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Review

Alloying influences on low melt temperature SnZn and SnBi solder alloys for electronic interconnections

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ABSTRACT

Due to its commercial potential and the technological challenges associated with processing, low temperature soldering is a topic gaining widespread interest in both industry and academia in the application space of consumer and “throw away” electronics. This review focuses on the latest metallurgical alloys, tin zinc (Sn–Zn) and tin bismuth (Sn–Bi), for lower temperature processed electronic interconnections. The fundamentals of solder paste production and flux development for these highly surface active metallic powders are introduced. Intermetallic compounds that underpin low temperature solder joint production and reliability are discussed. The influence of alloying on these alloys is described in terms of critical microstructural changes, mechanical properties and reliability. The review concludes with an outlook for next generation electronic interconnect materials.

1. Introduction

Lead had been the mainstay of electronic equipment design and manufacture however due to a combination of legislation and environmental factors it is playing an ever diminishing role. Now lead is mainly limited to high reliability microelectronics, such as sever level computing systems, engine control units (ECU) and military applications [1]. Sn–Ag, Sn–Cu and Sn–Ag–Cu (SAC) lead-free eutectic or near eutectic systems have emerged as the front runners in the replacement of Sn–Pb solders [2]. While various SAC alloy systems have been proposed by Japanese (SAC305, short for Sn–3.0Ag–0.5Cu), EU (SAC387, short for Sn–3.8Ag–0.7Cu) and US (SAC396, short for Sn–3.9Ag–0.6Cu) consortiums [3].

A solder alloy paste is essentially made up of powdered lead free solder alloy and flux medium in a 50:50 volume ratio approximately. Low melting point solder alloy are advantageous in so far as soldering can be achieved without thermally degrading components such as circuit board laminates, integrated circuit (IC) package encapsulates and heat sensitive devices. Coupled to this, low melting point alloys have low or no Ag content and are typically associated with reduced material costs when compared to SAC alloys.

However, the most likely low temperature solder candidate materials SnZn and SnBi are significantly different both chemically and metallurgically from conventional SAC based alloys. Zn and Bi are both soluble in Sn, resulting in a strengthening effect on the Sn matrix. However, the Zn content gives poor corrosion resistance, and highly active fluxes are required to remove Zn oxide during processing [4]. These SnZn powders react with solder paste flux mediums resulting in a much shorter solder paste shelf life [5]. Recently, advances in solder flux design and formulation have shown great promise in overcoming these issues [5,6]. In addition to materials selection and design paste related characteristics are influenced by solder alloy particle size. For surface mount technology (SMT) applications, the quality of printed paste through an aperture in a stencil is influenced by particle size. Due to the miniaturisation of electronic devices and increasing functionality the average solder particle size is decreasing. As a result next generation type 7 and 8 solder pastes are being developed by atomisation processes with average particle sizes of <3 μm. With smaller particles displaying greater oxide content due to increased surface area. More active fluxes to remove these oxides are required.

During the soldering process, interfacial reactions between the molten solder and the substrate occur forming intermetallic compounds (IMCs). IMC formation promotes bonding between the

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solder and the substrate. However, large IMCs present at the interface tend to decrease the mechanical properties of the entire joint due to their brittle nature [7–9]. Chen et al. mention that a lower Young's modulus (YM), smaller coefficient of thermal expansion (CTE) mismatch between the board and component as well as a more rounded IMC surface morphology enhance joint reliability [10]. Solder joint reliability test methods include drop, shock and accelerated temperature cycling (ATC) [10,11]. Interfacial reactions and the properties of product layers can be controlled by alloying, which we will detail in the upcoming sections [2].

Post reflow solder joints are responsible for both electrical and mechanical connections, one of the major concerns for ball grid arrays (BGA) and flip-chip technology is the reliability of the solder joint. Solder joints are subjected to fluctuating strains due to CTE mismatches between the chip carrier and the circuit board [12–14]. Therefore, the mechanical properties of solder joints, such as their fatigue and shear strengths, are the crucial issue in determining the reliability and integrity of electronic packaging [15–17]. Another important factor in solder joint reliability is microstructural ageing or evolution during electronic assembly and subsequent storage. Once a system is deployed and functioning in the field, the kinetics of solder aging is increased due to a combination of thermal and power cycling [18,19]. Coyle et al. detail the influence of soldering process variables on microstructural evolution and IMC morphology for accurate prediction of reliability of solder joints [17,20,21].

For components with noble metal pre-plated lead frames, creep corrosion is a potential reliability risk for long-term field applications [20,22]. Mixed flowing gas (MFG) test is an accelerated environmental test, where the temperature, relative humidity, and concentration of selected gases are carefully controlled and monitored, and is used to assess solder joints in such environments [23].

Another potential reliability risk with high-Sn-content lead free solder alloys (of around 95–99.3 wt.% [24]) is associated with undercooling in flip chip technology where solder bumps are subjected to random solidification times due to the large undercooling of the β-Sn phase [2,25]. This results in some bumps being solidified while others are not, leading to stress concentrations and subsequent early mechanically induced failures [26]. SnZn and SnBi alloys have far smaller undercooling compared to Sn-rich Pb-free alloys therefore negating this potential issue [27–30].

