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(54) **HIGH TEMPERATURE LEAD-FREE SOLDER COMPOSITIONS**

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(57) **ABSTRACT**

Disclosed is a high temperature, high performance lead-free solder alloy comprising effective amounts of tin, copper, silver, bismuth, and antimony and having a liquidus temperature above 215° C. More particularly, several lead-free solder alloys are disclosed that comprise about (i) at least about 90% Sn, 0.2 to 5.0% Cu, 0.05 to 5.0% Bi; or (ii) at least about 75% Sn, 0.5 to 7.0% Cu, 0.05 to 18% Sb; or (iii) at least about 67% Sn, 3 to 15% Ag, 0.01 to 18% Sb; (iv) at least about 78% Sn, 0.8 to 7.0% Cu, 4 to 15% Ag; (v) at least about 96% Sn, and at least one of 0.01 to 2.0% Ni, and 0.01 to 2.0% Co; (vi) at least about 90% Sn, 0.05 to 5.0% Bi, and 0 to 5.0% Sb; and (vii) at least about 90% Sn, 0.2 to 0.9% Cu, and 0.1 to 5.0% Bi.

HIGH TEMPERATURE LEAD-FREE SOLDER COMPOSITIONS

CROSS REFERENCES TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part application of U.S. application Ser. No. 10/056,667 filed Oct. 29, 2001 and claims priority upon U.S. Provisional application Ser. No. 60/244,506 filed Oct. 31, 2000 and U.S. Provisional application Ser. No. 60/243,796 filed Oct. 27, 2000.

FIELD OF THE INVENTION

[0002] The present invention relates to lead-free solder alloys that provide high temperature performance for micro-electronics and various other electronic applications. More particularly, the present invention relates to lead-free compositions containing effective amounts of tin, copper, silver, bismuth, antimony and which exhibit a melting temperature (liquidus temperature) above 225° C.

[0003] The present invention also relates to a surprising and unexpected discovery concerning the effect of bismuth in lead-free tin-copper compositions.

BACKGROUND OF THE INVENTION

[0004] Lead-containing solder alloys face a limited future due to lead toxicity and the control or prohibition of the use of lead on a global basis. Consequently, many efforts around the world have been undertaken to find suitable lead-free alternatives to Pb—Sn solder alloys. Some low and moderate temperature alloys (having melting temperatures below 215° C.) have been disclosed in the art. However, there remains a need for Pb-free alloys with a liquidus temperature above 215° C. that can withstand high temperature applications. In addition, there is a particular need for high temperature Pb-free alloys that possess high strength and high fatigue resistance in order to meet increasing performance requirements for solder interconnections as advancements in integrated circuit (IC) and related interconnections are made.

[0005] In electronics manufacturing, solder alloy is used to metallurgically join bare chips or packaged chips onto an adjacent level of a substrate and to connect leadframe or various other leads. This enables electronic devices to be constructed through the formation of a desirable band of intermetallics. In forming reliable solder joints, it is important that the solder alloy readily flows and wets commonly used metallization pads such as Cu, Ag, Au, Pd, Ni and other metallic surfaces in the assembly. These requirements are particularly important in view of today's high-speed automated manufacturing processes that employ mild fluxes that are compatible with electronic systems.

[0006] It would be beneficial to provide a class of solder compositions with a critical physical property, i.e., a high enough melting temperature to accommodate interconnection requirements without approaching a melting state during multiple-step production operations as well as while the product is in service. This high temperature performance is particularly important for chip level interconnections. Exposing solder compositions to temperatures near the melting temperatures of the compositions, causes product malfunction or a catastrophic failure. In order to avoid such

interconnecting disruption and failure, the melting temperature of this class of solder compositions must be above 215° C.

[0007] A Cu—Sn eutectic with a composition of 99.3% Sn, 0.7% Cu is considered a viable Pb-free alloy. However, the strength and fatigue resistance of the Cu—Sn eutectic is significantly inferior to 63 Sn/37 Pb that has been most widely used in electronic assemblies, particularly surface mount printed circuit boards. It would be desirable to provide a new class of solder compositions that exhibit dramatically increased strength and fatigue life as compared to currently known comparable solder compositions.

