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ABSTRACT

Owing to the great advancement in technology, the input/output terminals in electronic packaging have greatly increased resulting to a proportional increase in solder interconnection joints of electrical components. Therefore, in order to work in line with the mission and vision of the electronic industries which are the production of more powerful, efficient and miniaturized gadgets, it is imminent to introduce alloying elements to the existing lead free conventional solders which will possibly lead to the enhancement of electrical and mechanical properties of the interconnection joints. An attempt has been made to reveal an element of desirable properties which can meet the demands of the micro systems and electronics industries. A documentation of the benefits that the carbon nanotubes CNTs can yield has been presented in previous studies which therefore serve as the primary reason for embarking on this review report.

INTRODUCTION

The lead based solders have been used since antiquity dating back 2000 years with the near eutectic alloys 60Sn-40Pb and 63Sn-37Pb being the most widely used and longed yielded so many benefits in the course of electronic/component packaging due to their reliability, low cost and good wettability on copper substrate [1]. However, the lead (Pb) content of solders has been identified as poisonous element and as a result of this, various bodies came up with legislations to sensitize and limit the usage of leaded solders.

On July 1, 2006; the European Union Waste Electrical and Electro Equipment (WEEE) and Restriction of Hazardous Substance (RoHS) prohibited the intentional addition of lead to most consumer electronics produced in the EU [2]. More so, the Association Connecting Electronics Industries IPC came up with a roadmap for lead elimination in the United States of America [3]. The sole purpose of which is to keep the industry abreast of the lead implications so that companies can prepare themselves for any action they see fit. Hence, the legislative actions have therefore pushed the electronic industries to restrict the usage of lead free solders in America and Europe [4].

Based on the restriction in lead usage, there arises promising alternatives; the lead free solders. Some examples of these solder alloys are the Sn-Ag-Cu (SAC), Sn-Cu, Sn-Ag, Bi-Sb, Sn-Sb and several others. Lee considered it essential for the candidate to have melting temperature/physical properties similar and not poorer than those of Sn-Pb solders, good fatigue resistance, and adequate wetting properties to metallization used in the electronics industry, narrow plastic range, adequate shelf life and low cost [5]. More so, the conventional lead free solders have varying melting temperature which makes it possible for diversification in the mode of usage. The Sn-Sb alloy is one of the most promising candidates to replace the high melting point Sn-95wt%Pb alloy [6]. Shalaby et al. [7-9], revealed that the relatively high melting point and good electrical properties of the Sn-Sb solder makes it suitable in the step soldering technology, where soldering is applied more than once during manufacturing.

In recent times, research has shown that the addition of alloying elements often bring improvement in the properties of composite solders. Proper choice of foreign reinforcement additions could desirably introduce uniformly distributed intermetallic hard particles or non-coarsening particles [10]. Moreover, not only must
solders function traditionally as reliable electrical interconnects rather, they must also perform in more robust environments consisting of higher temperature and more severe mechanical loading [11]. Therefore, there is an urgent need to incorporate elements with desirable properties into the conventional solders.

Carbon nanotubes (CNTs) were first discovered as an elongated fullerenes and ever since then, it has subsequently been subjected to scientific and research exploration [12]. The exceptional mechanical and physical properties demonstrated by carbon nanotubes combined with their low density, has made this new form of carbon an excellent candidate for composite reinforcement [13-16]. CNTs have their elastic modulus in the range of 1-3 TPa, which is significantly higher than that of high strength steels at just 1/6th of the weight [17,18]. Carbon nanotubes have truly bridged the gap between the molecular realm and the macro-world and are destined to be a star in future technology [19]. Fig. 1 below shows the magnified image of a typical SWCNT. Incorporating this to solder matrix will yield good results in solder joint reliability. In light of the above facts, the review is focused on presenting detailed literature on the intermetallics, physical and mechanical properties of the CNT reinforced solders.

Fig. 1: (a) SEM image of SWCNT and (b) TEM micrograph of SWCNT produced by CVD process [20].

