

An Investigation of TiO₂ Addition on Microstructure Evolution of Sn-Cu-Ni Solder Paste Composite

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Abstract. In this research, varying fraction of titanium oxide (TiO₂) reinforcement particles was successfully incorporated into Sn-Cu-Ni solder paste in an effort to study the influence of TiO₂ addition on microstructure evolution of Sn-Cu-Ni solder paste composite. Sn-Cu-Ni solder paste composite was produced by mixing TiO₂ particle with Sn-Cu-Ni solder paste. The microstructure analysis was carried out by Scanning Electron Microscopy-Energy dispersive X-ray (SEM-EDX). The addition TiO₂ particle helps to refine the bulk solder microstructure and suppress the intermetallic compound (IMC) formation at the interface as will be discussed further.

1 Introduction

In microelectronic manufacturing industry lead solder paste widely used as electronic assembly due to their excellent reliability such as low melting point, better wettability, good mechanical, fatigue and creep properties [1, 2]. Unfortunately, lead is a known as toxic metal in electronic circuit. Since most of the electronic circuit waste could not be recycled and thus they will be dumped in the landfill. This phenomenon will cause lead pollution to the environment, especially soil pollution. Due to the band of lead solder paste usage in electronic assemblies, many research now focusing on lead free solder paste as interconnect material [3].

However, there are another challenge related to lead-free solder paste such as solder melting temperature, processing temperature, wettability, mechanical and thermo-mechanical fatigue (TMF) behaviors [4]. An attractive and potentially viable method of enhancing lead-free solder paste reliability is adopting composite approach to fabricate solder paste composite [5]. Composite solder is solder alloy which is intentionally incorporated with reinforcement particles [6]. Tang et al. [7] have studied the effect of adding TiO₂ nanoparticles on microstructure, microhardness and tensile properties of Sn-3.0Ag-0.5Cu-x TiO₂ composite solder. The microstructure of solder composite becomes

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more uniform and the size of Ag_3Sn and average grain size were decreasing. Apart from that, microhardness and tensile properties of composite solders have been improved.

In the current study, the influence of TiO_2 incorporated on Sn-Cu-Ni solder paste properties have not been studied in detail yet. The experimental data for this solder paste composite is still lacking. Therefore, an established data is needed. This research study was made to investigate the effect of various weight percentages of TiO_2 particles on the microstructure evolution and mechanical properties of Sn-Cu-Ni solder paste composite.

2 Experimental procedures

Sn-Cu-Ni solder paste (Nihon Superior Co. Ltd, Japan) with 20 to 38 μm particle size range and titanium oxide (TiO_2) reinforcement particulates (44 μm particle size from Sigma Aldrich) were mechanically mixed together in a various percentage (0, 0.25, 0.50, and 0.75 wt. %) to form composite Sn-Cu-Ni solder paste. The solder paste and reinforcement powder were pre-weight on a balance weight and mechanical mixing Sn-Cu-Ni solder paste with TiO_2 particles for 30 minutes to ensure the uniform distribution of the reinforcements. To produce a solder joint, about 0.1g of solder paste composite was then deposited on copper substrate and reflow soldering. After the reflow, the solder joint was then cleaned to remove flux residues.

The reflowed sample was first cross-sectioned perpendicularly to solder-copper interface of the solder joint and mounted in mounting cup using epoxy resin before metallographic sample preparation (grinding, polishing and etching using dilute solution of 5 vol. % nitric acid (HNO_3), 2% hydrochloric acid (HCl) in 93 vol. % methanol (CH_3OH)). Wetting angles were measured under optical microscope (ECLIPSE L300N) and using J-Image software.

The morphology of interfacial IMCs layer was observed by scanning electron microscope (SEM) JEOL JSM 6460LA coupled with energy dispersive X-ray spectroscopy (EDS). The IMC thickness was calculated by dividing the area of the IMC by its length and then takes averaged over five SEM images taken at a magnification of 3000x. J-image software was utilized to conduct the measurements of IMCs thickness form for as reflowed samples.

3 Results and discussion

Fig. 1 shows SEM image of the microstructure of monolithic and solder paste composite. The microstructure for both monolithic and solder paste composite composed of two regions which are the dark region known as eutectic region and light region as $\beta\text{-Sn}$. The eutectic region consists of Cu_6Sn_5 IMC phase. Microstructural observation shows that with the increasing amount of reinforcement particles up to 0.75 wt. %, the size of Cu_6Sn_5 IMCs were refined.

