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# Effect of Ni-Coated Carbon Nanotubes on Interfacial Intermetallic Layer Growth

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## Abstract

In the present study, Ni-coated carbon nanotubes (Ni-CNTs) were incorporated into the Sn-Ag-Cu matrix, to form a composite solder. The interfacial intermetallic compound layer thickness formed on electroless nickel immersion gold (ENIG) metallized Cu substrate was determined under the as-soldered condition. It was observed that the addition of 0.01 wt.% Ni-CNTs into the Sn-Ag-Cu solder matrix, affected the formation of intermetallic compounds during the soldering reaction. For the reaction between the composite solder and the ENIG/Cu substrate,  $(Cu_{1-x}Ni_x)_6Sn_5$  and  $(Cu_{1-y}Ni_y)_3Sn_4$  were formed. The test results revealed that the thickness of interfacial IMC decreased from 2.30  $\mu m$  to 1.84  $\mu m$  with the addition of Ni-CNTs. Shear tests were also conducted on the as-soldered solder joints. The shear test results revealed that the composite solder joint exhibited a  $\sim 15\%$  increase in yield strength and a  $\sim 17\%$  increase in ultimate shear strength, as compared to its monolithic counterpart.

## Introduction

Tin-lead (Sn-Pb) solders are the most prominent interconnect materials used in the electronic components, whereby they provide the necessary mechanical and electronic connection. However, in recent years, environmental concerns and strict legislative regulations on the use of Pb-containing substances in electronic devices have motivated the move towards lead-free solders. Sn-Ag-Cu alloys are considered one of the most promising candidates to replace the widely used Sn-Pb solders [1-3].

During the soldering process, metallurgical reaction between solder and Cu pad or pad with electroless nickel immersion gold (ENIG) metallization, forms a layer of intermetallic compound (IMC) at the solder/metallization interface. It is well known that the IMC is a controlling factor on the overall long-term reliability of the solder joints as its physical properties are dissimilar from those of the solders and metallized films. Due to the brittle nature of the IMC, excessive intermetallics growth degrades the interfacial integrity and this would be detrimental for the solder joint reliability. To address this issue and the trend of miniaturization, there is an increasing need to develop new interconnection materials which have improved properties, so as to fulfill the ever-stricter service requirements. One of the approach is to introduce filler material into the conventional solder (like Sn-Ag-Cu solders), forming a composite solder [4-9].

In our earlier study on Sn-Ag-Cu/Ni-CNTs composite solders [10], the experimental results revealed better wettability and no compromise on the melting temperature, with the addition of Ni-coated CNTs. Furthermore, the tensile results of the bulk composite solder samples also showed an improvement, as compared to the monolithic SnAgCu

samples. In order to ensure long-term reliability of SnAgCu/Ni-CNT composite solder, it is essential to investigate the influence of Ni-CNTs addition on the interfacial IMC growth.

Accordingly, in the present study, 95.8Sn-3.5Ag-0.7Cu solder reinforced with 0.01 wt.% of Ni-CNTs was synthesized. The interfacial IMC growth at the solder/ENIG metallization for both monolithic and SnAgCu/Ni-CNT composite solder was investigated under the as-soldered condition. Their corresponding shear strengths were also determined.

## Experimental Procedures

In this study, 95.8Sn-3.5Ag-0.7Cu solder (particle size range: 5-15  $\mu m$ ) was used as the matrix material and Ni-coated multi-walled carbon nanotubes (with outer diameter: 10-20nm and length:  $\sim 30 \mu m$ ) was used as the reinforcing material.

Firstly, the desired amount of solder powder and Ni-CNTs was pre-weighed. Prior to mixing, a ferrous spoon was used to break-up the Ni-CNTs agglomerates and to aid in improving the homogeneity of the mixture. Subsequently, the SnAgCu/Ni-CNT powder mixture was blended for 10 hours in a V-blender. The mixture was then uniaxially compacted and sintered at 175°C for 2 hours in an inert Argon atmosphere. Finally, the billet was extruded into an 8 mm diameter rod and used for the characterization studies. In the case of the monolithic SnAgCu material, the material was fabricated as stated above, without the blending process.

