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TECHNICAL PAPER

Performance of MWCNT-Reinforced SAC0307/Cu Solder Joint Under Multiple Reflow Cycles

Sanjay Tikale[1] · **K. Narayan Prabhu**[1]

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Abstract The evolution of interfacial microstructure and its effect on shear strength under multiple reflow cycles for multi-walled carbon nanotubes (MWCNT)-reinforced Sn0.3Ag0.7Cu solder/copper joint was investigated. The melting characteristics, wettability and mechanical properties of the solder alloy were assessed. The addition of MWCNT in the range of 0.01–0.05 wt% improved the wettability, melting behaviour and mechanical strength of the SAC0307 solder alloy. The nanoparticles in small weight fraction (0.01–0.05 wt%) addition were more effective in retarding intermetallic compounds growth at the interface. Amongst all compositions studied, the SAC0307–0.05MWCNT nanocomposite showed significant improvement in the performance of SAC0307/Cu solder joint under multiple reflow condition. The nanoparticles' reinforcement above 0.1 wt% of the solder alloy was ineffective in improving the solder performance due to increased clustering in the matrix.

Keywords Multi-walled carbon nanotubes · Nanocomposite · Multiple reflow cycles · Shear strength

1 Introduction

The legal restrictions imposed by international regulatory directives like The Waste Electrical and Electronic Equipment and Restriction of Hazardous Substances (WEEE and RoHS) on the use of lead-based solders have directed the research towards the development of lead-free solders [1]. The increasing demand for miniaturisation and high functioning electronic assemblies have motivated the research to develop the lead-free solders with enhanced physical, mechanical, thermal and electrical properties [2]. The addition of second phase materials like, metals, rare earth elements and nanoparticles in solder alloy, has been proved to be more effective in improving solder properties [3, 4]. Amongst many lead-free solders, ternary Sn–Ag–Cu solders have been considered as most promising candidates for replacing traditional Sn–Pb solders in electronic industries owing to their near eutectic compositions, good wettability and better thermal and mechanical properties [5, 6]. Low Ag content Sn–Ag–Cu alloys are generally less preferred in industries than high Ag content alloys because of their poor wettability and low mechanical strength. However, low Ag content alloys have good impact strength and are much cost-effective [7].

The solder joints often undergo multiple reflow cycles during manufacturing, service and repair works. The exposure to an elevated temperature accelerates the diffusion process and increase the intermetallic compounds (IMC) growth at the joint interface. Undesirable thick IMC at the interface deteriorate the joint strength due to its inherent brittle nature. In order to improve the performance of the solder joint under different thermal conditions, the IMC morphology needs to be refine and its growth must be arrested. Many studies have shown that the tensile strength, hardness and melting characteristics of solder have

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✉ K. Narayan Prabhu
prabhukn_2002@yahoo.co.in

Sanjay Tikale
Sanjaytikale@gmail.com

[1] Department of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal 575 025, India

improved with the addition of nanoparticles [8–10]. The exceptional mechanical and thermal properties of CNT have made them suitable candidate for reinforcement to develop the composite solder alloy. Studies done by Dele-Afolabi et al. [11] on Sn–5Sb solder alloy with MWCNT addition showed a decrease in solder melting temperature and suppression of IMC growth at the interface. CNT dispersion in the solder matrix acted as the reinforcement and enhanced the strength of the nanocomposite solder. Nai et al. [12] observed the improvement in wettability, yield strength and ultimate tensile strength of Sn–Ag–Cu solder alloy with MWCNT addition. The present study is focused on the assessment of the performance of SAC0307 solder alloy with MWCNT reinforcement in different weight fractions subjected to multiple reflow condition.