The refinement of Cu_6Sn_5 IMC phases is in conjunction with the theory of heterogeneous nucleation [8] During soldering, reinforcement particles may be finely dispersed in the molten solder and precipitate on the top of the substrate. These areas then become the heterogeneous nucleation sites for Cu_6Sn_5 IMC. With an increasing amount of reinforcement particles, it will result in decreasing the surface energy of Cu_6Sn_5 grains. These situations will then result in decreasing the growth velocity of Cu_6Sn_5 grains. According to heterogeneously nucleation theory, the Cu_6Sn_5 will nucleate on reinforcement surface in order to reduce the thermodynamic barrier [9]. The increasing amount of reinforcement particles in the solder has caused more reinforcement particles precipitate on

the top of the substrate, thus produce more nucleation site. It is believed that the more production of the nucleation site, the more Cu_6Sn_5 refinement process has occurred.

Previous studies reported that reinforcement particles may attribute in alter the microstructure become finer and thus improved the properties[8-10]. The effect of TiO_2 particles on Sn-0.3Ag-0.5 solder resulting in smaller grain size with an increase in TiO_2 proportion. The refinement effect of Si_3N_4 was also found by Salleh et al. with the addition of Si_3N_4 into monolithic solder, the β -Sn grains refine greatly and the size of Cu_6Sn_5 IMCs decrease [9].

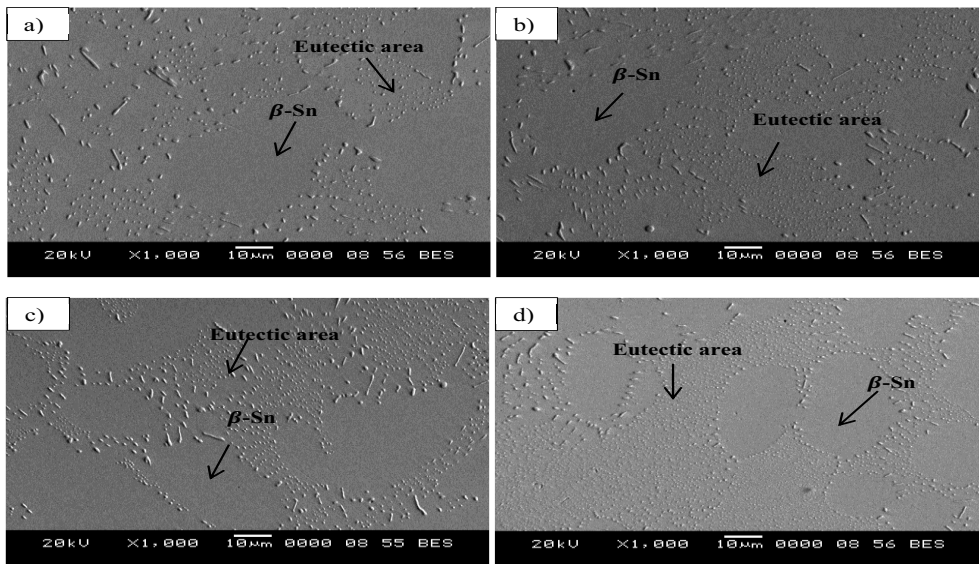


Fig. 1. Microstructure of Sn-Cu-Ni solder paste reinforced with TiO_2 at different percentage (a) 0 %, (b) 0.25 %, (c) 0.50 % and (d) 0.75 %.

4 Intermetallic compound formation

The intermetallic compounds (IMCs) layer for monolithic and solder paste composite is shown in Fig. 2. It can be seen that the scallop-like IMCs layer was observed along Cu substrate interface. The Cu_6Sn_5 was detected by SEM-EDX analysis, while Cu_3Sn phase was not detected. The thin Cu_3Sn phase was hardly to be detected for first reflow cycle and accelerated test such as thermal aging can possibly reveal this phase. It can be observed that the morphology of the interfacial Cu_6Sn_5 layer does not change too much with TiO_2 particle addition into Sn-Cu-Ni solder paste. The scallop type of IMC layer was not changed even when TiO_2 particle added. However, the addition of TiO_2 particles suppressed the growth of interfacial Cu_6Sn_5 layer. Fig. 3 shows the average IMC layer thickness for both monolithic and Sn-Cu-Ni solder paste composite with various weight percentages.

