

## LEAD-BASED SOLDERS FOR HIGH TEMPERATURE APPLICATIONS

### CROSS REFERENCE TO RELATED APPLICATIONS

None STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

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### BACKGROUND OF THE INVENTION

The invention relates to high temperature solders for use in microelectronics that are destined for use in "harsh" environments.

As microelectronics are used in more rigorous or "harsh" applications, solder used in such applications has had to be improved to survive such conditions. The need for solders useful in such environments is increasing, with applications in automotive, avionics, and telecommunications arenas. Major difficulties with solders which are cycled repeatedly from low to high temperatures include adverse reactions with the substrate, and degradation and cracking due to thermal fatigue. Very high lead solders (98–100 wt. % lead) are known to be capable of good fatigue life, but are not used because of manufacturability problems, e.g., the wetting ability of the solders onto the required substrates is poor, and because alloy grain size coarsens with concomitant fatigue life degradation when exposed to high temperatures.

Current high-temperature solder technology uses, e.g., lead based alloys containing 10% tin (Sn) (i.e., "90-10" alloy) or 10% Sn and 2% silver (Ag) (i.e., "10-88-2"). These alloys have adequate fatigue life for most applications today, but are viewed to be inadequate for future applications in harsh environments; their thermal fatigue performance is adequate but not optimal; they suffer unacceptable loss of mechanical properties after prolonged exposure at elevated temperature (since there is reaction with substrates, producing brittle intermetallic phases and a weak solute depleted region near the substrate); they have a wide melting range, which is undesirable for use in electronics assembly; and a low solidus point, precluding use in applications at higher temperatures.

Cocks U.S. Pat. No. 5,120,498 teaches the addition of 0.01 to 10% lithium (Li) to improve the wettability of alloys on glass, containing at least two elements from the following: lead (Pb), tin, indium (In), cadmium (Cd), bismuth (Bi), mercury (Hg), antimony (Sb), silver, gold (Au) and gallium (Ga). However, these alloys contain substantial amounts of the aforesaid elements; furthermore the proportion of lead in the composition does not constitute the majority, i.e., less than about 95%, of the alloy. The presence of these elements lowers the melting point of these compositions, rendering them unsuitable for the highest temperature applications.

According to M. Schwartz in *Brazing* (ASM International, Metals Park, Ohio 1987), 0.2–3% Li is used in Ag-based brazing alloys to enhance wettability, and 0.2% Li is used in palladium (Pd)/nickel (Ni) alloys to enhance wettability. However, these alloys melt at several hundred degrees above the desirable range for solders.

According to W. Hofmann and H. Hanneman (*Z. Metallkunde* Vol. 20, pp. 47–49, 1938), the addition of sodium (Na) considerably delays the recrystallization of Pb.

### BRIEF SUMMARY OF THE INVENTION

The invention relates to high-temperature solder compositions, particularly high lead solders exhibiting

improved wettability to metal substrates, an advantageously well-controlled melting range, and excellent thermal fatigue properties. An embodiment of the invention relates to a high lead solder composition comprising a minor amount, typically about 0.0005–0.1 wt %, based on the total weight of the solder composition, of an alkali metal selected from the group consisting of Na, potassium (K), and Li, with lead making up about 98% or more of the composition.

A further embodiment additionally comprises an amount of a grain-size controlling additive ("GCA"), e.g., 0.001–0.5 wt % (based on the total weight of all the components in the solder composition) selected from the group consisting of cesium (Ce), barium (Ba), lanthanum (La), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), thorium (Th), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), yttrium (Y), lutetium (Lu), scandium (Sc), Mg, Na, selenium (Se), tellurium (Te), oxides thereof and mixtures thereof, in an amount effective to control the Pb grain size within the alloy to  $\leq 300 \mu\text{m}$ , more preferably  $\leq 200 \mu\text{m}$ , after exposure for 200 hours at 200° C.

In yet another embodiment, 0–1 wt % of an element selected from the group consisting of Sn, In, Bi, Sb, Ag, Au, and Ga, and mixtures thereof, may be included in the solder composition.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention addresses the problem of wettability of very high lead alloys, i.e., greater than about 98%, preferably greater than about 99%, more preferably greater than about 99.5%, to metal substrates, which is accomplished herein through the addition of an alkali metal selected from the group consisting of Na, K and Li in an amount of about 0.0005–0.1 wt % (i.e., 5–1000 ppm), preferably about 0.0005–0.05 wt % (i.e., 5–500 ppm), more preferably about 0.0005–0.01 wt % (i.e., 5–100 ppm.) The wettability at these levels of addition is surprisingly achieved, since an amount of alkali metal in the high lead solder above the basic range results in a degradation in the physical properties of the alloy. Not only does the wettability of the lead alloy decrease, but at amounts above the basic range the lead is more susceptible to oxidation, and the alloy also becomes more brittle.

The high lead alloys of the invention advantageously include other additives. For example, an amount of a grain-size controlling additive effective to control the Pb grain size within the alloy to  $\leq 300 \mu\text{m}$ , preferably  $\leq 200 \mu\text{m}$ , after exposure for 200 hours at 200° C., may be desirably included. This feature (maintaining and controlling a small grain size) is important to maximizing the fatigue life of the high lead alloy at high temperatures, e.g., 200° C. Such additives may be selected from the group consisting of Ce, Ba, La, Pr, Nd, Sm, Eu, Gd, Th, Y, Dy, Ho, Er, Tm, Yb, Lu, Sc, Mg, Na, Se, Te, oxides thereof and mixtures thereof.

Other elements may be added, at up to about one percent each, in order to modify various physical and mechanical properties of the alloy such as the rate of dissolution of the substrate during soldering, and oxidation resistance.

For example, Sn, In, Bi, Sb, Ag, Au and Ga may be added up to 1% each, in order to modify various other mechanical and physical properties of the solder such as strength, creep rate, substrate dissolution protection, and oxidation and corrosion resistance.

The solder may be made by adding the aforementioned alkali metal (including the aforementioned additional