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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2004/0258556 A1****Kim et al.**(43) **Pub. Date: Dec. 23, 2004**(54) **LEAD-FREE SOLDER ALLOYS AND METHODS OF MAKING SAME**(22) Filed: **Oct. 2, 2003****Related U.S. Application Data**(75) Inventors: **Choong-Un Kim**, Arlington, TX (US);
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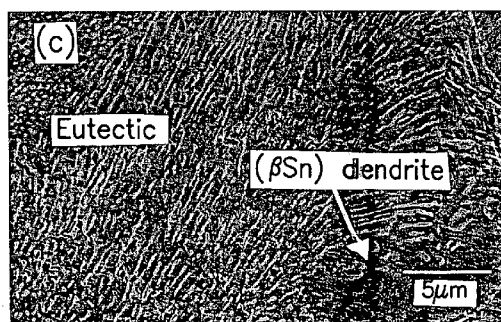
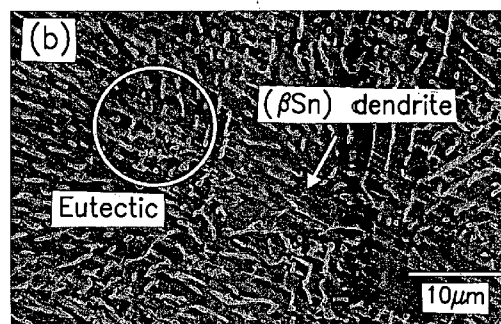
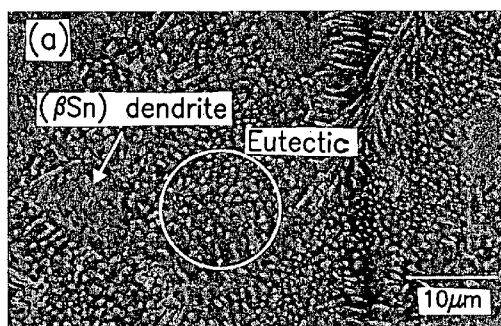
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SHELTON, CT 06484-6212 (US)(73) Assignees: **Nokia Corporation**, Espoo (FI); **Board of Regents, University of Texas System**, Austin, TX(21) Appl. No.: **10/678,655**(57) **ABSTRACT**

According to one aspect of the invention, a modified Sn—Ag—Cu, lead-free solder alloy is disclosed. The alloy comprises an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the alloy in an amount effect to form an intermetallic interface between the alloy a substrate, the intermetallic interface having a composite structure without scallop formation and including Sn islands.



