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ZINC MICRO-ALLOYING ADDITIONS IN Sn-0.7Cu LEAD-FREE SOLDER ALLOYS. SHORT REVIEW

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Abstract

Sn-Pb solder alloy has been replaced with lead-free solder alloys due to the negative effect for environment and human health. The additions of Zinc (Zn) micro-alloying element in Sn-0.7Cu lead-free solder alloy were reported by several researchers in improving the performance of Sn-0.7Cu solder alloy. This paper reviews the research findings available on the additions of zinc micro-alloying in Sn-0.7Cu solder alloy. It can be concluded that zinc micro-alloying additions were reported to improve the mechanical properties, phase analysis and microstructure of the solder free solder joint.

Keywords: *Lead-free solder, soldering, intermetallic, micro-alloying, phase formation, mechanical properties, microstructure analysis, review*

Introduction

Solder alloys are the most important material in application of electronic packaging as an interconnection material. Recently, Sn-Pb solder were banned by European Union in 2002 due to containing toxic materials in electronic packaging [1–5]. Due to the regulation, industries and researchers are developing lead-free solders in replacing conventional lead solders. In the development of lead-free solders, several criteria needs to be met such as having a low melting temperature, ease of handling, good workability, ductility and excellent wetting angles on Cu substrates [6]. Currently, Sn-0.7Cu solder alloy of near eutectic composition is one of the popular low cost solder alloy used and also an interest to industries and researchers to develop a high reliability lead-free solder alloy by improving this solder alloy as a base material [7-8].

Sn-0.7Cu solder alloy gives several advantages such as, low cost, good electric conductivity and environmental friendly. However, Sn-0.7Cu solder alloy still needs improvement and further development. One method in improving the solder alloy is by implementing micro-alloying techniques where equilibrium states of binary alloy system can be influenced by micro-alloying. Micro-alloying is defined as development and creation of new alloy through minor or trace element addition into Sn-0.7Cu through solidification. The function of micro-alloying element is to influence the crystallography, morphology, orientation, phase stability and the thermal expansion of intermetallic phase in the solder alloy [7]. Micro-alloying also may influence the phase formation and microstructural stability of solder and joints. According to Laurila et al., micro-alloying are divided into two major categories, (i) solubility in Cu_6Sn_5 intermetallic, and (ii) not extensively soluble in Cu_6Sn_5 intermetallic [9]. The addition of Zn micro-alloying element into the Sn-Cu solder were majorly reported to improve its microstructure, mechanical properties, and their phase formation.

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Effect of Zn to Phase Analysis in Sn-Cu Solder Alloy

In general, common primary intermetallics that form in a Sn-Cu lead-free solder alloy are hexagonal, rods, hollow and plate like shape of Cu_6Sn_5 IMC [8]. While result of X-ray Diffraction (XRD) identified only body-centered tetragonal (Bct) β-Sn and Cu_6Sn_5 IMC phase in the entire Sn-0.7Cu solder alloy [10]. It is reported that after ageing at 150°C for 5 days, Zn microalloying addition may stabilize the hexagonal η- Cu_6Sn_5 where the thickness of the interfacial Cu_6Sn_5 and Cu_3Sn will reduced [11]. With additions of Zn into Sn-Cu solder alloy, it is reported that Zn atom being occupied with Sn1C site unit cell and the hybridization between Zn-d and Sn-s stabilizes the meta-stable hexagonal Cu_6Sn_5 phase [12].

In other related study, after the addition of 1.0 wt % of Zn micro-alloying into the Sn-0.7Cu solder alloy, the IMC layer at Sn-0.7Cu-1.0Zn/Cu interface were identified as Cu_6Sn_5 and Cu_6Zn_8. Conversely, to form a continuous Cu-Zn layer during reflow process, the amount of Sn-0.7Cu-1.0Zn is small to supply zinc element.

