Using Nanoparticles and Carbon Nanotubes to Enhance the Properties of a Lead-free Solder

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ABSTRACT

In the present study, using the powder metallurgy route, varying amount of nano-sized Y_2O_3 particulates and Ni-coated carbon nanotubes (Ni-CNTs) were intentionally incorporated into the Sn-3.5Ag-0.7Cu solder to develop two nanocomposite solder systems. The samples were extruded and characterized in terms of their wettability, thermal, microstructural and tensile properties. Characterization results established that composite technology coupled with nanotechnology in electronic solders can lead to improvement in mechanical performance (in terms of better 0.2% yield strength (up to 13% increase) and better ultimate tensile strength (up to 17% increase). With the addition of reinforcements, better wettability of the nanocomposite solders was also observed and with no compromise on the melting temperature. These advanced interconnect materials will hence benefit the microelectronics packaging and assembly industry. An attempt is also made in this study to correlate the properties of the resultant nanocomposite solders with the increasing presence of reinforcements.

Keywords: nanoparticles, carbon nanotubes, composites, lead-free solder.

1 INTRODUCTION

In the electronics industry, solders play an important role in various levels of electronics assembly sequence and also as an interconnection between the silicon chip and substrate. In order to ensure the proper functioning of the electronics assembly, it is crucial for solders as the interconnecting material, to provide the necessary electrical, mechanical and thermal continuity [1]. However, with the miniaturization of electronic components and the ever-increasing functional and service requirements, conventional solder technology can no longer guarantee the device reliability. Hence, in order to fufill these ever-demanding challenges, a new generation of solders which is equipped with a combination of good thermal, electrical and mechanical properties must be developed. Composite solder with intentionally incorporated reinforcements in the solder matrix is developed [2 – 6].

In this study, an attempt was made to synthesize two nanocomposite systems, namely, SnAgCu/Ni-CNT and SnAgCu/Y_2O_3 solder composites, using the powder metallurgy technique. Characterization studies such as differential scanning calorimeter test and wettability test were carried out to analyze the melting temperature and the wettability of the composite solders, respectively. Furthermore, the mechanical performance of the composite solders was assessed using the tensile tests. Particular emphasis was also placed on correlating the increasing presence of reinforcements with the thermal and mechanical results of the resultant composite solders.

2 EXPERIMENTAL PROCEDURES

In this study, two types of reinforcement were used, namely, (i) nickel-coated multi-walled carbon nanotubes (Ni-CNT) (outer diameter: 10 – 20 nm and length: ~ 30 μm) and (ii) yttria (Y_2O_3) particulates (size range: 32 – 36 nm). The 95.8Sn – 3.5Ag – 0.7Cu (in wt. %) solder was used as the matrix alloy. For the case of SnAgCu/Ni-CNT composite solder, the size of solder powder ranged from 2 – 11 μm was used. While for the case of SnAgCu/Y_2O_3 composite solder, the size of solder powder ranged from 25 – 45 μm was used.

The processing procedures involved blending the pre-weighed solder powders and the desired amount of reinforcement, to achieve a homogeneous mixture. The mixture was then uniaxially compacted and sintered at 175 °C. Finally, it was extruded at room temperature, employing an extrusion ratio of 20:1. Following extrusion, the samples were subjected to the various characterization studies mentioned below.

Differential scanning calorimeter (DSC) was used to determine the melting point of the samples. A sample of weight less than 20 mg was firstly placed in a ceramic pan and heated to a temperature of 250 °C.

Solder wettability was determined with respect to the contact angle. Firstly, the extruded solder rods were cut into 5 mm thick discs. One disc was then placed on a copper substrate with fluxing and heated in a furnace to 250 °C. Flux was introduced to remove the possible oxides resulted from oxidation in both solder and substrate. The contact angle of the solder sample was then measured. A representative picture of the measured contact angle (θ) of the solder sample on the copper substrate is shown in Figure 1.

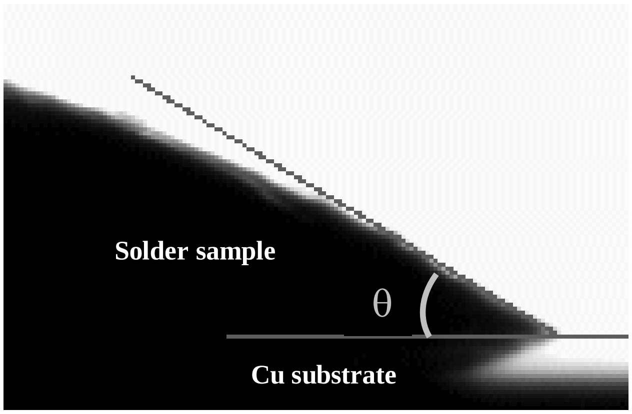


Figure 1: Representative picture showing the measured contact angle (θ) of the solder sample on the copper substrate.