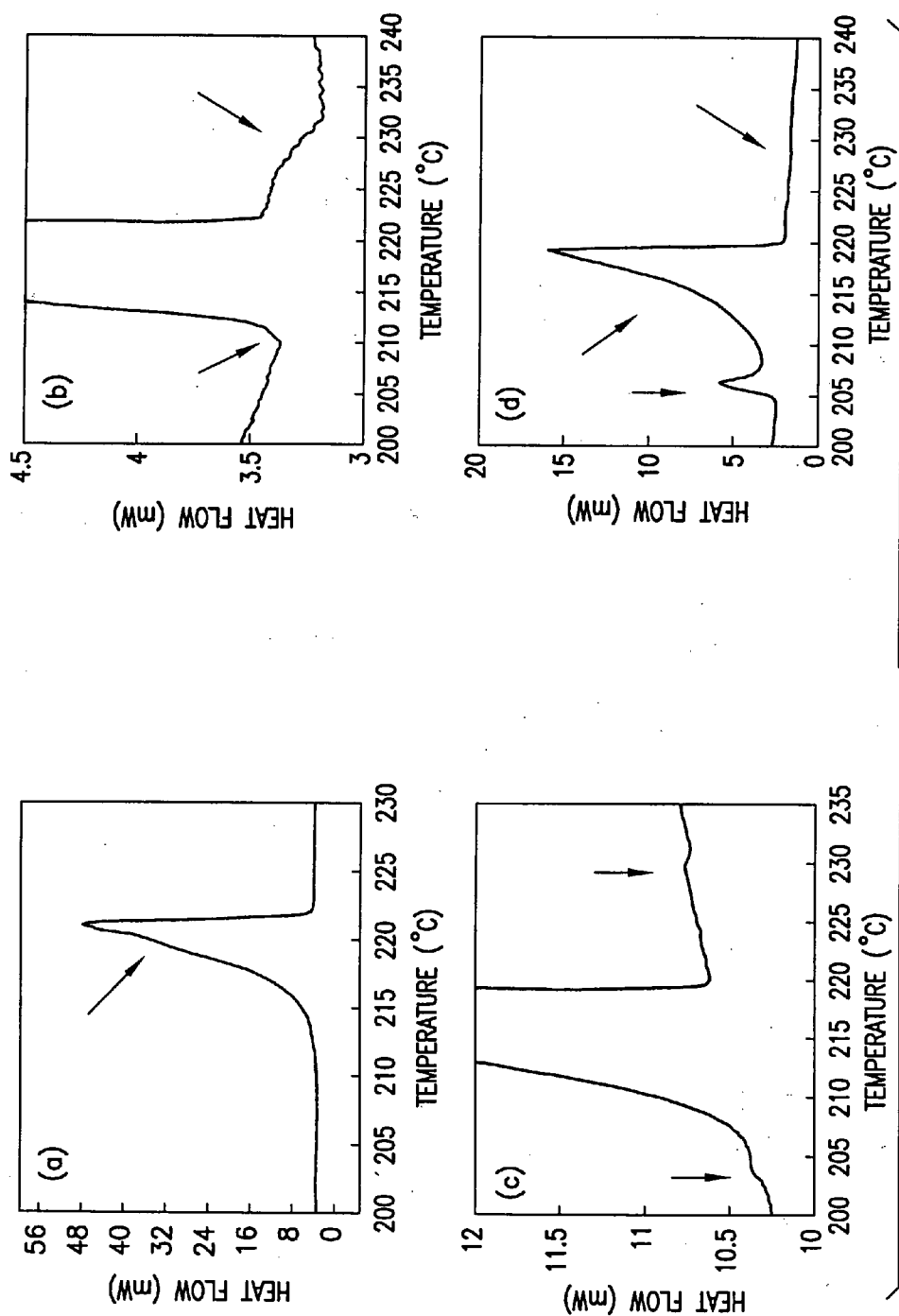


FIG.1

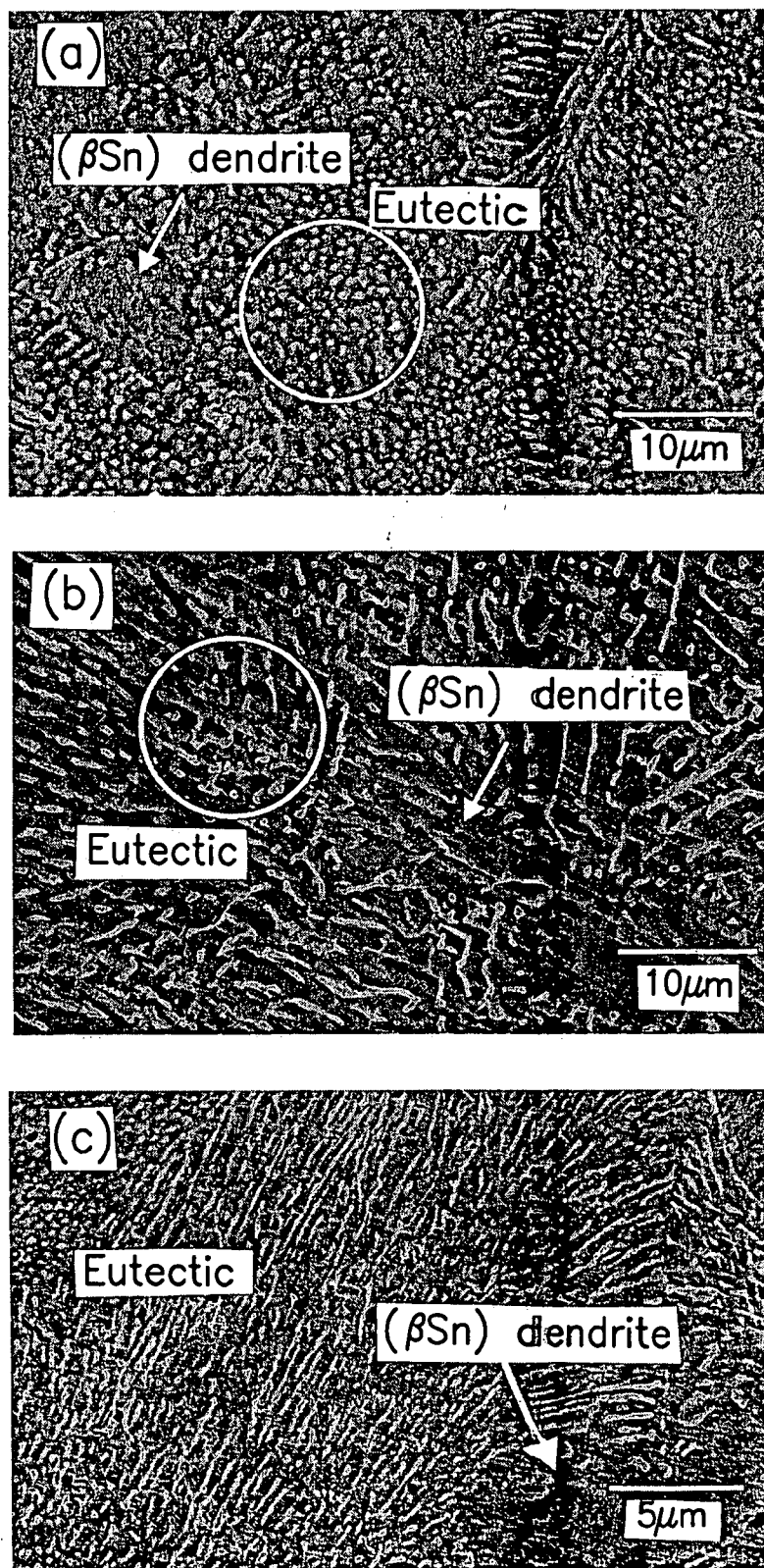


FIG 2

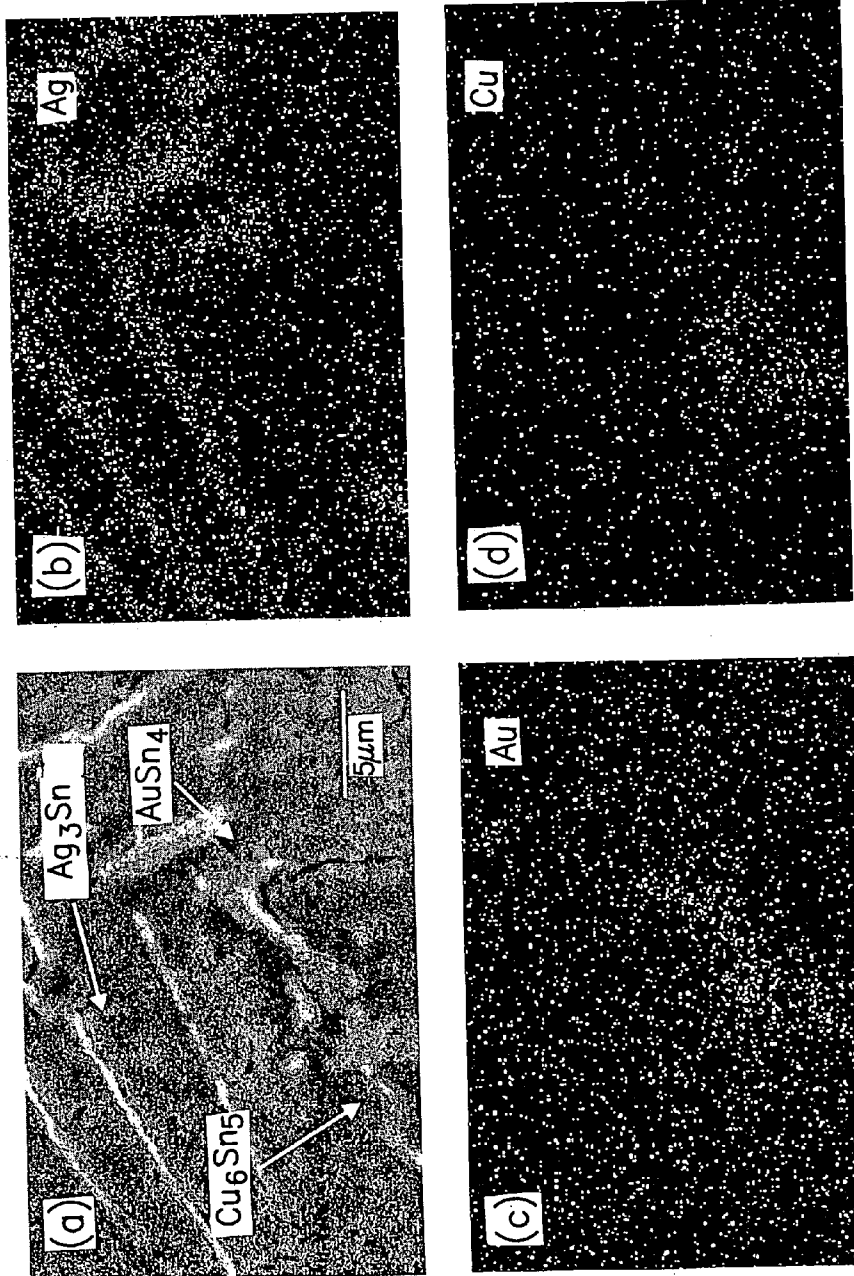


FIG.3

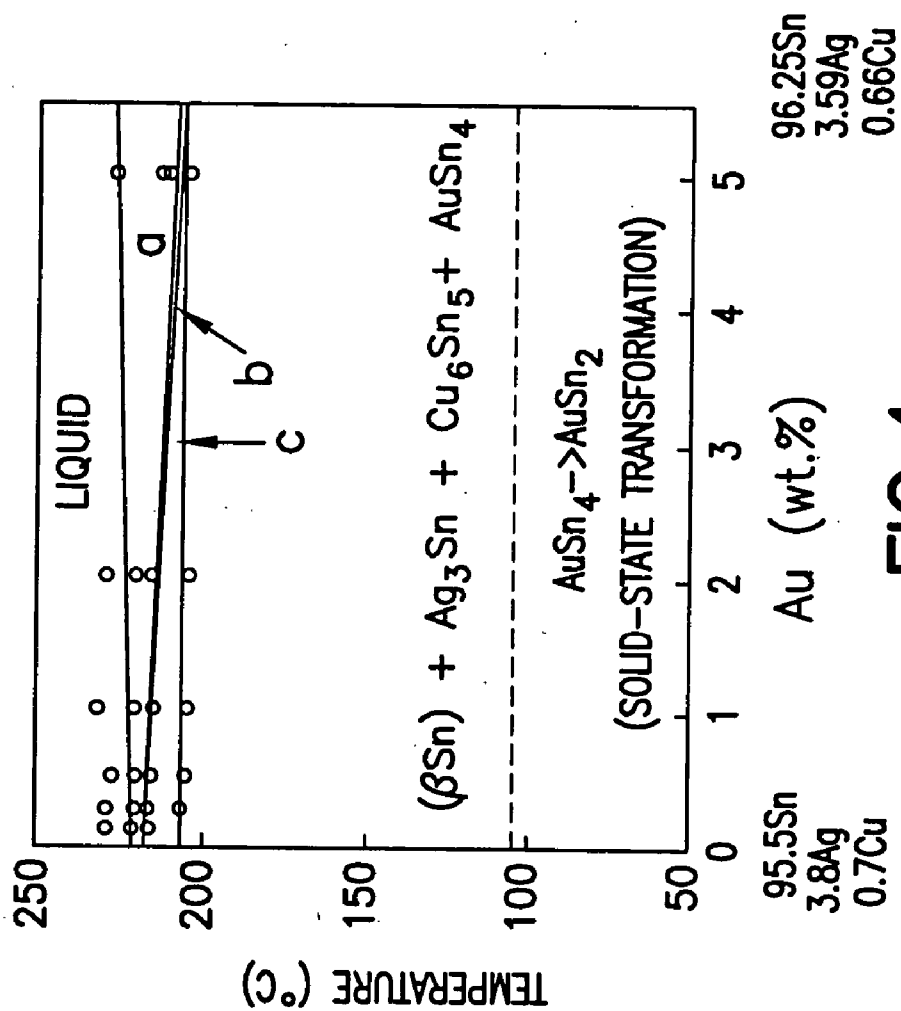


FIG. 4

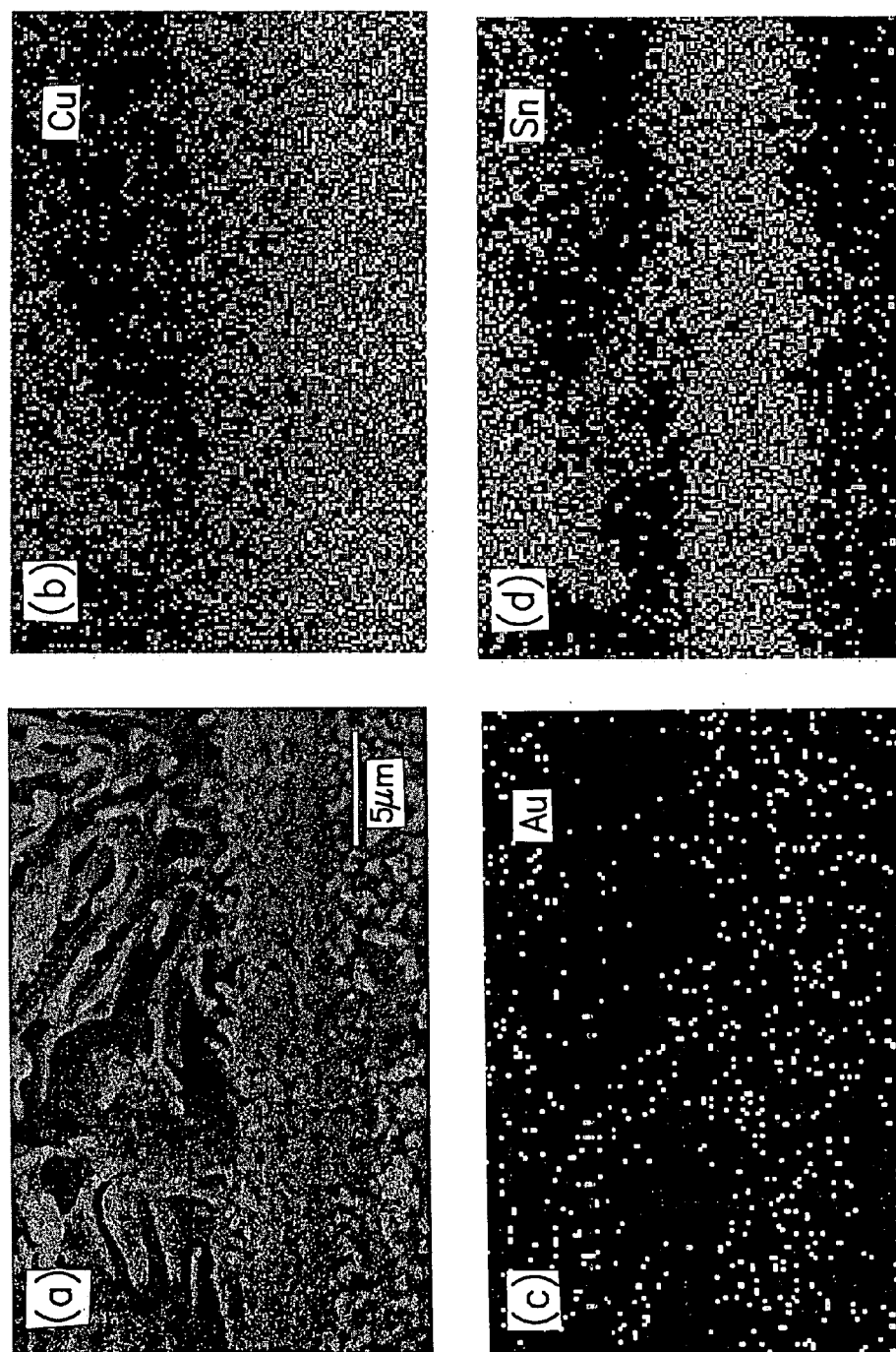


FIG. 5

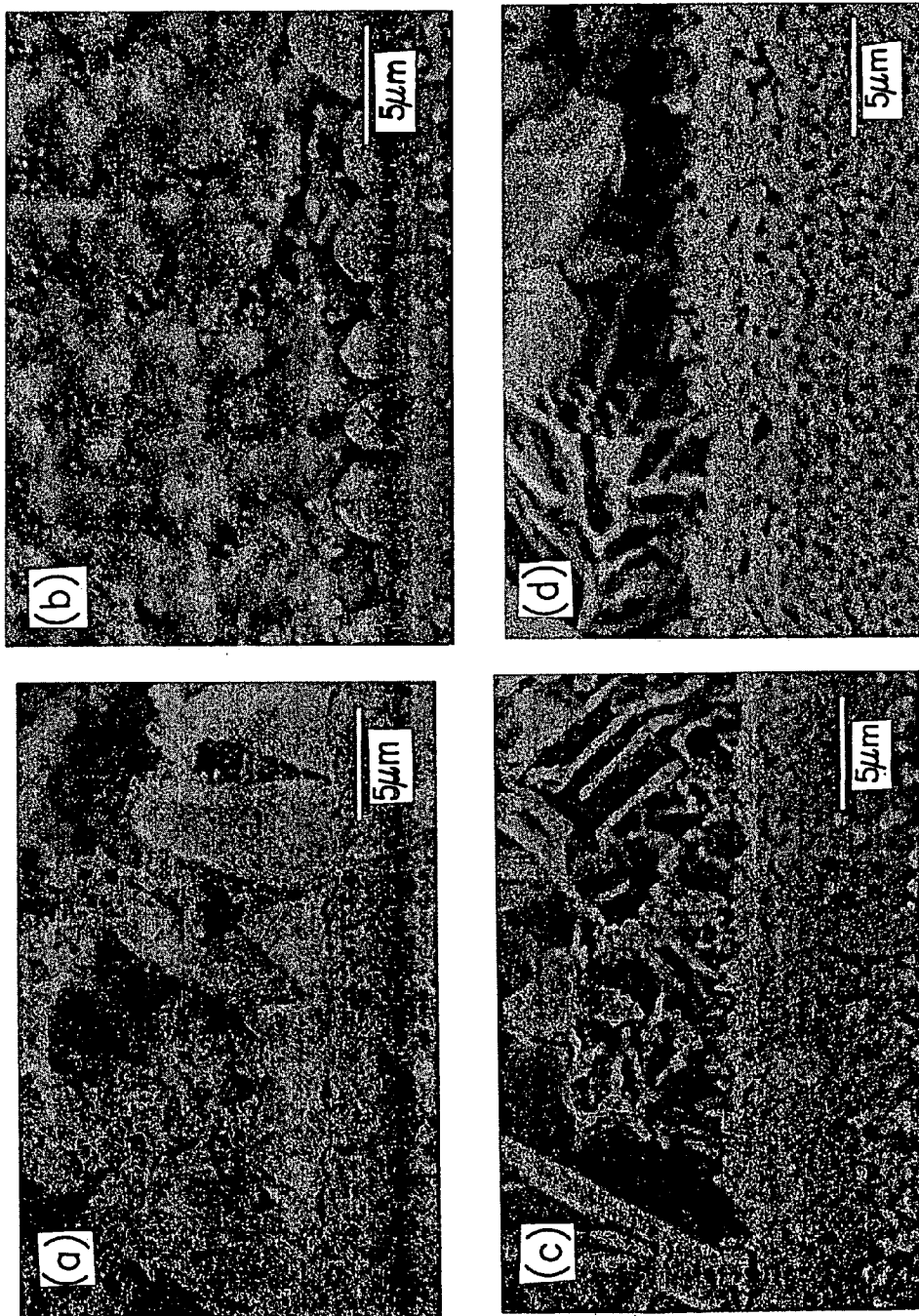


