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(54) **COST-EFFECTIVE LEAD-FREE SOLDER ALLOY FOR ELECTRONIC APPLICATIONS**

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CPC ***B23K 35/262*** (2013.01); ***B23K 35/26*** (2013.01); ***C22C 13/00*** (2013.01); ***C22C 13/02*** (2013.01); *B23K 35/0244* (2013.01)

(57) **ABSTRACT**

A lead-free silver-free solder alloy may comprise tin, copper, bismuth, cobalt, and antimony. Alternatively, the alloy may comprise gallium in lieu of cobalt. The alloy may further comprise nickel, germanium, or both. The copper may be present in an amount from about 0.5% to 0.9% by weight of the solder. The bismuth may be present in an amount from about 1.0% to about 3.5% by weight of the solder. The cobalt may be present in an amount from about 0.02% to about 0.08% by weight of the solder. Where gallium is used in lieu of cobalt, the gallium may be present in an amount from about 0.2% to about 0.8% by weight of the solder. The antimony may be present in an amount between about 0.0% to about 0.09% by weight of the solder. The balance of the solder is tin.

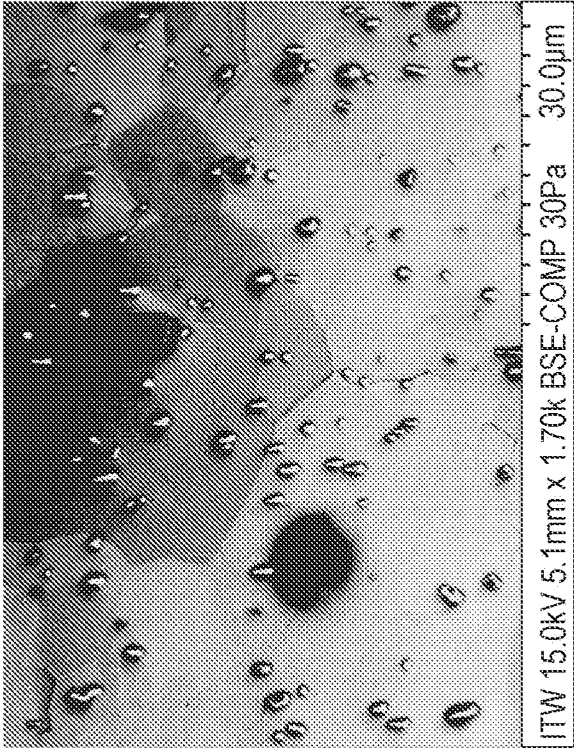

FIG. 1B
(Prior Art)

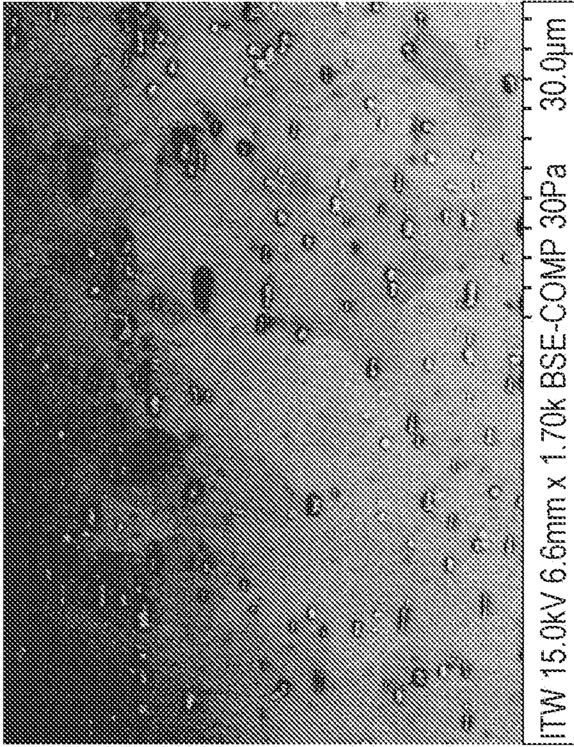

FIG. 1A
(Prior Art)

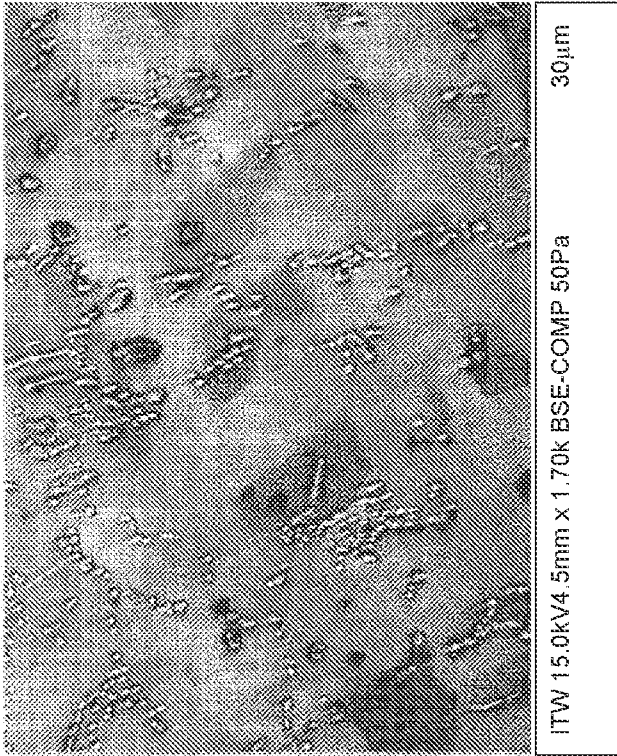

FIG. 2B

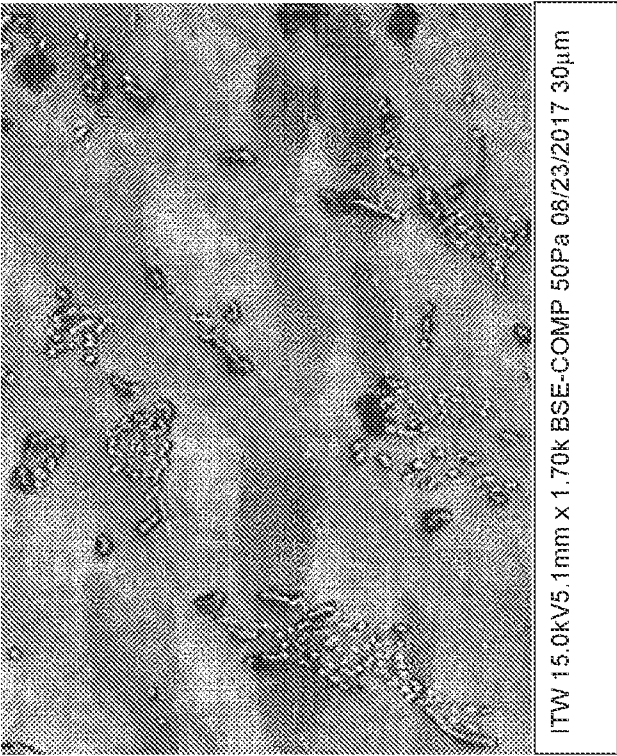

FIG. 2A

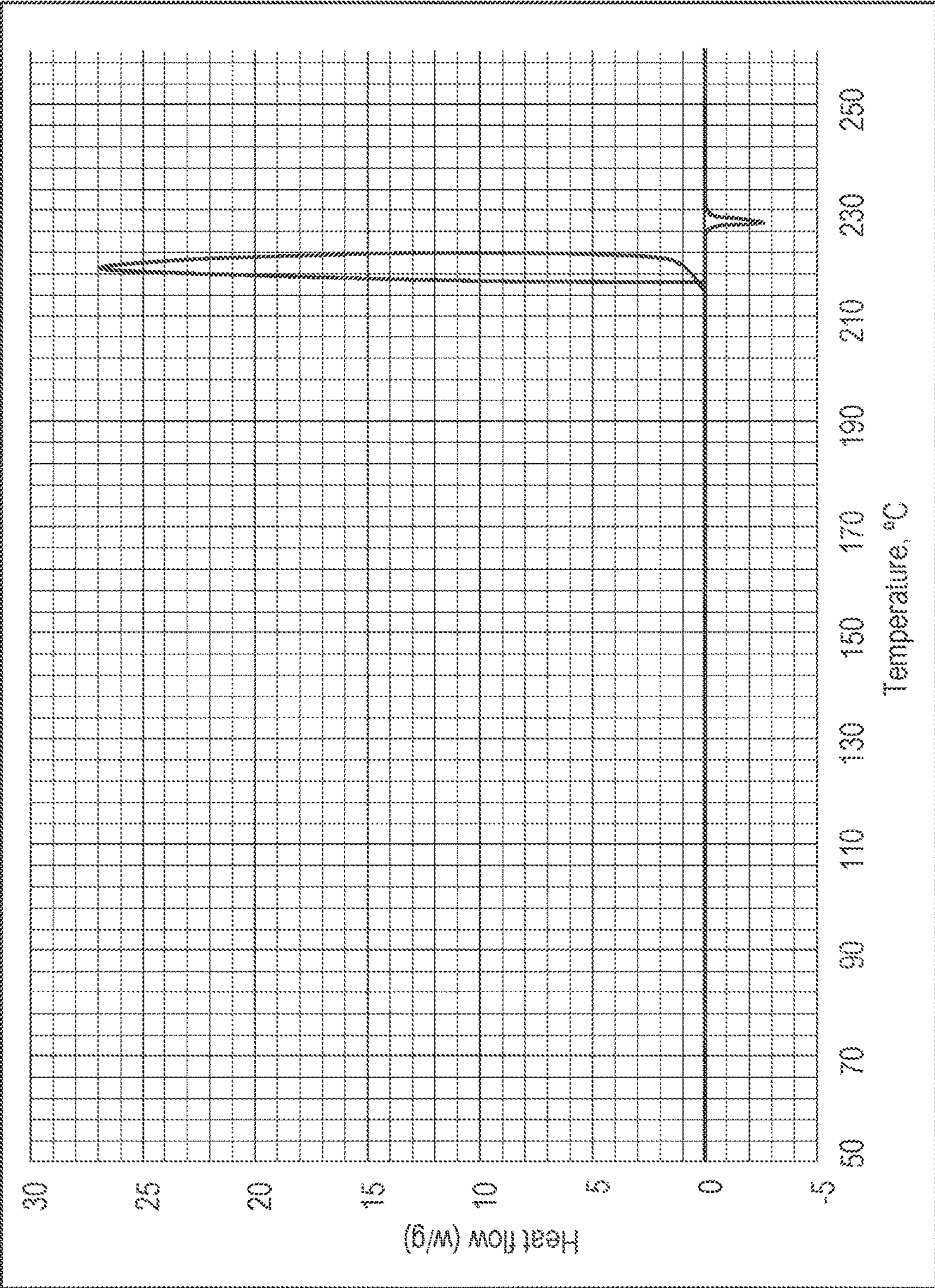

FIG. 3
(Prior Art)