2 Materials and Methods

2.1 Melting Characteristics and Wettability Assessment

99Sn–0.3Ag–0.7Cu (in wt%) solder alloy paste added with mildly activated rosin flux (ROL0) was reinforced with different weight fractions of MWCNT. Nanotubes having the diameter range of 10–25 nm with an average length of 100–300 nm were used for the reinforcement. The transmission electron microscope (TEM) image of MWCNT used is presented in Fig. 1. The MWCNT were first cleaned with concentrated HCl (37%) and routed through the surfactant assisted process using polyvinylpyrrolidone (PVP-10) in dimethylacetamide (DMAc) solution [13]. The surfactant-treated MWCNT in 0.01, 0.05, 0.1 and 0.5 weight percentage of SAC0307 solder alloy, respectively, were mechanically blended with solder paste using stirrer to make different nanocomposite solder systems. These different nanocomposites are designated hereafter as, SAC0307–*x*MWCNT, where *x* represents weight percentage. The change in melting characteristics of SAC0307 solder alloy due to the addition of MWCNT were investigated using differential scanning calorimetry (DSC) under N_2 atmosphere. The heating/cooling rate of 10 °C/min for the temperature range of 30–300 °C was adopted for analysis. The influence of different weight fractions of MWCNT addition on the wettability of the solder was determined as a function of the spreading area of the reflowed solder sample. Stereomicroscope (STEMI 2000-C) was used to capture the images of reflowed samples. The spreading area was estimated with the help of image analyser software.

2.2 Solder Joint Shear Test

The effect of MWCNT addition on shear strength of SAC0307 solder was investigated using the single-lap-shear soldered joint samples under tensile pull test. The pure copper plates with the dimension of 55 mm (l) × 6 mm (w) × 1.5 mm (t) were used as substrate. A layer of 10 mm long, 6 mm wide and 0.2 mm thick (0.1 gm) solder paste was placed in between the Cu plates using mechanical fixture [14]. Samples were reflowed in a programmable reflow oven for the reflow time of 100 s using the thermal reflow profile shown in Fig. 2 [15]. Samples were subsequently reflowed for 1, 2, 4 and 6 reflow cycles to assess the effect of multiple reflows on joint properties. Tensile pull test was performed using Instron 5967 tensile testing machine under a strain rate of $1 \times 10^{-2}\ s^{-1}$.

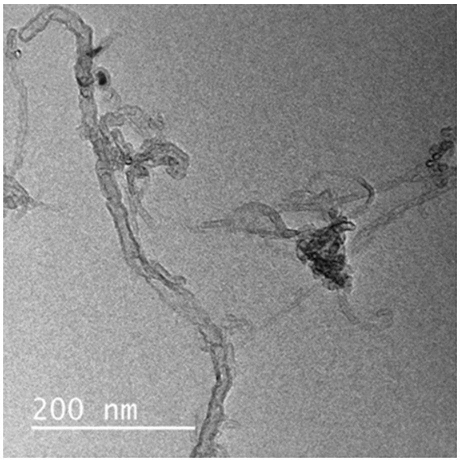


Fig. 1 TEM image of MWCNT

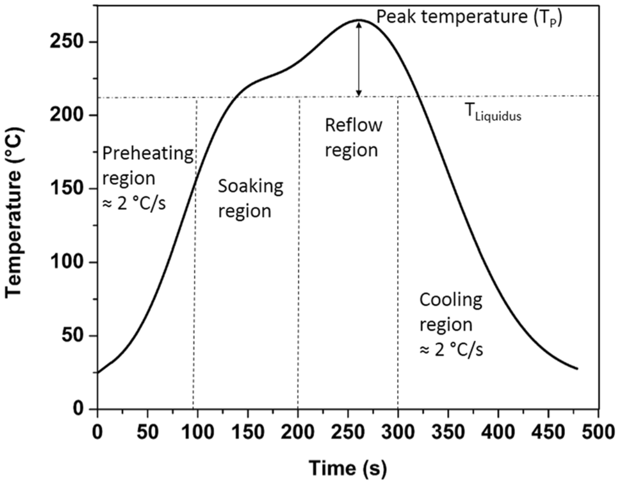


Fig. 2 Thermal reflow profile

2.3 Microstructure Study

The development of solder microstructure and IMC growth with MWCNT addition under multiple reflow condition was studied with the help of scanning electron microscopy (SEM). The reflowed samples were cut, polished and etched for 1–2 s with etchant solution (92% CH_3OH + 5% HNO_3 + 3% HCl). The compositions of different phases in the microstructure were analysed using energy dispersive spectroscopy (EDS) and X-ray diffraction spectroscopy (XRD). The interfacial IMC thickness was measured through SEM image analysis using image analyser software (Axio Vision SE64 Rel. 4.9). An average IMC thickness of uneven IMC layer at the interface was calculated by using the relation $\bar{x} = A_i/L_x$ where A_i represents the area and L_x is the length of IMC layer obtained from SEM micrograph.