FIG. 6

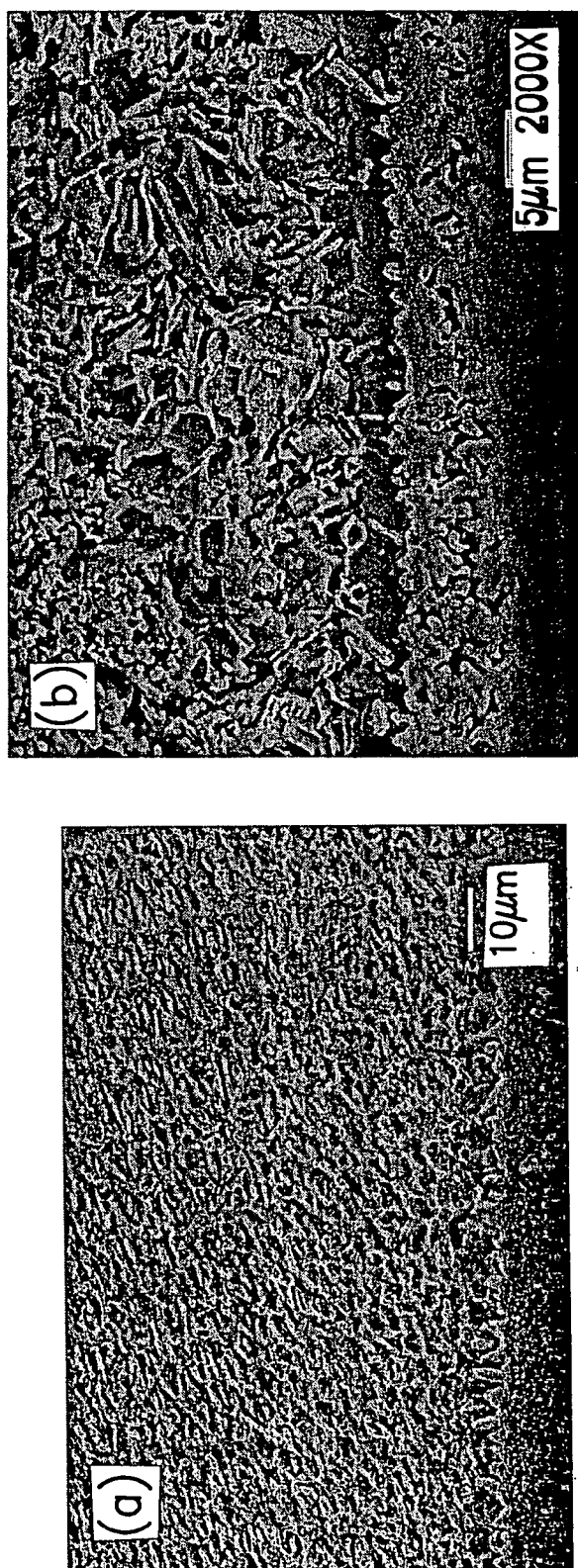


FIG. 7

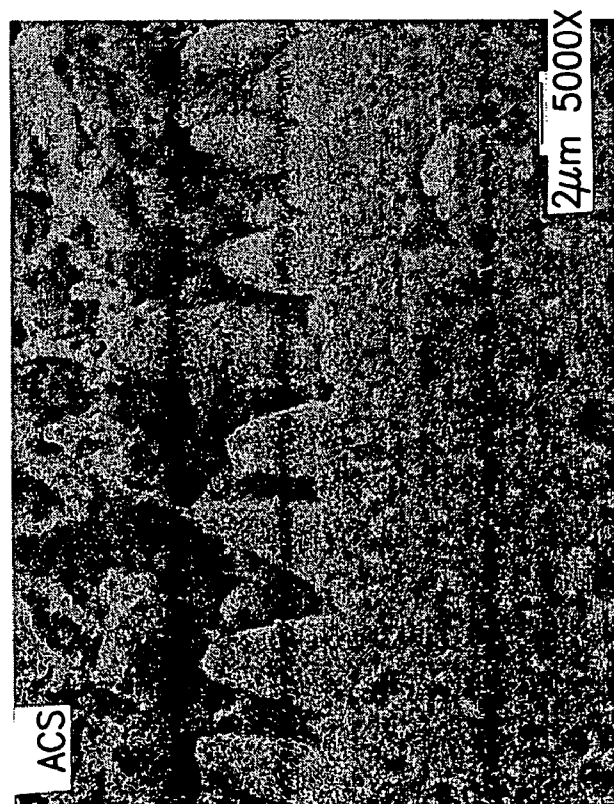
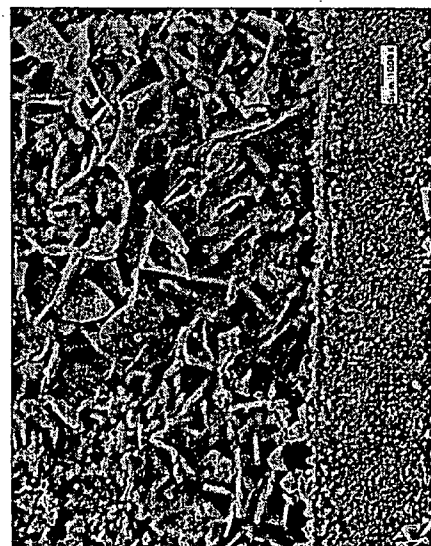


FIG.8(a)



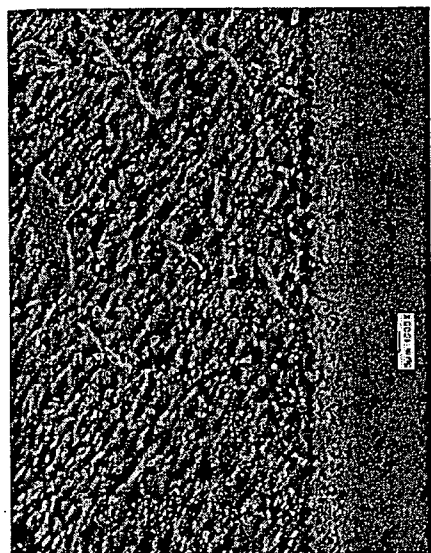
FIG.8(b)

FIG.8



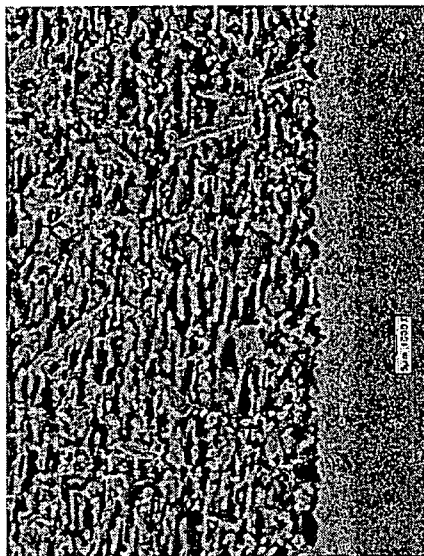
As-prepared

FIG. 9(a)