[0008] Solder joints perform as electrical, thermal, and mechanical interconnections in many electronic systems such as telecommunication, computer, avionics and automotive electronics. During the service life of electronic components, solder joints are inevitably exposed to thermal stresses as the result of temperature fluctuation, power on/off switching, and/or harsh environmental conditions. This coupled with mis-matched thermal expansion characteristics in the interconnected materials of semiconductor, ceramic, metal, and polymeric materials in the system, may result in thermo-mechanical fatigue in solder joints. Furthermore, as electronic circuitry becomes increasingly denser and the clock speed of microprocessors continues to reach ever-higher frequencies, one of the design objectives of electronic systems is increased heat dissipation.

[0009] In addition, the number of solder joints on each printed circuit board (PCB) continues to rise. The presence of several thousands or tens of thousands of solder joints in a typical electronic circuit is not uncommon. As will be appreciated, a single solder joint failure can result in a failed system. Consequently, requirements on the higher liquidus temperature along with the desired strength and fatigue resistance of solder joints are heightened. The recent developments in high pin count integrated circuit (IC) packages such as ball grid array (BGA), chip scale package (CSP), and direct-chip-attach technologies such as "flip chip" further demand higher performance in fatigue resistance for solder alloys.

[0010] A number of lead-free solders have been proposed in the art. A summary of these lead-free alloys is outlined in Chapter 15 of the book "Modern Solder Technology for Competitive Electronics Manufacturing", authored by Dr. J. S. Hwang and published by McGraw-Hill. Although satisfactory in many respects, these alloys do not exhibit high enough liquidus temperatures to satisfy high temperature performance either during multiple-step circuitry manufacturing or for certain end-use applications. Therefore, there is an acute need for a new class of lead-free solder compositions that exhibit a melting point of at least 215° C. and/or that exhibit improved strength and fatigue resistance over comparable currently known solder compositions.

SUMMARY OF THE INVENTION

[0011] Accordingly, it is a primary object of the present invention to provide a lead-free solder. It is an advantage of this invention to provide a lead-free solder that is capable of withstanding the high temperature production steps and/or exposure to high temperatures in microelectronic and electronic applications.

[0012] It is a further advantage of this invention to provide a lead-free solder that has a melting temperature range above 215° C., and particularly, above 225° C.

[0013] It is a further advantage of this invention to provide a lead-free solder that is readily adaptable to established or conventional electronic manufacturing processes and infrastructure without requiring major changes in materials, processes and components.

[0014] It is a further advantage of this invention to provide a lead-free solder that offers high-strength and high fatigue resistance. Such characteristics would enable the solder to withstand the increasingly adverse and harsh conditions associated with many microelectronic and electronic applications.

[0015] Additional objects and advantages of the invention will be set forth in part in the description which follows.

[0016] To achieve the foregoing objects and in accordance with this invention, as embodied and broadly described herein, the solder alloys of this invention have Sn as a major constituent and effective amounts of Cu, Ag, Bi, or Sb. The solder demonstrates compatible and desired melting temperature, good strength and fatigue resistance. The solder alloys of this invention also exhibit significant improvements in strength by using Bi as a doping constituent in the Cu—Sn matrix. The solder exhibits compatible high melting temperature, high strength, and high fatigue resistance.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] While the present invention will be described in connection with several preferred embodiments, it will be understood that such description is not intended to limit the invention to those embodiments.

[0018] The present invention provides a high temperature, high performance lead-free solder alloy that exhibits a melting temperature that is compatible with established component and circuitry manufacturing techniques. The preferred solder alloys are as follows:

[0019] (i) at least about 90% Sn, 0.2 to 5.0% Cu, and 0.05 to 5.0% Bi;

[0020] (ii) at least about 75% Sn, 0.5 to 7.0% Cu, and 0.05 to 18% Sb;

[0021] (iii) at least about 67% Sn, 3 to 15% Ag, and 0.01 to 18% Sb;

[0022] (iv) at least about 78% Sn, 0.8 to 7.0% Cu, and 4 to 15% Ag;

[0023] (v) at least about 96% Sn, at least one of 0.01 to 2.0% Ni, and 0.01 to 2.0% Co;

[0024] (vi) at least about 90% Sn, 0.05 to 5.0% Bi, and 0 to 5.0% Sb; and

[0025] (vii) at least about 90% Sn, 0.2 to 0.9% Cu, and 0.1 to 5.0% Bi.

[0026] All compositions are expressed in weight percent.

[0027] The upper limit of Sn in each of the compositions (i)-(vii) varies with each composition. However, these upper limits are generally as follows. Solder alloy (i) may contain Sn up to about 99%. Solder alloy (ii) may contain Sn up to

about 99%. Solder alloy (iii) may contain Sn up to about 97%. Solder alloy (iv) may contain Sn up to about 96%. Solder alloy (v) may contain Sn up to about 99%. Solder alloy (vi) may contain Sn up to about 99%. Solder alloy (vii) may contain Sn up to about 99%.