2. Melting temperature

2.1. SnZn based alloys

Sn–Cu, Sn–Ag and SAC solder alloys have melting points in the range 217–227 °C, see Table 1, which is significantly higher than that of 63Sn37Pb (183 °C) [5]. Careful reflow profile selection has allowed successful soldering within the tolerance ranges of the majority of boards and components. However, there are higher hierarchy level interconnections and heat-sensitive electronic components which cannot withstand temperatures above 210 °C. Even though SAC alloys have been widely used by the industry as the most promising candidates for reliable Pb-free solder its relatively high melting temperature has become their drawback to wider applications within the electronics industry [27,31]. Eutectic Sn–9Zn solder alloy is a promising candidate for low temperature processing because of its relatively low melting temperature (198.5 °C), superior mechanical properties at room temperature, and relatively low cost compared with SAC alloys [32]. Melting temperature is merely increased by 0.5 °C with 4 wt.% Ag addition [33]. Low additions of Cu can reduce the melting point however melting points are increased at levels >1 wt.% [34].

EI-Daly and his co-workers showed that Ni and Sb (0.5 wt.%) in Sn–6.5Zn solder alloy were effective in reducing undercooling, while the melting temperature and pasty range remained at the hypoeutectic Sn–6.5Zn level [35,36]. Recently, Ni particles were used to reinforce Sn–8Zn–3Bi solders and subsequent results indicated that 1 wt.% Ni addition increased the melting temperature of Sn–8Zn–3Bi alloy by 2.3 °C, and expanded its solidification range by 1 °C [37].

Shiue et al. found that the melting point of Sn–Zn based alloys can be effectively decreased by indium addition, but the difference between solidus and liquidus temperature is broadened with an incremental increase of In content in Sn–9Zn solders [38]. McCormack et al. added 5 wt.% In into Sn–9Zn to reduce the melting temperature from 198 to 188 °C and the wetting behaviour was similar to that of Sn–Pb alloy [39]. The addition of Bi to Sn–Zn binary alloys confers several important advantages. It lowers the liquidus temperature of the Sn–9Zn eutectic. Kim and his co-workers found that 8 wt.% Bi in Sn–8Zn lowers melt temperature to 186 °C [28]. Chen et al. reported that Ga (3 wt.%) addition decreases the melting point of Sn–9Zn solder by 7 °C, while the melting range and undercooling increases [40]. Alloying influences on thermal properties of Sn–Zn based alloys can be found in Table 2.

2.2. SnBi based alloys

With a low melting temperature of 138 °C, the application of 42Sn–58Bi solders are gaining considerable attention in the electronics industry. It is reported that adding trace amount of RE (0.1 wt.% Ce and La), 0.5 wt.% Ag, or 0.5 wt.% Co has little influence on the melting temperature of Sn–58Bi based solders, each exhibiting a short pasty range of less than 4 °C, which ensures the formation of a reliable solder joint [41,42]. On the other hand, Shen et al. found that trace Cu addition (0.1 wt.%) decreases both melting point and pasty range of Sn–Bi based solder while Zn (2 wt.%) plays a reverse effect [43]. Shlaby reported that the addition of 2 wt.% In or Ag into the SnBi reduces the melting temperature of the solder [44]. Alloying influences on thermal properties of Sn–Bi based alloys can be found in Table 3.

3. Wetting and interfacial reaction

3.1. SnZn based alloys

Sn–Zn has some significant drawbacks as a solder which have inhibited its use to niche applications. Zn is readily oxidised to Zn oxide/hydroxide and $ZnCl_2$, leading to poor wettability and reduced solder joint reliability [36]. Takemoto and Funaki have attributed the poor wetting performance of Sn–Zn to a low electrode potential of Zn compared to the Cu-based substrates which excessively accelerates the preferential anodic dissolution of Zn resulting in no dissolution of Sn [45]. Suganuma et al. have linked heat exposure to Kirkendall void formation along the interface between the Cu–Zn IMC layer and the solder [27]. For an Au/Ni/Cu substrate, an $AuZn_3$ IMC layer forms at the interface and becomes detached from the interface during reflow, presumably due to the mismatch in CTE and weak adhesion between the $AuZn_3$ IMC layer and Ni layer caused by the depletion of Au. To ensure the reliability, detachment of the $AuZn_3$ IMC needs to be prevented. Interestingly, for the $AuZn_3$ IMC layer formed at Sn–9Zn/ENIG (Electroless Nickel Immersion Gold) interfaces but the detachment did not occur, due to different adhesion strength of the $AuZn_3$/Ni in the Sn–9Zn/Au/Ni/Cu joint and the $AuZn_3$/Ni–P in the Sn–9Zn/ENIG joint [46].

It has been found that 0.05 wt.% RE elements (Ce and La) addition, improves wetting performance due to a reduction in the interfacial tension between the solder alloy and the Cu substrate