4 days at 165°C

FIG. 9(b)



25 days at 165°C

FIG. 9(c)

FIG. 9

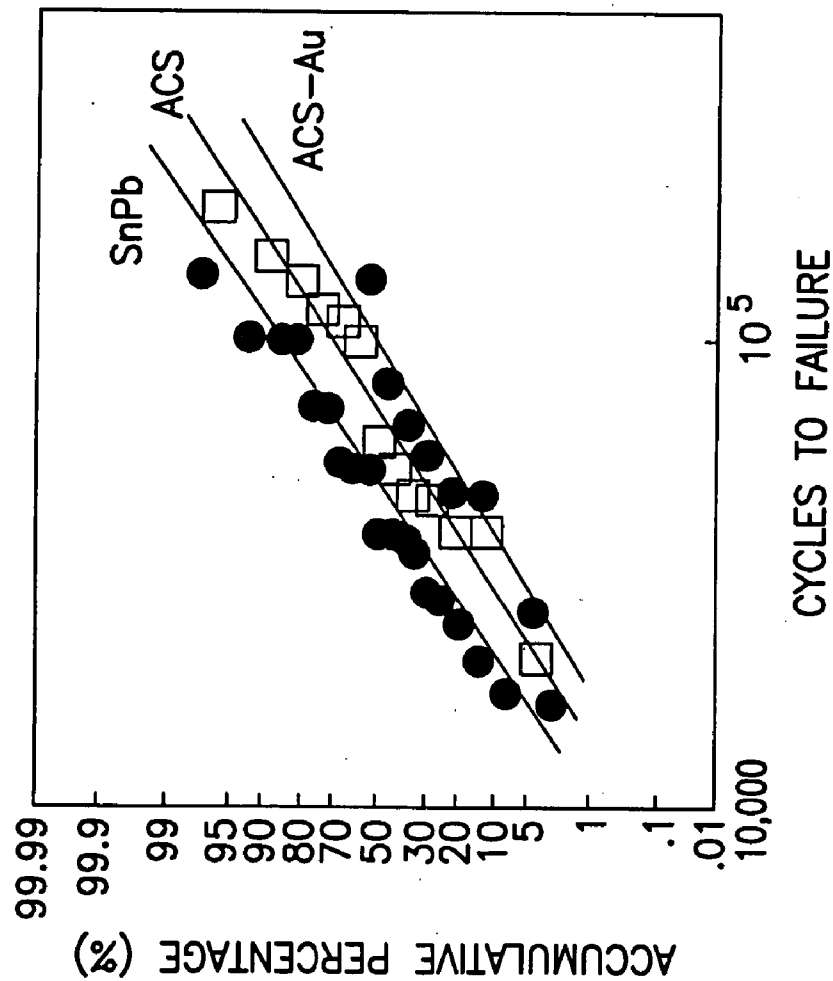


FIG.10

LEAD-FREE SOLDER ALLOYS AND METHODS OF MAKING SAME

PRIORITY STATEMENT

[0001] This application claims priority under 35 U.S.C. § 119(e) from provisional U.S. Patent Application Ser. No. 60/479,639, filed on Jun. 19, 2003, which is herein incorporated by reference.

TECHNICAL FIELD

[0002] This invention relates generally to lead-free solder alloys and methods of making such lead-free solder alloys. More particularly, the invention relates to the addition of alloying additives that change the mechanism of interface reaction between Sn-base lead-free solders and Cu substrates. These additives in small quantities can change the interface reaction mechanism in such a way that reliability of a solder joint during processing and subsequent use can be substantially improved.

BACKGROUND

[0003] Interface reaction between molten solder and Cu is required for solder joint formation, but should be kept at a minimum for various reasons. For example, excessive reaction consumes Cu through the formation of Cu—Sn intermetallics. The consumption of Cu is a particularly concerning factor for microelectronic devices because the consumption may cause structural and electrical failure of the interconnects. Also, excessive growth of the Cu—Sn intermetallic compounds may threaten packaging reliability. It is known that Cu—Sn intermetallics do not grow in a homogeneous layer, but undergo instability resulting in rough interface morphology, which adds more intermetallics to solder joints. As intermetallics are brittle in nature, such a microstructure may weaken the resistance of solder joints against failure by mechanical shock and fatigue.

[0004] With the continuing thrust toward lead-free solder technology, the concern of excessive interface reaction and resulting solder embrittlement is becoming more important than ever, particularly because a majority of lead-free solders are based on the Sn-rich alloy systems such as Ag—Sn and Ag—Cu—Sn (ACS). Higher processing temperatures in combination with higher concentration of Sn in the solder increases the possibility of excessive reaction with Cu.

[0005] Reaction barrier layers such as Ni, Fe—Ni and Fe—Pd layers may be employed to address excessive reaction and joint embrittlement. These layers do react with Sn in molten solder, but not as readily as Cu. Slower reaction kinetics with these coating layers enable better control of interface reaction. However, the use of such layers may have some shortcomings. For example, the number of preparatory steps before soldering is increased. Also, these layers may offer limited effectiveness unless they are relatively thick. In the case of microelectronics or high-density packaging applications, the layers cannot be arbitrarily thick because of other considerations such as electrical resistance and increased mechanical stresses in metal layers.

[0006] U.S. Pat. No. 6,231,691 to Anderson et al. discloses a modified Sn—Ag—Cu lead-free solder alloy. The solder microstructure retains a fine, uniform microstructure. However, such a microstructure may not be optimum for the increasingly demanding environments of lead-free solders.

[0007] Accordingly, there is a need for new and improved lead-free solders and methods of making such lead-free solders.

SUMMARY OF THE PREFERRED EMBODIMENTS

[0008] The foregoing and other problems are overcome, and other advantages realized, in accordance with the presently preferred embodiments of these teachings.

[0009] In accordance with an embodiment of the invention, the influence of Au addition on the phase equilibria of Ag—Cu—Sn near eutectic alloys and on the interface reaction with a Cu substrate was determined. From the thermal and microstructural characterization of 3.8Ag-0.7Cu—Sn alloys containing various amount of Au, it is found that the Au promotes the formation of quaternary eutectic reaction at $204.5 \pm 0.3^\circ \text{C}$. The equilibrium phases in the quaternary eutectic microstructure are found to be AuSn_4 , Ag_3Sn , (βSn), and Cu_6Sn_5 . While the addition of Au to 3.8Ag-0.7Cu—Sn alloys is also found to increase liquidus temperature and the temperature ranges of the phase equilibria field for primary phases, such influences from Au are found to be less pronounced when the alloys were reacted with a Cu substrate. Due to the formation of an Au—Cu—Sn ternary interface intermetallic, it is found that a majority of Au added to the solder may be depleted from the melt. The depletion of Au reduces the impact of Au on phase equilibria of the solder alloys in the joint. It is further found that the involvement of Au in interface reaction results in the change of the interface phase morphology from a conventional scallop structure to a novel composite structure of $(\text{AuCu})_6\text{Sn}_5$ grains and finely dispersed (βSn) islands.

[0010] In accordance with another embodiment of the present invention, an inventive method is to include minor amounts of noble (Au) and/or transition metals (Ni, Pd, Fe, Co, Zn, Cr) in molten solder. These additives have greater affinity to Cu—Sn intermetallics than to the melt, and thus segregate to the interface during intermetallic formation. With formation of ternary intermetallics (Cu—Sn—X), the interface microstructure may change from a Cu—Sn single layer interface to a composite layer containing Sn rich islands. Excessive interface reaction may be reduced because the composite layer acts as a buffer for intermetallic instability. Furthermore, the presence of a soft Sn phase in brittle Cu—Sn intermetallic increases the shock and fatigue resistance of the joint. The formation of a composite interface layer can also be beneficial in increasing the shelf-life of printed circuit board components. Copper in printed circuit boards may be treated with Sn or Sn-bearing alloys. This treatment enhances solderability, as well as protects Cu from oxidation. However, solid-state interface reaction may occur during board storage prior to its usage, thereby reducing solderability. The presence of Applicants' composite layer at the interface can advantageously act as a buffer for further reaction.

[0011] In accordance with a further embodiment of the invention, a modified Sn—Ag—Cu, lead-free solder alloy is disclosed comprising an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the alloy in an amount effective to form an intermetallic interface between the alloy and a substrate. The intermetallic interface has a composite structure without scallop formation and including Sn islands.

[0012] In accordance with another embodiment of the invention, a Pb-free solder consists essentially of, in weight %, greater than about 90% Sn, about 0.25-7% Ag, about 0.1-5% Cu, and comprises an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form an intermetallic interface between the solder and a substrate. The intermetallic interface advantageously has a composite structure without scallop formation and including Sn islands.

[0013] A further embodiment of the invention is a solder joint comprising a Pb-free alloy having a composition consisting essentially of, in weight %, greater than about 90% Sn, about 0.25-7% Ag and about 0.1-5% Cu. The solder joint also comprises an additive selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free alloy in an amount effective to form an intermetallic interface between the alloy and a soldered component, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

[0014] In accordance with another embodiment of the invention, a Pb-free solder consists essentially of, in weight %, greater than about 90% Sn, about 3.6-3.8% Ag, about 0.6-0.7% Cu, and comprises an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form an intermetallic interface between the solder and a substrate. The intermetallic interface advantageously has a composite structure without scallop formation and including Sn islands.

[0015] A further embodiment of the invention is a solder joint comprising a Pb-free alloy having a composition consisting essentially of, in weight %, greater than about 90% Sn, about 3.6-3.8% Ag and about 0.6-0.7% Cu. The solder joint also comprises an additive selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free alloy in an amount effective to form an intermetallic interface between the alloy and a soldered component, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

[0016] Another embodiment of the invention is a soldering process for a component. The soldering process comprises: melting and solidifying a Pb-free solder consisting essentially of, in weight percent, greater than about 90% Sn, about 3.6-3.8% Ag, about 0.6-0.7% Cu, and comprising an additive selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free solder in an amount effective to form an intermetallic interface between the solder and a soldered component, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

[0017] Another embodiment of the soldering process comprises: melting and solidifying a Pb-free solder consisting essentially of, in weight percent, greater than about 90% Sn, about 0.25-7% Ag, about 0.1-5% Cu, and comprising an additive selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free solder in an amount effective to form an intermetallic interface between the solder and a soldered component, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

[0018] Yet another embodiment of the invention is a modified Sn—Ag—Cu, lead-free solder alloy having a composition of, in weight %, of about 3.6-3.8Ag, about 0.6-0.7Cu, greater than about 0.9Sn, and comprising an additive element of Au, the alloy having a quaternary eutectic reaction at $204.5 \pm 0.3^\circ \text{C}$., wherein the alloy comprises a eutectic microstructure with equilibrium phases of AuSn_4 , Ag_3Sn , (βSn), and Cu_6Sn_5 .