3 Results and Discussion

3.1 Melting Behaviour and Wettability of the Composite Solder

The DSC curves for heating and cooling cycle for SAC0307 and SAC0307–0.05MWCNT compositions are shown in Fig. 3. The heating DSC curve for SAC0307 solder shows a primary melting peak around 219 °C which corresponds to the melting of an eutectic impurity in the solder. The addition of MWCNT results in slight decrease (around 1.5 °C) of onset and melting temperature of SAC0307 solder alloy. Undercooling of the solder is the temperature difference between the onset temperature of heating cycle and the onset temperature of cooling cycle of DSC curve. The nanoparticles in low weight fraction (0.01–0.05 wt%) addition marginally lower the pasty range and undercooling of the solder alloy. The decrease in onset and peak melting temperature can be attributed to the increase in surface free energy in the melt due to the addition of active nanoparticles. Excess surface free energy increases the instability and reduces the heat required for the melting of alloy which reduces the onset and melting temperatures. Solder alloys with lower melting temperature and smaller pasty range provide shorter reflow cycle time, low porosity and improved mechanical properties leading to improvement in the quality of the solder joint.

The stereo-macrographs of reflowed samples for different wt% of MWCNT addition showing spreading area are presented in Fig. 4. Spreading area analysis reveals that the nanoparticle addition in the range of 0.01–0.05 wt% increases the spreading area by 15% which indicates an improvement in the wettability of SAC0307 solder. The dispersed MWCNT in the melt reduces the surface tension of liquid solder and also decreases the solder-flux interfacial energies which enhances the solder wettability. However, the addition over of 0.05 wt% MWCNT decreases solder spreading by about 25%. The high concentration of MWCNT increases the viscosity of the solder melt and forms a network structure by agglomeration which inhibits the melt flow and reduces the spreading of the liquid solder.

3.2 Solder Joint Microstructure

The SAC0307 solder forms Cu_6Sn_5 IMC layer at the interface and Ag_3Sn IMC particles in β-Sn matrix after solidification on Cu substrate. The elemental compositions of different phases are confirmed with the help of EDS and XRD analysis. Figure 5 shows the SEM micrographs for monolithic and reinforced solder joint interface after 1

