

Influence of multi-walled carbon nanotubes on melting temperature and microstructural evolution of Pb-free Sn-5Sb/Cu solder joint

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Abstract. In this study, the effects of multi-walled carbon nanotubes on the melting temperature and microstructural evolution of the Sn-5Sb/Cu joints are evaluated. Plain and carbon nanotubes (CNTs) reinforced Sn-5Sb solder systems with solder formulations Sn-5Sb, Sn-5Sb-0.01CNT, Sn-5Sb-0.05CNT and Sn-5Sb-0.1CNT were prepared through the powder metallurgy route and thereafter samples were subjected to thermal and microstructural evaluation. As retrieved from the DSC scans, a slight decline in the peak temperature was observed in the composite solders which is indicative of the CNTs role in exciting surface instability in the host Sn matrix. In order to prepare the solder joints and analyze the interfacial intermetallic compound (IMC) evolution, respective solder systems were placed on copper (Cu) substrate and subjected to both reflow soldering and isothermal aging (170°C) conditions. From the IMC thickness result, considerable retardation in the IMC layer growth was observed in the CNTs reinforced solder joints, especially the 0.05wt.% CNTs solder system owing to the inhibition of Sn atoms diffusion by reinforcement material.

1. Introduction

Taking into consideration the ongoing miniaturization of electronic products, residual stress increase in interconnection joints is imminent owing to the space restriction and the thermal fluctuation experienced during the service life of the products. Meanwhile, due to a sharp rise in the input/output terminals during electronic packaging [1-3], achieving high reliability and maintaining an acceptable level of performance efficiency is a major point of call for researchers in the development of excellent lead-free solder alternatives.

As highlighted in the study of [4] alloying lead-free solders with small-scale content of foreign elements is a viable way of influencing the microstructure, the reaction growth rate and the physical properties of the phases formed. In recent times, nano-sized particles have been employed as reinforcement materials in lead free solders due to their effectiveness in restricting grain boundary sliding through uniform distribution of the particles at the grain boundaries [5,6]. A typical nano-



material that has caught the interest of researchers and has shown to be a promising reinforcement material is the carbon nanotubes (CNTs)

Consolidating on the advantages of CNTs, [7-9] reported that the Sn-Ag-Cu (SAC) solder system reinforced with single-walled carbon nanotubes (SWCNTs) exhibited a slight decline in the melting temperature as against that of the plain solder. Similarly, Han et al. fabricated a composite solder system through the incorporation of Ni-CNTs dispersoids [10]. The authors observed an insignificant alteration in the melting temperature of Ni-CNTs doped solders which ranged from 219.4°C to 220.8°C. Elsewhere, Mayappan et al. reported that the addition of CNTs inhibited the growth of Cu₆Sn₅ and Cu₃Sn from 1.69×10^{-10} - 1.02×10^{-10} cm²/s and 4.9×10^{-11} - 2.5×10^{-11} cm²/s respectively [11].

In the studies of Xu et al., the authors revealed the evolution of a retarded overall IMC (Cu₆Sn₅ and Cu₃Sn) layer growth in CNTs reinforced solder than those of the unreinforced counterpart after subjecting both solder systems to 336 h aging condition with a continuous current density of 1.2×10^4 A/cm² [12]. So far, investigations [13,14] have shown the SAC solder to be the preferential candidate for lead-free soldering application hence instigating the neglect of other lead-free solder counterparts. Belonging to this category is the Sn-5Sb solder whose unique melting temperature of 240°C makes it a dual purpose solder suitable for step soldering and high temperature application in electronic packaging [15]. However, the solder experiences extreme IMC layer growth during its operational lifetime which poses great danger to the mechanical integrity of the joints developed [16].

In the present study, plain and composite Sn-5Sb solder systems were developed through the powder metallurgy method. The thermal properties of the developed solder systems and the intermetallics evolution of these solder systems on a Cu substrate were investigated. With the inclusion of the CNTs phase, it is envisioned that the developed joint will function decently in a robust operating environment.

2. Experimental Procedure

Multi walled carbon nanotubes (MWCNTs) having a diameter range of 15-20nm and a length range of 0.5-2µm (see Figure. 1), was used as the reinforcing material in this study. The Sn-5Sb, Sn-5Sb-0.01CNT, Sn-5Sb-0.05CNT and Sn-5Sb-0.1CNT solder samples were prepared by the ball milling process at 800rpm for 6h using a planetary mono mill (Fritsch Pulverisette 7). Cold compaction of the milled powders was performed on the universal testing machine (INSTRON 3382) using a pressure of 80MPa to form a 20mm solder pellet.