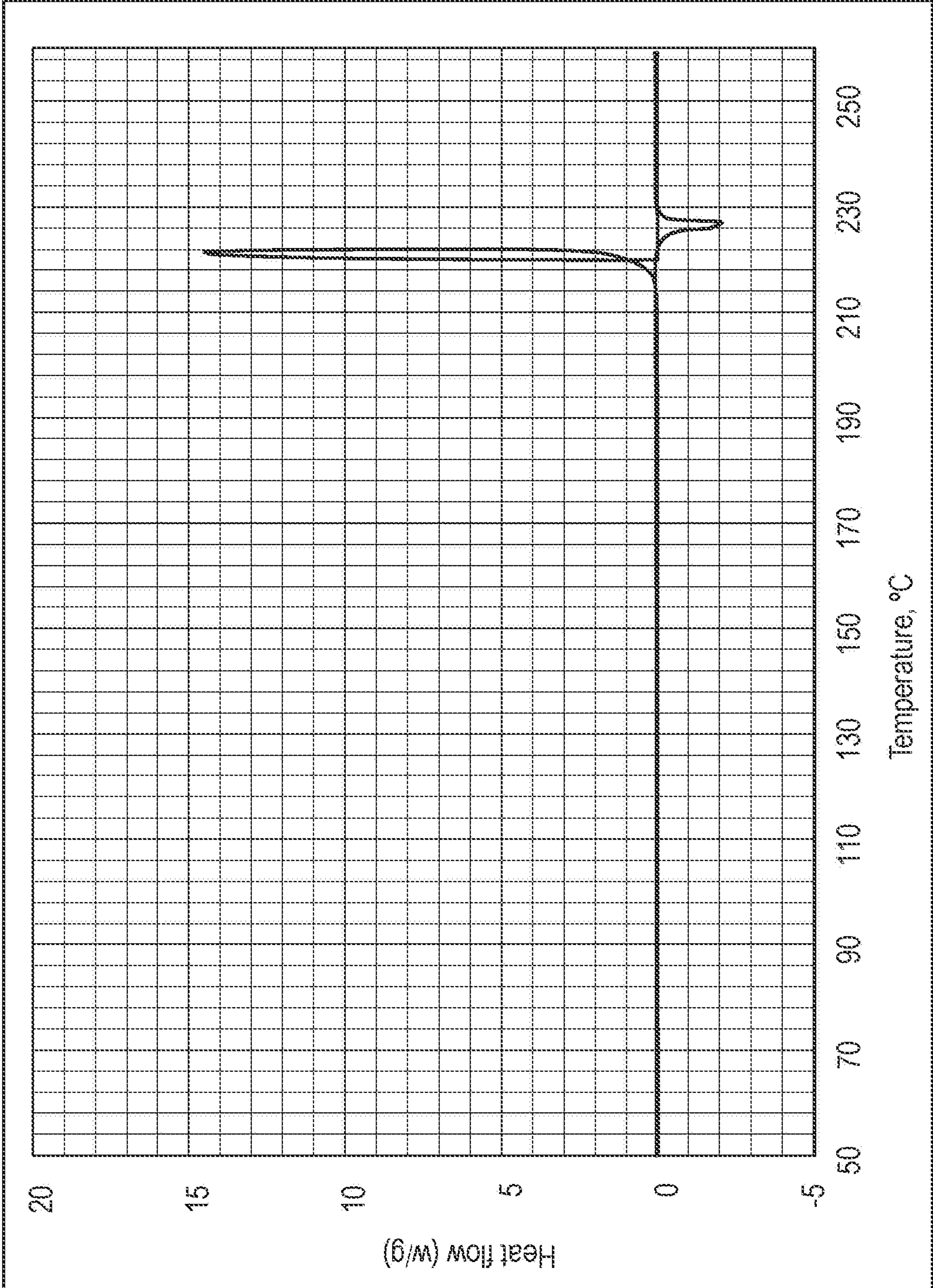

FIG. 4

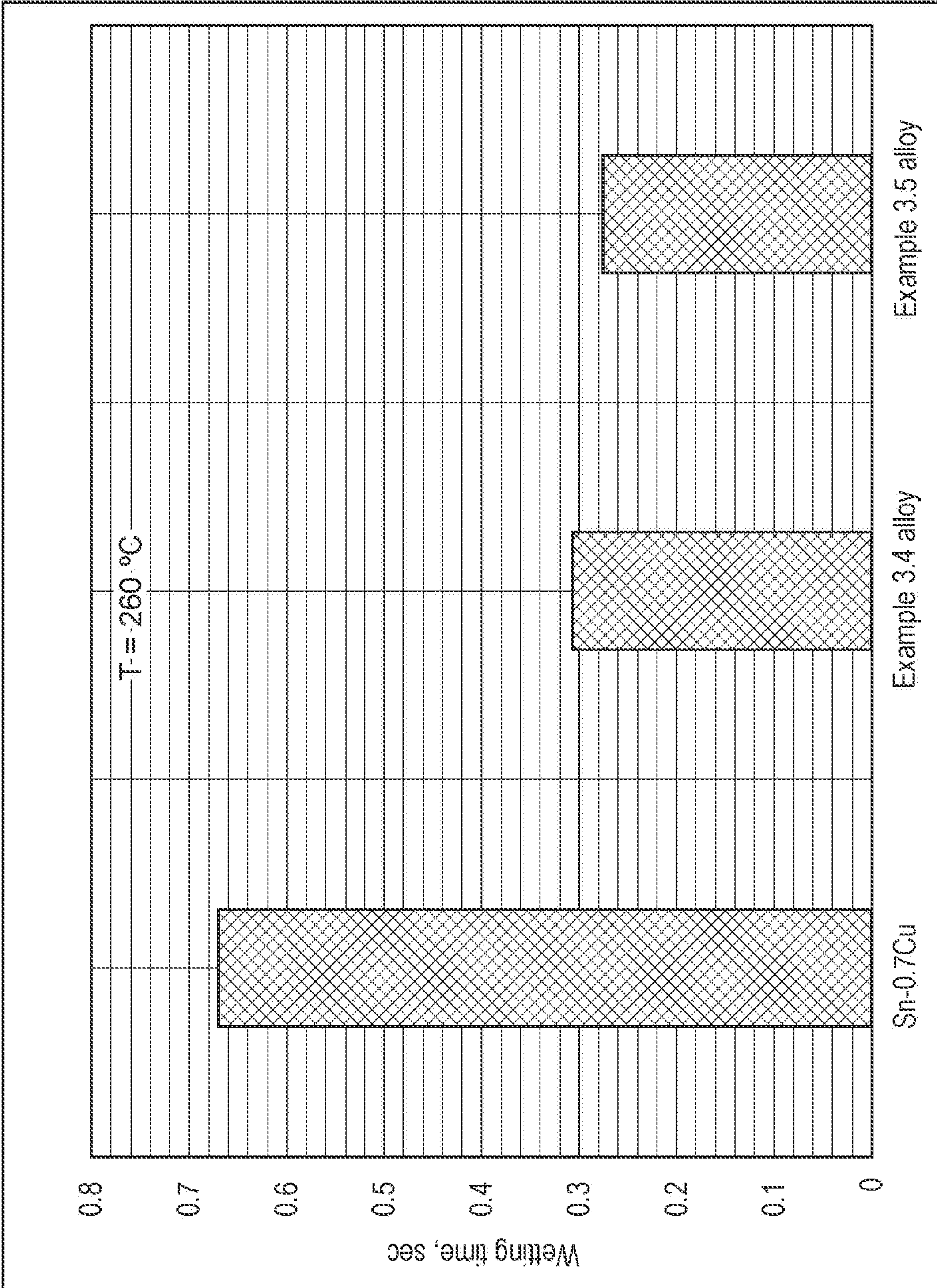

FIG. 5A

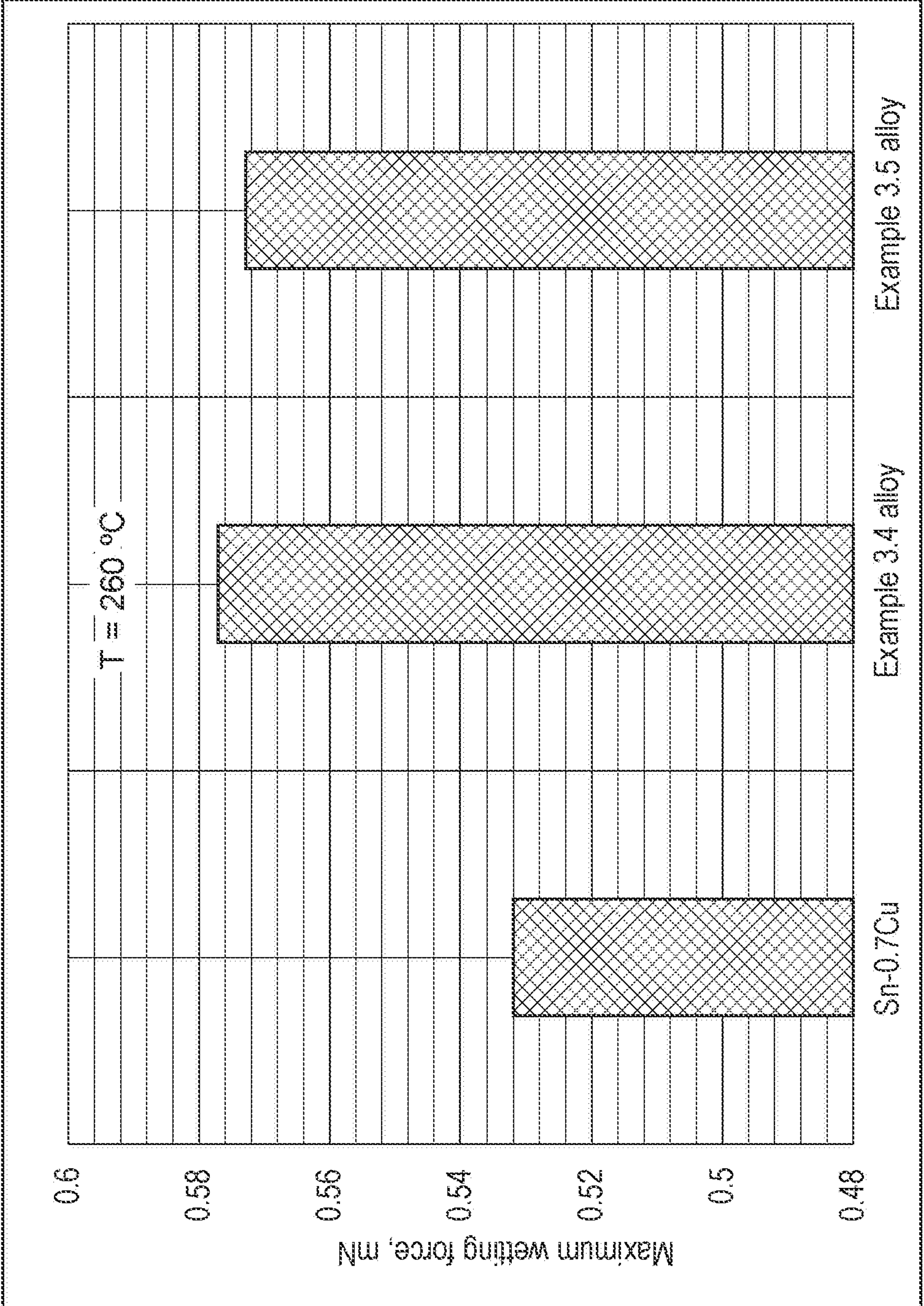

FIG. 5B

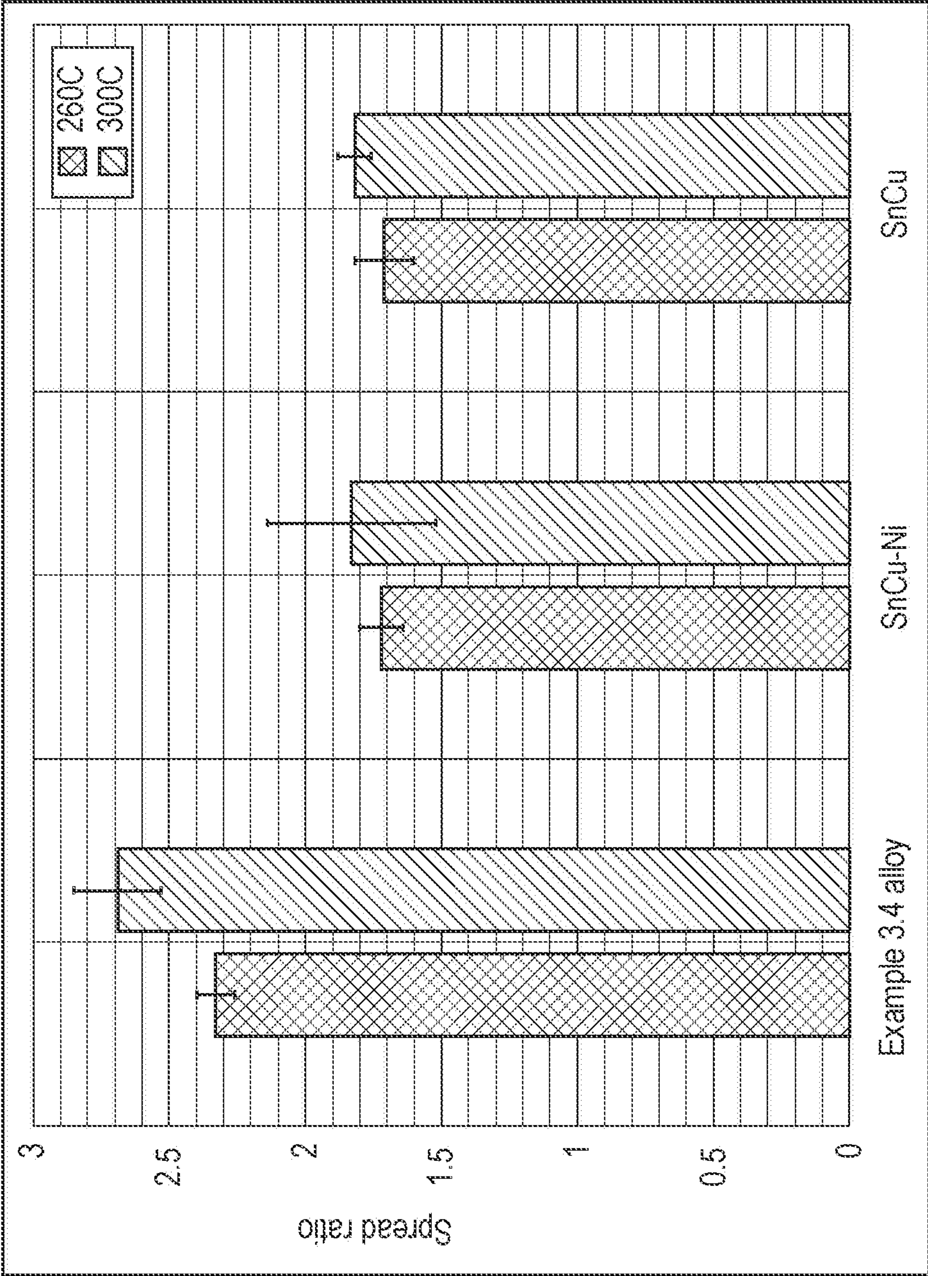

FIG. 6A

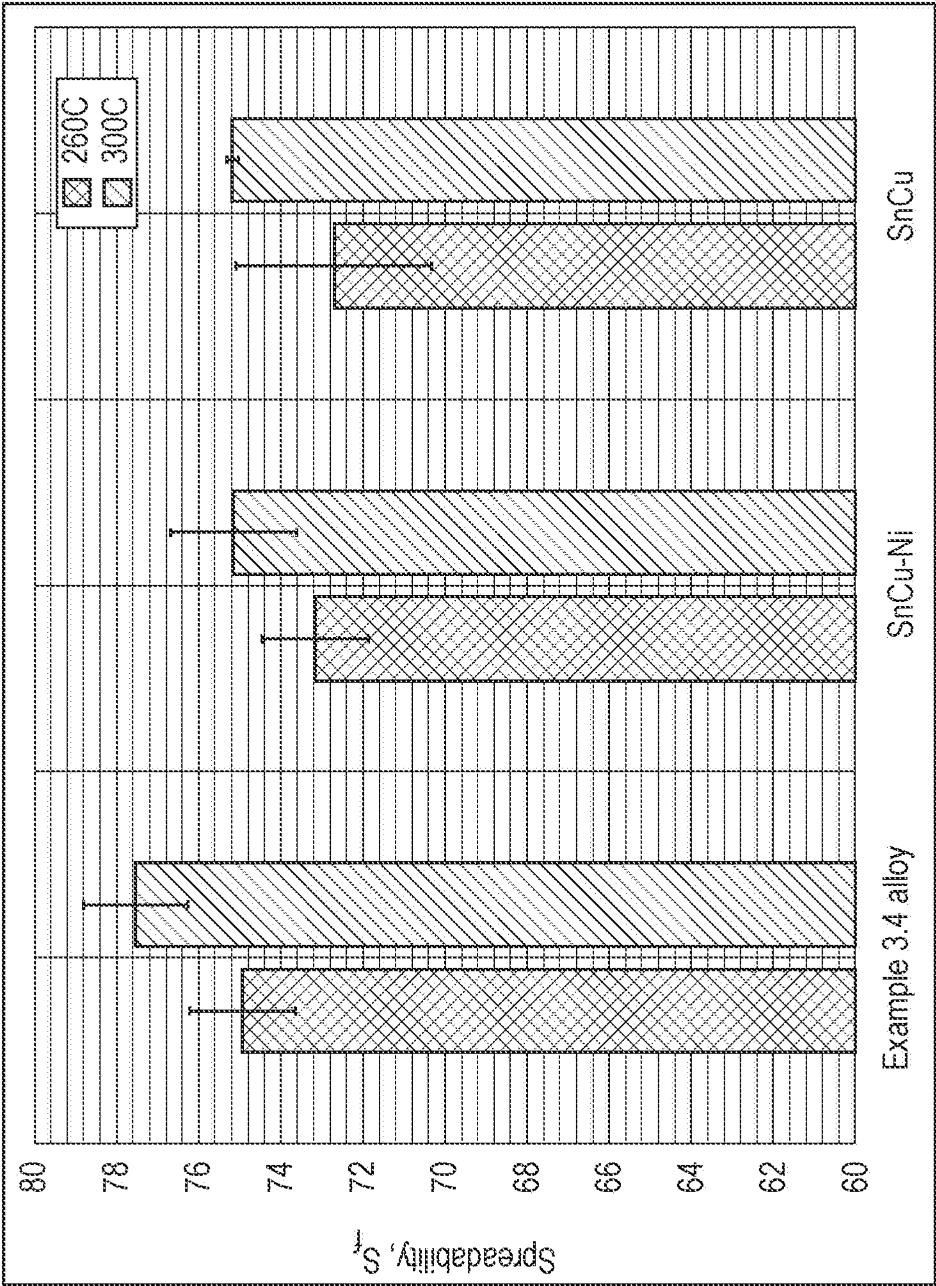

FIG. 6B

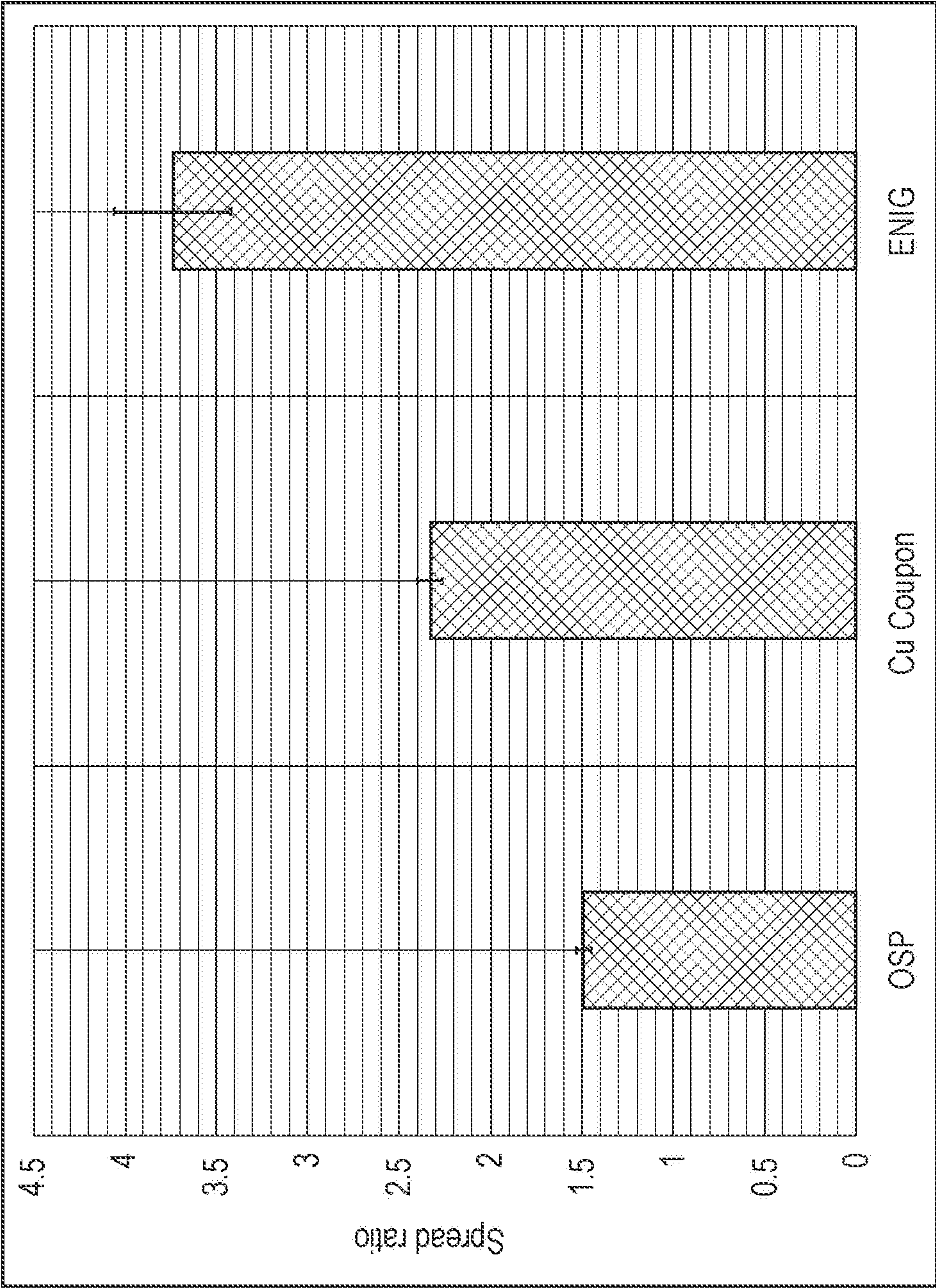

FIG. 7A

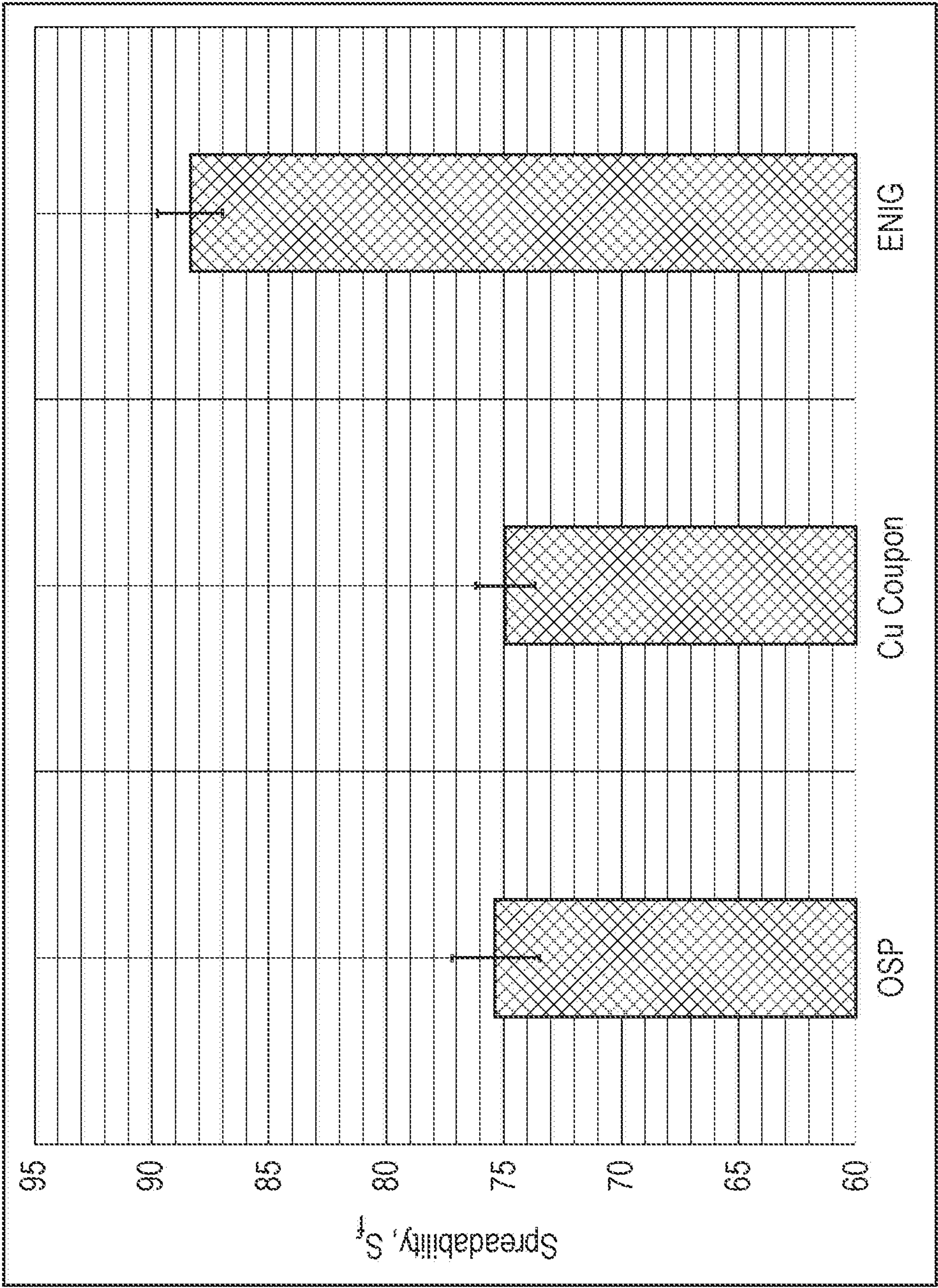

FIG. 7B

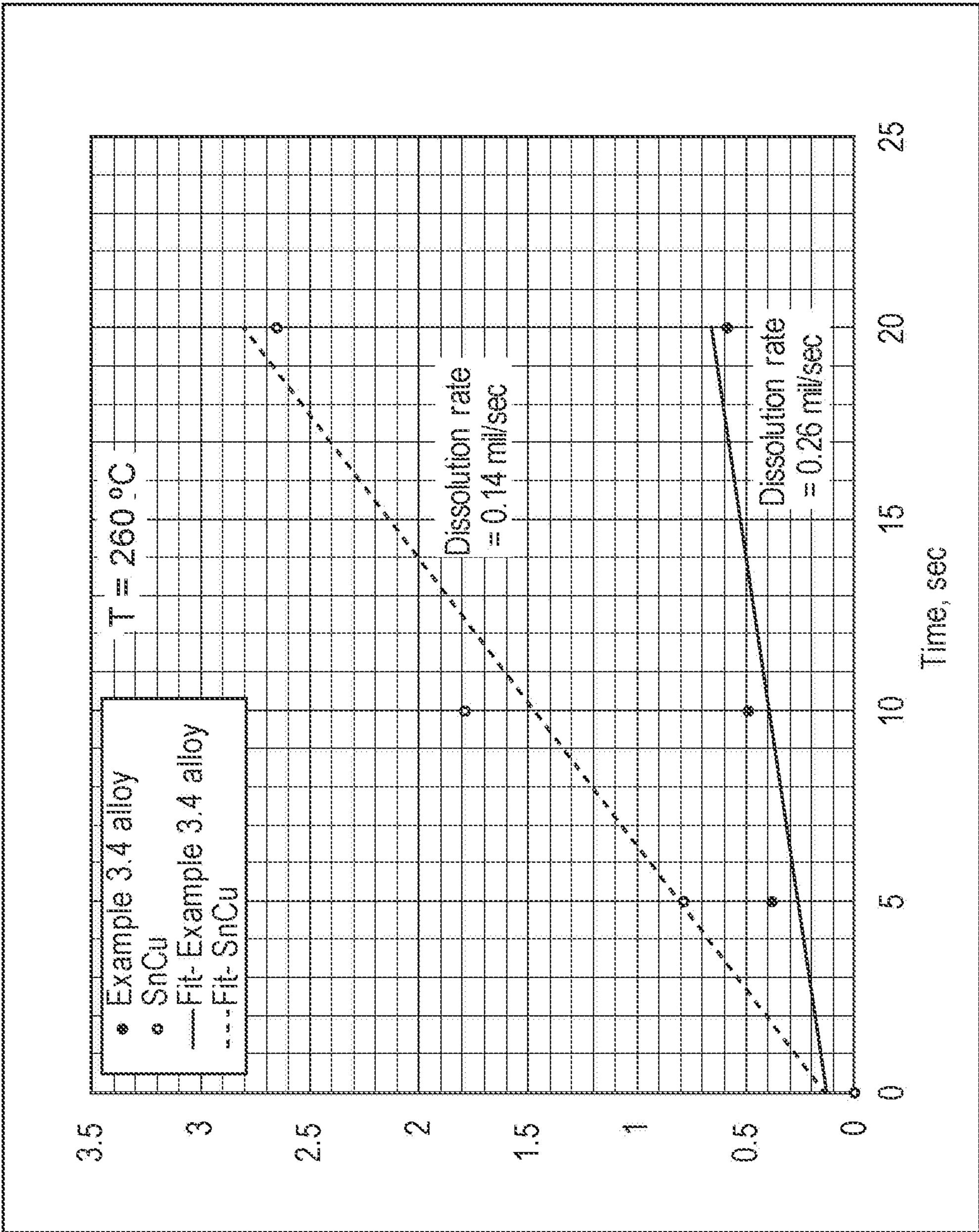

FIG. 8A

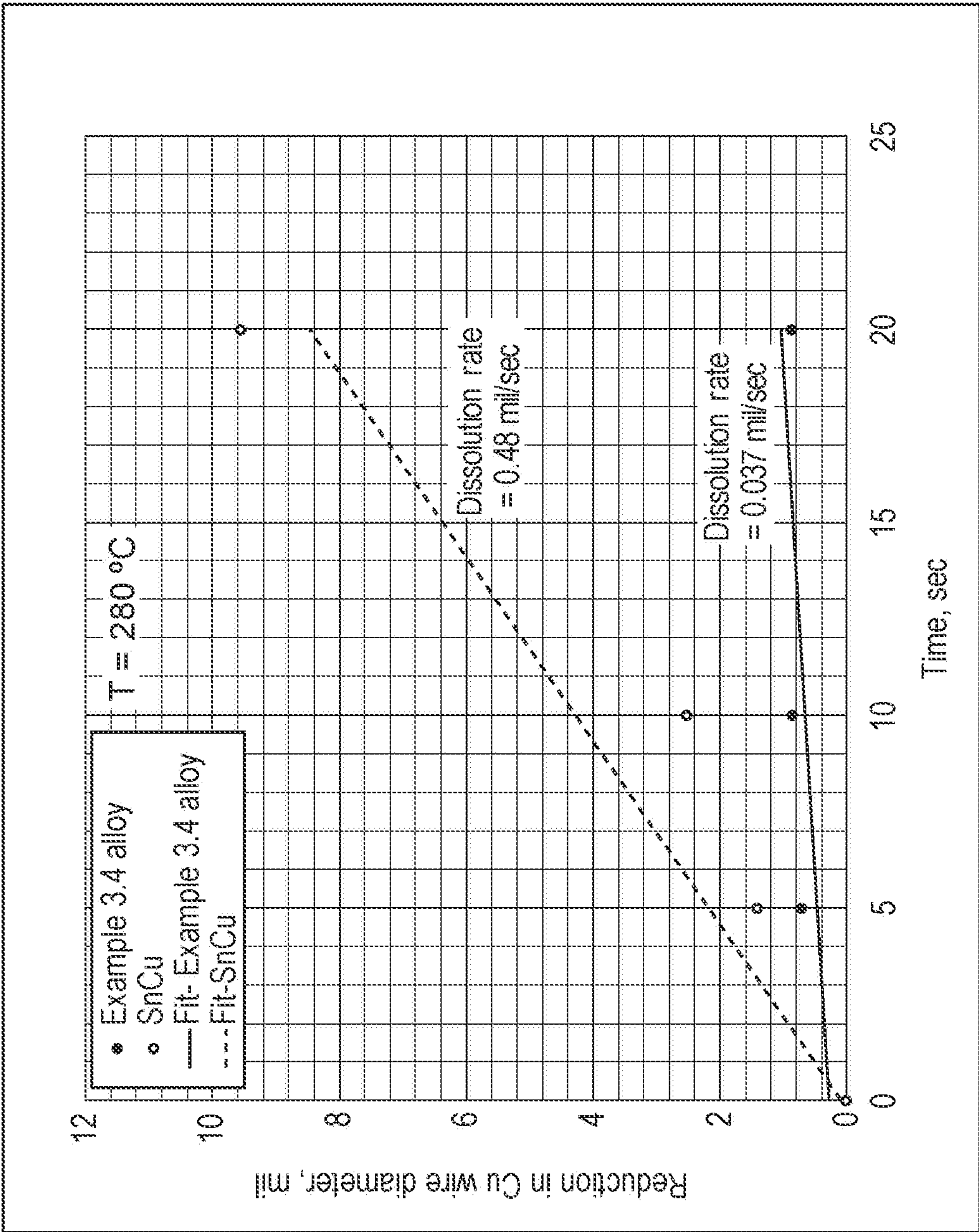

FIG. 8B

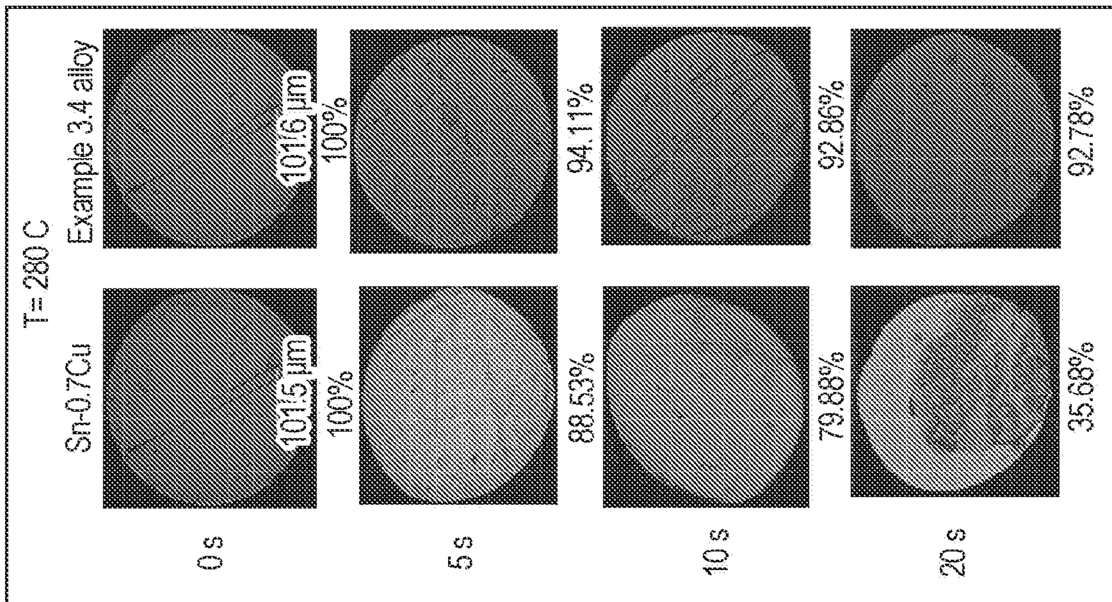

FIG. 9B

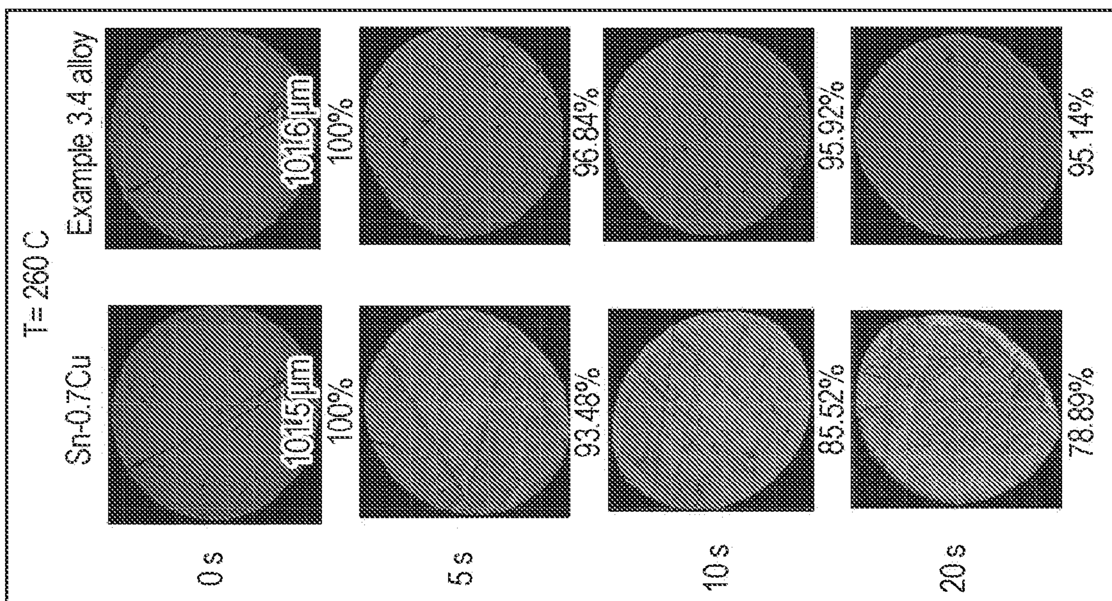

FIG. 9A

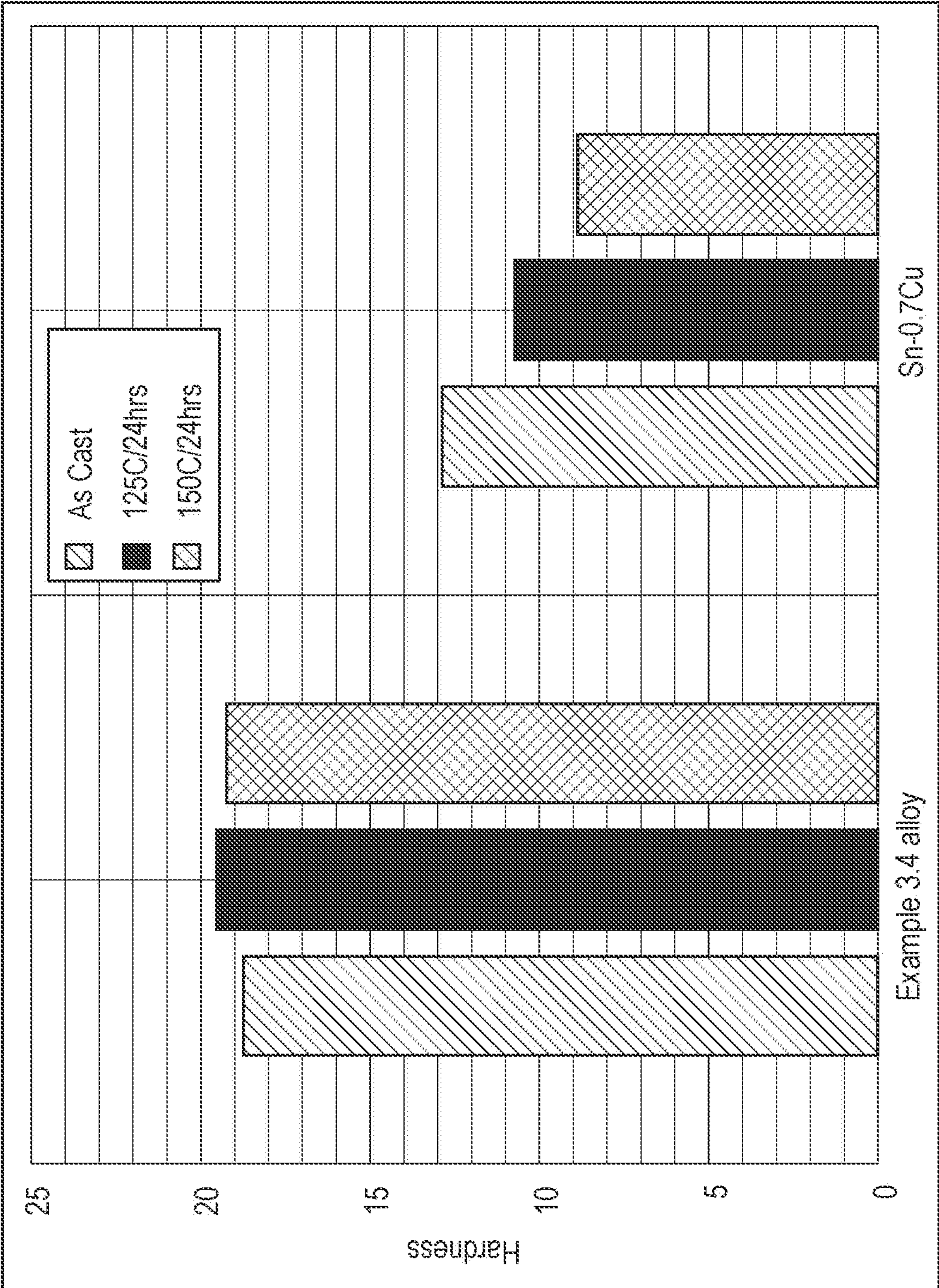

FIG. 10A

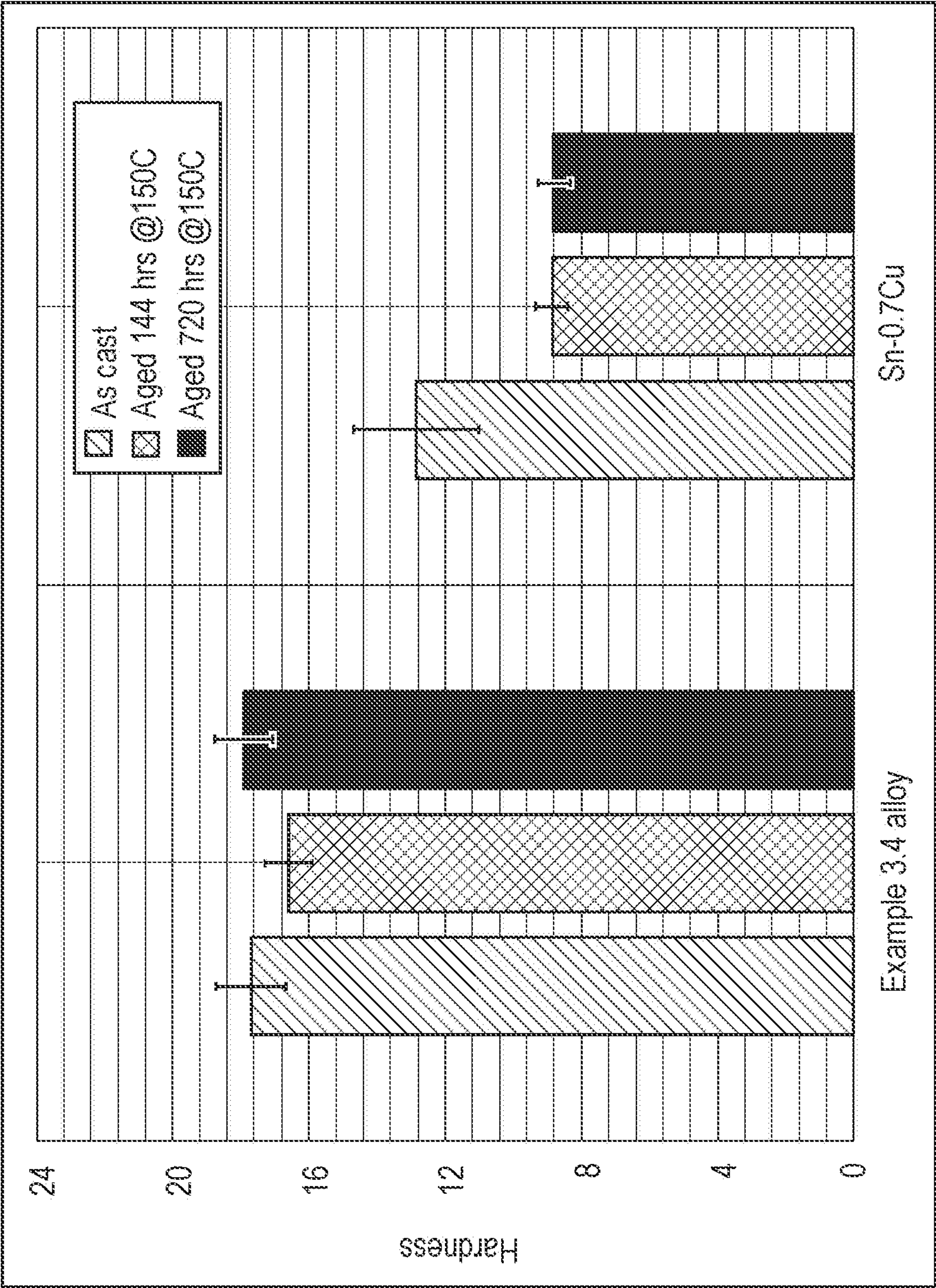

FIG. 10B

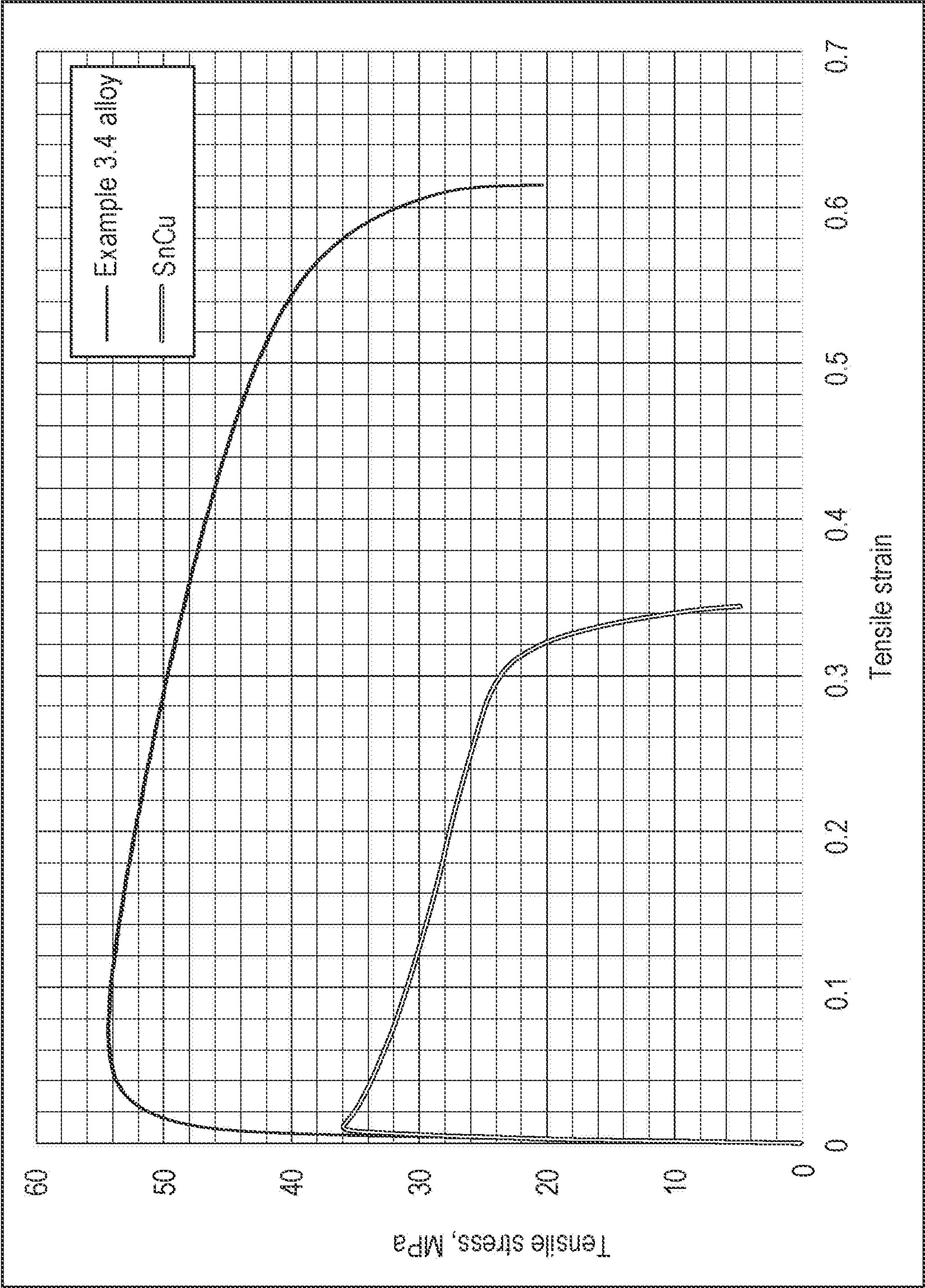

FIG. 11