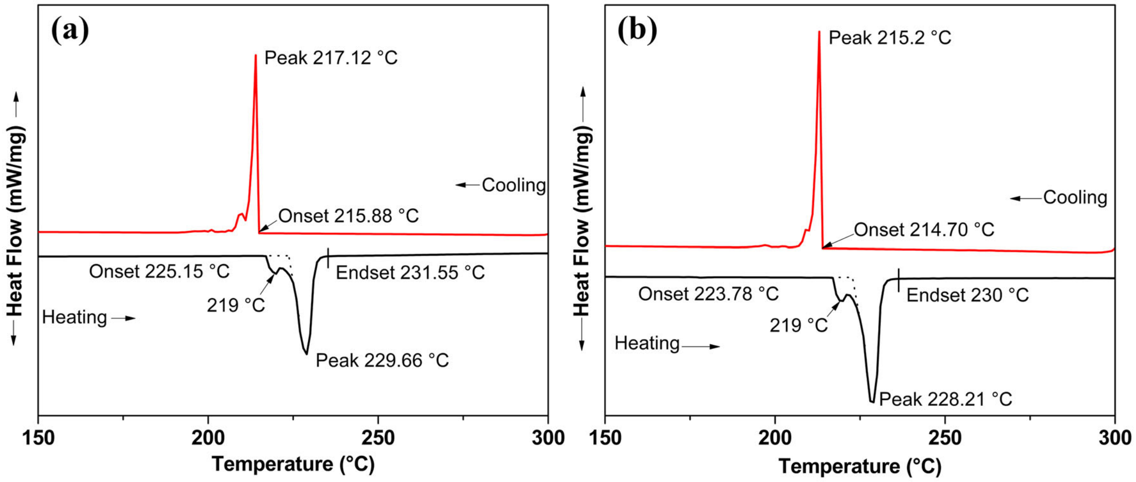


Fig. 3 DSC curves for **a** SAC0307, **b** SAC0307–0.05MWCNT

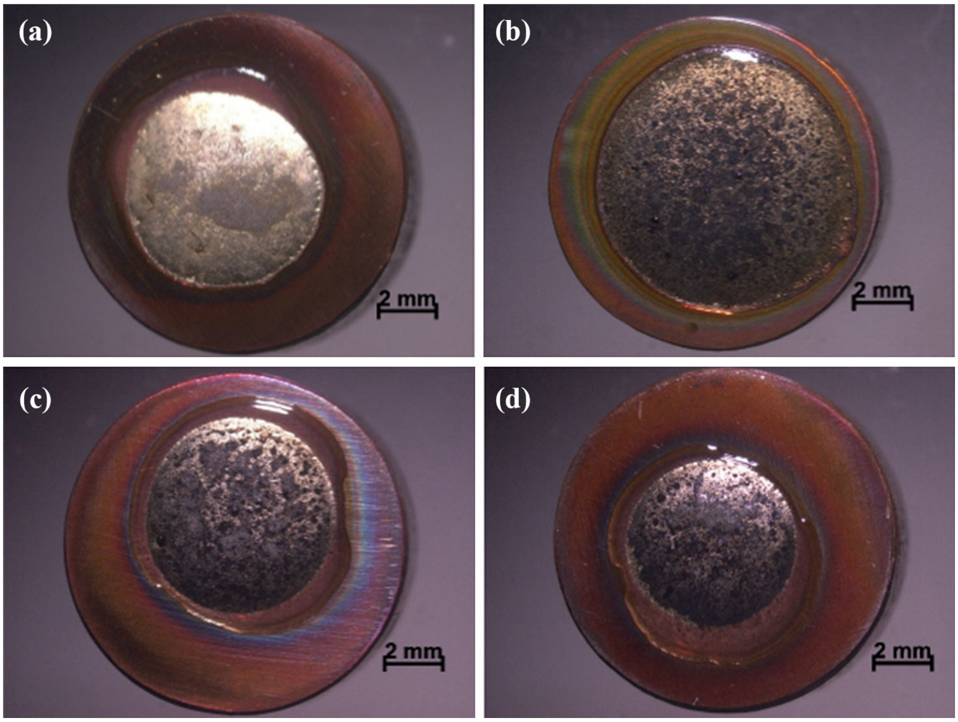


Fig. 4 Stereo images of reflowed samples for, **a** SAC0307, **b** SAC0307–0.05MWCNT, **c** SAC0307–0.1MWCNT, **d** SAC0307–0.5MWCNT