Microstructural analysis of the metallographically polished samples is carried out using the Field-Emission Scanning Electron Microscope (FE-SEM) equipped with Energy Dispersive Spectroscopy (EDS). This is aimed to investigate: (i) the presence and distribution of reinforcements, (ii) the presence of porosity and (iii) the presence and distribution of intermetallic compounds (IMCs) in the solder matrix.

The tensile properties of the extruded samples in the form of smooth bars were determined in accordance with ASTM test method E8M-96 using a crosshead speed set at 0.254 mm/min on round tension test specimens of 5 mm diameter and 25 mm gauge length. The 0.2% yield strength (0.2% YS), ultimate tensile strength (UTS) and ductility values were determined by plotting the stress–strain curves.

3 RESULTS AND DISCUSSION

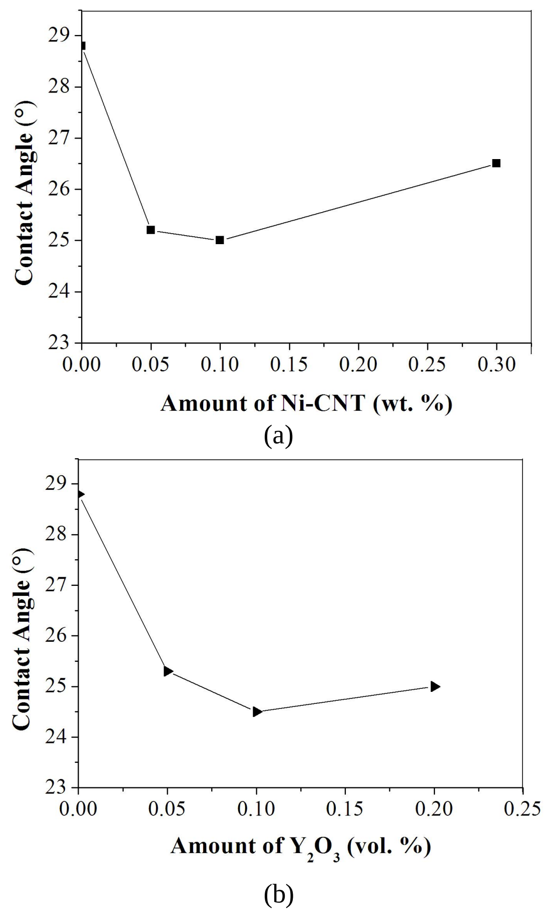
The DCS results of the nanocomposite samples showed that there was no influence on the melting point of the composite solders when either Ni-CNTs or Y_2O_3 particulates were incorporated into the solder matrix. The melting points of the composite samples were comparable to that of the monolithic Sn-Ag-Cu solder, as shown in Table 1. This finding is crucial, as it signified that when utilizing these nanocomposite solders in the fabrication of interconnects, there was no need to make any changes to the existing solder processes.

Wetting is crucial for soldering, as it plays an essential role in ensuring good bonding between the solder material and the substrate. Wettability between the solder and substrate is an important issue in the reliability of electronic packaging and understanding the wetting behavior of the composite solder is one of the key steps before industrial application [1, 7]. It is generally described by the contact angle (θ) to the substrate and it has been generally accepted that the smaller the contact angle, the better the wettability [8]. The wettability results of the solder samples measured with respect to the contact angle, revealed that additions of nano-sized Y_2O_3 particulates and Ni-CNT in the respective solder matrices, improved the wetting behavior (see Figure 2).

Table 1: Melting point results of SnAgCu/Y_2O_3 and SnAgCu/Ni-CNT nanocomposite solders.

Material	Reinforcement	Melting Point (°)
SAC*	-	221.9
SAC/0.05Y	0.05 vol.%	220.5
SAC/0.1Y	0.1 vol.%	221.5
SAC/0.2Y	0.2 vol.%	222.0
SAC**	-	220.0
SAC/0.05Ni-CNT	0.05 wt.%	220.1
SAC/0.1Ni-CNT	0.1 wt.%	219.4
SAC/0.3Ni-CNT	0.3 wt.%	220.8

* SAC: 95.8Sn – 3.5Ag – 0.7Cu (size range: 25 – 45 μm).
** SAC: 95.8Sn – 3.5Ag – 0.7Cu (size range: 2 – 11 μm).