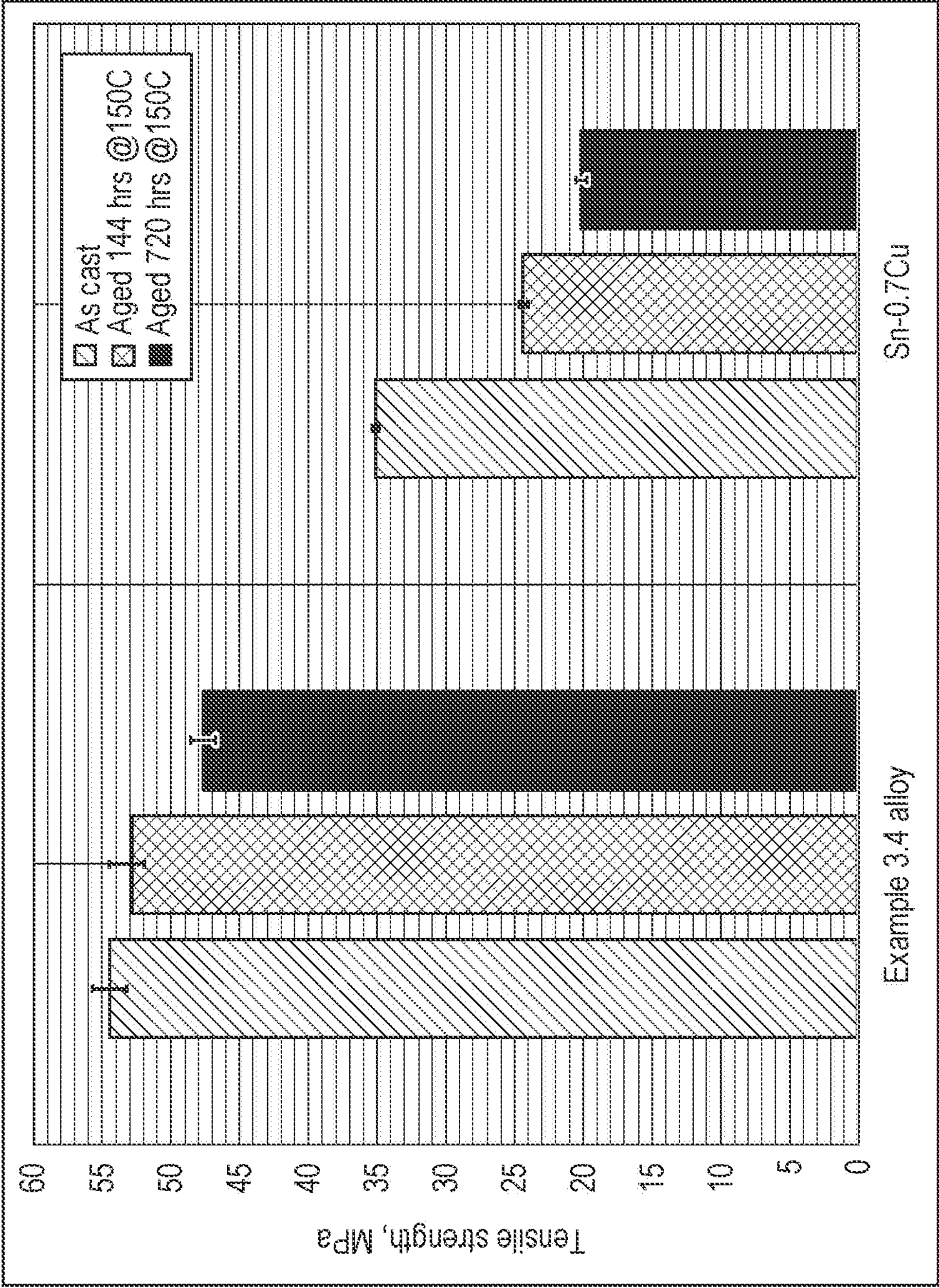

FIG. 12

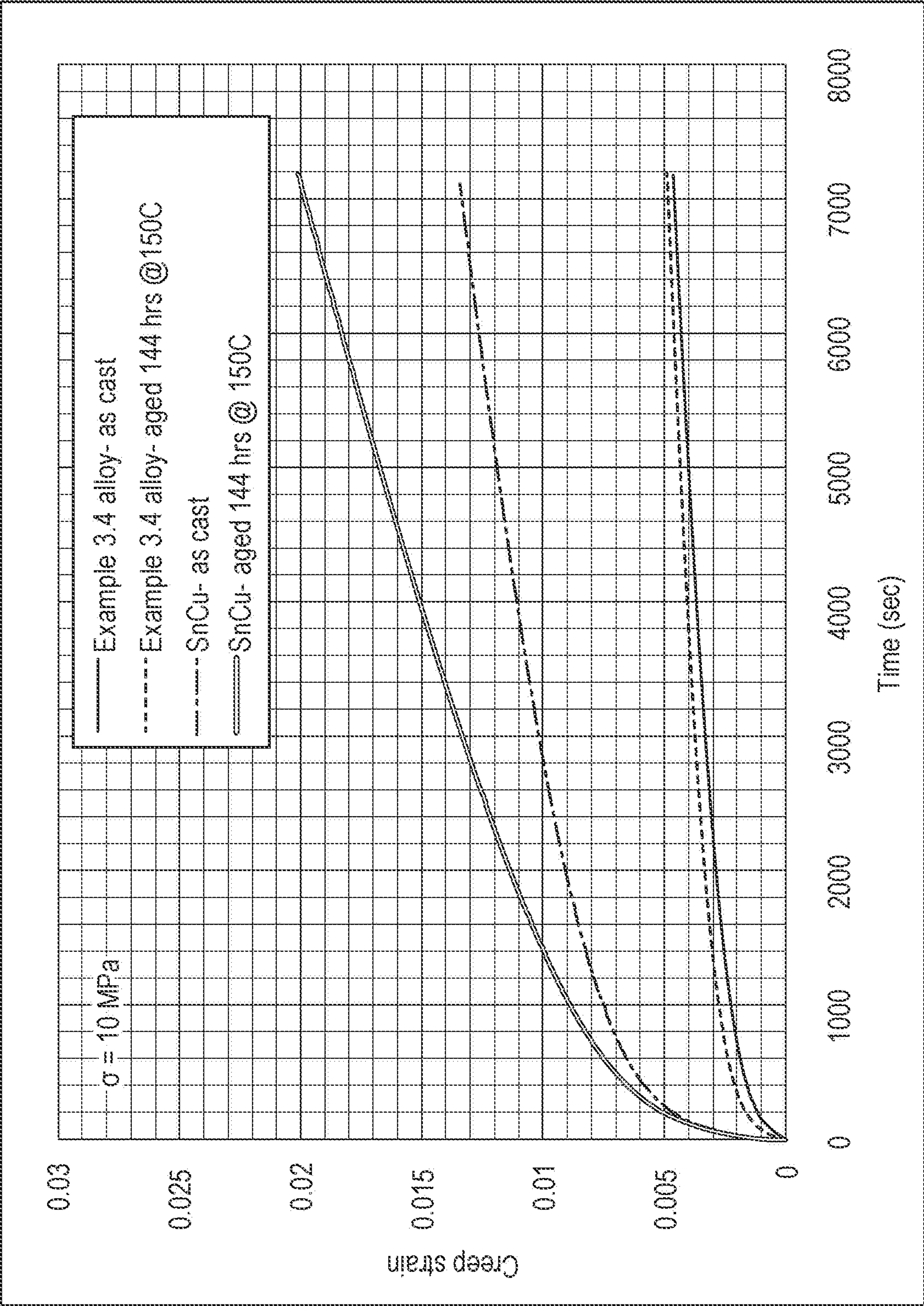

FIG. 13

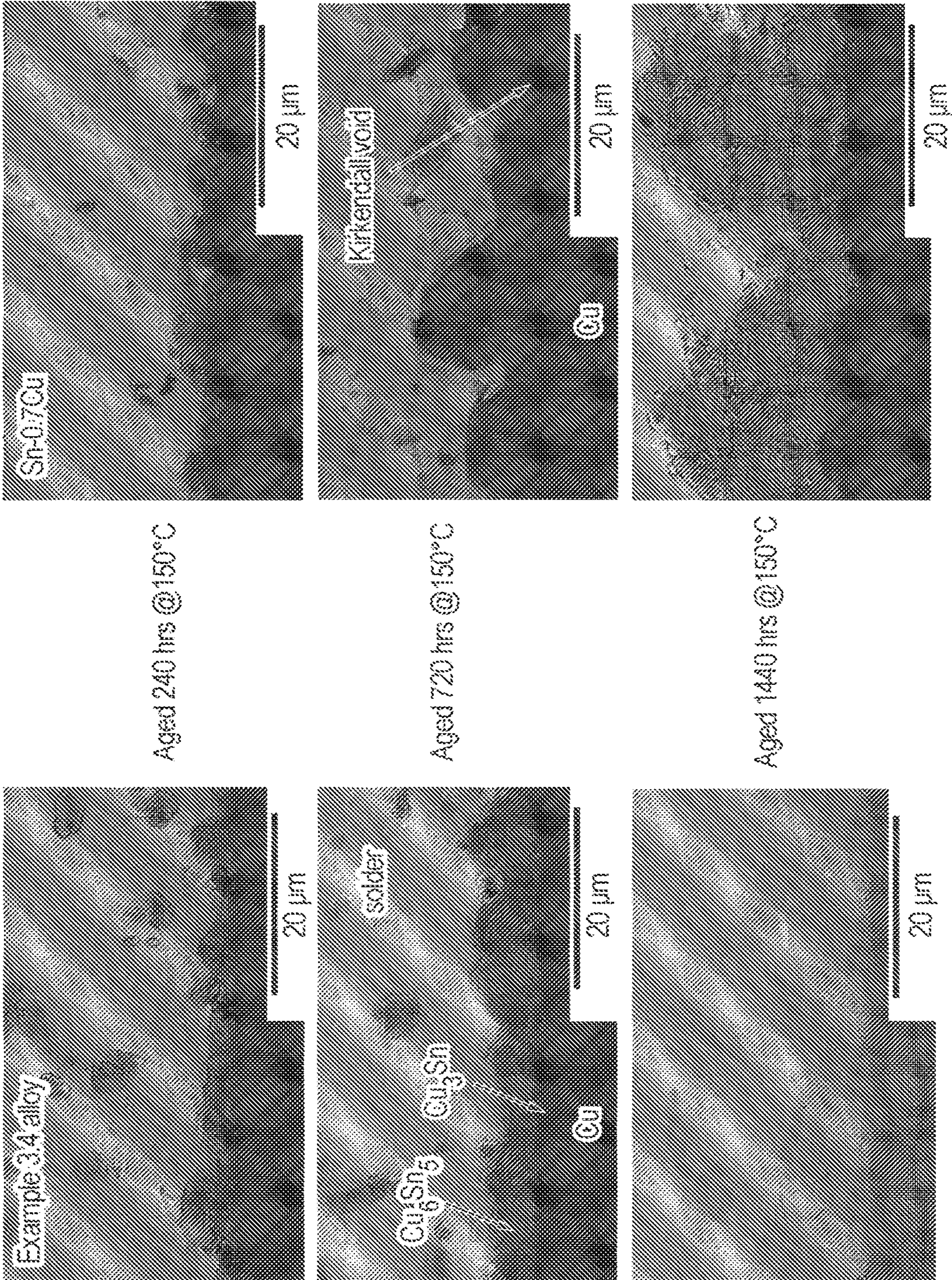

FIG. 14A

FIG. 14B
(Prior Art)

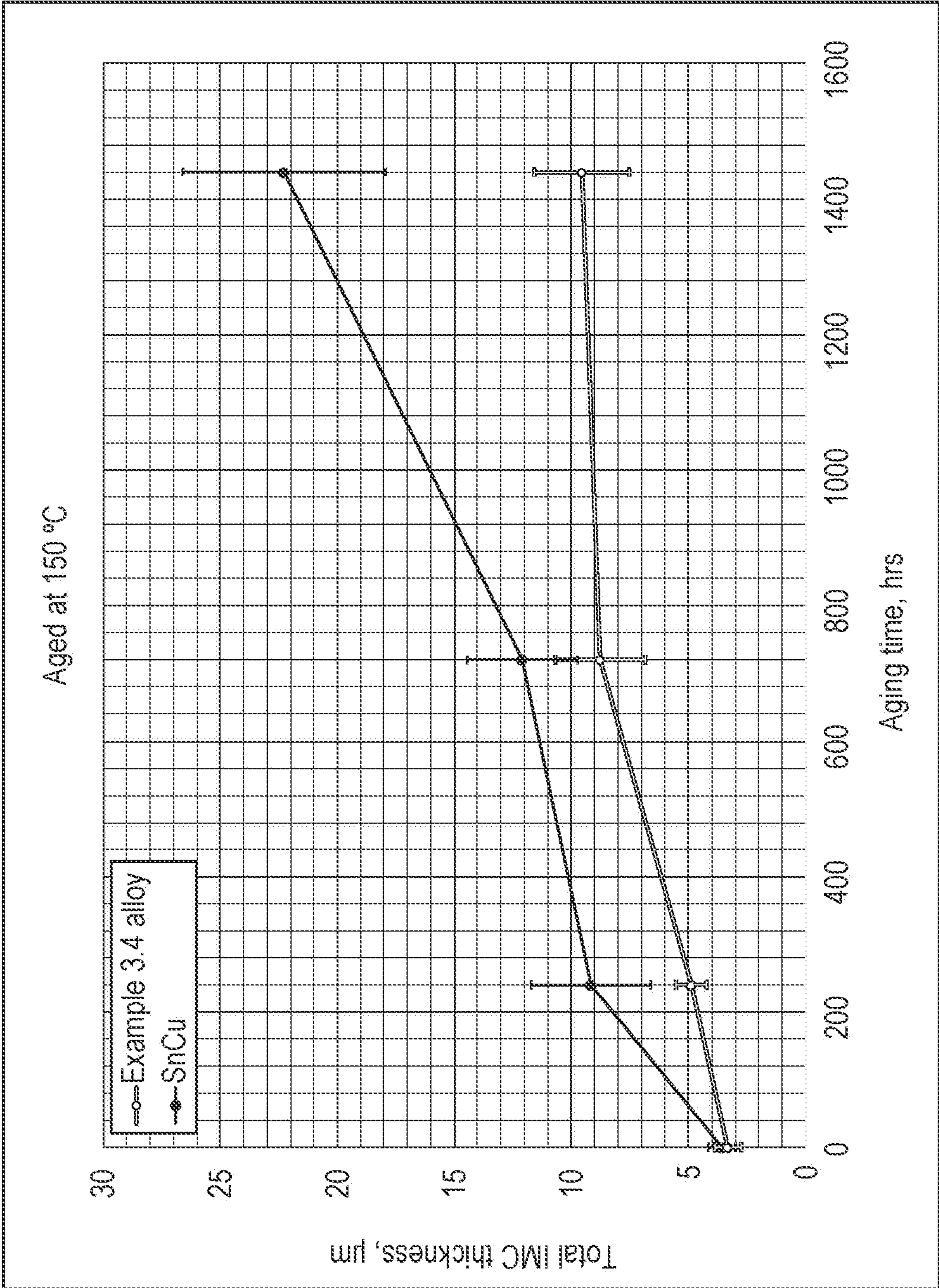

FIG. 15

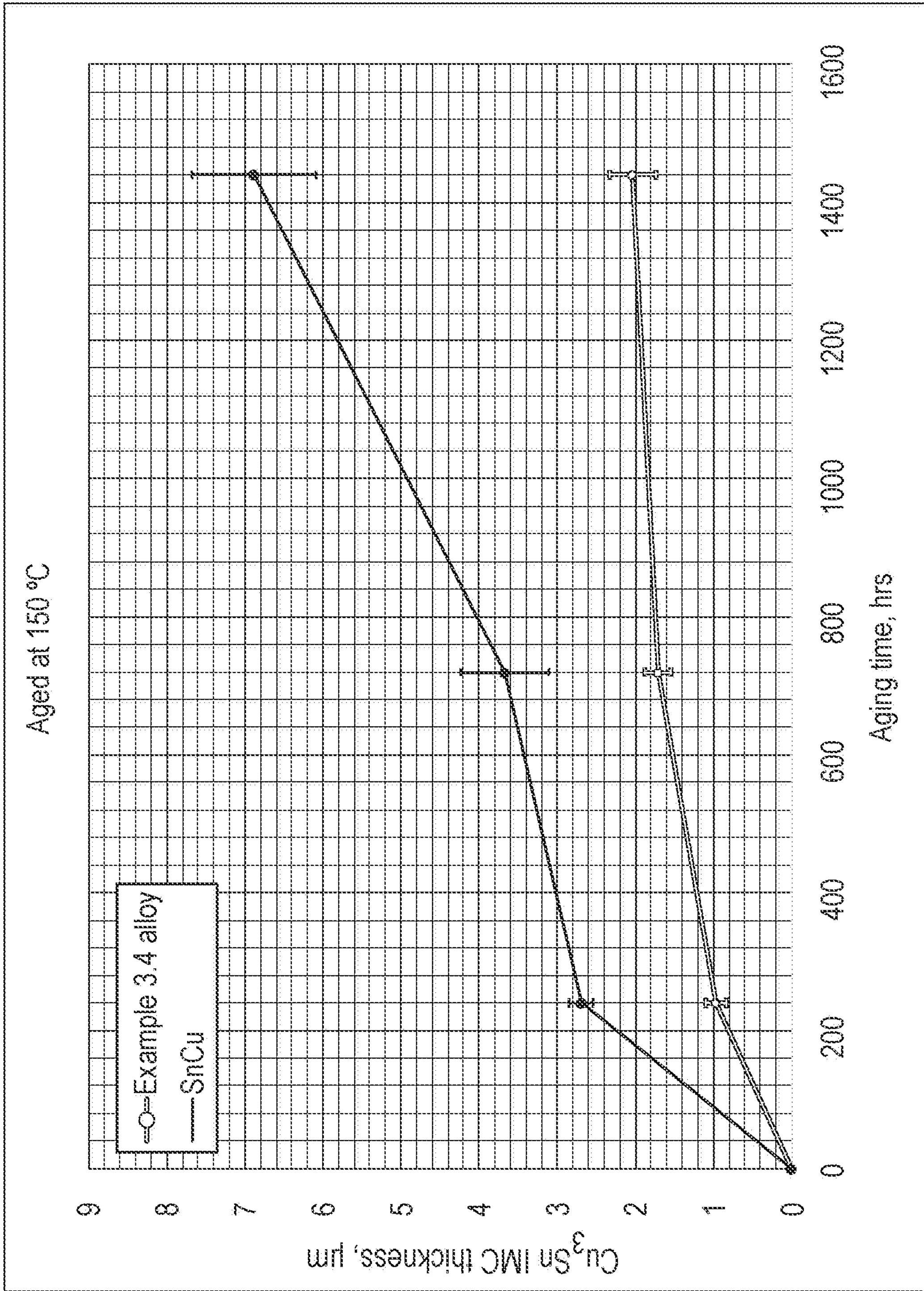

FIG. 16

COST-EFFECTIVE LEAD-FREE SOLDER ALLOY FOR ELECTRONIC APPLICATIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of U.S. Provisional Pat. Application No. 62/583,271, filed Nov. 8, 2017, the entire contents of which are incorporated herein by reference.

FIELD

[0002] The present disclosure generally relates to lead-free, silver-free solder alloys for electronic applications.

BACKGROUND