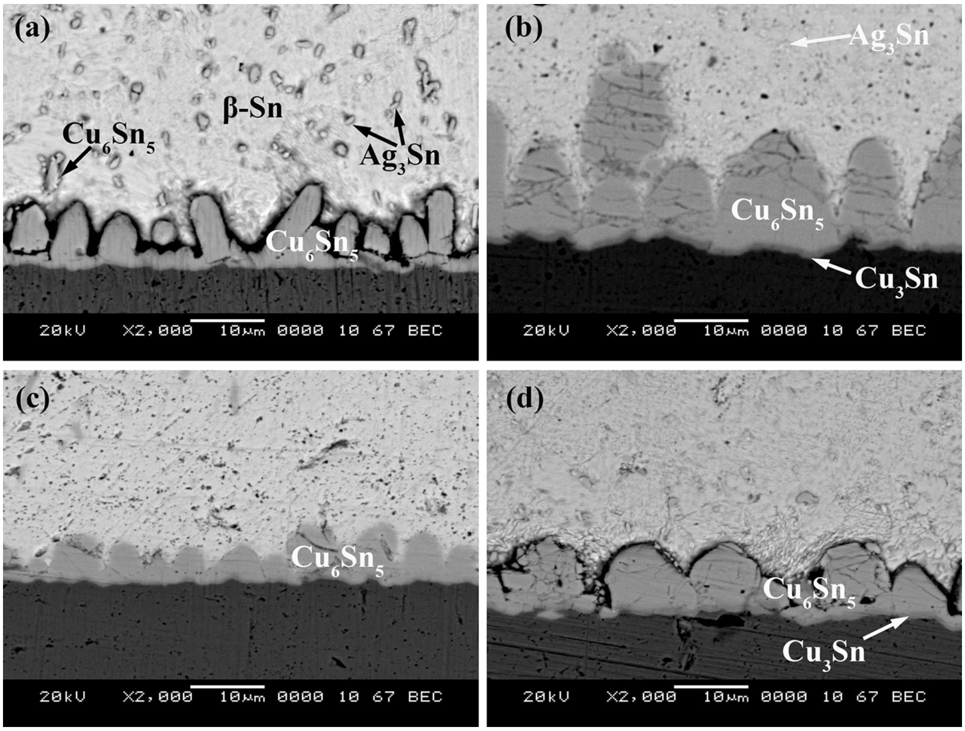


Fig. 5 SEM images of joint interface for SAC0307 **a** 1-reflow, **b** 6-reflows and SAC0307–0.05MWCNT, **c** 1-reflow, **d** 6-reflows

reflow and 6 reflows. The morphology of Cu_6Sn_5 IMC layer for monolithic SAC0307 solder alloy appears as elongated structure and with an increase in reflow cycles it become coarser. The average IMC layer thickness measure around 6 µm and 11 µm after 1 reflow and 6 reflows, respectively. A thin layer of Cu_3Sn IMC is formed between the substrate and Cu_6Sn_5 IMC layer after four reflows. The MWCNT reinforcement suppresses the growth of IMC layer under multiple reflows and also changes the morphology of Cu_6Sn_5 IMC layer to rounded scallop form. The IMC layer thickness is suppressed by 30% with 0.05 wt% MWCNT addition compared to unreinforced solder under multiple reflow condition. The effective adsorption of MWCNT between the IMC groves creates a barrier for dissolution of Cu atoms in bulk and restricts the diffusion of Sn from the bulk solder to IMC leading to suppression of the IMC growth under multiple reflows [11]. The addition above 0.1 wt% appears to be ineffective in IMC growth suppression owing to the increase in the agglomeration and entanglement associated with excessive addition of MWCNT. Figure 6 shows the EDS mapping graphs for 0.05 wt% and 0.5 wt% MWCNT added solder matrix samples, respectively. Elemental mapping confirms the presence of agglomeration of MWCNT in the matrix with high weight fraction addition. The coagulation reduces the effectiveness of MWCNT drastically and nullifies all the positive effects of their addition to the solder alloy.

3.3 Mechanical Strength of the Solder Joint

The joint shear strength for different nanocomposites of SAC0307 solder with respect to different reflow cycles are plotted in Fig. 7. The addition of MWCNT in the range of 0.01–0.1 wt% improves the joint strength under multiple reflows compared to monolithic SAC0307 alloy. The joint strength of the solder increases around 15% with second reflow cycle and decreases on higher reflows irrespective of the nanocomposition. The addition of 0.05 wt% MWCNT yield the maximum (around 23%) increase in the joint shear strength compared to monolithic solder alloy under multiple reflows. The improvement in shear strength can be attributed to the thin and uniform Cu_6Sn_5 IMC layer along with uniform dispersion of finer spheroidal shaped Ag_3Sn IMC in the matrix. The effective dispersion of MWCNT in the bulk strengthens the solder matrix and improves the joint shear strength under stress. However, the excessive addition of MWCNT (above 0.1 wt%) results in lower joint shear strength compared to unreinforced solder. The decrease in joint shear strength is due to the drastic reduction in wettability and IMC coarsening at the joint interface. Thick IMC layer is brittle and has low fracture strength. The excessive IMC growth often produces microcracks in the layer when exposed to repeated reflow cycles. These factors largely deteriorate the joint strength under applied stress.