Melting Point and Density:

Niranjani V.L., et al. [21] examined the melting temperature of SAC 387 alloy and SAC 387 + SWCNT. The onset (solidus) and peak (liquidus) melting temperatures for base alloy was determined to be 216.4°C and 220°C respectively while both the onset and peak temperatures decreased to 215.8°C and 218.4°C respectively for 0.1wt% SWCNT of base alloy reinforcement. Fig. 2 below shows the DSC scans for three solder samples. More so, Kumar et al [20] compared results of Sn-Ag-Cu CNT reinforced solders and Sn-Ag-Cu without reinforcement. They observed a considerable depression in both the onset and peak melting temperatures of reinforced solders with 1wt% SWCNT reinforcement dropping from 217.7°C to 213°C. Similar results demonstrating the melting point reduction for Sn-3.8Ag-0.7Cu was reported by Kumar et al [22]. From all the facts in the literature above, the possible reasons for the melting point reduction in reinforced solders could be attributed to the increase in the surface instability with higher surface free energy rendered by the addition of carbon nanotubes [23].

The DSC results of all the composite samples showed that there was no influence on the melting point of the solder when higher weight percentages of CNTs were added into the solder matrix. [24]. Han Y.D., et al [25] disclosed that with the addition of Ni-CNTs into the SAC solder matrix, there was no significant change to the melting point of the composite solders with melting point of solder samples ranging from 219.4°C to 220.8°C. Furthermore, the investigation of Chantaramanee et al [23] indicated that loading the SAC solder with Ag-coated nanotubes in the range of 0.01wt% to 0.10wt% slightly affected the peak temperature by 1°C. Table 1 show the melting temperatures of all solder samples with varying proportion of SWCNT addition. The findings above implied that the existing soldering processes can still be retained when using these composite solders as interconnects. [25,26]
A novel study by T.T. Dele-Afolabi et al. (2014) explores the advancement in environmental biology, specifically focusing on the application of carbon nanotubes (CNTs) in solder composites. The research highlights the significant influence of CNT incorporation on the physical properties of the solder matrix. DSC (Differential Scanning Calorimetry) scans (Fig. 2) illustrate the thermal behavior of three distinct samples: SAC387 base alloy, SAC387 + 0.05%CNT, and SAC387 + 0.1%CNT. These scans provide insights into the melting points and phase transitions of the materials, showcasing how the addition of CNTs affects thermal stability.

<table>
<thead>
<tr>
<th>Material</th>
<th>SWCNTs (wt%)</th>
<th>Melting temperature</th>
<th>Onset Temperature</th>
<th>Peak Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC 305</td>
<td>-</td>
<td>218.70</td>
<td>218.50</td>
<td>220.16</td>
</tr>
<tr>
<td>SAC 305 - 0.01 Ag-coated</td>
<td>0.01</td>
<td>218.50</td>
<td>218.39</td>
<td>220.07</td>
</tr>
<tr>
<td>SAC 305 - 0.04 Ag-coated</td>
<td>0.04</td>
<td>218.00</td>
<td>219.15</td>
<td>222.00</td>
</tr>
<tr>
<td>SAC 305 - 0.10 Ag-coated</td>
<td>0.10</td>
<td>218.44</td>
<td>218.35</td>
<td>220.83</td>
</tr>
</tbody>
</table>

Table 1: Melting temperatures of SAC305 Ag-coated SWCNTs solder composites at different weight percentages of SWCNT additions [23]

In addition to the thermal properties, the study also evaluates the density and coefficient of thermal expansion (CTE) of the composite solders. These results are compared with those of monolithic solders, revealing a density trend decrease in solder samples incorporated with CNTs, due to their significantly lower density compared to Sn-Ag-Cu solder. The reduction in CTE can be attributed to the judicious selection of CNTs, which have a much lower CTE than the base alloy, and the ability of well-bound CNTs to constrain the expansion of the solder matrix. Table 2 provides a detailed comparison of melting points, densities, and CTE values for both monolithic and composite solders.