Effect of Zn to Microstructure in Sn-Cu Solder Alloy

Microstructure studies were majorly reported as proofs in the improvement of Zn micro-alloying of Sn-0.7Cu solder alloy. Sample preparation for microstructure observations were normally prepared by soldering the solder alloy on a Cu pad and commonly done in a reflow oven with the temperature profile of 1.5 minutes of dwell time, at a peak temperature of 250°C with a cooling rate of 1°C/s [15]. For microstructure observations of solder joints, normally samples are cross-sectioned by mounting and polishing steps and final polishing by using oxide polishing suspension (OPS). Sn grain structure, intermetallic compound (IMC) particles, and the network structure in bright-field images will appear in cross-section. The etching process could also be used to reveal the IMC phases and microstructure in 3D for bright-field images [16] where optical microscope (OM) and secondary electron microscope (SEM) could be used for the observation . Back-scattered electron (BSE) mode in SEM could be used to observe the IMCs composition contrast, and energy dispersive X-ray spectroscopy (EDS/EDX) to analyze the compositional.

Commonly, Cu_6Sn_5 (primary and interfacial) and interfacial Cu_3Sn IMCs could be observed after reflow soldering [11]. It is reported that by adding a small amount of Zn into Sn-0.7Cu, the microstructure of Sn-0.7Cu, Sn-0.7Cu-0.2Zn and Sn-0.7Cu-1.0Zn is similar, but the β-Sn phase was refined in Sn-0.7Cu-0.2Zn compared to Sn-0.7Cu [17]. For Sn-0.7Cu-1.0Zn, some dispersed particles appeared and located at the boundary between the refined β-Sn phase and eutectic phase where EDX detected particles named Cu-Zn IMC precipitates. In Sn-0.7Cu-0.2Zn the coarse of β-Sn phase and lamellar eutectic structure (Sn-rich matrix phase and Cu-Sn IMC phase of elongated shape is interplacing [17]. Figure 1 illustrates the effects of Zn on the microstructure of Sn-0.7Cu by addition of Zn micro-alloying.

Gouda [17] indicates that the cooling rates affects the microstructure of Sn-0.7Cu-0.5Zn alloy. It is also reported that by additions of Zn, β-Sn dendrite were able to be suppressed and its grain size could be reduced [7]. In another study, Cu-Zn intermetallic were reported to form in less than 0.5 wt% of Zn micro-alloying additions into the Sn-0.7Cu solder alloy [18]. Figure 2 show the present of the β-Sn and Cu_6Sn_5 IMCs phase in the Sn-0.7Cu solder alloy with additions of 1.0 wt% of Zn [21].

With addition of certain amount of zinc micro-alloying, the driving force of the Cu-Zn IMC formation is higher compare to Cu-Sn IMC formation. Besides that, the thickness of the IMC layer could be decreased. It is reported that a thickness of 8 μm of interfacial IMC on Sn-0.7Cu solder alloy after 20 days aging compared to 3.5 μm on Sn-0.7Cu-0.2Zn and Sn-0.7Cu-1.0Zn [19]. Incorporation of Zn into the Cu_6Sn_5 crystal could modify the interdendritic eutectic [20]. Similarly, it can cause the formation of CuZn intermetallic within the interdendritic region during the last stage of solder solidification [20].

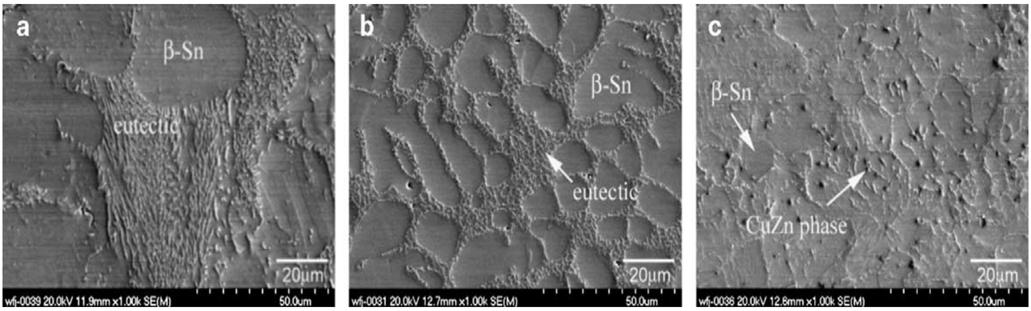

Fig. 1. The phase form in different composition of zinc addition a) Sn-0.7C b) Sn-0.7Cu-0.2Zn c) Sn-0.7Cu-1.0Zn [17].