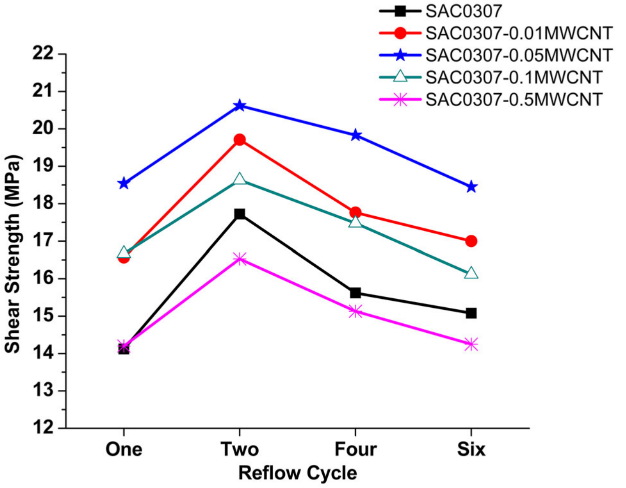
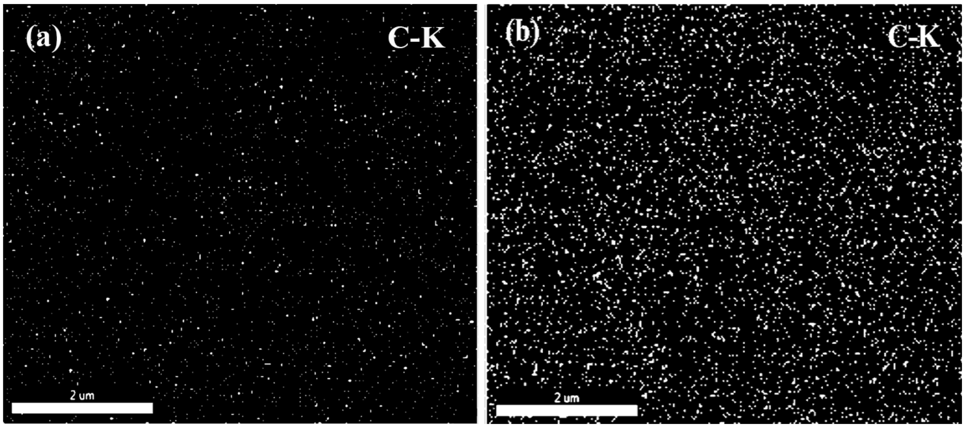


Fig. 7 Joint shear strength of MWCNT-reinforced SAC0307 solder with respect to different reflow cycles

The SEM images of fractured surface for different compositions of SAC0307 alloy samples after shear test are shown in Fig. 8. Samples with minor addition (0.01–0.05 wt%) of MWCNT result in ductile failure with small dimples on fractured surface whereas, samples with high nanoparticles content (0.1–0.5 wt%) fails with mix-mode of failure, possessing coarser dimples on the fractured surface. Thick IMC layer with microcracks and increased porosity with high concentration and clustering of MWCNT are the probable reasons for increase in the brittleness of the solder joint.

Fig. 6 EDS mapping showing MWCNT distribution for SAC0307 solder with MWCNT addition **a** 0.05 wt% and **b** 0.5 wt%



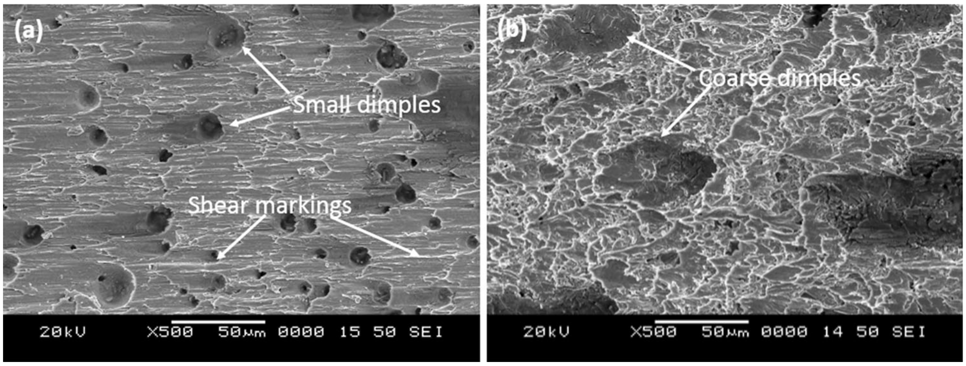


Fig. 8 SEM images of fractured samples for, **a** 0.01–0.05 wt% MWCNT addition, **b** 0.1–0.5 wt% MWCNT addition

4 Conclusion

The addition of MWCNT in low weight fraction marginally lowered the melting temperature of SAC0307 solder alloy. However, the thermal behaviour of the solder was not affected significantly with MWCNT addition. Under multiple reflow condition, the MWCNT reinforcement in the range of 0.01–0.05 wt% enhanced the solder wettability and improved the joint strength. The high concentration of nanoparticles significantly decreased the wettability and deteriorated the performance of the solder joint. The addition of 0.05 wt% MWCNT in the SAC0307 solder was found to be most effective in improvement of the solder performance under multiple reflow cycles.

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