Differential scanning calorimetry (DSC) analysis was carried out using Mettler Toledo DSC 823e model to study the melting properties of the solder samples. Solder samples were heated up from 30°C till 600°C at 10°C/min heating rate. Thereafter, solder samples were reflowed on a pure (99.99%) Cu substrate with a thin layer flux application. After the reflow process, some of the samples were held back and subjected to solid-state isothermal aging for 500 hours.

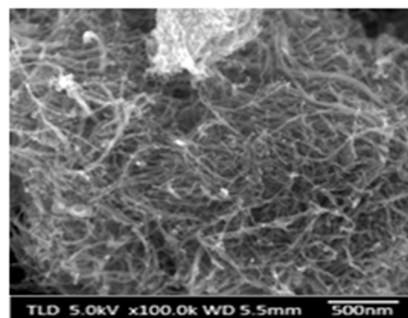


Figure 1. SEM image of MWCNTs.

3. Results and Discussion

3.1. Melting temperature analysis

Considering the surging technological advancement in electronics packaging, it is pertinent to comprehensively study the melting temperature properties of the solder interconnection materials. Figure 2 and Table 1 presents both the differential scanning calorimetry (DSC) scans and the melting temperature data for both the plain and composite solder systems respectively.

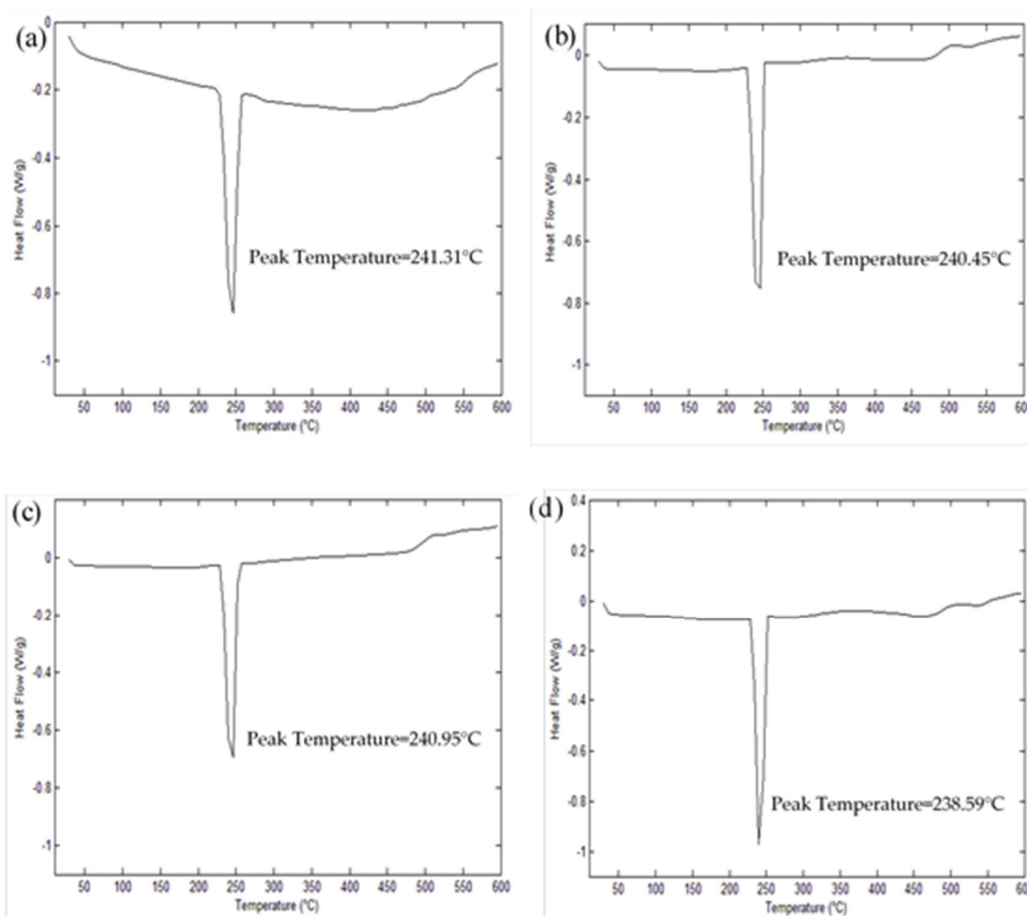


Figure 2. Differential scanning calorimetry scans of (a) Sn-5Sb, (b) Sn-5Sb-0.01CNT, (c) Sn-5Sb-0.05CNT and (d) Sn-5Sb-0.1CNT composite solders.