For the preparation of solder joint samples, a solder preform (1.0mm by 3.0mm by 0.2mm thick) was firstly cut from the respective extruded solder rod and placed on the ENIG/Cu substrate. The sample was then heated in a reflow oven (Heller 1800). The peak temperature was set at  $\sim 245^\circ C$ . Flux was also introduced to remove the possible oxides which resulted from the oxidation of the solder and substrate.

The samples were subsequently mounted in a resin, metallographically polished and etched for a few seconds with 8 vol.% hydrochloric acid in 92 vol.% methanol. The samples were observed under the EVO 50 XVP Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS). This is aimed to investigate: (i) the effect of Ni-CNTs on the thickness of interfacial IMC formed between the solder and ENIG/Cu substrate, and (ii) the phases present in the IMC layer.

The average thickness of the interfacial IMC was determined using image analysis. Firstly, representative SEM micrographs were taken showing the IMC layer (see Fig. 1). This IMC layer was then traced out and analyzed using the Scion Image Analysis software. Due to the unevenness of the IMC layer along the interface, an average value of IMC thickness ( $\bar{h}$ ) was determined from the following equation:

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$$\bar{h} = \frac{A}{L_x} \quad (1)$$

where the  $A$  is the area of IMC layer obtained from the micrograph and the  $L_x$  is the length of the IMC along the interface.

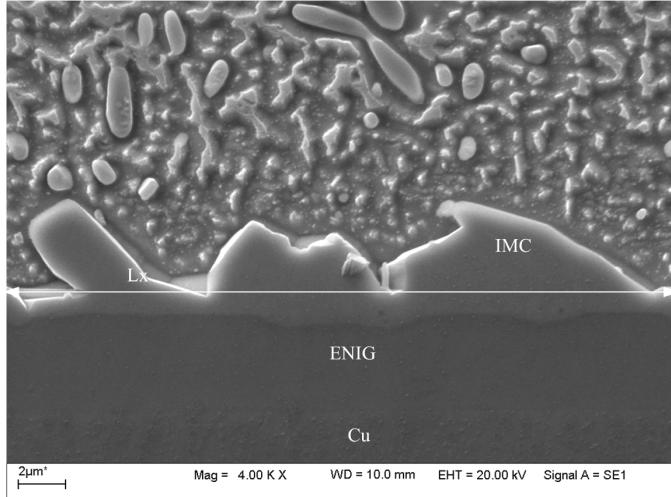


Fig. 1. Representative SEM micrograph showing the interfacial IMC layer formed in the composite and monolithic solder joints.

For shear tests, a micro-lap-shear solder joint sample was used. Prior to testing, the samples were further ground using 1200 grit SiCp paper and polished, to remove any excess solder at the edges. Shear tests were conducted on a micro-force test system from Instron. The test was conducted at room temperature. At least five samples were tested under each condition and the results were averaged.

## Results and Discussion

Fig. 2 shows the typical interfacial IMC layer of the SAC and SAC/Ni-CNT solders on the ENIG metallization under the as-soldered condition and the EDS analysis of the IMC formed at the interface.

During the soldering process, the molten solder comes in contact with the substrate and a layer of IMC is formed at the solder/substrate interface (see Fig. 2). Ahat *et al.* [11] reported that the strength was inversely proportional to the thickness of the IMC layer. In order to avoid the rapid diffusion of Cu atoms from the Cu substrate into the Sn-based solder, a barrier coating such as Ni film is used. However, there are cases whereby rapid diffusion still exists through the breached regions in the Ni film. Thus the Ni layer is often coated with another layer of Au to overcome this issue. The Au layer also serves to protect against oxidation [12].

For the solder/ENIG/Cu couple, the interfacial IMC layer consists of  $(Cu_{1-x}Ni_x)_6Sn_5$  and/or  $(Cu_{1-y}Ni_y)_3Sn_4$  [13, 14]. During the reflow process, the upper-most Au layer completely dissolved into the molten solder. Therefore, the Ni layer was exposed and it directly reacted with the molten solder, to form the Cu-Ni-Sn interfacial IMC layer [15-17].