[0019] A further embodiment of the invention includes forming a composite interface layer between a copper substrate and a Sn-based lead free solder. The method comprises the steps of providing a Sn-based lead free solder and adding an additive element to the Sn-based lead free solder in an amount effective to form an intermetallic interface layer between the solder and the copper substrate. The intermetallic interface layer has a composite structure without scallop formation and including Sn islands, wherein the additive element is selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof.

[0020] In further accordance to an embodiment of the invention, a composite, intermetallic layer on a Cu substrate is disclosed. The composite, intermetallic layer has a composite structure without scallop formation and including Sn islands, wherein a molten solder comprises an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form the composite, intermetallic layer between the solder and the Cu substrate.

[0021] In addition to the above Sn—Ag—Cu ternary alloys and as further described hereinafter, pure Sn and binary alloys of, in wt. %, i) Sn more than about 90% and Cu about 0.1%-5% and ii) Sn more than about 90% and Ag about 0.25-7% may be employed in the above solders, joints and processes with the additives to achieve the advantageous composite structure.

[0022] Further, it is contemplated that embodiments of the present invention may be used in any suitable form. For example, the afore-referenced noble and/or transition metal additives may be i) added to a starting solder alloy, ii) added to a pre-Sn layer by, for example, dipping or co-plating (e.g. a PCB or other suitable article may be dipped into an Sn—Au alloy thereby extending the shelf life of the article) or iii) added as a coating layer on top of a Cu substrate such that the layer allows dissolution of the additives. If the targeted additives are added to the solder, sufficient alloying additives or elements should be present in the molten solder to modify the interface mechanism by ternary intermetallic formation.

[0023] These and other features, aspects and advantages of embodiments of the present invention will become apparent with reference to the following description in conjunction with the accompanying drawings. It is to be understood, however, that the drawings are designed solely for the purpose of illustration and not as a definition of the limits of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] FIGS. 1(a), 1(b), 1(c) and 1(d), collectively referred to as FIG. 1, show DCS results for 0.1Au-ACS in (a-b), 2.0Au-ACS in (c) and 5.0Au-ACS (d) tested at a heating rate of $1^\circ \text{C}/\text{min}$. Arrows indicate reaction points. In each case, 4 reaction points were found.

[0025] FIGS. 2(a), 2(b) and 2(c), collectively referred to as FIG. 2, are SEM micrographs showing the microstructure of (a) 0.5Au-ACS, (b) 1.0Au-ACS, and (c) 2.0Au-ACS alloys. All samples were heat treated at 600° C. for one week followed by quenching. Note the presence of Sn dendrite (arrows) and eutectic microstructures containing Ag_3Sn , Cu_6Sn_5 , (βSn) and AuSn_4 (circles).

[0026] FIGS. 3(a), 3(b), 3(c) and 3(d), collectively referred to as FIG. 3, show a SEM micrograph (a) and EDS x-ray mapping results (b-d) showing the quaternary eutectic microstructure found in 2.0Au-ACS alloys. Signals in (b), (c) and (d) represent Ag, Au and Cu, respectively. Note the presence of AuSn_4 phase located between Ag_3Sn and Cu_6Sn_5 .

[0027] FIG. 4 is an isopleth phase diagram comparing CALPHAD and experimental results. Left axis of this diagram represents Sn-3.8Ag-0.7Cu alloy. Phase fields denoted by a, b, and c are $\text{L}+\text{Ag}_3\text{Sn}$, $\text{L}+\text{Ag}_3\text{Sn}+(\beta\text{Sn})$ and $\text{L}+\text{Ag}_3\text{Sn}+(\beta\text{Sn})+\text{Cu}_6\text{Sn}_5$, respectively. The ratio of Ag, Cu and Sn is fixed throughout the calculation to be consistent with the alloys used in the study.

[0028] FIGS. 5(a), 5(b), 5(c) and 5(d), collectively referred to as FIG. 5, show an SEM micrograph (a) and EDS x-ray mapping results (b-d) showing the microstructure of the interface layer for a 1.0Au-ACS solder joint reflowed at 260° C. for 3 minutes. Signals in (b), (c) and (d) represent Cu, Au and Sn, respectively. Note the presence of the porous interface layer. Also note that the interface layer contains more Au than any other areas.

[0029] FIGS. 6(a), 6(b), 6(c) and 6(d), collectively referred to as FIG. 6, are SEM micrographs showing the cross sectional microstructure of (a) ACS, (b) 0.25Au-ACS, (c) 1.0Au-ACS and (d) 2.0Au-ACS. All the joints were reflowed at 260° C. for 3 minutes. Notice that the alloys containing less than 0.25% Au (a-b) form a conventional interface microstructure with scallops. Alloys containing more than 0.25% Au form a composite interface structure consisting of small $(\text{AuCu})_6\text{Sn}_5$ grains and (βSn) islands.

[0030] FIGS. 7(a) and 7(b), collectively referred to as FIG. 7, show (a) Sn-3.8Ag-0.7Cu with 1.0Ni addition, and (b) Sn-3.8Ag-0.7Cu with 1.0Fe addition. Both microstructures advantageously show the composite IMC formation with (βSn) islands. IMC in (a) is $(\text{Cu, Ni})_6\text{Sn}_5$ and in (b) is $(\text{Cu, Fe})_6\text{Sn}_5$.

[0031] FIGS. 8(a) and 8(b), collectively referred to as FIG. 8, show a comparison of interface structure for ACS (a) and 2.0Au-ACS (b). Note the scallops in (a).

[0032] FIGS. 9(a), 9(b) and 9(c), collectively referred to as FIG. 9, show the change in interface microstructure with aging time after soldering with Au bearing Ag—Cu—Sn alloys ((a)-as prepared; (b)-4 days at 165° C.; (c)-25 days at 165° C.).

[0033] FIG. 10 is a plot of accelerated fatigue testing showing improved reliability by Au addition.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS:

[0034] Preferred embodiments of the present invention pertain to lead-free solders for electronic devices. Such devices include, for example, copper plated printed circuit

boards. With an ever increasing concern on environmental safety and also a desire for more reliable solder alloys suitable for modem packaging structure, research has been conducted on the Ag—Cu—Sn (ACS) ternary alloys with near eutectic composition. These alloys are determined to be one of the most promising Pb-free solders because they provide various advantageous properties over other Pb-free solders, such as excellent wettability, reasonable compatibility with the existing processes, and superior mechanical strength. Some ACS alloys are used in a few advanced packaging structures, and their usage is expected to grow in the next few years.

[0035] However, the influence of impurities on the metallurgical and mechanical properties of ACS alloys is of particular note because a significant change in the properties can result from contaminants. The source and type of contaminants may vary considerably depending on the structure of solder joints and processes used during soldering. The substrate that solders react with is a significant source. In order to prevent oxidation and also to enhance wettability or suppress excessive reaction, Cu substrates may be coated with various metallic thin films such as Au, Ni and Pd. For example, in the case of Au, Au readily reacts with molten solder and results in an instantaneous dissolution of the Au-layer during reflow process. This may affect the solderability because it can induce substantial changes in the melting temperature and reactivity of the molten solder. The mechanical reliability of the solder joint is also a concern because, in the case of Pb—Sn solder, the dissolution of Au exceeding 3-5 wt. % may promote the formation of large AuSn_4 intermetallics.

[0036] In order to determine the influence of Au on the solderability of ACS alloys, the change in the phase equilibria of ACS alloys by Au addition was investigated. However, the study of quaternary alloy system, ACS alloy plus Au, poses considerable challenges not only because the number of elements and phases to consider is large, but also because the interface reaction may further change the solder chemistry. Following the complete dissolution of Au, molten Sn in the solder reacts with the substrate underneath Au, such as Cu or Ni. With the reaction at the interface, the chemistry and thus the phase equilibria of the solder is further changed. For example, the formation of Cu_6Sn_5 phase at the solder/Cu interface drains Sn from solder but adds Cu (in addition to Au) to the solder.

[0037] In order to access the influence of Au on the phase equilibria of ACS alloys, an investigation was conducted in two different steps, as described in detail below in the Example. The first step was to investigate the change in the phase equilibria of the bulk alloy without generating the complexities of chemistry change from interface reaction. For this investigation, 3.8Ag-0.7Cu—Sn system was chosen as a base alloy, and a known amount of Au was added. The quaternary alloys (Au-ACS) were then subjected to thermal and microstructural characterization to determine the nature of quaternary phase equilibrium. The second step was to examine the change in the phase equilibria when those quaternary alloys were forced to react with Cu substrate. In this step, particular attention was paid to the microstructural change in the solder and interface because any difference in the parent alloy and the reacted alloy would indicate the direction of chemistry change and also the change in the phase equilibria. It is surprisingly determined that the addi-

tion of Au impacts the phase equilibria of the chosen ACS alloys in several ways. The first notable change is the creation of quaternary eutectic reaction by the Au addition. The Au forms an AuSn₄ phase that induces quaternary eutectic reaction at 204.5° C. with other equilibrium phases in the base ACS alloy—(βSn), Ag₃Sn, and Cu₆Sn₅. It is also determined that AuSn₄ exists in the eutectic microstructure when Au is added to the ACS alloys used in this investigation. It is further found that the addition of Au extends the primary phase field where Ag₃Sn phase forms. This may increase the chance for growth of Ag₃Sn primary phase and may decrease the mechanical reliability. However, this investigation finds that the change by Au addition on the microstructure of the ACS alloy itself is less dramatic when the quaternary alloy is reacted with Cu due to the formation of (AuCu)₆Sn₅ ternary intermetallic compound. The intermetallic layer acts as a sink for Au in the melt and limits Au content in the solder. Furthermore, the mechanism of interface reaction is completely changed by the formation of (AuCu)₆Sn₅. The intermetallic layer is found to be composite structure of fine grained (AuCu)₆Sn₅ and (βSn) islands. This unique microstructure is believed to be beneficial for enhancing fracture toughness of the intermetallic layer considering that finely dispersed (βSn) phase may be effective in arresting cracks and releasing strain energy. Set forth below in the Example are further details of this investigation.