(b)

Figure 2: Wettability test results of: (a) SnAgCu/Ni-CNT and (b) SnAgCu/Y_2O_3 nanocomposite solders.

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With 0.1 vol.% of Y_2O_3 addition and 0.1 wt.% of Ni-CNT addition in the solder matrix, the contact angle decreased by ~ 15% and ~ 13%, respectively. This could be attributed to the change in surface tension of the liquid composite solder when reinforcements were added. Liu et al. [9] and Tai et al. [10] also reported that the addition of 1 vol. % of Ni particulates in Sn-Ag solder and 0.5 vol. % of Ag particulates in Sn-Cu solder improved the wettability of the composite solders on Cu substrate which is consistent with the observations made in this study.

Microstructural characterization studies conducted on the composite and monolithic materials revealed uniform presence of intermetallic compounds dispersed throughout the solder matrix. Figure 3 shows a representative FE-SEM micrograph of the microstructure of the monolithic and composite solder samples. In this study, three phases namely: β-Sn, Ag_3Sn and Cu_6Sn_5 [11 – 13] were found in the solder matrix and their presence were confirmed with the EDS spectrum. For solder materials synthesized using the powder metallurgy route, Ag_3Sn and Cu_6Sn_5 intermetallic compounds exhibited granular morphology as shown in Figure 3.

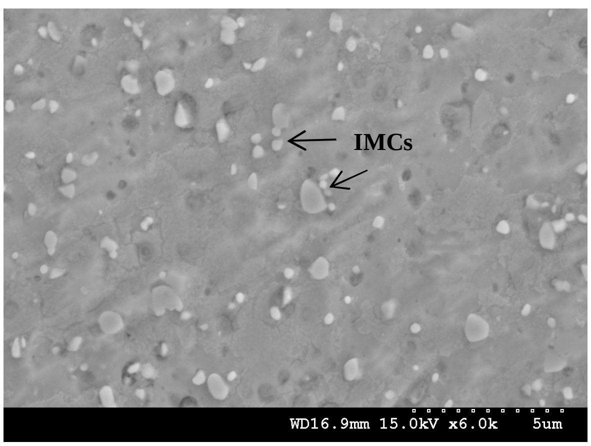

Figure 3: Representative FE-SEM micrograph showing the presence of the intermetallic compounds (IMCs) in the monolithic and composite solders.

For both composite systems synthesized in this study, reasonably uniform distribution of the reinforcements was observed. This could be attributed to: (a) suitable blending parameters and (b) high extrusion ratio used in secondary processing. Theoretically, when secondary processing with a large enough deformation is introduced, homogeneous distribution of reinforcements can be achieved regardless of the size difference between matrix powder and reinforcement particulates [14].

For SnAgCu/Ni-CNT composite samples, Ni-CNT clusters were uniformly dispersed throughout the solder matrix. As the length of the Ni-CNTs used in the present study is ~ 30 μm, their high aspect ratio and the strong van der Waals forces cause the Ni-CNTs to attract one another [15 – 17]. Thus the Ni-CNTs have a tendency to entangle together, resulting in Ni-CNT clustering rather than single, homogeneously dispersed Ni-coated CNTs (see Figure 4).

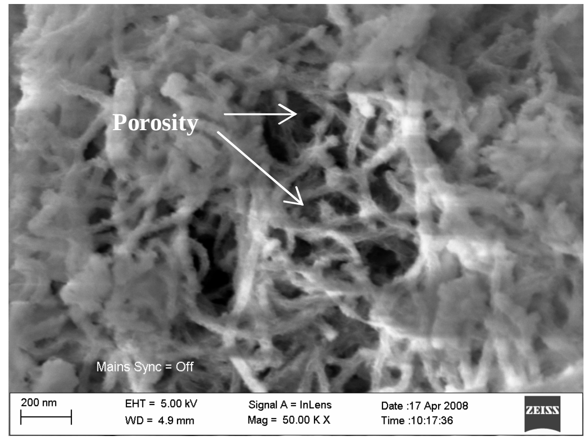

Figure 4: Representative FE-SEM fractograph showing the presence of Ni-coated CNTs in the SnAgCu/Ni-CNT composite solders.

