.0 wt. percent of either Se or Te.

17. An article according to claim 16, wherein the alloy may also contain up to about 5.0 wt. % Ga.

18. A solder composition, comprising a lead-free solder alloy containing at least about 75.0 wt. % Sn, between about .5 and 6.5 wt. % Ag, between about .1 and 10.0 wt. % In, between about .5 and 8.0 wt. % Bi, and between about 0.01 and 5.0 wt. % Ga.



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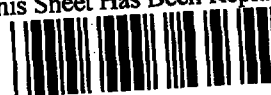
19. An article comprised of the solder of claim 1 in the form of a paste, cream, preform, wire, ribbon or bar.

20. A solder composition comprised of a lead-free alloy including at least about 75 weight percent Sn, between about 0.1 and 8.0 weight percent Ag, between about 0.1 and 10.0 weight percent In, and the absence of Co.

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HIGH STRENGTH LEAD-FREE SOLDER MATERIALS**ABSTRACT**

Disclosures are lead-free solder alloys having tensile properties exceeding those of near-eutectic 60Sn-40Pb (wt. %) alloys. The alloys are based on the Sn-Cu-Ga, Sn-Cu-Ga-In, Sn-Cu-Ga-In-Zn, Sn-Cu-In, Sn-Ag-In, Sn-Ag-Bi-Se/Te, Sn-Ag-In-Bi-Se/Te, and Sn-Ag-In-Bi-Ga systems.

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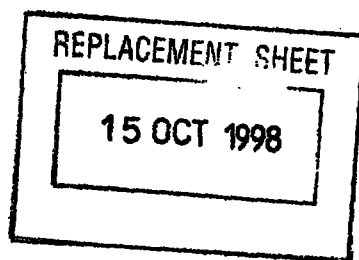




TEXT OF THE ABSTRACT

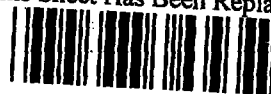
HIGH STRENGTH LEAD-FREE SOLDER MATERIALS

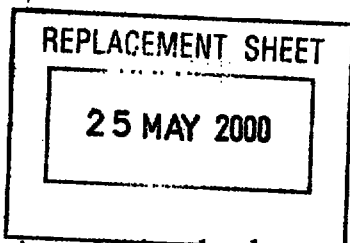
Disclosures are lead-free solder alloys having tensile properties exceeding those of neareutectic 60 Sn-40 Pb (wt.%) alloys. The alloys are based on the Sn-Cu-Ga, Sn-Cu-GA-In and Sn-Cu-Ga-In-Zn Systems.



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An additional advantage of the present invention is that the solder composition has physical attributes equivalent or superior to traditional lead containing solders.

Additional objects and advantages of the invention will be set forth in part in the description which follows and in part will be obvious from the description, or may be learned by practice of the invention. The object and advantages of the invention may be realised and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

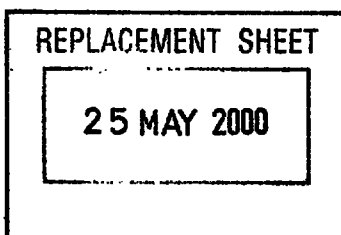
To achieve the foregoing objects and in accordance with the purpose of the invention, as embodied and broadly described herein, the solder composition of this invention is comprised of a lead-free alloy including tin, copper, gallium and indium. Tin comprises at least about 75 weight percent of the alloy composition, the copper between 0.1 and 9.5 weight percent, the gallium between 0.01 and 5.0 weight percent and the indium between greater than 0 and about 6 weight percent.

Preferably, the tin comprises at least 85 weight percent of the alloy copper between 0.3 and 4.5 weight percent and gallium between 0.05 and 1.0 weight percent.

In embodiments of the invention, the alloy may further include zinc, selenium and/or tellurium. Preferably, the solder may comprise between 0 and 9 percent zinc and either selenium or tellurium in an amount between 0 and 1.0 weight percent.

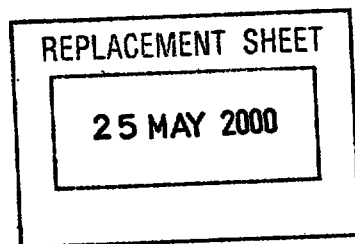
Detailed Description of the Invention

Lead-free solder alloys containing Sn (at least 75.0 and preferably 85.0 wt. %), Cu (between 0.3 and 4.5 wt. %) and Ga (between 0.05 and 1.0 wt. %) have tensile properties (according to ASTM E8-96) exceeding 40 MPa, preferably 45 MPa and more preferably 50 MPa. For a variety of purposes such as further increasing the strength or decreasing the liquidus temperature, the alloys may also contain one or more of the following elements: In (not more than 6.0 wt %), Zn (not more than 9.0 wt. %), either Se or Te (not more than



CLAIMS

1. A lead-free alloy solder composition comprising at least about 75 weight percent Sn, between about 0.1 and 9.5 weight percent Cu, between about 0.01 and 5 weight percent Ga and between greater than 0 and about 6 weight percent In, the composition having a tensile strength of at least 48Mpa.
2. The composition of Claim 1 including at least 85% weight percent Sn, between 0.3 and 4.5 weight percent Cu and between 0.05 and 1.0 weight percent Ga.
3. The composition of Claim 1 or 2 including between about 0 and 9.0 weight percent Zn, and either Se or Te in an amount of not greater than 1.0 weight percent.
4. An article comprising a paste, cream, preform, wire, ribbon or bar made of the composition of any one of Claim 1 to 3.



HIGH STRENGTH LEAD-FREE SOLDER MATERIALS

ABSTRACT

Disclosures are lead-free solder alloys having tensile properties exceeding those of near-eutectic 60Sn-40Pb (wt. %) alloys. The alloys are based on the Sn-Cu-Ga, Sn-Cu-Ga-In, Sn-Cu-Ga-In-Zn, Sn-Cu-In, Sn-Ag-In, Sn-Ag-Bi-Se/Te, Sn-Ag-In-Bi-Se/Te, and Sn-Ag-In-Bi-Ga systems.