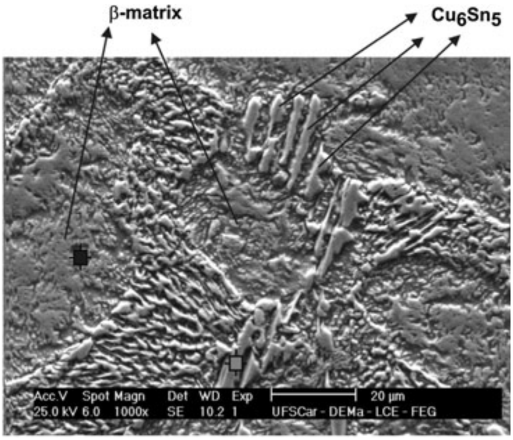

Fig. 2. The present of the β-matrix alloy and Cu_6Sn_5 due to addition of zinc [21].

Effect of Zn to Mechanical Properties in Sn-Cu Solder Alloy

Mechanical properties of a solder joint can be analysed using either its shear strength, tensile strength or hardness. Leonardo et. al [22], conducted a test on Sn-0.7Cu with additions of 4 wt%, 9 wt% and 12% of Zn. For the 4 wt% and 12 wt% of Zn alloys, the ultimate tensile strength and elongation results are in correlation with the secondary dendrite arm spacing. Meanwhile, with 9 wt% of Zn, ultimate tensile strength and elongation results correlates to the formation of needle width in the Zn-rich phase [22]. Figure 3 show the stress-strain curve results for the sample of solder alloys with additions of high amount of Zn.

The cooling rate had an effect on the dendritic size. As the cooling rates increased the size of the dendritic decreased [23]. According to Harris et. al, the present of small Cu_6Sn_5 in Sn-0.7Cu may improve their hardness and resistance of fatigue [24].

Microhardness test could be used to evaluate the relationship between the microstructure and the mechanical properties. Microhardness measurement is used to detect the hardness of different structures of different soft solders where it can be used to determine the mechanical properties of the different phases of the structure [25]. Hardness characterizes the durability and suitability of solder during working. Generally the hardness of a bulk solder will decrease after aging [26]. In conducting a microhardness test, a low test load is needed. For an example a microhardness tester with a test load of 300 g and dwell time is 10 seconds could be used [27]. Figure 4 illustrates the pit image on the solder ball surface after the Vickers hardness test.

