The effect of CNT and Cu on interfacial intermetallic growth of Sn-Ag-Cu solder

M H Nur Liyana¹, M A Azmah Hanim¹, Shamsuddin Sulaiman¹ and O Saliza Azlina²

¹Department of Mechanical and Manufacturing Engineering, Universiti Putra Malaysia, 43400 UPM Serdang Selangor, Malaysia.
²Faculty of Mechanical & Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat, Johor, Malaysia.

*Corresponding author: liyanamh92@gmail.com

Abstract. In this study, the effect of copper and carbon nanotubes (CNT) composition on interfacial growth of various Sn-Ag-Cu (SAC) solder joints were investigated. SAC is proven to have good reliability and mechanical properties but lacking in terms of melting point and wettability. Thus, Sn-4.0 wt%Ag-0.3wt%Cu (SAC403) and Sn-4.0 wt%Ag-0.7 wt%Cu (SAC407) were reinforced with CNT with various weight percentages of 0 to 0.1wt%. The wetting angle and intermetallic compound (IMC) thickness is measured using optical microscope (Olympus BX5/M) and Olympus Stream Essentials software. The high Cu content alloys formed a long Cu₆Sn₅ whisker which act as an obstacle to crack propagation. CNT improves wettability and IMC layer growth for both SAC403 and SAC407 by lowering the wetting angle and IMC thickness compared to the plain solder.

1. Introduction
These environmental concerns have been raised due to the use of lead, Pb containing solder in electronic products in recent years. Lead was stated by Environmental Protection Agency (EPA) as one of the top 17 chemicals that poses the greatest threat to human life and the environment [1]. Besides that, the waste electrical and electronic equipment (WEEE) has claimed that the use of lead in consumer electronic will be banned after January 2006 [2]. Thus, many researcher are trying to develop a lead free solder alloys which meant elimination of lead in solder system used in microelectronic packaging processes in the industry.

Some of the examples of lead free solder alloys that researcher had produced are the Sn-Sb, Bi-Sb, Sn-Ag, Sn-Cu, SAC and others. SAC lead free solder is a well-known studied material proven to have good reliability and mechanical properties. The advantages of this alloy system are its relatively low melting temperature compared with Sn-Ag binary eutectic alloy and good solderability. However, there are still some problems needed to be resolved such as the argument about the best composition which has been discussed by various authors [3-6].

Recently, research has shown that the addition of alloying element, nanoparticles and any other suitable foreign material often bring improvement to the properties of composite solder. Uniform distributed intermetallic compound could be desirably introduced when we have proper choice of foreign reinforcement addition [7] since IMC formed are mainly influenced by the type of solders used [8]. Besides that, solder system should function as reliable electric interconnects and environment consisting of higher temperature and more severe mechanical loading [9].
CNTs exhibit remarkable physical, mechanical, electrical and thermal properties and consist of hollow cylinders formed by rolling graphene sheets. Due to their impressive physical properties and unique structures, attention towards CNTs are steadily increasing since their discovery [10]. Intense interest from researchers has been generated in utilizing these unique structures and outstanding properties, for example, in hydrogen storage, supercapacitors, biosensors, electromechanical actuators, and nanoprobes for high-resolution imaging and so on as mention by Lu [11] and Saether et al. [12].

Recently, nanoparticles, especially CNTs reinforcement into solder joints has been proven to be able to enhance the mechanical and electrical properties of solder alloys by inhibits IMC growth and phase-rich grain growth [13]. CNTs were widely incorporated into polymers, metals and ceramics to form composites in order to apply those excellent properties of CNTs to engineering applications [14]. Therefore, in order to work in line with electronic industries which focus on the production of more powerful, efficient and miniaturized gadgets, it is recommended to introduce alloying elements to the lead free conventional solders which will possibly lead to the enhancement of electrical and mechanical properties of the interconnecting joints. This research has been made to reveal whether an element of desirable properties can meet the demands of the electronics industries. In the present work, CNT is added as reinforcement to the SAC lead free solder of different copper ratio which are SAC 403 and SAC 407 to study its effect on interfacial growth of the solder.

2. Methods

Highly pure Sn (99.9%), Ag (99.9%), Cu (99.9%) and multi walled carbon nanotubes (MWCNTs) was prepared in powder form according to their respective weight. All the powders were ball milled using a Fritsch Planetary Mono Mill with 6 hour duration to ensure most importantly the homogenous dispersion of carbon nanotube. For compaction process, the powders were weighed according to the required weight for the study and cold compacted at pressure of 80 MPa to form a specific thickness solder tablet using 20 mm diameter cylindrical die using Specac Model and Instron universal testing machine. The solder tablet were cut into several pieces and weighed before placed on the copper substrate and were heated in the furnace until it melts at 300°C for 20 minutes. Then the samples were cold mounting, grind and polished before sample morphology observation using optical microscope. The thickness of IMC and wetting angle ($\theta$) is measured using optical microscope (Olympus BX5/M) and Olympus Stream Essentials software as shown in Figure 1.