[0028] In yet another preferred embodiment of the invention, there is provided a solder alloy containing about 96.0% Sn, 3.0% Cu, and 1.0% Bi. The alloy has a liquidus temperature at 304° C. (a melting temperature from about 225° C. to 304° C.). The tensile strength and fatigue life of the alloy are 55 MPa and 4215 cycles, respectively.

[0029] In another preferred embodiment of the invention, there is provided a solder alloy containing about 82% Sn, 3% Cu, and 15% Sb. The alloy has a liquidus temperature at 295° C. (a melting range from about 240° C. to 295° C.). The tensile strength and fatigue life of the alloy are 87 MPa and 5881 cycles, respectively.

[0030] In a further preferred embodiment of the invention, there is provided a solder alloy containing about 90% Sn and 10% Ag. The alloy has a liquidus temperature at 275° C. (a melting temperature from about 224° C. to 275° C.). The tensile strength and fatigue life of the alloy are 52 MPa and 9821 cycles, respectively.

[0031] In yet another preferred embodiment of the invention, there is provided a solder alloy containing about 85% Sn and 15% Sb. This alloy may contain relatively minor amounts of copper. The alloy has a liquidus temperature at 290° C. (a melting temperature from about 240° C. to 290° C.). The tensile strength and fatigue life of the alloy are 73 MPa and 7619 cycles, respectively.

[0032] In another preferred embodiment of the invention, there is provided a solder alloy containing about 75% Sn, 10% Ag, and 15% Sb. The alloy has a liquidus temperature at 290° C. (a melting temperature from about 235° C. to 290° C.). The tensile strength and fatigue life of the alloy are 98 MPa and 3752 cycles, respectively.

[0033] In a still further preferred embodiment of the invention, there is provided a solder alloy containing about 87% Sn, 3% Cu, and 10% Ag. The alloy has a liquidus temperature at 288° C. (a melting temperature from about 218° C. to 288° C.), and the tensile strength and fatigue life of the alloy are 75 MPa and 4355 cycles, respectively.

[0034] In another preferred embodiment of the invention, there is provided a solder alloy containing about 99.3% Sn, 0.2% Ni, 0.5% Co. The alloy has a liquidus temperature at 231° C., and the tensile strength and fatigue life of the alloy are 42 MPa and 4350 cycles, respectively.

[0035] In another preferred embodiment of the invention, there is provided a solder alloy containing about 98.5% Sn, 1% Bi, 0.5% Sb. The alloy has a liquidus temperature of 232° C., and the tensile strength and fatigue life of the alloy are 36 MPa and 3891 cycles, respectively.

[0036] Preferably, the high temperature lead-free solder materials described herein exhibit liquidus temperatures of at least about 215° C.; and typically greater than about 225° C.; and for certain compositions, greater than about 235° C.; for certain compositions, greater than about 250° C.; for certain compositions, greater than about 265° C.; for certain compositions, greater than about 285° C.; for certain com-

positions, greater than about 300° C.; and for certain compositions; greater than about 305° C.

[0037] Preferably, the high temperature lead-free solder materials described herein exhibit significantly greater strength and/or fatigue life, than a corresponding composition without the noted incorporation of one or more particular elements such as Bi, Sb, or Ag. For certain preferred compositions, the incorporation of the particular element significantly increases tensile strength (and other properties) by amounts of at least 10%, 20%, 30%, 40%, 50%, 75%, 100%, 125%, 150%, 175%, 200%, or more.