<table>
<thead>
<tr>
<th>Material</th>
<th>MWCNTs (wt%)</th>
<th>Tm (°C)</th>
<th>Density (g/cm³)</th>
<th>CTE (x 10⁻⁶/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC</td>
<td>-</td>
<td>221.9</td>
<td>7.440 ± 0.070</td>
<td>22.9 ± 0.7</td>
</tr>
<tr>
<td>SAC-0.01CNT</td>
<td>0.01</td>
<td>221.2</td>
<td>7.371 ± 0.010</td>
<td>19.8 ± 1.3</td>
</tr>
<tr>
<td>SAC-0.04CNT</td>
<td>0.04</td>
<td>220.9</td>
<td>7.364 ± 0.004</td>
<td>19.3 ± 1.3</td>
</tr>
<tr>
<td>SAC-0.07CNT</td>
<td>0.07</td>
<td>221.4</td>
<td>7.337 ± 0.009</td>
<td>19.3 ± 0.8</td>
</tr>
</tbody>
</table>

Table 2: Melting, density and CTE results of monolithic and composite solders [24]

Wetting Properties:

Wettability is a critical factor in joint formation, influencing the adhesion and long-term reliability of electronic devices. The study investigates the wetting properties of SAC305 solder composites with 0.01wt% Ag-coated SWCNTs and observes a contact angle decrease of 45.5%, reaching an optimum contact angle of 13.8° ± 0.9°. These results indicate the promising potential of CNT-reinforced solders in improving joint formation and reliability. Further investigations are necessary to explore the full extent of CNT incorporation in solder matrices and their impact on electrical and mechanical properties.
when the Ag-coated SWCNTs reinforcement was used [25]. Table 3 presents the contact angles of solder composites with varying proportion of Ag-coated SWCNT.

**Table 3:** Contact angles of solder composites with different weight percentages of Ag-coated SWCNT [23]

<table>
<thead>
<tr>
<th>Material</th>
<th>SWCNTs (wt%)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC</td>
<td>-</td>
<td>25.24 ± 6.80</td>
</tr>
<tr>
<td>SAC-0.01 Ag-coated</td>
<td>0.01</td>
<td>13.76 ± 0.92</td>
</tr>
<tr>
<td>SAC-0.04 Ag-coated</td>
<td>0.04</td>
<td>17.60 ± 2.10</td>
</tr>
<tr>
<td>SAC-0.07 Ag-coated</td>
<td>0.07</td>
<td>14.65 ± 1.37</td>
</tr>
<tr>
<td>SAC-0.10 Ag-coated</td>
<td>0.10</td>
<td>18.03 ± 0.90</td>
</tr>
</tbody>
</table>

**Intermetallics Formation:**

One way to influence the interfacial reactions and the resulting product layers in a given system is to alloy solder with small amounts of additional elements [32]. As observed from the EDX results [25,33], the morphology of the Ag₃Sn and Cu₆Sn₅ intermetallic phases showed a uniform distribution throughout the solder matrix. The functionalized carbon nanotubes (FCNT) in the SAC solder can lead both to an increase or decrease in the IMC growth, depending on their concentration [34]. A low concentration of the FCNT (0.01%) led to an increase in the IMC thickness, and a higher concentration of the non-dopants (0.1%) lead to a decrease in the IMC thickness. In the same light, the average thickness of the IMCs at the anode side increased by 0.35μm after exposure to electrical current for 260h while that in the unreinforced solder joints increased by 3.21μm, which was 9.2 times thicker than that of composite sample. Fig. 3, reveals that the IMC thickness of the CNT – SnAg solder after 400h aging treatment was 2.7μm, which was one half of the non – mixed SnAg solder.

**Fig. 3:** IMC thickness of non-mixed Sn–Ag and CNT-SnAg samples [35]

S.M.L Nai et al [36] determined the average value of IMC thickness from the following equation;

\[
\bar{t} = \frac{A}{L_x} \tag{1}
\]

Where \( \bar{t} \) = average value of IMC thickness  
\( A \) = area of IMC thickness obtained from micrograph  
\( L_x \) = Length of the IMC along the interface

The study confirmed that the aging conditions of the IMC layer growth investigation was diffusion controlled in both the unreinforced and composite solder joint samples. It can be seen from Table 4 below that the composite solder joints exhibited lower diffusion coefficients (ranging from 5.8 x 10⁻¹⁴ cm²/s to 7.3 x 10⁻¹⁴ cm²/s), as compared to that of the SAC solder joint (8.5 x 10⁻¹⁴ cm²/s).