[0003] Solder alloys are widely used for manufacturing and assembly a variety of electronic devices. Traditionally, solder alloys have been tin-lead based alloys. Tin-lead based alloys were used to prepare solder with desired materials properties, including a suitable melting point and pasty range, wetting properties, ductility, and thermal conductivities. However, lead is a highly toxic, environmentally hazardous material that can cause a wide range of harmful effects. As a result, research has focused on producing lead-free solder alloys with desired materials properties.

[0004] The present disclosure relates to a low cost lead-free solder alloy providing desired materials properties including—as compared to certain prior art alloys—a lower undercooling temperature, minimal copper dissolution, improved mechanical properties, and long-term reliability under demanding environmental conditions.

SUMMARY

[0005] According to one aspect of the present disclosure, a lead-free and silver-free alloy comprises: 0.5 to 0.9 wt. % copper; 1.0 to 3.5 wt. % bismuth; 0.02 to 0.08 wt. % cobalt; 0.0 to 0.09 wt. % antimony; and balance tin, together with any unavoidable impurities. Optionally, the alloy further comprises 0.001 to 0.01 wt. % germanium and/or 0.01 to 0.1 wt. % nickel.

[0006] According to another aspect of the present disclosure, a lead-free and silver-free alloy comprises: 0.6 to 0.8 wt. % copper; 1.2 to 1.8 wt. % bismuth; 0.04 to 0.06 wt. % cobalt; 0.02 to 0.08 wt. % antimony; and balance tin, together with any unavoidable impurities. Optionally, the alloy further comprises 0.004 to 0.008 wt. % germanium and/or 0.03 to 0.07 wt. % nickel.

[0007] According to another aspect of the present disclosure, a lead-free and silver-free alloy comprises: 0.7 wt. % copper; 1.5 wt. % bismuth; 0.05 wt. % cobalt; 0.05 wt. % antimony; and balance tin, together with any unavoidable impurities. Optionally, the alloy further comprises 0.006 wt. % germanium and/or 0.05 wt. % nickel.

[0008] According to another aspect of the present disclosure, a lead-free and silver-free alloy comprises: 0.5 to 0.9 wt. % copper; 1.0 to 3.5 wt. % bismuth; 0.2 to 0.8 wt. % gallium; 0.0 to 0.09 wt. % antimony; and balance tin, together with any unavoidable impurities.