[0038] More specifically, the particularly preferred high temperature, lead-free solder compositions described herein exhibit unexpected increases in strength and high temperature properties upon the incorporation of a particular element in the noted proportion(s). The incorporation of the element in each specific solder composition is critical to achieving the combination of the noted high temperature characteristics and the significant strength properties. For example, a particularly preferred solder composition in accordance with the present invention, i.e., at least about 90% Sn, 0.2 to 5.0% Cu, and 0.05 to 5.0% Bi exhibits a liquidus temperature greater than 225° C. and a tensile strength that is at least 20% greater than a corresponding Sn/Cu alloy as a result of the incorporation of the Bi in the noted amounts. The specific range of 0.05 to 5.0% Bi is critical in achieving the noted combination of high temperature and high strength properties. This is entirely unexpected and surprising. In yet another example, a particular preferred solder composition in accordance with the present invention, i.e. at least about 75%, 0.5 to 7.0% Cu, and 0.05 to 18.0% Sb exhibits a liquidus temperature greater than 225° C. and a tensile strength that is at least 20% greater than a corresponding Sn/Cu alloy as a result of the incorporation of Sb in the noted amounts. The specific range of 0.05 to 18.0% Sb is critical in achieving the noted combination of high temperature and high strength properties. This is entirely unexpected and surprising. In yet another example, a particularly preferred solder composition in accordance with the present invention, i.e. at least about 78% Sn, 0.8 to 7.0% Cu, and 4.0 to 15.0% Ag exhibits a liquidus temperature greater than 225° C. and a tensile strength that is at least 20% greater than a corresponding Sn/Cu alloy as a result of the incorporation of the Ag in the noted amounts. The specific range of 4.0 to 15.0% Ag is critical in achieving the noted combination of high temperature and high strength properties. This is entirely unexpected and surprising. In yet a further example, a particular preferred solder composition in accordance with the present invention, i.e. at least about 90% Sn, 0.5 to 5.0% Bi, and 0 to 5.0 Sb exhibits a liquidus temperature greater than 225° C. as a result of the incorporation of the Bi and Sb in the noted amounts. The specific range of 0.05 to 5.0% Bi and 0 to 5.0% Sb is critical in achieving the noted high temperature property. This is entirely unexpected and surprising. In a further example, a particularly preferred solder composition in accordance with the present invention, i.e. at least about 90% Sn, 0.2 to 0.9% Cu, and 0.1 to 5.0% Bi exhibits a liquidus temperature greater than 225° C. and a tensile strength that is at least 20% greater than a corresponding Sn/Cu alloy as a result of the incorporation of the Bi in the noted amounts. The specific range of 0.1 to 5.0% Bi is critical in achieving the noted combination of high strength and high temperature properties. This is entirely

unexpected and surprising. The reference to a corresponding composition of Sn/Cu, refers to a eutectic Sn/Cu composition of 99.3 Sn/0.7 Cu.

[0039] The present invention also provides a high temperature lead-free solder alloy that is significantly superior to a Cu—Sn eutectic composition in strength and fatigue resistance. The solder alloy of this aspect of the present invention comprises at least about 90% Sn, 0.2 to 0.9% Cu, and 0.1 to 5.0% Bi.

[0040] Specifically, it has been surprisingly discovered that Bi enhances SnCu alloys. For example, Sn0.7 Cu imparts a shear strength of 20 MPa, tensile strength of 24 MPa and a fatigue life of 1125 cycles. Under the identical testing conditions, Sn0.7 Cu1.0 Bi has a shear strength of 32 MPa, tensile strength of 41 MPa and a fatigue life of 11,228 cycles. Similar superior properties were obtained for Sn0.7 Cu3.0 Bi. In the meantime, the discovered alloys deliver the high liquidus temperature (>225) for high temperature usefulness.

[0041] For reference purposes, it is believed that 63 Sn/37 Pb solder has generally been measured with the ultimate tensile strength being 47 MPa and the low-cycle fatigue life at 0.2% strain being 3650 cycles. The tensile strength and fatigue life of a solder alloy of 99.3 Sn/0.7 Cu are 24 MPa and 1125 cycles, respectively, which is well below that for a 63 Sn/37 Pb composition that has been used as the industry standard for surface mount assemblies.

[0042] It has been discovered that the strength of SnCu was enhanced by Sb, increasing with increasing Sb. And simultaneously, SnSb was strengthened by Cu, its strength increases with increasing Cu. For example, Sn₂Cu₃Sb has tensile strength of 60 MPa vs. SnSb of 34 MPa and SnCu of 24 MPa.

[0043] The present invention solder alloy demonstrates a higher strength and fatigue life than a Sn/Cu eutectic composition.

[0044] In a preferred embodiment of this aspect of the invention, there is provided a solder alloy containing about 98.3% Sn, 0.7% Cu, and 1% Bi. The tensile strength and fatigue life of the alloy are 48 MPa and 9165 cycles, respectively. The fatigue life of this composition is 770% higher than that of 99.3 Sn/0.7 Cu, and the tensile strength is 200% higher than that of 99.3 Sn/0.7 Cu.

[0045] It will be appreciated that all of the solder alloy compositions of the present invention may contain a variety of one or more elements. Examples of such elements include, but are not limited to Ga, Se, Te, Ba, Ca, Mg, Zn, Si, Sb, In, Au, Ag, Pd, Pt, Fe, Ni, Co, Ti and combinations thereof. Generally, the amounts of such elements are less than 1% collectively.