**Table 4:** Diffusion coefficient (D) of monolithic and composite solder systems [36]

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount of CNTs (wt%)</th>
<th>D (x 10⁻¹⁴ cm²/s)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC</td>
<td>-</td>
<td>8.5</td>
<td>0.986</td>
</tr>
<tr>
<td>SAC-0.01 CNT</td>
<td>0.01</td>
<td>7.3</td>
<td>0.980</td>
</tr>
<tr>
<td>SAC-0.04 CNT</td>
<td>0.04</td>
<td>5.8</td>
<td>0.969</td>
</tr>
<tr>
<td>SAC-0.07 CNT</td>
<td>0.07</td>
<td>6.5</td>
<td>0.982</td>
</tr>
</tbody>
</table>
**Tensile Properties:**

The tension test is a common test for determining mechanical properties of materials such as ductility, toughness, elastic modulus and strain-hardening capability. Kumar *et al* [20] observed that all compositions of Sn-Ag-Cu with varying wt% of carbon nanotubes addition exhibited high UTS and comparable ductility. Their observation was linked directly to the critical reduction in the average size/morphology of the secondary phases in the composite solder specimens. Also, in a similar research, results revealed an overall improvement in 0.2% yield strength (YS) and ultimate tensile strength for the composite solders due to presence of CNTs addition. However, when the addition CNTs reached 0.07wt%, the composite sample showed a decrease in microhardness value. Furthermore, the investigation of Kumar *et al* [22] revealed that the SWCNT addition increased the Young’s Modulus of Sn-3.8Ag-0.7Cu. The elongation measurement of indicated an increasing trend of the elongation with increase in CNTs content compared with the Sn-58Bi solder alloy [37]. However, when the addition of CNTs content exceeded 0.03%, the elongation of composite samples decreased. Meanwhile, Fig. 4 and 5 illustrates the exploration of Niranjaini *et al* [21], and reveals that the addition of 0.05% SWCNT resulted in the increase of yield strength and ultimate tensile strength at all temperatures and strain rates, although the increase in strength values at 75°C was marginal.

**Fig. 4:** The variation of yield strength of SAC387, SAC387 + 0.05% SWCNT, SAC387 + 0.1% SWCNT with temperature at constant strain rate of 5 x 10^{-4} s^{-1} [21]

**Fig. 5:** The variation of ultimate tensile strength of SAC387, SAC387 + 0.05% SWCNT, SAC387 + 0.1% SWCNT with temperature at constant strain rate of 5 x 10^{-4} s^{-1} [21]

**Shear Strength:**

According to Nai *et al* [36], the solder joint samples revealed that the 0.2% yield stress and ultimate shear stress increased most significantly with the addition of 0.01wt% of CNTs by values of 19% and 33% respectively, while the strength was marginal for the 0.04wt% and 0.07wt% CNT addition as compared to that of monolithic solder joint. The result above is similar to another research as their observation also showed that strength improvement was only marginal at higher amount of CNTs addition (0.04% and 0.07%) [39]. Which can be attributed to small clusters of CNTs which resulted in small cracks on the surface of solder matrix acting as nucleation sites for plastic instability and lower strength.

Furthermore, Han Y.D *et al*.[40], indicated that the improvement in mechanical properties of the SAC-Ni coated CNTs composite joints over the monolithic SAC solder joints can be attributed to the following mechanisms which was also indicated in the investigations of Goh C.S. *et al*, [41-43]; (1) generation of
geometrically necessary dislocations to accommodate thermal and elastic modulus mismatch between solder matrix and Ni-CNTs (2) Load transfer due to the presence of Ni-CNTs, and (3) thinner IMC layer in the composite solder joints. More so, the authors also observed a decrease in the ultimate shear strength values of both the monolithic and the composite solder joints as the thermal cycles increased.