EXAMPLE

[0038] The base ACS alloy used in this example was 3.8Ag-0.7Cu—Sn (all weight percent) obtained from Multicore Co. in the form of a rod. This alloy has a near eutectic composition. For the study of phase equilibrium in bulk, quaternary alloys containing Au were made by adding Au to the base alloy. Six different compositions were chosen and are listed below in Table 1. The quaternary alloys were made using the following procedure. The weighted Au-wire (99.99% pure) and ACS rods were placed in quartz tubes. The tubes were evacuated, back-filled with high purity Ar, sealed and placed in a furnace at 600° C. for a duration of one week for alloying. For better mixing of the alloy, occasional vibration of the tubes was applied during this one-week period. After completion of alloying, the tubes were quenched by ice bath in order to maintain the compositional homogeneity of the alloy.

TABLE 1

Name	(Wt. %)			
	Au	Ag	Cu	Sn
ACS	0	3.80	0.70	Bal.
0.1Au-ACS	0.10	3.80	0.70	Bal.
0.25Au-ACS	0.25	3.79	0.70	Bal.
0.5Au-ACS	0.50	3.78	0.70	Bal.
1.0Au-ACS	1.00	3.76	0.69	Bal.
2.0Au-ACS	2.00	3.72	0.69	Bal.
5.0Au-ACS	5.00	3.61	0.67	Bal.

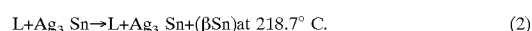
[0039] The phase transformations occurring in the quaternary alloys were characterized by conducting differential scanning calorimetry (DSC) analysis. Samples for DSC analysis were taken from five different places, and the measurement was repeated until five consistencies were achieved. In order for identification of phase formed in the

quaternary alloys, samples were also taken, polished, and etched followed by optical and scanning electron microscopy (SEM).

[0040] The results obtained from DSC and microstructural characterization were compared with results from CALPHAD (CALculation of PHase Diagram). In the CALPHAD, thermodynamic data of ternary Ag—Cu—Sn system published by Moon et. al. was used. See, *Electron. Mater.* 29, 1122 (2000). The additional parameters for the analysis of Au-ACS quaternary system were obtained from extrapolation of thermodynamic functions fitted to constitutional binary systems: Au—Ag, Au—Cu, and Au—Sn. See, *Metal. Trans.*, 19, 409 (1988); *Thermochimica Acta*. 130, 1 (1988); and *Calphad*, 22, 335 (1998), respectively. Also, the extrapolation technique introduced by Muggianu et al. was employed. See, *J. Chim. Phys.* 72, 85 (1975). All references cited in the specification are incorporated by reference.

[0041] In order to investigate the influence of interface reaction on Au-ACS alloys, the quaternary alloys were subjected to reaction with a Cu substrate. The reaction was induced by placing 30 mg solder balls on a Cu plated printed circuit board and then immersing the board into a bath containing rosin mildly activated flux. The temperature of the bath was maintained at 260° C., and the reaction time was three minutes. After completion of reaction, cross-sectional characterization of the interface microstructure was conducted.

[0042] The base ACS alloy chosen for this example has a composition slightly off from the eutectic and shows two primary reactions prior to the eutectic reaction at 217° C.:



[0043] where L and E represents the liquid phase and the eutectic phase, respectively. As apparent from these reaction equations, two different types of Ag₃Sn and (βSn) phase exist in the alloys: one formed as the primary phase and the second as eutectic phase. With the addition of Au, a gradual change in the phase equilibria and also development of a new phase field occur.

[0044] The change in the phase equilibria by addition of Au may be detected by monitoring the phase transition temperatures. FIG. 1 displays the DSC results taken from 0.1 (a-b), 2.0 (c), and 5.0 (d) Au-ACS alloys. As shown in FIG. 1(a), the addition of 0.1% Au does not seem to result in a significant change in the phase equilibria of the ACS alloy. The DSC result appears to indicate a presence of one eutectic reaction initiating at 216° C. and terminating at 223° C. However, a closer examination of the peak (FIG. 1(b)) reveals that the peak includes signals of several reactions. As marked in FIG. 1(a), the slope of the peak changes at 220° C. In addition, the presence of peak tail is noticeable at about 228° C. The detailed analysis reveals that there are a total of four reactions occurring at 228, 223, 220, and 216° C. (in solidification sequence). The occurrence of four reactions suggests that the addition of 0.1% Au changes the (L+Ag₃Sn+(βSn)+Cu₆Sn₅) phase field. In the case of ACS alloys, this phase field exists only at the eutectic point at 217° C. However, due to the addition of 0.1% Au, it is

changed to span from 216° C. to 220° C., suggesting a possibility of the quaternary eutectic reaction at a higher Au content. The DSC results shown in Figure(c) and (d) provide further evidence of the quaternary eutectic reaction. Note the presence of an additional peak at 204.5° C. prior to the major peak. The temperature of the 204.5° C. peak remains constant in alloys having Au concentration above 0.5%, indicating the occurrence of the quaternary eutectic reaction. Table 2 below summarizes the phase transition temperatures for the Au-ACS alloys tested. The order of reaction is from high to low temperature.

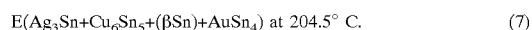
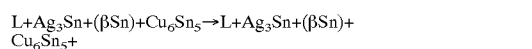
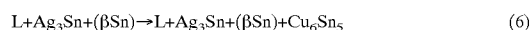
TABLE 2

Alloy (Wt. %)	1 st rxn.	2 nd rxn.	3 rd rxn.	4 th rxn.
0.1Au-ACS	228.0	223.0	220.0	216.0
0.25Au-ACS	228.0	219.8	216.2	206.0
0.5Au-ACS	226.6	219.3	215.1	204.5
1.0Au-ACS	230.6	220.1	214.4	204.2
2.0Au-ACS	228.5	219.8	214.8	204.3
5.0Au-ACS	226.8	213.2	211.0	204.8

[0045] The DSC data shown in Table 2 indicate at least two influences of Au on the phase equilibria of ACS alloys. The first is that Au solubility in the ACS alloy is less than 0.25% and the second is that the quaternary eutectic reaction occurs.

[0046] Microstructural examination of the Au-ACS alloys confirms these findings. SEM and EDS characterization of Au-ACS alloys with Au content less than 0.25% does not show any Au-rich phases. The microstructure looks similar to ACS alloys and consists of Ag₃Sn, Cu₆Sn₅ and (βSn). However, the alloys containing more than 0.5% Au show the presence of AuSn₄ intermetallic phase as a part of quaternary microstructure.

[0047] FIG. 2 shows the SEM microstructure of 0.5Au-ACS (a), 1.0Au-ACS (b), and 2.0Au-ACS (c). Note the presence of quaternary eutectic microstructure, as indicated in the micrographs. FIG. 3 presents the EDS analysis conducted on the quaternary eutectic microstructure. It can be seen that the quaternary eutectic microstructure consists of AuSn₄, Ag₃Sn, Cu₆Sn₅, and (βSn). Further examination of the microstructure reveals that AuSn₄ exists only in the eutectic microstructure, suggesting that AuSn₄ does not form by an off-eutectic reaction in the alloys tested here. Therefore, the phase formation reaction that the Au-ACS alloys experience during solidification process appears to be similar to those of the ACS alloys (eqs. (1)-(3)) when Au content is less than 0.25%. When Au exceeds 0.5%, the reaction changes to include the quaternary eutectic reaction:



[0048] FIG. 4 shows the phase diagram of the Au-ACS system obtained from the CALPHAD analysis. During the calculation, the ratio of the weight fractions of Ag, Cu, and Sn were maintained at 3.8, 0.7, and 95.5, respectively. Therefore, this isopleth phase diagram is constructed to present the change in the phase equilibria of 3.8Ag-0.7Cu—

Sn alloy by Au addition. It can be seen that the calculation is generally in agreement with the experimental results. The CALPHAD result does not show the solubility limit of Au in the ACS alloys. However, the general trend matches well with the experimental results. In addition to the formation of quaternary eutectic, this phase diagram shows another noteworthy influence of Au on the phase equilibria of ACS alloys: the expansion of the (L+Ag₃Sn) phase field. It is observed that the Ag₃Sn phase formed by off-eutectic phase (primary Ag₃Sn phase) tends to grow into a large plate. The expansion of Ag₃Sn primary phase field does suggest the possibility that more and larger Ag₃Sn compounds may form by the primary reaction. The presence of such larger phases may be detrimental to the mechanical stability of the solder not only because they may be brittle, but also because they may produce local sites of stress concentration. When the microstructure of slowly cooled samples is inspected, it is observed that the Ag₃Sn primary phases grow larger with increasing Au content. However, such an influence may be less concerning when Au-ACS alloys are reacted with a Cu substrate, for the reasons explained below.

[0049] Interface reaction may introduce further changes in the phase equilibria of ACS alloys because it alters the solder composition. When Au-ACS alloys are reacted with Cu, it is found that the formation of Au—Cu—Sn ternary intermetallic compound reduces the change induced by Au addition on the phase equilibria of ACS alloy. It is observed that the AuSn₄ phase is absent from the solder microstructure when Au-ACS alloys are reacted with Cu substrate. No evidence of AuSn₄ phase was found in the solder microstructure for 2% Au content. Rather, the majority of Au present initially in the solder is found at the interface in the form of a (AuCu)₆Sn₅ phase.

[0050] FIG. 5 show EDS micrographs of the interface formed for 1.0Au-ACS alloys and a Cu plate at 260° C. for 3 minutes. The secondary electron image in FIG. 5(a) shows an interface compound layer formed between solder matrix (top side) and Cu plate (bottom side). Note that the interface layer contains more Au than the solder matrix. This result indicates that Au in the molten solder diffuses preferentially to the reaction layer during the reflow process and forms a ternary Au—Cu—Sn compound. XRD analysis reveals that this ternary compound has a Cu₆Sn₅ crystal structure. It is believed that the close proximity of crystal structure and chemistry between Au and Cu may allow Au to prefer the interface Cu₆Sn₅ over the molten solder.

[0051] A surprising influence of Au on the interface reaction is the complete change in the reaction mechanism. FIGS. 6 compares cross-sectional SEM microstructures of various Au-ACS solder joints after reflow process at 260° C. for 3 minutes: ACS (a), 0.25Au-ACS (b), 1.0Au-ACS (c), and 2.0Au-ACS (d). It may be seen that the solder joint with ACS and 0.25Au-ACS shows the well-documented scalloped morphology of Cu₆Sn₅ interface microstructure. It has been observed that the first phase formed at the Cu interface is Cu₆Sn₅ when a Cu substrate is reacted with Sn-bearing solder alloys. With further reaction, a few Cu₆Sn₅ grains preferentially grow to result in scallops.