As can be observed from the peak temperature values, a minimal drop was observed in the melting temperature of composite solders as compared with the plain solder system. This is consistent with previous findings [7]. Across the board, the 0.1wt.% CNTs reinforced solder system showed the lowest value for both the onset temperature (T_{onset}) and peak temperature (T_m). More so, it is worthy of note that the peak temperature of 0.1wt.% CNTs composite solder system showed a 2.72°C from 241.31°C for the plain solder counterpart to 238.59°C . As it was observed in the literature [3.9], the slight decline in the peak temperature of the composite solder systems can be attributed to the multi-walled carbon nanotubes role in exciting surface instability in the host Sn matrix owing to the higher surface free energy potentials of the CNTs.

Sample	Peak Temperature T_m (°C)	Solidus Temperature T_{end} (°C)	Liquidus Temperature T_{onset} (°C)	Pasty Range
Sn-5Sb	241.31	253.42	231.80	21.62
Sn-5Sb-0.01CNT	240.45	253.00	231.36	20.64
Sn-5Sb-0.05CNT	240.95	253.39	231.98	21.41
Sn-5Sb-0.1CNT	238.59	250.33	230.97	19.36

Table1. Thermal parameters for plain and composite solders from DSC scans.

3.2. Interfacial IMC formation

The representative optical micrographs and the SEM-EDX evaluation for the intermetallic evolution results of as reflow and 500h aged samples are presented in Figures 3 and 4 respectively. From the optical micrographs of both the as-reflow and aging conditions, a remarkable IMC layer growth retardation can be observed in the composite solder system. In particular, the composite solder system having 0.05wt.% CNTs reinforcement showed superior IMC layer growth retardation for all subjected conditions as compared with other solder systems.

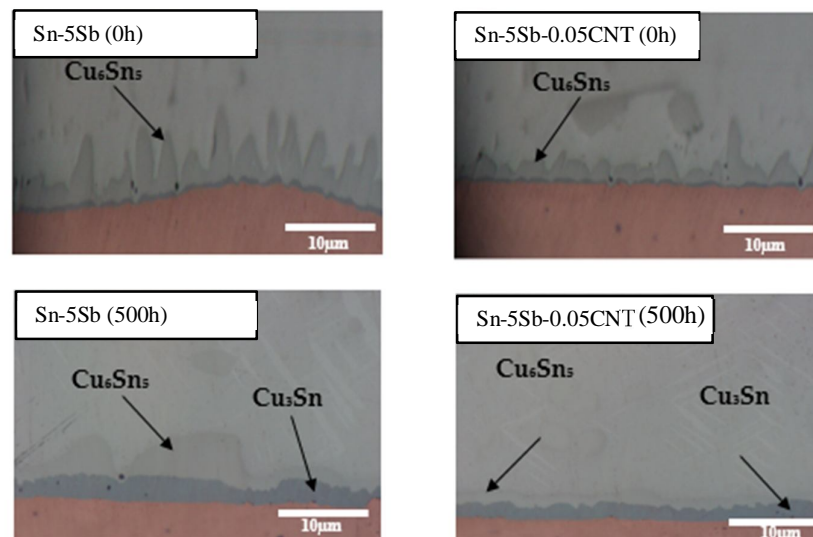


Figure 3. Optical micrographs of interfacial IMC layer of the as reflow and 500h aged solder joint samples.

Figure 5 presents the plot of total IMC layer thickness against different solder systems, wherein the degree of IMC layer growth retardation can be observed in the composite solder systems. For the Sn-5Sb plain solder and Sn-5Sb-0.05CNT composite solder, IMC thicknesses of $3.04\mu\text{m}$ and $2.60\mu\text{m}$ were recorded respectively for both solder formulations. In a similar way, the IMC layer thickness recorded for the Sn-5Sb and Sn-5Sb-0.05CNT after 500h of isothermal aging were $7.69\mu\text{m}$ and $6.73\mu\text{m}$ respectively which indicates a drop of $0.96\mu\text{m}$ in the composite sample as compared to that of the plain solder. Therefore, the IMC layer growth suppression experienced in the composite solder formulations can be attributed to the inhibitory role played by multi-walled carbon nanotubes in impeding Sn atoms diffusion from the solder matrix which is needed in the growth of the underlying Cu_3Sn IMC layer. This finding is in line with the previous investigations [17,18].

