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Processing and mechanical behavior of Cu-Bi alloys with high volume fraction of Bi: Suitability for high temperature soldering application

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ABSTRACT

This work evaluates potential of Cu-Bi alloys comprising high volume fraction of Bi for high temperature soldering application. Cu-Bi alloys with 20, 40 and 60 vol% Bi are processed using liquid phase sintering (LPS). Effects of various sintering parameters, such as sintering time, temperature and relative green density, are studied to establish experimental conditions for preparing Cu-Bi alloys with optimum microstructure. Compression tests at different temperatures, ranging from RT to 260 °C, and strain rates, ranging from 5×10^{-4} to $1\times10^{-2}\ s^{-1}$, are conducted to assess effects of temperature, strain rate and Bi content on the overall mechanical response of the material. The sintered density increases with increase in the green density and, with some exception, also with the sintering period and the sintering temperature. On the other hand, overall densification decreases with green density. Yield strength and strain-hardening exponent of Cu-Bi alloys decrease with increase in both the mechanical testing temperature and the volume fraction of Bi in the alloy. In addition, a set value of strain rate sensitivity can also be attained by optimizing the Bi content in Cu-Bi alloy and the test temperature. Microstructurally aware finite element analysis is performed to gain insights into deformation processes. Finally, a rationale for using Cu-Bi alloys as high temperature solders is presented.

1. Introduction

Development of solder alloys for high temperature applications, e.g., at temperatures greater than 250 °C [1], is an active area of research. Besides the traditional applications in microelectronic devices designed to operate at high temperatures, e.g., in automobiles, gas and petroleum extraction, etc., the high temperature solders may soon find applications in consumer microelectronic devices, such as mobile phones, laptops and other hand-held devices, also. This is because of dramatic increase in the service temperature of solder joints in the advanced microelectronic packages: For example, it is generally thought that the solder joints may soon be exposed to temperatures greater than 135 °C for extended periods of time (> 1000 h) [2]. The increase in the service temperature of solder joints in these microelectronic devices is mainly attributed to the continued increase in the processing capacity of the electronic gadgets, which is accompanied by substantial decrease in their form factor and adoption of 3 – D device architecture [2].

Traditional choices of solders include Pb-Sn, Pb-Ag, Sn-Sb, Sn-Cu, Zn-Al, Au-Sn, Au-Si, etc. [1]. The usage of the first two solders in the above list is discontinued as these are Pb-based and hence do not meet the restriction of hazardous substances (RoHS) guidelines [3]. The drawbacks associated with Sn-Sb and Sn-Cu alloys include extensive formation of intermetallic compounds (IMCs), which are brittle and may also be porous [1]. Zn-Al alloys have a very high eutectic temperature of 380 °C. However, Zn-6 wt% Al, a widely used Zn-Al solder alloy,[1] is very hard and brittle due to formation of fine dendritic microstructure [1]. Although Zn-6 wt% Al does not comprise of any IMC, it is often required to add a third element, such as Cu, Mg or Ge, for reducing brittleness of this alloy, which, in turn, results in formation of unwanted IMCs and a decrease in the melting temperature [1]. Based on computer coupling of phase diagrams and thermochemistry (CALPHAD) studies, Sn-25Au-20Sb, Au-18Ge-10In, Au-30Sn-24In, etc., have also been proposed as potential high temperature solders [4]. However, due to formation of Au_5Sn IMC, the mechanical integrity of Au-Sn based alloys also becomes a major reliability issue. On the other hand, use of Au in these solders makes them very expensive for commercial applications.

Besides Sn, Au and Zn based alloys, Bi based alloys have also

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[1] It should be noted that with specific alloy composition and microstructure, Al-Zn alloys can be superplastic and can be used as high temperature solders for joining Al alloys.

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been proposed for soldering applications. For example, Sn-Bi alloys have been used previously to form solder joint with Cu and brass; however, melting temperature of these alloys is only 139 °C [5]. Other Bi containing solders include Sn-Ag-Bi (SAB) solders with melting temperature of 217 °C. However, the SAB solders are susceptible to formation of IMCs [8]. Bi-Ag solders have a eutectic temperature of 263 °C; however, they are also brittle [1]. On the other hand, Cu-Bi alloy, comprising high volume fraction of Bi and prepared using liquid phase sintering (LPS), will have a reflow (or soldering) temperature of 271 °C (i.e., equal to the melting temperature of Bi [8]). This temperature is still not too high as compared to common Pb-free, Sn based solders. Thus, Cu-Bi alloys, comprising high volume fraction of Bi, can be used for regular reflow soldering also besides high temperature soldering application. However, Cu-Bi alloy system has never been proposed as a possible high temperature solder [1, 5–7], and hence we explore such a possibility in this work. Below we summarize unique and attractive features of Cu-Bi system, which qualify it as a potential candidate for high temperature soldering application.

Cu-Bi system is a 2-phase alloy system comprising a low melting phase (LMP), Bi, having a melting temperature of only 271 °C [8], and a high melting phase (HMP) Cu. It is a unique 2-phase system with very limited mutual solubility between its micro-constituents [8], however, with excellent wetting properties. Contact angle close to 0° facilitates spreading of liquid Bi over the surface of solid Cu. In addition, the dihedral angle between Cu and liquid Bi is approximately 0° [9,10], resulting in uniform spreading of liquid Bi all around Cu, including narrow crevices. It should be noted that a low value of dihedral angle creates excellent wetting between liquid Bi and the grains of Cu powders. Furthermore, Cu-Bi does not react to form any IMC, and hence neither the continued exposure to high temperatures nor the repetitive liquefaction of Bi results in formation of new, and perhaps, undesired IMCs [8]. Besides mechanical integrity, the cost effectiveness is also an important factor that should be taken into account while selecting an ideal solder alloy. In this regard, Cu-Bi alloys may be potential candidates as both Cu and Bi are relatively inexpensive as compared to Au, In, Ag and Sb, which are used in currently used solders [7].