[0052] Surprisingly, the interface microstructure of 1.0, and 2.0 Au-ACS alloys show completely different interface microstructure, as can be seen from FIGS. 6(c) and (d). Note that the interface phase, (AuCu)₆Sn₅, does not show the

same scallop formation. Rather, the interface appears to consist of small $(\text{AuCu})_6\text{Sn}_5$ grains with finely dispersed pores. Further analysis of the microstructure reveals that the pore is the site where (βSn) phase is removed by etching. Accordingly, the interface microstructure was found to include $(\text{AuCu})_6\text{Sn}_5$ grains with finely dispersed (βSn) islands.

[0053] The interface microstructure with Au-ACS alloys containing Au higher than 5.0% was not tested in this example. However, it is believed that the same mechanism would be active in the alloy with a higher Au content, for example including but not limited to, up to about 5.5 weight %. This value is given based on the quaternary eutectic point of Ag—Cu—Sn—Au occurring at 5.5 weight % Au. While not wishing to be bound by theory, it is believed that the change in the interface reaction is related to the formation of the Au—Cu—Sn ternary compound. As illustrated by **FIG. 6**, the new interface microstructure may be developed when the Au concentration in the initial solder exceeds about 0.25 weight %. This suggests that there may exist a needed concentration of Au in the interface layer for the initiation of the new reaction. Although Au prefers the interface, sufficient Au should also present in the melt in order for chemical equilibrium between the growing intermetallic phase and the solder. It is possible that after exceeding the amount of Au needed in the melt, Au may participate in the interface reaction and promote new mechanism.

[0054] The influence of Au on the solder joint is a matter of practical concern because experimental evidence suggests that AuSn_4 compounds may result in embrittlement of Pb—Sn solder. Furthermore, since the addition of Au increases the liquidus temperatures, poor wettability may occur when excessive amount of Au is added to the solder. However, such an assessment needs consideration of the phase equilibria. For example, a phase that may be detrimental to solder reliability is one formed by the primary reaction. Unlike phases in the eutectic microstructure, intermetallic phases formed by off-eutectic reaction have an opportunity to grow into a large compound. When the intermetallic phases are formed by eutectic reaction, they may be less of a concern because they are fine-sized and evenly dispersed. Therefore, if the formation of AuSn_4 phase does not occur by off-eutectic reaction, the addition of Au may be beneficial. This example supports such a possibility.

[0055] Further positive influences of Au were determined in this investigation. For instance, the addition of Au induces a formation of quaternary eutectic microstructure. Also, due to a preferred reaction of Au with interface Cu_6Sn_5 phase upon reacting with the Cu substrate, a majority of Au is located in the interface, and not in the bulk of the solder joint. Even more beneficial is that the addition of Au modifies the microstructure of interface intermetallic phase, resulting in the suppression of the scallop formation. Since the scallop formation may make the solder joint susceptible to mechanical failures, its suppression by Au addition can have beneficial influence on the joint reliability. It is especially beneficial in applications where solder joint is small and the Cu substrate layer is thin. Furthermore, the composite interface microstructure that includes finely dispersed ductile (βSn) phase can add an additional benefit to the solder reliability. One of the weakest links in a solder joint is the intermetallic layer at the interface. With fine dispersion

of (βSn) phase in the matrix, the fracture toughness and thus fatigue resistance of the layer can be enhanced.

[0056] A new and useful alloy may be developed using the findings of this investigation. As described above, the addition of Au into the ACS system results in the quaternary eutectic reaction occurring at 204.5°C ., which is substantially lower than 217°C . of the eutectic ACS alloy. The quaternary Au-ACS alloy may have various advantageous properties in addition to lower melting point. A notable advantage is the potential improvement of solder reliability owing to suppression of scallop formation and also to the development of composite interface microstructure.

[0057] A similar advantageous composite effect may be achieved by using Au or other suitable additive as described herein, in a coating layer. For example, a coating layer of Sn (or SnPb) containing Au may be employed. For instance, Sn may be coated as a surface finish in order to protect the substrate from oxidation and contamination. This process may be referred to as pre-tinning and may be completed by dipping a Cu substrate into a molten bath of Sn. However, the formation of Cu_6Sn_5 intermetallic compounds and subsequent growth to form scallops during storage may decrease both wettability and reliability of the joint. With the addition of Au or other suitable additive into the bath, the interface reaction will result in the composite structure, which would advantageously prevent further growth of intermetallic compounds. Also, Au or other suitable additives may be used as a coating layer in Under Bump Metallization (UBM) or Ball Limiting Metallization (BLM) processes known to those in the art. Upon the melting of the solder, Au may dissolve immediately into the melt.

[0058] The amount of Au that may be added to the solder from surface coating may not be sufficient to induce the reaction for composite formation because the mass of solder is quite large compared to a few micron thick Au coating. For this, it may be necessary to adjust the coating thickness to ensure that the Au addition is sufficient for the given amount of solder. One skilled in the art would understand how to adjust the thickness of Au layer to exceed the minimum Au amount needed for composite formation.

[0059] It should be noted that additions of Au may potentially expand the Ag_3Sn primary phase field. However, depletion of Au to the interface reduces the Au content in the solder, and thus the expansion should not have a significant impact.

[0060] **FIG. 7** advantageously shows (a) Sn-3.8Ag-0.7Cu with 1.0Ni addition, and (b) Sn-3.8Ag-0.7Cu with 1.0Fe addition. More particularly, SEM microstructures of (a) 1.0Ni-94.07Sn-3.74Ag-0.69Cu solder joint reflowed at 260°C for 3 minutes, and (b) 1.0Fe-94.07Sn-3.74Ag-0.69Cu solder joint reflowed at 285°C for 3 minutes are shown therein. Both microstructures show the composite IMC formation. IMC in (a) is $(\text{Cu, Ni})_6\text{Sn}_5$ and in (b) is $(\text{Cu, Fe})_6\text{Sn}_5$.

[0061] **FIG. 8** also shows the advantageous change in microstructure as a result of the present invention. The conventional scalloped microstructure of the base ACS alloy is shown in (a), wherein Applicants' improved fatigue resistant Au enriched microstructure with the absence of scallop formation is shown in (b).

[0062] **FIG. 9** further demonstrates the change in interface microstructure with aging time after soldering with the Au

bearing Ag—Cu—Sn alloy having a composition of 1.0Au-94.07Sn-3.74Au-0.69Cu. The interface structure is stabilized by the Sn islands which act as a Cu sink. Once all of the Sn from the Sn islands is consumed, the interface may turn into a continuous intermetallic composite layer further stabilizing the layer and slowing the reaction kinetics. The interdiffusion between Sn and Cu leads to the growth of Cu—Sn IMCs (intermetallic compounds) even during the aging. These coarsened IMCs may be detrimental to the mechanical load. In the case of the composite IMC, however, Sn islands act as Cu traps, consuming Cu to turn into ternary compounds. Thus, the intermetallic layer does not grow by Cu—Sn interdiffusion.

[0063] FIG. 10 shows accelerated fatigue testing results and improved reliability of solder joints by Au addition. The compositions tested were 1.5Au-92.66Sn-3.69Ag-0.68Cu. This testing simulated the mechanical failure of solder joints. Failures in Pb—Sn and ACS may occur primarily by crack growth through brittle interface phases. This figure advantageously demonstrates that lifetime of the composite IMC sample (1.5Au-ACS) is longer than that of scallop IMC sample (ACS & 0.25Au-ACS). Accordingly, reliability of the solder joint may be improved by forming the composite IMC structure in the interface.

[0064] Embodiments of the present invention improve processability and reliability of solders in many ways. For example, if the composite layer is induced during the pre-Sn stage, for example by dipping a printed circuit board into the alloys of the invention, the shelf-life of the board or any similar structure will be increased substantially. The presence of Sn islands in the intermetallic layer traps diffusing Cu and retards further growth of Cu—Sn intermetallics during storage.

[0065] Also, the composite layer in a solder joint, either formed during the pre-Sn stage or during the soldering process, will also suppress the further growth of intermetallic phases. Considering the buffering role of Sn islands against continuous interface reaction, the interface reaction will be much more stable. Therefore, the processability of the solder will be much more flexible. The presence of Sn islands in the composite will further increase the failure resistance of the joint. The Sn is a much softer phase than the intermetallics, and thus its presence in islands will improve the toughness of the interface.

[0066] Moreover, having Sn islands finely dispersed in the interface layer benefits the shock and fatigue resistance of solder joints. For example, the soft and ductile Sn islands can dissipate the strain energy applied to the joint resulting in arresting crack growth. Also, the mechanism of the composite layer produces a microstructure that is much finer than the normal scallop formation. For a majority of cases, we observed that the volume fraction of Sn islands may range from as low as about 20 percent to about 60%, and the size of the Sn islands may be between about 0.2 to about 0.8 μm . While the size of the IMCs in the composite may be slightly larger than Sn islands (about 0.3-1.2 μm), the IMCs are substantially smaller (more than a factor of about 5) than the scallops. The fine size of the Sn islands is especially beneficial because it provides numerous arresting points for crack propagation. If Sn islands are larger in size, they may not be as effective in enhancing the mechanical properties of the interface even if the fraction of the Sn islands is the

same. Thus, it is advantageous to have Sn islands dispersed in finer scale than the course.

[0067] The present invention may be simple to implement yet effective in resolving problems previously encountered in the prior art, as described above. It may not be necessary to use special metal layers, such as reaction barrier layers, as a coating to control interface reaction and to improve solder reliability. Additionally, due to the small amounts of additives employed, the cost of alloying and processing is not significantly increased. It should be noted that the mechanism of composite formation may not necessarily be determined by the composition, but supply of additives. Accordingly, the minimum amount of additives may differ depending upon the processing conditions and amount of total solder. For example, a minimum amount of greater than about 0.25 wt. % of Au may be employed for reflow conditions described herein, including about 0.3 wt. % Au and even greater than about 1 wt. %. Similarly, about 0.5 wt. % or greater of Ni, Pd, Fe, Co, Zr and Cr (and combinations thereof) may be employed for reflow conditions described herein. Sufficient amount of the additives should be present to maintain a supply of the additives for a given condition of reflow and joint formation for the desired composite structure. Thus, the additives should be present in an amount that is effective to, for example, form an intermetallic interface having a composite structure without scallop formation and including Sn islands, as described herein. As a further example, the additives described herein may be present in amounts or combination greater than about 0.5-1 wt. % up to about 5-8 wt. %.