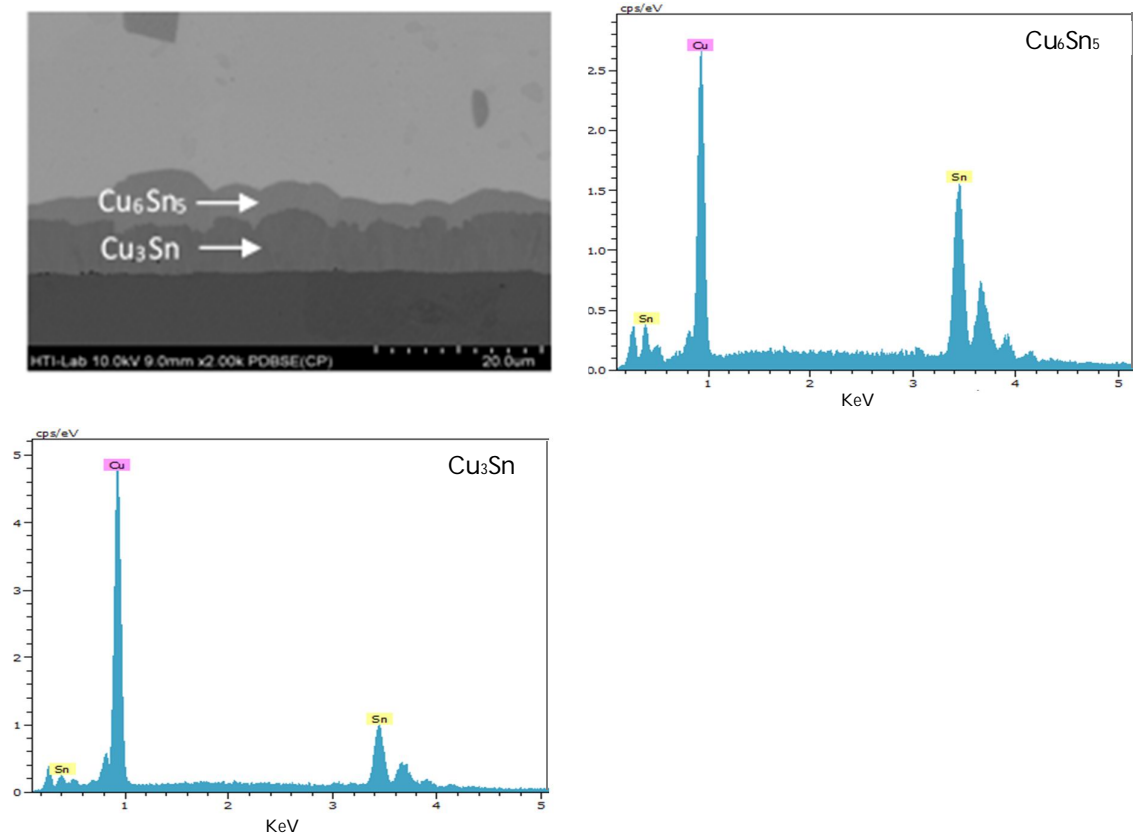


Figure 4. FESEM micrograph of the aged solder joint and the respective EDX spectrums of the interfacial IMC layers.

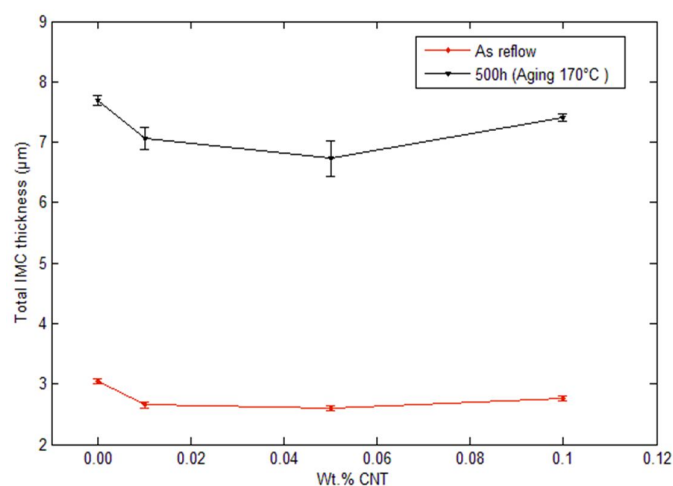


Figure 5. Overall IMC layer thickness against different solder systems subjected to as-reflow and aging conditions.

4. Conclusion

The Sn-5Sb solder systems with different weight fractions of multi-walled carbon nanotubes were fabricated by utilizing the powder metallurgy process. The melting properties and interfacial IMC layers for both the plain and composite solder systems were studied. The peak temperature of composite solder systems indicated a slight decrease which is indicative of MWCNTs role in exciting surface instability in the solder matrix. However the reduction was negligible and has no tendency towards disrupting the already established soldering routine of Sn-5Sb solder during electronic hardware packaging. More so, the interfacial IMC thickness of plain and composite solder joints were compared. It was observed that the as reflowed samples showed a marginal IMC layer suppression in the composite solder formulations as against that of the plain solder. However, the IMC layer growth suppression became remarkable in the composite solders after 500h of isothermal aging. This suggests that CNTs existence in solder matrix was effective in subduing the IMC layer growth.

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