[0009] According to another aspect of the present disclosure, a lead-free and silver-free alloy comprises: 0.6 to 0.8 wt. % copper; 1.2 to 1.8 wt. % bismuth; 0.4 to 0.6 wt. % gallium; 0.02 to 0.08 wt. % antimony; and balance tin, together with any unavoidable impurities. Optionally, the alloy further comprises 0.004 to 0.008 wt. % germanium and/or 0.03 to 0.07 wt. % nickel.

[0010] According to another aspect of the present disclosure, a lead-free and silver-free alloy comprises: 0.7 wt. % copper; 1.5 wt. % bismuth; 0.5 wt. % gallium; 0.05 wt. % antimony; and balance tin, together with any unavoidable impurities. Optionally, the alloy further comprises 0.006 wt. % germanium and/or 0.05 wt. % nickel.

[0011] It is to be understood that both the foregoing general description and the following detailed description describe various embodiments and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter. The accompanying drawings are included to provide a further understanding of the various embodiments, and are incorporated into and constitute a part of this specification. The drawings illustrate the various embodiments described herein, and together with the description serve to explain the principles and operations of the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The following is a description of the examples depicted in the accompanying drawings. The figures are not necessarily to scale, and certain features and certain views of the figures may be shown exaggerated in scale or in schematic in the interest of clarity or conciseness.

[0013] FIG. **1**A is a SEM micrograph of a prior art tin-copper alloy in as cast condition.

[0014] FIG. **1**B is a SEM micrograph of a prior art tin-copper alloy that has been aged at 125 degree C for 24 hours.

[0015] FIG. **2**A is a SEM micrograph of an alloy according to the present disclosure in as cast condition.

[0016] FIG. **2**B is a SEM micrograph of an alloy according to the present disclosure that has been aged at 125 degree C for 24 hours.

[0017] FIG. **3** is a differential scanning calorimetry (DSC) chart for a prior art tin-copper alloy.

[0018] FIG. **4** is a differential scanning calorimetry (DSC) chart for an alloy according to the present disclosure.

[0019] FIG. **5**A is a bar chart showing a comparison between the wetting time of two alloys according to the present disclosure and a prior art tin-copper alloy.

[0020] FIG. **5**B is a bar chart showing a comparison between the maximum wetting force of two alloys according to the present disclosure and a prior art tin-copper alloy.

[0021] FIG. **6**A is a bar chart showing a comparison between the spread ratio of an alloy according to the present disclosure and prior art tin-copper-nickel and tin-copper alloys.

[0022] FIG. **6**B is a bar chart showing a comparison between the spreadability of an alloy according to the present disclosure and prior art tin-copper-nickel and tin-copper alloys.

[0023] FIG. **7**A is a bar chart showing the spread ratio of an alloy according to the present disclosure on three different substrates.

[0024] FIG. **7**B is a bar chart showing the spreadability of an alloy according to the present disclosure on three different substrates.

[0025] FIG. **8**A is a line chart showing a comparison between the copper wire dissolution rate of an alloy accord-

ing to the present disclosure and a prior art tin-copper alloy at 260° C.

[0026] FIG. **8**B is a line chart showing a comparison between the copper wire dissolution rate of an alloy according to the present disclosure and a prior art tin-copper alloy at 280° C.

[0027] FIG. **9**A shows a comparative series of optical micrographs comparing the copper wire dissolution rate of an alloy according to the present disclosure and a prior art tin-copper alloy at 260° C.

[0028] FIG. **9**B shows a comparative series of optical micrographs comparing the copper wire dissolution rate of an alloy according to the present disclosure and a prior art tin-copper alloy at 280° C.

[0029] FIG. **10**A is a bar chart showing a comparison between the hardness of an alloy according to the present disclosure and a prior art tin-copper alloy.

[0030] FIG. **10**B is a bar chart showing a comparison between the hardness of an alloy according to the present disclosure and a prior art tin-copper alloy, where both alloys have been isothermally aged at 150° C.

[0031] FIG. **11** is a line chart showing stress-strain curves for an alloy according to the present disclosure and a prior art tin-copper alloy.

[0032] FIG. **12** is a bar chart showing a comparison of the ultimate tensile strength of an alloy according to the present disclosure and a prior art tin-copper alloy.

[0033] FIG. **13** is a line chart showing creep strain as a function of time for an alloy according to the present disclosure and a prior art tin-copper alloy both as cast and after aging for 144 hours at 150° C.

[0034] FIG. **14**A shows a series of micrographs of the interface between an alloy according to the present disclosure and an underlying copper substrate after aging at 150° C. for 240, 720, and 1440 hours.

[0035] FIG. **14**B shows a series of micrographs of the interface between a prior art tin-copper alloy and an underlying copper substrate after aging at 150° C. for 240, 720, and 1440 hours.

[0036] FIG. **15** is a line chart showing total IMC thickness as a function of aging time at 150° C. for an alloy according to the present disclosure and a prior art tin-copper alloy.

[0037] FIG. **16** is a line chart showing Cu_3Sn IMC thickness as a function of aging time at 150° C. for an alloy according to the present disclosure and a prior art tin-copper alloy.

[0038] The foregoing summary, as well as the following detailed description, will be better understood when read in conjunction with the figures. It should be understood that the claims are not limited to the arrangements and instrumentality shown in the figures. Furthermore, the appearance shown in the figures is one of many ornamental appearances that can be employed to achieve the stated functions of the apparatus.

DETAILED DESCRIPTION

[0039] In the following detailed description, specific details may be set forth in order to provide a thorough understanding of embodiments of the present disclosure. However, it will be clear to one skilled in the art when disclosed examples may be practiced without some or all of these specific details. For the sake of brevity, well-known features or processes may not be described in detail. In addition, like or identical reference numerals may be used to identify common or similar elements.

[0040] Novel lead-free and silver-free solder alloy compositions that are suitable for a variety of electronics applications are described below. These solder alloy compositions may be used in various forms. For example, the solder alloy compositions may be used in the form of a bar, wire, solder powder, solder paste, or another predetermined preform. These solder alloy compositions are tin based.

[0041] The compositions shown in Tables 1 to 6 have been found to exhibit desirable properties that are superior to certain prior art alloys. For example, the lead-free and silver-free solder compositions described in Tables 1 to 6 provide a narrow pasty range, excellent wetting and spreading performance, a significant reduction of undercooling temperature, improved mechanical properties, and long-term reliability over time under demanding environmental conditions. The "pasty range" may be defined as the temperature range between which the alloy is fully solid and completely liquid (the range between the solidus and liquidus on a phase diagram).

[0042] Table 1 provides several compositions according to the present disclosure that comprise tin, copper, bismuth, cobalt, and antimony.

TABLE 1

Element	Composition Range 1.1 (wt. %)	Composition Range 1.2 (wt. %)	Example 1.1 (wt. %)	Example 1.2 (wt. %)	Example 1.3 (wt. %)
Copper (Cu)	0.5 - 0.9	0.6 - 0.8	0.7	0.7	0.8
Bismuth (Bi)	1.0 - 3.5	1.2 - 1.8	1.5	1.5	1.5
Cobalt (Co)	0.02 - 0.08	0.04 - 0.06	0.05	0.02	0.05
Antimony (Sb)	0.0 - 0.09	0.02 - 0.08	0.05	0.05	0.05
Tin (Sn)	Balance	Balance	Balance	Balance	Balance

[0043] Tables 2 and 3 provide several more compositions according to the present disclosure. As shown, these compositions may additionally comprise germanium or nickel.

TABLE 2

Element	Composition Range 2.1 (wt. %)	Composition Range 2.2 (wt. %)	Composition Range 2.3 (wt. %)	Composition Range 2.4 (wt. %)
Copper (Cu)	0.5 - 0.9	0.5 - 0.9	0.6 - 0.8	0.6 - 0.8
Bismuth (Bi)	1.0 - 3.5	1.0 - 3.5	1.2 - 1.8	1.2 - 1.8
Cobalt (Co)	0.02 - 0.08	0.02 - 0.08	0.04 - 0.06	0.04 - 0.06
Antimony (Sb)	0.0 - 0.09	0.0 - 0.09	0.02 - 0.08	0.02 - 0.08
Germanium (Ge)	0.001 - 0.01		0.004 - 0.008	
Nickel (Ni)		0.01 -0.1		0.03 - 0.07
Tin (Sn)	Balance	Balance	Balance	Balance

TABLE 3

Element	Example 3.1 (wt. %)	Example 3.2 (wt. %)	Example 3.3 (wt. %)	Example 3.4 (wt. %)	Example 3.5 (wt. %)
Copper (Cu)	0.7	0.7	0.7	0.7	0.7
Bismuth (Bi)	1.5	1.5	1.5	1.5	1.5
Cobalt (Co)	0.05	0.05	0.02	0.03	0.04
Antimony (Sb)	0.05	0.05	0.05	0.05	0.05
Germanium (Ge)	0.006		0.006	0.006	0.006
Nickel (Ni)		0.05			0.05
Tin (Sn)	Balance	Balance	Balance	Balance	Balance

[0044] Table 4 provides several alternative compositions according to the present disclosure that comprise tin, copper, bismuth, gallium, and antimony. According to these embodiments shown in Table 3, gallium is used in lieu of cobalt.

TABLE 4

Element	Composition Range 4.1 (wt. %)	Composition Range 4.2 (wt. %)	Example 4.1 (wt. %)	Example 4.2 (wt. %)	Example 4.3 (wt. %)
Copper (Cu)	0.5 - 0.9	0.6 - 0.8	0.7	0.7	0.8
Bismuth (Bi)	1.0 - 3.5	1.2 - 1.8	1.5	1.5	1.5
Gallium (Ga)	0.2 - 0.8	0.4 - 0.6	0.5	0.2	0.5
Antimony (Sb)	0.0 - 0.09	0.02 - 0.08	0.05	0.05	0.05
Tin (Sn)	Balance	Balance	Balance	Balance	Balance

[0045] Tables 5 and 6 provide several more compositions according to the present disclosure. As shown, these compositions may additionally comprise germanium or nickel.

TABLE 5

Element	Composition Range 5.1 (wt. %)	Composition Range 5.2 (wt. %)	Composition Range 5.3 (wt. %)	Composition Range 5.4 (wt. %)
Copper (Cu)	0.5 - 0.9	0.5 - 0.9	0.6 - 0.8	0.6 - 0.8
Bismuth (Bi)	1.0 - 3.5	1.0 - 3.5	1.2 - 1.8	1.2 - 1.8
Gallium (Ga)	0.2 - 0.8	0.2 - 0.8	0.4 - 0.6	0.4 - 0.6
Antimony (Sb)	0.0 - 0.09	0.0 - 0.09	0.02 - 0.08	0.02 - 0.08
Germanium (Ge)	0.001 - 0.01		0.004 - 0.008	
Nickel (Ni)		0.01 - 0.1		0.03 - 0.07
Tin (Sn)	Balance	Balance	Balance	Balance

TABLE 6

Element	Example 6.1 (wt. %)	Example 6.2 (wt. %)	Example 6.3 (wt. %)	Example 6.4 (wt. %)	Example 6.5 (wt. %)
Copper (Cu)	0.7	0.7	0.7	0.7	0.7
Bismuth (Bi)	1.5	1.5	1.5	1.5	1.5
Gallium (Ga)	0.5	0.5	0.2	0.3	0.4
Antimony (Sb)	0.05	0.05	0.05	0.05	0.05
Germanium (Ge)	0.006		0.006	0.006	0.006
Nickel (Ni)		0.05			0.05
Tin (Sn)	Balance	Balance	Balance	Balance	Balance

[0046] Controlled additions of bismuth, antimony, and/or cobalt to a tin-copper system are used to refine the alloy's grain structure and increase the alloy's mechanical strength. More specifically, cobalt may be added to the alloy to refine the grain structure and reduce the undercooling temperature. Bismuth and antimony both dissolve in tin and may be added to the alloy to provide solid solution strengthening. Bismuth decreases the solidus temperature of the alloy and reduces its surface tension, thus improving the wettability. Antimony increases the mechanical strength of the alloy. In small amount (0-0.09 wt. %), adding antimony does not affect the melting characteristics of the alloy. In greater

amounts, the addition of antimony may increase the melting temperature of the alloy. Optionally, nickel may be added to improve further the mechanical properties of the alloy. In addition, elements such as germanium or phosphorus may be added to improve the alloy's oxidation resistance. The proper synergy between the mechanisms described above, which is achieved though the specific composition ranges claimed in the instant application, optimizes the alloy's mechanical properties and any resulting solder joints' resistance to thermal cycles.

[0047] FIGS. **1**A and **1**B show scanning electron microscope ("SEM") micrographs of areas of the surface of an alloy comprising 99.3 wt. % tin and 0.7 wt. % copper. FIGS. **2**A and **2**B show SEM micrographs of areas of the surface of an alloy according to the composition of Example 3.4 shown in Table 3. FIGS. **1**A and **2**A show the alloys as cast; whereas FIGS. **1**B and **2**B show the alloys after aging for 24 hours at a temperature of 125° C. As can be seen from the SEM micrographs, the grain structure of the tin-copper alloy (shown in FIGS. **1**A and **1**B) coarsens during aging at an elevated temperature. In contrast, the Example 3.4 alloy maintains its finer, more uniform grain structure during aging at 125° C. (compare FIG. **2**A to FIG. **2**B). The microstructure contains Cu_6Sn_5 precipitates. Bismuth and antimony each dissolve in the tin matrix, and thus provide solid solution strengthening. Cobalt acts as a micro-alloying element to refine the microstructure. The finely distributed Cu_6Sn_5 precipitates and solid solution strengthening stabilize the microstructure during aging at an elevated temperature.