[0068] Accordingly, the advantageous composite effect is not limited to the given Sn-3.8Ag-0.7Cu alloy of the Example. The mechanism of the composite formation is not limited to this specific alloy and, for example, we may include near eutectic Ag—Sn, Cu—Sn binary alloys, as well as ternary Ag—Cu—Sn alloys whose composition is near eutectic, and also pure Sn in the solders, processes and joints described herein. The following compositions also may be employed (wt. %) with the additives as described herein: Pure Sn+additives; Sn—Cu binary alloys: Sn more than about 90% and Cu about 0.1%-5%; Sn—Ag binary alloys: Sn more than about 90% and Ag about 0.25-7%; Sn—Ag—Cu ternary alloys: Sn more than about 90%, Ag about 0.25-7% and Cu about 0.1-5%. The foregoing is particularly useful for reflow or processing temperatures up to about 300° C. Similarly, Applicants' mechanism of composite formation and additives as described herein may be employed with the following ternary base alloys (wt. %, balance Sn): 4.7Ag-1.7Cu; 3.5Ag-0.9Cu; 4.0Ag-0.5Cu and 3.0Ag-0.5Cu.

[0069] The foregoing description has provided by way of exemplary and non-limiting examples a full and informative description of the best way presently contemplated by the inventors for carrying out the invention. However, various modifications and adaptations may become apparent to those skilled in the relevant arts in view of the foregoing description, when read in conjunction with the accompanying drawings and appended claims. However, all such and similar modifications of the teachings of this invention will still fall within the scope of this invention. Further, while the descriptions herein are provided with a certain degree of specificity, the present invention could be implemented with either greater or lesser specificity, depending on the needs of

the user. Further, some of the features of the present invention could be used to advantage without the corresponding use of other features. As such, the foregoing description should be considered as merely illustrative of the principles of the present invention, and not in limitation thereof, as this invention is defined by the claims which follow.

What is claimed is:

1. A Pb-free solder consisting essentially of, in weight %, greater than about 90% Sn, about 3.6-3.8% Ag, about 0.6-0.7% Cu, and comprising an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form an intermetallic interface between the solder and a substrate, the intermetallic interface having a composite structure without scallop formation and including Sn islands.

2. The Pb-free solder of claim 1, wherein the additive element is Au and the composite structure comprises $(\text{AuCu})_6\text{Sn}_5$ grains and dispersed (βSn) islands.

3. The Pb-free solder of claim 2, wherein the substrate is a copper electrical component.

4. The Pb-free solder of claim 3, wherein the electrical component is a printed circuit board.

5. The Pb-free solder of claim 2, wherein concentration of the Au in the solder is greater than about 0.25 weight %.

6. The Pb-free solder of claim 5, wherein the concentration of Au in the solder is about 1 weight %.

7. The Pb-free solder of claim 5, wherein the concentration of Au in the solder is about 2 weight %.

8. A solder joint comprising a Pb-free alloy having a composition consisting essentially of, in weight %, greater than about 90% Sn, about 3.6-3.8% Ag, about 0.6-0.7% Cu, and comprising an additive selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free alloy in an amount effective to form an intermetallic interface between the alloy and a soldered component, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

9. The solder joint of claim 8, wherein the additive element is Au and the composite structure comprises $(\text{AuCu})_6\text{Sn}_5$ grains and dispersed (βSn) islands.

10. The solder joint of claim 9, wherein the soldered component is an electrical component having a copper substrate.

11. The solder joint of claim 10, wherein the electrical component is a printed circuit board.

12. The solder joint of claim 8, wherein concentration of the Au in the solder is greater than about 0.25 weight %.

13. The solder joint of claim 12, wherein the concentration of Au in the solder is about 1 weight %.

14. The solder joint of claim 12, wherein the concentration of Au in the solder is about 2 weight %.

15. A Pb-free solder consisting of, in weight %, greater than about 90% Sn, about 3.6-3.8% Ag, about 0.6-0.7% Cu, and comprising an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form an intermetallic interface between the solder and a substrate, the intermetallic interface having a composite structure without scallop formation and including Sn islands.

16. A Pb-free solder joint consisting of, in weight %, about 90% Sn, about 3.6-3.8% Ag, about 0.7% Cu, and comprising an additive selected from the group consisting of

Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free alloy in an amount effective to form an intermetallic interface between the alloy and a soldered component to form a joint, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

17. A soldering process for a component comprising:

melting and solidifying a Pb-free solder consisting essentially of, in weight percent, about 90% Sn, about 3.6-3.8% Ag, about 0.6-0.7% Cu, and comprising an additive selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free solder in an amount effective to form an intermetallic interface between the solder and a soldered component, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

18. The soldering process of claim 17, wherein molten solder is solidified in contact with an electrical component having a copper substrate to form a solder joint.

19. The soldering process of claim 18 wherein the additive is Au in an amount greater than about 0.25 weight %.

20. A modified Sn—Ag—Cu, lead-free solder alloy comprising an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the modified Sn—Ag—Cu, lead-free solder alloy in an amount effective to form an intermetallic interface between the alloy a substrate, the intermetallic interface having a composite structure without scallop formation and including Sn islands.

21. The modified Sn—Ag—Cu, lead free solder alloy of claim 20, wherein the additive element is Au and the composite structure comprises $(\text{AuCu})_6\text{Sn}_5$ grains and dispersed (βSn) islands.

22. The modified Sn—Ag—Cu lead free solder alloy of claim 21 wherein greater than about 0.25 weight % of the additive element is added to the alloy.

23. A method of making a lead-free alloy comprising:

melting and solidifying a Pb-free alloy consisting essentially of, in weight percent, greater than about 90% Sn, about 3.6-3.8% Ag, about 0.6-0.7% Cu, and comprising an additive selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free alloy in an amount effective to form an intermetallic interface between the alloy and a substrate, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

24. The method of claim 23, wherein the additive element is Au and the composite structure comprises $(\text{AuCu})_6\text{Sn}_5$ grains and dispersed (βSn) islands.

25. The method of claim 24, wherein greater than about 0.25 weight % of the additive element is added to the alloy.

26. A modified Sn—Ag—Cu, lead-free solder alloy comprising an additive element of Au, the modified Sn—Ag—Cu, lead-free solder alloy having a quaternary eutectic reaction at $204.5 \pm 0.3^\circ \text{C}$., wherein the alloy comprises a eutectic microstructure with equilibrium phases of AuSn_4 , Ag_3Sn , (βSn) , and Cu_6Sn_5 .

27. The modified Sn—Ag—Cu, lead free-solder alloy of claim 26, having a composition comprising, in weight %, about 3.6-3.8Ag, about 0.6-0.7Cu, greater than about 0.9Sn.

28. A method of forming a composite interface layer between a copper substrate and a Sn-based lead free solder comprising the steps of:

providing a Sn-based lead free solder;

adding an additive element to the Sn-based lead free solder in an amount effective to form an intermetallic interface layer between the solder and the copper substrate, the intermetallic interface layer having a composite structure without scallop formation and including Sn islands, wherein the additive element is selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof.

29. The method of claim 28, wherein the additive element is Au in an amount greater than about 0.25 weight %.

30. The method of claim 29, wherein the composite structure comprises (AuCu)₆Sn₅ grains and dispersed (βSn) islands.

31. The method of claim 30, wherein the Sn-based lead free solder is provided in molten form.

32. The method of claim 28, wherein a coating layer is provided for the copper substrate.

33. The method of claim 28, wherein the Sn-based lead free solder is selected from the group consisting of Ag—Sn, Cu—Sn binary and ternary Ag—Cu—Sn alloys and Sn.

34. The method of claim 33, wherein the Cu—Sn binary alloy comprises, in weight %, greater than about 90% Sn and between about 0.1-5% Cu.

35. The method of claim 33, wherein the Ag—Sn binary alloy comprises, in weight %, greater than about 90% Sn and between about 0.25-7% Ag.

36. A composite, intermetallic layer on a Cu substrate, the composite, intermetallic layer having a composite structure without scallop formation and including Sn islands, wherein a molten solder comprises an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form the composite, intermetallic layer between the solder and the Cu substrate.

37. The solder of claim 1 comprising a base solder alloy of 3.8Ag-0.7Cu—Sn.

38. The solder of claim 5 comprising a base solder alloy of 3.8Ag-0.7Cu—Sn.

39. The solder of claim 1, wherein the Sn islands are about 0.2-0.8 μm.

40. The solder of claim 5, wherein the Sn islands are about 0.2-0.8 μm.

41. The solder of claim 1, wherein intermetallic size is about 0.3-1.2 μm.

42. The solder of claim 5, wherein intermetallic size is about 0.3-1.2 μm.

43. A Pb-free solder consisting essentially of, in weight %, greater than about 90% Sn, about 0.25-7% Ag, about 0.1-5% Cu, and comprising an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form an intermetallic interface between the solder and a substrate, the intermetallic interface having a composite structure without scallop formation and including Sn islands.

44. The solder of claim 43 comprising 4.7Ag-1.7Cu.

45. The solder of claim 44, wherein the additive element is Au.

46. The solder of claim 43 comprising 3.5Ag-0.9Cu.

47. The solder of claim 43 comprising 4.0Ag-0.5Cu.

48. The solder of claim 43 comprising 3.0Ag-0.5Cu.

49. A Pb-free solder consisting of, in weight %, greater than about 90% Sn, about 0.1-5% Cu an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form an intermetallic interface between the solder and a substrate, the intermetallic interface having a composite structure without scallop formation and including Sn islands.

50. A Pb-free solder consisting of, in weight %, greater than about 90% Sn, about 0.25-7% Ag and an additive element selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the solder in an amount effective to form an intermetallic interface between the solder and a substrate, the intermetallic interface having a composite structure without scallop formation and including Sn islands.

51. A soldering process for a component comprising:

melting and solidifying a Pb-free solder consisting essentially of, in weight percent, about 90% Sn, about 0.25-7Ag, about 0.1-5% Cu, and comprising an additive selected from the group consisting of Au, Ni, Pd, Fe, Co, Zn, Cr and combinations thereof, present in the Pb-free solder in an amount effective to form an intermetallic interface between the solder and a soldered component, the intermetallic interface having a composite structure free from scallop formation and including Sn islands.

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