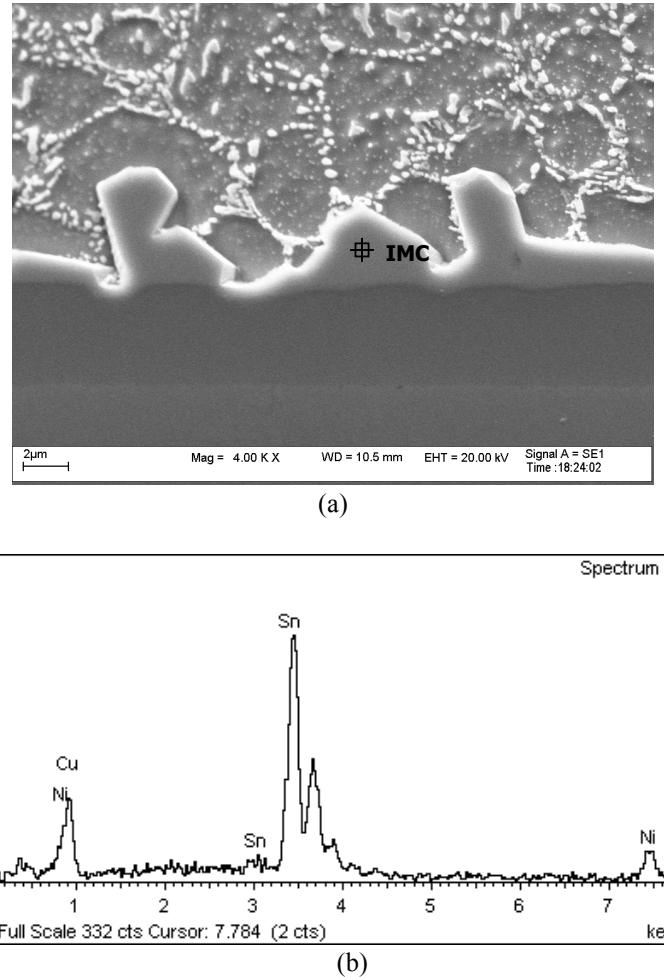


Fig. 2 (a) Representative micrograph showing the IMC layer formed at the interface of monolithic SAC and SAC/0.01Ni-CNT solder joints. (b) EDS analysis showing the Cu, Ni and Sn phases present in the interfacial IMC.

The results as presented in Fig. 3 revealed that with the addition of Ni-CNTs, the average thickness of the interfacial IMC layer evidently decreased (by ~ 20%, from 2.30  $\mu m$  to 1.84  $\mu m$ ).

During soldering, reaction took place. The Sn and Cu atoms mainly diffused from the solder to react with the interfacial Ni film, to form the Cu-Ni-Sn IMC layer. With the addition of Ni-CNTs, the presence of the Ni coating on the CNT resulted in its reaction with Sn in the solder matrix and thus intermetallics were formed. The reaction mechanism is believed to be such that the Ni-CNTs in the solder matrix restrained the diffusion of the Sn atoms towards the interface of the ENIG metallized substrate. Hence, the presence of Ni-CNTs as reinforcements in the composite solder joints can effectively slow down the growth of the IMC layer.

Furthermore, solders not only serve as an electrical interconnection, they are also subjected to mechanical loading while in use. Thus it is essential to assess the mechanical performance of such composite solder joints. In order to better mimic the actual service conditions used in the electronics industry, the shear tests were conducted on miniature lap-

shear solder joints. Fig. 4 presents the shear test results of the as-soldered monolithic SAC and composite solder joint samples. With the addition of 0.01 wt.% of Ni-CNTs, the average yield strength and ultimate shear strength values increased by ~ 15% and ~ 17%, respectively (see Fig. 4).