[0048] As shown in FIGS. **3** and **4**, the melting characteristics of solder alloys were determined by differential scanning calorimetry ("DSC"). The undercooling (i.e., the temperature difference between the onset of heating temperature and the onset of cooling temperature) was measured for the solder alloys. Undercooling occurs because precipitation of crystals is not spontaneous, but requires activation energy. FIG. **3** shows the DSC curve for an alloy comprising 99.3 wt. % tin and 0.7 wt. % copper. FIG. **4** shows the DSC curve for an alloy according to the composition of Example 3.4 shown in Table 3. In addition, data from the DSC analysis is shown in Table 7.

(T_2) is at 211° C., providing an undercooling (ΔT) of 16° C. For the Example 3.4 alloy (for example), T_1 is at approximately 225° C. and T_2 is at approximately 220° C., providing an undercooling (ΔT) of approximately 5° C.

[0050] FIGS. **5**A and **5**B show a comparison between the wetting time (FIG. **5**A) and the maximum wetting force (FIG. **5**B) of a tin-copper alloy (Sn-0.7Cu), the Example 3.4 alloy, and the Example 3.5 alloy. The wetting experiments were performed according to IPC (Association Connecting Electronics Industries) standard IPC-TM-650. This standard involves a wetting balance test that involves determining the total wetting time and maximum wetting force. A shorter wetting time corresponds to a higher wettability. A shorter wetting time and a higher wetting force reflects better wetting performance and correlates with spread and fillet formation under a given soldering process.

[0051] Wetting performance of solder can also be expressed in terms of spread ratio and spreadability. The spread area indicates how much solder is on the soldering pad substrate, and can be indicated as a spread ratio. A spread test was performed in accordance with the IPC (IPC J-STD-004B, TM 2.4.46) and JIS Z 3197 standards. Spread ratio and spreadability were investigated for three different substrates: bare copper (Cu), Organic Solderability Preservative (OSP) coated copper, and Electroless Nickel Immersion Gold (ENIG) plated copper. The solder alloys (circular preform) were melted onto the substrate being tested using flux. The wetted area was measured using an optical microscope before and after the test. The spread ratio is calculated by wetted area after reflow/melt divided by wetted area before reflow/melt. The solder height was measured to calculate the spreadability (or spread factor). Spreadability was calculated using the following formula, where S_R = spreadability, D = diameter of solder (assumed to be spherical), H = height of spread solder, and V = volume of solder (g/cm³) (estimated from mass and density of tested solder):

$$S_R = \frac{D-H}{D} \times 100 \text{ where } D = 1.248 \times V^{1/3}$$

TABLE 7

Alloy	Alloy Composition	Onset of Heating, T_1 °C	Onset of Cooling, T_2 °C	Undercooling ($\Delta T = T_1 - T_2$)	Pasty Range, °C
Prior Art	Sn-0.7Cu	227	211	16	3.0
Example Alloy	Sn-0.7Cu-1.5Bi-0.05Sb-0.006Ge	225.02	199.12	25.89	3.32
Example 3.3	Sn-0.7Cu-1.5Bi-0.05Sb-0.02Co-0.006Ge	224.71	216.26	8.44	2.84
Example 3.4	Sn-0.7Cu-1.5Bi-0.05Sb-0.03Co-0.006Ge	225.14	220.16	4.97	2.51
Example 3.5	Sn-0.7Cu-1.5Bi-0.05Sb-0.04Co/0.05N i-0.006Ge	224.99	218.4	6.59	3.14

[0049] As can be seen by comparing FIGS. **3** and **4**, and in Table 7, the Example 3.3, 3.4, and 3.5 alloys exhibit a noticeable reduction in undercooling as compared to the prior art tin-copper alloy. For the tin-copper alloy, the onset of heating (T_1) is at 227° C. and the onset of cooling

[0052] FIG. **6**A shows a comparison between the spread ratio of the Example 3.4 alloy as compared to prior art SnCu-Ni and SnCu alloys on a bare copper substrate at two different temperatures (260° C. and 300° C.). FIG. **6**B shows a comparison between the spreadability of the Exam-

ple 3.4 alloy as compared to prior art SnCu-Ni and SnCu alloys at two different temperatures (260° C. and 300° C.).

[0053] FIG. **7**A shows a comparison between the spread ratio of the Example 3.4 alloy on three different copper substrates (OSP, bare copper, and ENIG) at 255° C. FIG. **7**B shows a comparison between the spreadability of the Example 3.4 alloy on three different copper substrates (OSP, bare copper, and ENIG) at 255° C.

[0054] FIGS. **8**A, **8**B, **9**A, and **9**B show a comparison between the copper dissolution rate of a tin-copper alloy (Sn-0.7Cu) and the Example 3.4 alloy (Alloy-3) at 260° C. (FIGS. **8**A and **9**A) and at 280° C. (FIGS. **8**B and **9**B). As can be seen in these figures, the copper dissolution rate is considerably slower for the Example 3.4 alloy as compared to the tin-copper alloy. The copper dissolution tests were performed using pure copper wire that was washed, degreased, cleaned in acid solution, rinsed, and dried. The tests were conducted at two temperatures: 260° C. and 280° C. The copper wires were exposed to molten solder for 5 seconds, 10 seconds, and 20 seconds. Cross sections of the copper wires were analyzed by optical microscopy, including to perform area measurement and analysis.

[0055] FIG. **10**A shows the hardness values of an Example 3.4 alloy according to the present disclosure as compared to a prior art tin-copper alloy (comprising 99.3 wt. % tin and 0.7 wt. % copper). As can be seen from the bar chart, the hardness of the Example 3.4 alloy is 50-100% higher than the hardness of the prior art tin-copper alloy. Further, the Example 3.4 alloy remains hard after aging at an elevated temperature, in contrast to the prior art tin-copper alloy, as shown in FIG. **10**B, which shows the result of hardness testing as cast, after aging 144 hours at 150° C., and after aging 720 hours at 150° C.

[0056] The coefficient of thermal expansion (CTE) of the alloys according to the current disclosure was also measured. Mismatches between the CTE of a solder and an underlying substrate can lead to fatigue failure during cyclic loading. As the CTE mismatch increases, so too does the shear strain, which decreases the thermal cycle life of a component. Cracks may start and propagate at sites of stress concentration due to a CTE mismatch. Cracking in solder joints may be reduced by reducing the difference between the CTE of a solder and an underlying substrate. Table 8 shows the CTE of an alloy according to the present disclosure compared to a prior art tin-copper alloy and with reference to the CTE of an example underlying substrate.

TABLE 8

Alloy	Alloy/Substrate Composition	Temperature Range, °C	CTE, ppm/°C
Prior Art	Sn-0.7Cu	30 - 150	27.15
Example 3.4	Sn-0.7Cu-1.5Bi-0.05Sb- 0.03Co-0.006Ge	30 - 150	21.89
Example Substrate	Copper	30 - 150	16.7

[0057] A tensile stress-strain chart of an example alloy according to the present disclosure (Example 3.4 alloy) as compared to a prior art tin-copper alloy is shown in FIG. **11**. Casting solders were machined and cut into rectangular pieces of size 100 mm × 6 mm × 3 mm. Samples were isothermally aged at 150° C. for up to 720 hours. Tensile tests were conducted at room temperature at a strain rate of 10^{-2} s^{-1}. The ultimate tensile strength and yield strength of the alloys are shown in Table 9. The significant improvement of tensile strength shown in the Example 3.4 alloy may be due to the addition of bismuth and solid solution strengthening effect. The Example 3.4 alloy is also shown to be more ductile than the prior art tin-copper alloy. The tensile strength properties of the Example 3.4 alloy and prior art tin-copper alloy after aging at 150° C. are shown in FIG. **12**. Both the Example 3.4 alloy and the prior art tin-copper alloy show a reduction in ultimate tensile strength after aging at an elevated temperature, but the reduction is considerably more marked for the prior art tin-copper alloy, which exhibited a 32 % reduction in tensile strength.

TABLE 9

Alloy	Alloy Composition	Ultimate Tensile Strength, MPa	Yield Strength, MPa
Tin-Copper	Sn-0.7Cu	35.08 ± 0.24	31.32 ± 2.97
Example 3.4	Sn-0.7Cu-1.5Bi-0.05Sb- 0.03Co-0.006Ge	54.45 ± 1.25	52.3 ± 1.35

[0058] Creep deformation is a major failure mode of solder joints in microelectronic packaging because of the high homologous temperatures involved. Solder experiences thermo-mechanical stresses due to different coefficient of thermal expansion (CTE) between the chip and other layers within the packages. These stresses can cause plastic deformation over a long period of service. Solder alloys may undergo creep deformation even at room temperature. In real life applications, electronic modules can operate over a temperature range of -40° C. to +125° C., which is in the range of 0.48 to 0.87 T_m (fraction of the melting temperature of the solder). For devices under stress, this is a rapid creep deformation range. Thus, a thorough understanding of creep deformation in lead-free solder is an important concern for the electronic packaging industry. Casting solders were machined and cut into rectangular pieces of size 120 mm × 6 mm × 3 mm. Samples were isothermally aged at 150° C. for up to 144 hours. Creep tests were conducted at room temperature at a stress level of 10 MPa. As shown in FIG. **13**, the Example 3.4 alloy shows superior creep resistance as compared to a prior art tin-copper alloy. The creep resistance exhibited by the Example 3.4 alloy may be due to the addition of microalloys to refine the microstructure and strengthening mechanisms such as solid solution and precipitation hardening.

[0059] During a soldering operation, materials from the solid substrate dissolve and mix with the solder, allowing intermetallic compounds (IMCs) to form. A thin, continuous, and uniform IMC layer tends to be important for good bonding. Without IMCs, the solder/conductor joint tends to be weak because no metallurgical interaction occurs in the bonding. However, a thick IMC layer at the interface may degrade the reliability of the solder joints because a thick IMC layer may be brittle. IMC layers formed between solder and OSP substrate as a function of exposure time and temperature were examined. Solder alloys were melted on an OSP substrate and reflowed in an Electrovert OmniExcel 7 Zone Reflow oven using flux. Solder alloy samples were then exposed to an elevated temperature at

150° C. for up to 1440 hours. IMC layers were evaluated at different periods of aging time.

[0060] FIGS. **14**A and **14**B show a comparison between the IMC layer growth of the Example 3.4 alloy and a tin-copper alloy (Sn-0.7Cu) after aging at 150° C. for up to 1440 hours. As can be seen in these figures, both the Example 3.4 alloy and the tin-copper alloy exhibit IMC layer growth. However, the tin-copper alloy shows signs of brittleness, as shown by the presence of Kirkendall voids (for example, after aging for 720 hours). Both alloys show formation of Cu_6Sn_5 and Cu_3Sn layers at the boundary between the solder and the copper substrate. FIG. **15** shows the total IMC thickness as a function of aging time. As shown in FIG. **15**, the IMC layer for the tin-copper alloy is much thicker than for the Example 3.4 alloy. The addition of microalloys to refine the microstructure may limit diffusion, thus also limiting total IMC growth. The lower IMC thickness in the Example 3.4 alloy likely makes the Example 3.4 alloy suitable for a longer life application at elevated temperatures. FIG. **16** shows the total Cu_3Sn thickness as a function of aging time. At the interface between Cu_6Sn_5 and Cu substrate, a new IMC layer of Cu_3Sn forms for both alloys. In the Example 3.4 alloy, the addition of microalloys suppresses the growth of Cu_3Sn, which may limit the formation of Kirkendall voids.

[0061] Some of the elements described herein are identified explicitly as being optional, while other elements are not identified in this way. Even if not identified as such, it will be noted that, in some embodiments, some of these other elements are not intended to be interpreted as being necessary, and would be understood by one skilled in the art as being optional.

[0062] While the present disclosure has been described with reference to certain implementations, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the present method and/or system. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the present disclosure without departing from its scope. For example, systems, blocks, and/or other components of disclosed examples may be combined, divided, re-arranged, and/or otherwise modified. Therefore, the present disclosure is not limited to the particular implementations disclosed. Instead, the present disclosure will include all implementations falling within the scope of the appended claims, both literally and under the doctrine of equivalents.

1-20. (canceled)

21. A lead-free, silver-free solder alloy consisting of:
- 0.5 to 0.9 wt% copper;
- 1.0 to 3.5 wt% bismuth;
- 0.02 to 0.08 wt% cobalt;
- 0.02 to 0.09 wt% antimony;
- 0.01 to 0.2 wt% nickel;
- optionally 0.001 to 0.01 wt% germanium; and
- balance tin, together with any unavoidable impurities.

22. The lead-free, silver-free solder alloy of claim **21** consisting of:
- 0.5 to 0.9 wt% copper;
- 1.0 to 3.5 wt% bismuth;
- 0.02 to 0.08 wt% cobalt;
- 0.02 to 0.09 wt% antimony;
- 0.01 to 0.2 wt% nickel; and
- balance tin, together with any unavoidable impurities.

23. The lead-free, silver-free solder alloy of claim **21** consisting of:
- 0.5 to 0.9 wt% copper;
- 1.0 to 3.5 wt% bismuth;
- 0.02 to 0.08 wt% cobalt;
- 0.02 to 0.09 wt% antimony;
- 0.001 to 0.01 wt% germanium;
- 0.01 to 0.2 wt% nickel; and
- balance tin, together with any unavoidable impurities.

24. The lead-free, silver-free alloy of claim **21**, wherein:
- the copper is present at a concentration of about 0.7 wt%;
- the bismuth is present at a concentration of about 1.5 wt%;
- the cobalt is present at a concentration of about 0.04 wt% or about 0.05 wt%; or
- the antimony is present at a concentration of about 0.05 wt%.

25. The lead-free, silver-free alloy of claim **21**, wherein:
- the copper is present at a concentration of about 0.7 wt%;
- the bismuth is present at a concentration of about 1.5 wt%;
- the cobalt is present at a concentration of about 0.04 wt% or about 0.05 wt%; and
- the antimony is present at a concentration of about 0.05 wt%.

26. The lead-free, silver-free alloy of claim **21**, wherein germanium is present at a concentration of about 0.006 wt% and/or the nickel is present at a concentration of about 0.05 wt%.

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