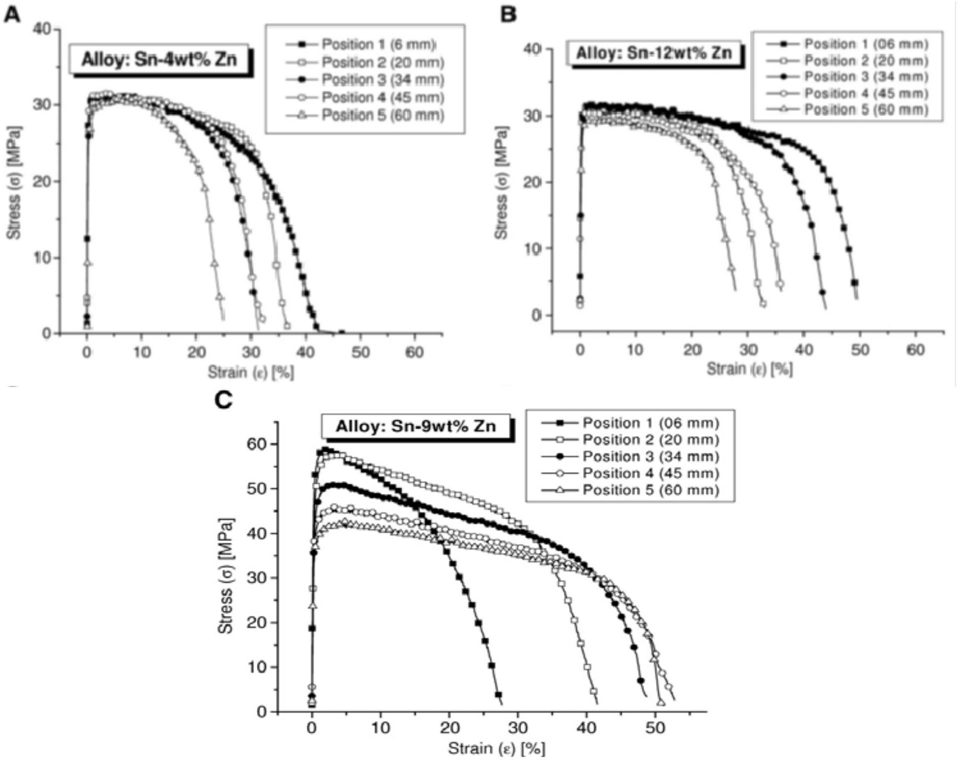

Fig. 3. The stress-strain curve for A) 4 wt%, B) 9 wt% and C) 12 wt% of Zn addition in Sn-0.7Cu solder alloys [22].

For tensile properties, the ultimate tensile strength (σ_u) and elongation (δ) could be correlated with the microstructure results [21]. The ultimate tensile strength of solder joints may decrease when the molten solder temperature and reaction time is increase. Ultimate tensile strength (UTS) also may be increased with increasing the ageing time. UTS in Sn-0.7Cu solder alloy are smaller compared to other solder alloys. In Sn-0.7Cu, it is reported that cracks may propagate along the large IMC or solder interface [28].

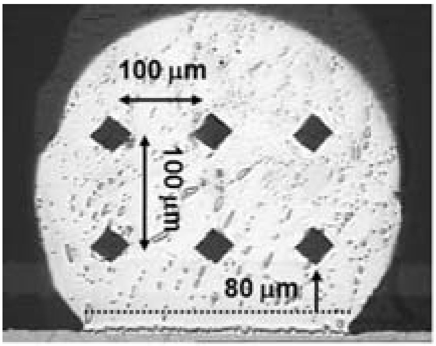

Fig. 4. Hardness indentation at the surface sample [15]

Other mechanical properties of a solder joint can be studied is by using shear test to determine the shear strength of the solder joint. Several studies have compared the shear strength between Sn-0.7Cu and Sn-0.7Cu-1.0Zn solder alloy under different shear strain rates at 0.1/s, 1/s and 10/s [14]. Then the zinc effects were further analyzed based on the shearing fractography and microstructure of interfacial IMC layer. In this study, shear test was carried out by SHIDMADZU servo-hydraulic test system at room temperature with 1 kN load cell. As a result, according to Gao et, al. the maximum shear strength of Sn-0.7Cu solder alloy at 10/s was measured as 35 MPa [14]. Important to realize, the shear strength of Sn-0.7Cu-1.0Zn solder alloy higher than Sn-0.7Cu alloy when a small amount of Zn has added.

Conclusions

Based on previous reported study, the addition of Zn micro-alloying element into the Sn-0.7Cu have influence the microstructure and properties of the Sn-0.7Cu solder alloys. With the additions of Zn, it can improve their nucleation growth of β-Sn and lead to the increase of nucleation temperature. With additions of Zn, Cu-Zn intermetallic formation could be introduced where generally these could affect the performance of a solder joint.

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