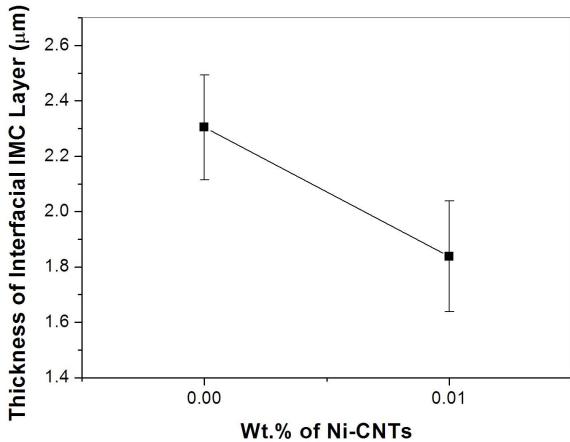


Fig. 3 Thickness of Cu-Ni-Sn IMC layer for monolithic SAC and SAC/0.01Ni-CNT composite solder joints.

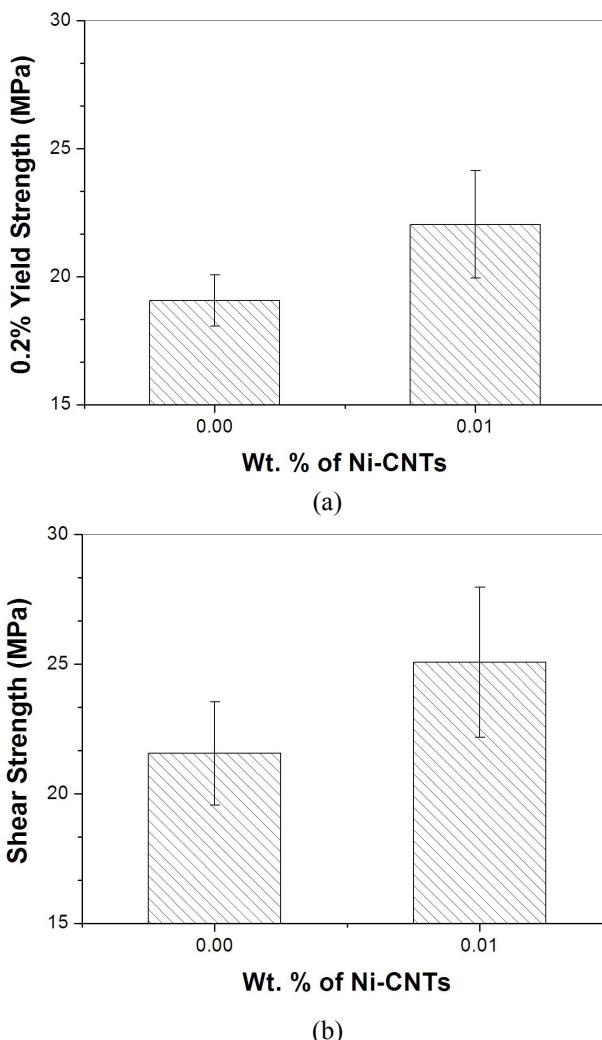


Fig. 4 Shear test results of as-soldered monolithic SAC and SAC/0.01Ni-CNT composite solder joint samples, (a) 0.2% yield strength, (b) ultimate shear strength.

The improvement in mechanical properties can be attributed to the following strengthening mechanisms: (i) generation of geometrically necessary dislocations to accommodate thermal and elastic modulus mismatch between solder matrix and Ni-CNTs [18, 19] and (ii) load-bearing effects due to presence of Ni-CNTs [20].

Although it was reported that thicker intermetallic layers formed between solder and substrate could significantly degrade the mechanical properties of the solder joints [11, 21], there were also opposing findings in the literature. Deng *et al.* [22] reported that intermetallic thickness does not play a critical role in controlling the shear strength of solder joints. In view of this, ongoing studies are being conducted to assess the contribution of the thickness of the intermetallic layer on the shear properties of the solder joint.

### Conclusions

- (1) After reflow, Cu-Ni-Sn intermetallic compound layer was formed at the solder/metallized substrate interface. The interfacial IMC layer of the composite solder joint (with addition of 0.01 wt.% Ni-CNTs) was observed to grow slower than that of the monolithic Sn-Ag-Cu solder joint.
- (2) The shear test results revealed that the composite solder joints exhibited an improvement in strength values (in terms of ~ 15% increase in yield strength and ~ 17% increase in ultimate shear strength).

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