The results of ambient temperature tensile tests revealed that the average strength values peaked with the addition of 0.05 wt.% of Ni-CNTs (see Table 2). An improvement of 8% for 0.2% YS and 12% for UTS was observed when compared to that of the monolithic SnAgCu material. For the case of SnAgCu/Y_2O_3 composite solders, an increasing trend of average 0.2% YS and UTS was observed with increasing addition of nano-sized particulates. The 0.2% YS increased by 13% and UTS increased by 17% with the addition of 0.2 vol.% Y_2O_3 (see Table 2).

The improvement in strength of the composite solders can be attributed to: (a) the progressive increase in dislocation density due to coefficient of thermal expansion (CTE) mismatch ($\Delta\sigma_{CTE}$) [18] between SnAgCu and reinforcements, and (b) the elastic modulus (EM) mismatch ($\Delta\sigma_{EM}$) [35] between solder matrix and reinforcement. The strength of a reinforced matrix can be defined by [18]:

$$\sigma_{my} = \sigma_{mo} + \Delta\sigma \qquad (1)$$

where σ_{my} and σ_{mo} are the yield strength of the reinforced and unreinforced matrix, respectively. $\Delta\sigma$ represents the total increment in yield stress of the reinforced SnAgCu matrix and is estimated by [19]:

$$\Delta\sigma = \sqrt{(\Delta\sigma_{CTE})^2 + (\Delta\sigma_{EM})^2} \qquad (2)$$

As observed in Figure 4, porosity was also present within the Ni-CNT clusters. For the SnAgCu/Ni-CNT composite solder samples, bonding occurs only between: (i) the Sn-Ag-Cu solder and Sn-Ag-Cu solder particles and (ii) Sn-Ag-Cu solder particles and reinforcements. Thus, with the addition of increasing amount of Ni-CNTs in the solder matrix, there will be some areas present in the solder matrix where Ni-CNTs come into contact with each other rather than with the solder particles. This is due to strong van der Waals forces between the CNTs, which resulted in mutual attraction of the nanotubes [15 – 17]. Small clusters of Ni-CNTs were formed and this consequently hindered effective bonding between the Ni-CNTs and the solder particles, resulting in cluster related porosity. Porosity acted as potential stress concentration sites that were favored for the formation of micro-cracking, which intensify failure. Existing literature [20] also reported that porosity at microscopic level could be detrimental to material's strength. The superior mechanical properties of CNTs cannot be fully realized in the synthesized composite solders due to the weak interfacial bonding between the Ni-CNT and the solder material. This hence limits further strength improvement of the composite solders with increasing addition of Ni-CNTs (> 0.05 wt.% Ni-CNTs).

Table 2: Tensile test results of SnAgCu/Y_2O_3 and SnAgCu/Ni-CNT composite solders.

Material	0.2% YS (MPa)	UTS (MPa)	Ductility (%)
SAC*	31 ± 2	35 ± 1	41± 8
SAC/0.05Y	32 ± 3	39 ± 3	31 ± 0
SAC/0.1Y	33 ± 3	38 ± 4	29 ± 2
SAC/0.2Y	35 ± 3	41 ± 4	29 ± 2
SAC**	48 ± 1	52 ± 1	22 ± 1
SAC/0.05Ni-CNT	52 ± 1	58 ± 3	17 ± 1
SAC/0.1Ni-CNT	48 ± 0	52 ± 0	18 ± 0
SAC/0.3Ni-CNT	48 ± 1	52 ± 1	14 ± 1

* SAC: 95.8Sn – 3.5Ag – 0.7Cu (size range: 25 – 45 μm).
** SAC: 95.8Sn – 3.5Ag – 0.7Cu (size range: 2 – 11 μm).

Ductility of both sets of composite sample was observed to decrease with increasing amount of reinforcements in the solder matrix (see Table 2). This can be attributed to the presence of reinforcements serving as crack nucleation sites, resulting in decreasing ductility under tensile loading conditions. This observation is also reported by several investigators working on other composite systems [2, 21].

4 CONCLUSIONS

The following conclusions can be drawn from the experimental findings of this study:

1. Two Sn-3.5Ag-0.7Cu based solder composite systems containing varying amount of Y_2O_3 particulates and Ni-coated CNTs were successfully synthesized using the powder metallurgy technique.
2. No significant change in the melting point of composite solders was observed, which indicated that existing soldering processes can be used when utilizing such composite materials for interconnects.
3. With the addition of reinforcement, results revealed improvement in wettability (in terms of smaller contact angles made with the copper substrate).
4. Tensile results revealed that the best overall mechanical properties were achieved in nanocomposite solders reinforced with 0.2 vol.% of Y_2O_3 particulates and 0.05wt. % of Ni-CNTs.

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