[0046] In certain aspects, it is preferred that the solder compositions contain only the specifically noted elements as described herein. That is, in these particularly preferred compositions, other elements or compounds which would affect the basic and material properties of the resulting solder compositions are excluded. However, it is to be understood that the present invention in its broadest aspects, includes the incorporation of additional elements and compounds that affect the characteristics of the resulting solder compositions.

[0047] The previously noted lead-free solder alloys of this invention can be prepared at the molten states of the major constituents by general heating techniques known in the art. The alloys can also be used in various physical forms such as pastes, powders, bars, wires, and preforms or in any soldering processes such as reflow oven soldering, wave machine soldering, selective soldering (laser, white beam, etc.) and hand soldering or in any materials fabrication such as various deposition and coating techniques.

[0048] While the invention has been described with respect to its preferred embodiments, it is to be understood that variations and modifications thereof will become apparent to those skilled in the art. The foregoing disclosure is not intended or to be construed to limit the scope of the invention described herein.

I claim:

1. A high temperature, lead-free solder alloy consisting essentially of:

at least about 90% Sn;

0.2 to 5.0% Cu; and

0.05 to 5.0% Bi;

the high temperature, lead-free alloy having a liquidus temperature greater than 225° C. and exhibiting a tensile strength that is at least 20% greater than a corresponding composition of Sn/Cu.

2. The high temperature, lead-free solder alloy of claim 1, wherein the alloy includes about 90 to 99% Sn, 0.2 to 5.0% Cu, and 0.05 to 5.0% Bi.

3. The high temperature, lead-free solder alloy of claim 2, wherein the solder alloy comprises about 96.0% Sn, 3.0% Cu, and 1.0% Bi.

4. A high temperature, lead-free solder alloy consisting essentially of:

at least about 75% Sn;

0.5 to 7.0% Cu; and

0.5 to 18.0% Sb;

the high temperature, lead-free alloy having a liquidus temperature greater than 225° C. and exhibiting a tensile strength that is at least 20% greater than a corresponding composition of Sn/Cu.

5. The high temperature, lead-free solder alloy of claim 4, wherein the alloy includes about 75 to 99% Sn, 0.5 to 7.0% Cu, and 0.05 to 18% Sb.

6. The high temperature, lead-free solder alloy of claim 5, wherein the solder alloy comprises about 82% Sn, 3% Cu, and 15% Sb.

7. A high temperature, lead-free solder alloy consisting essentially of:

at least about 78% Sn;

0.8 to 7.0% Cu; and

4.0 to 15.0% Ag;

the high temperature, lead-free alloy having a liquidus temperature greater than 225° C. and exhibiting a tensile strength that is at least 20% greater than a corresponding composition of Sn/Cu.

8. The high temperature, lead-free solder alloy of claim 7, wherein the alloy includes about 78 to 96% Sn, 0.8 to 7.0% Cu, and 4 to 15% Ag.

9. The high temperature, lead-free solder alloy of claim 8, wherein the solder alloy comprises about 87% Sn, 3% Cu, and 10% Ag.

10. A high temperature, lead-free solder alloy consisting essentially of:

at least about 90% Sn;

0.05 to 5.0% Bi; and

0 to 5.0% Sb;

the high temperature, lead-free alloy having a liquidus temperature greater than 225° C.

11. The high temperature, lead-free solder alloy of claim 10, wherein the alloy includes about 90 to 99% Sn, 0.05 to 5.0% Bi, and 0 to 5.0% Sb.

12. The high temperature, lead-free solder alloy of claim 11, wherein the solder alloy comprises about 98.5% Sn, 1% Bi, and 0.5% Sb.

13. A high temperature, lead-free solder alloy consisting essentially of:

at least about 90% Sn;

0.2 to 0.9% Cu; and

0.1 to 5.0% Bi;

the high temperature, lead-free alloy having a liquidus temperature greater than 225° C. and exhibiting a tensile strength that is at least 20% greater than a corresponding composition of Sn/Cu.

14. The high temperature, lead-free solder alloy of claim 13, wherein the alloy includes about 90 to 99% Sn, 0.2 to 0.9% Cu, and 0.1 to 5.0% Bi.

15. The high temperature, lead-free solder alloy of claim 14, wherein the solder alloy comprises about 98.3% Sn, 0.7% Cu, and 1% Bi.

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