Nevertheless, addition of small amount of Bi into Cu has been shown to embrittle the material [11,12]. This is because Bi can penetrate into the grain boundaries of Cu, resulting in reduction in the grain boundary cohesion and, eventually, the true tensile strength of the alloy as compared to pure Cu [13,14]. However, the mechanical properties of Cu-Bi alloys comprising high volume fraction of Bi (e.g., $>20\%$) have not been studied in detail. Interestingly, most of the studies focused on the mechanical behavior of Cu-Bi system have either been conducted above melting temperature of Bi [15] or have been focused on the embrittlement of Cu due to addition of minor amount of Bi [11,12]. In addition, the solder joints used in most of the electronic packages are often under compressive stresses and hence the embrittlement in tension may not be a significant deterrent against its usage as solder. Nevertheless, it is important to evaluate the thermo-mechanical integrity of Cu-Bi alloys, the proposed solder system, in compression for providing an objective rationale for their usage as solders, especially for high temperature applications.

In this study, LPS is utilized to prepare a 2-phase Cu-Bi alloy with substantially high Bi content ($>20\%$). LPS was performed above the melting temperature of Bi (i.e., above 271 °C) and well below the melting temperature of Cu (i.e., below 1085 °C), so that only LMP is liquefied. LPS was preferred as it is a low temperature process and does not require any post melting homogenization processing. In addition, it is also compatible with reflow soldering process and hence may be integrated with existing microelectronic practices without requiring significant modification in the process-flow [16,17]. The mechanical behavior of various Cu-Bi alloys is studied in compression by analyzing effects of the strain rate and the temperature on their stress-strain response. Finite element analysis (FEA) was performed to elucidate the roles of Cu and Bi in bearing stresses and accommodating strains. Following the aforementioned analysis, the mechanical responses of Cu-Bi alloys are compared with other commonly used solders. Finally, it is suggested that Cu-Bi alloys with high volume fraction of Bi can potentially be used for high temperature soldering applications.

2. Details of experiments and numerical analysis

2.1. Materials and experimental procedure

Cu-Bi composite solders with Cu as high melting phase (HMP) dispersions and Bi as low melting phase (LMP) matrix was prepared using LPS, which is a relatively low temperature and rapid processing route for attaining uniform microstructure with very high density, as compared to other metallurgical alloying techniques, such as complete melting, solid state sintering, etc. [18]. Three different Cu-Bi alloys comprising high volume fraction of Bi with Cu-Bi volume ratios of 4:1, 3:2 and 2:3 (i.e., 20 vol% Bi, 40% vol. Bi and 60 vol% Bi, respectively) were selected for the experiments. It should be noted that alloys comprising high volume fraction of Bi ($>10\%$) can be easily fabricated by LPS and, as it will be shown later, their mechanical properties is primarily determined by Bi, which is the dominant mechanically compliant phase of the composite solder. Nevertheless, a solder should not only be moderately mechanically compliant, but it should also possess very high thermal and electrical conductivities. These additional requirements warrant maintaining a high volume fraction of Cu, which is the dominant thermally and electrically conductive phase, in a Cu-Bi solder. The selection of particular compositions of 20, 40 and 60 vol% of Bi in Cu-Bi alloys in this study is arbitrary; however, it is aimed towards testing Cu-Bi alloys having good combination of mechanical compliance and thermal and electrical conductivities, and comprising low, intermediate and high volume fractions of Bi.

Spherical powders of high purity ($>99.9\%$) Cu and Bi were used in this study. The average sizes of both Cu and Bi powders were 10–40 μm. Before mixing, Cu powders were etched using 10% HCl solution for 10–15 min for removing native surface oxide layer. Subsequently, the powders were thoroughly rinsed with deionized water and finally, rinsed with ethyl alcohol. The rinsed Cu powders were dried by storing in vacuum ($\approx 1.3 \times 10^{-2}$ Pa) at room temperature for 12 h. Cu and Bi powders of appropriate quantity were mixed thoroughly in a N_2-filled glove-box for 30 min. Mixing in N_2 atmosphere prohibited oxidation of Cu powders. After mixing, approximately 0.4 g of powder mixture was taken out of the glove box for preparing one sample. Compaction of mixed powder was conducted in a steel die, producing cylindrical green pellets of 5.1 mm diameter and 2.35–2.70 mm height. The exact height of the samples depended on the compaction pressure, which varied from 4 to 12 MPa. The volume of the green pellets was measured using geometric method, i.e., by measuring the diameter and the height of the sample using a Vernier caliper. The relative green density was measured by dividing the green density by the respective theoretical density, which are 9124, 9288 and 9452 kg/m^3 for Cu- 20 vol% Bi, Cu- 40 vol% Bi and Cu- 60 vol% Bi, respectively.

Cu-Bi pellets with different compositions were sintered at temperatures ranging from 300 to 500 °C for either 30, 60 or 90 min. To prevent oxidation, sintering was performed in a tubular vacuum furnace operating at a pressure of 1.3×10^{-2} Pa. Densities of sintered pellets were measured by Archimedes principle by immersing them in water. Before such measurement, a thin layer