In the development of Sn-Ag-Cu and Ag-coated CNTs through ultrasonic technique mixing, it had been observed that the ultimate shear strength increased most with 0.01 wt% of Ag-coated SWCNTs, with an increase of 11% [23] It can be seen in Fig. 6 that the 0.01 wt% of Ag-coated showed a higher increase than the other wt% CNTs reinforcement.

![Fig. 6: Shear strength of composite solder joints as a function of wt% SWCNTs [23]](image)

E.K. Choi et al [44] fabricated the MWCNTs reinforced Sn nanocomposites by an electro-deposition process and observed that with increase in CNT concentration in the bath from 0 to 100g/l, the shear energy increased more than 50% from $1.3 \times 10^{-5} \text{J}$ to $2.1 \times 10^{-5} \text{J}$ indicating that the mechanical reliability of solder joints can be substantially improved by using a composite solder reinforced with CNTs. Furthermore, Ko et al [35] produced Sn-3.5Ag CNT reinforced composite solder by the surface impact mixing (SIM) process and revealed that the shear strength slowly increased with SIM time until 24h. The joint strengths of the reflowed solder according to varying SIM process time are shown in Fig 7. The significant increase in shear strength may be attributed to the CNTs covering the entire solder ball surface after 24h of the SIM process.

![Fig. 7: Joint strengths of CNT-SnAg solder balls with varying SIM process time [35]](image)

Fracture Analysis:

Kumar K.M et al and Ning J.[20,45], indicated in their investigations that the fractured surface during the tensile deformation of the composite solder specimens was vertically aligned to the carbon nanotubes and the alignment might be one of the beneficial reason for increase in the strength of composite solders. Furthermore, the investigation made on SAC and SAC+CNTs revealed that for the CNT-based composites, crack ran through the SWCNTs that remained in the matrix of the solders which made it evident that the fracture occurred mostly by the failure of matrix and not by the interfacial debonding of solder matrix [20].

In their work, Han 2012 Y.D. [40], observed an elongated dimple like structures in both the monolithic SAC and SAC+Ni-CNTs composite solder joints which were subjected to different thermal cycles. Furthermore, they noted a dimple size increase as the thermal cycles increased which could be attributed to the coarsening of the intermetallic particles during thermal cycle tests. The same attribute was also stated in the works of Dutta
Let al and Zhu S.M. et al. [46,47]. Fig 8 below shows SEM fractographs of SAC and SAC/0.05Ni-CNT at 0 cycle with SAC and SAC/0.05Ni-CNT at 2000 cycles.

Fig. 8: Representative SEM fractographs of: (a) monolithic SAC at 0 cycle (b) SAC/0.05Ni-CNT at 0 cycle (c) monolithic SAC at 2000 cycles (d) SAC/0.05Ni-CNT at 2000 cycles [40]

Niranjaini V.L. et al. [21] compared the fracture mechanism of SAC 387 alloy and SAC 387+CNTs at different strain rates and temperature and observed that the fracture remained ductile in both the base alloy and composite at higher temperatures or higher strain rates even though the % elongations changed significantly with change in temperature and strain rate. The ductile failure mode is as well consistent with the observations reported by others [48,49].

Conclusion:

The review discourse has documented a tremendous improvement in the melting temperature, intermetallics formation and mechanical properties of CNTs reinforced solders. From the wettability results of CNTs solders, one can easily conclude that the significant reduction in the contact angle of solders on substrate will enhance the solder joint formation. More so, the reinforced CNT solders exhibited higher yield and ultimate tensile strength when compared to the unreinforced solders. The intermetallics phases observed in the literature for CNTs solder indicated a tremendous decrease in IMC thickness compared with the base alloy after aging treatment which indicates that the reinforced solders will resist failure under shock loading and some other aggressive working operations. However, the CNT reinforced solders showed no significant reduction in the melting properties when compared with solders reinforced with some other elements. Therefore, it is recommended for the current and future research to pay closer attention to this effect.

REFERENCES