![Optical micrograph of wetting angle between solder and Cu substrate.](image)

**Figure 1.** Optical micrograph of wetting angle between solder and Cu substrate.
3. Results and discussions

3.1. Intermetallics compound (IMC)

Figure 2 presents both type of solder showing fluctuated IMC thickness. For SAC 403, the lowest is at 0.01 wt% CNT which is 1.34 µm and the highest is 10.64 µm at 0.1 wt% CNT. For SAC 407, the lowest IMC is at 0.1 wt% CNT which 6.89 µm while the highest is at 0.01 wt% which is 27.76 µm. These shows CNT improved the IMC formation at certain wt%. However, experimental result shows mostly the IMC formation of SAC 407 is higher than SAC 403 except at 0.1 wt% CNT. Sakuyama et al., [15], in his study found that when copper is added to Sn-Sb solder, Cu₆Sn₅ IMC formed. Thus, in this study, when ratio of copper added to the solder is high, more Cu₆Sn₅ IMC formed and increase the total thickness of the IMC. This is also been reported by Yuan et al. [16] and Mookam et al. [17]. Moreover, previous study from Dele et al., stated that CNT balanced the Sn-Sb alloy in dissolving the Cu substrate by hindering the diffusion of Sn atom which is important for Cu₃Sn IMC formation because CNT creates a diffusion-bounded matrix by only embedded itself between the grain boundaries of Sn, Ag and Cu even when there is high tendency of diffusion mechanism at the grain boundaries [18]. Figure 3 shows the optical microstructure of SAC 403 and SAC 407 at 0 wt% CNT. The solder bulk and Intermetallic compound (IMC) form were observed and showed that IMC thickness of SAC407 is higher than SAC403 without CNT.

![Figure 2. IMC thickness of SAC 403 and SAC 407 at different wt. % of CNT.](image)

![Figure 3. Optical microstructure of cross-section on copper board of: a) SAC 403 and b) SAC 407.](image)
Other than the interfacial IMCs, there is also large IMCs formed in the solder which is also known as floating IMC. Kim et al. found large Ag$_3$Sn IMCs formed at the interfacial and in the Sn-3.9Ag-0.6Cu solders. It is usually observed for high Ag content solder joints [19]. Besides that, a long hexagonal faceted Cu$_6$Sn$_5$ IMCs are found dispersed in high Cu content solder joints with Cu substrate. Figure 4 shows the optical micrograph of the floating IMCs found in bulk solder for both SAC403 and SAC407.

![Floating IMC](image)

**Figure 4.** Optical microstructure of floating IMC found in: a) SAC 403 b) SAC 407.

### 3.2. Wetting angle

Figure 5 shows the wetting angle of both solder fluctuated with ratio of CNT added. For SAC 403 lowest angle is at 0.05 CNT wt% which is 10.315°. For SAC 407 lowest angle is at 0.005 CNT wt% which is 9.35°. For plain solder, SAC407 has lower wetting angle than SAC403. Wettability of solder is a measurement of how well the molten solder spread over on a substrate during reflow process. It is a very important factor during interconnection joint formation. A very good wetting is when the value of contact angle ($\theta$) is less than 30° [20]. Dele et al, stated that, the fluidity of solder alloys and wetting angle were influenced by IMC phases formed from solder-substrate chemical reaction [18]. The diffusion of Sn atoms needed for IMC formation is blocked at some part where CNT presence in solder alloys become precipitate float and interfacial IMCs. These obstacle will affect the flow to move to other side area making the spread area bigger which gives better wettability and less contact angle. An increase in flux-copper surface energy or decrease in flux-solder surface energy will lead to decrease contact angle. CNT increase the flux-solder surface tension because of chemical reactions stated by Kumar et. al.[21]. CNT improved the spreading area by enforcing the orbital interaction between the tin atoms and copper atoms resulting in good wettability.

![Wetting angle](image)

**Figure 5.** Wetting angle of SAC 403 and 407 at various percentage of CNT.
4. Conclusion
CNT improve the wettability and thickness of IMC for both SAC403 and SAC407. The lowest wetting angle for SAC403 is at 0.05 CNT wt% while for SAC407 is at 0.005 CNT wt%. Other than that, SAC 403 has the lowest IMC thickness at 0.01 wt% CNT while SAC 407 at 0.1 wt% CNT. Compared to SAC407, we can propose that SAC403 has the best result with lowest thickness of IMC and lower wetting angle at 0.05 wt% CNT.

5. References
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