The reduction on interfacial IMC layer thickness is due to the presence of TiO_2 particles and the mechanism of suppression on this IMC thickness was discussed by Haseeb et al. [11]. They suggested that the decreasing in the thickness of interfacial IMC is due to discrete particle effect that preferentially being absorbed at the grain boundaries of IMC scallops. However, in this research, TiO_2 particles are believed has been distributed homogeneously at the diffusion path for the IMC growth thus suppressed the growth of the IMC layer.

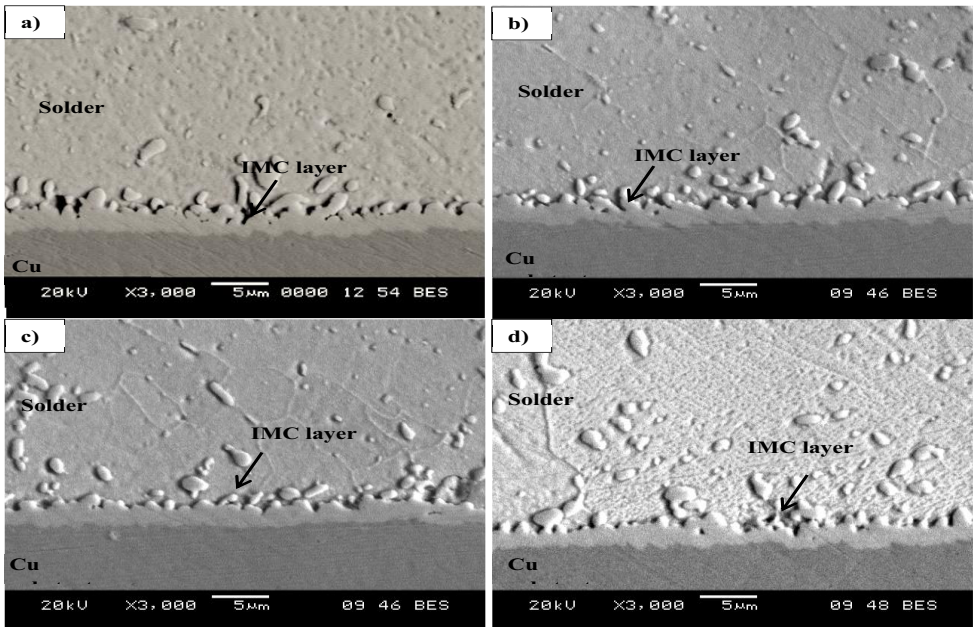


Fig. 2. Scanning electron microscope (SEM) images of the Intermetallic compound (IMC) formation for (a) 0, (b) 0.25, (c) 0.50 and (d) 0.75 of TiO_2 solder composite.

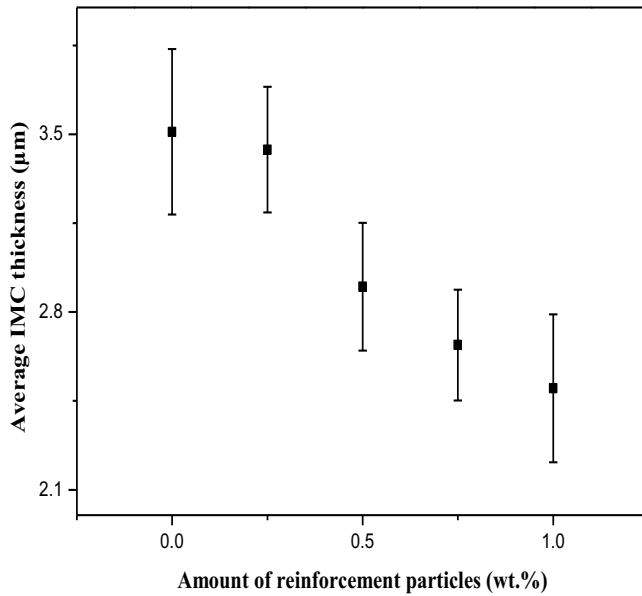


Fig. 3. Average intermetallic compound layer thickness of Sn-Cu-Ni solder paste reinforced with TiO_2 particles.

5 Conclusion

The effect of TiO₂ particles addition on microstructure evolution of Sn-Cu-Ni-TiO₂ solder joints was investigated. The addition of TiO₂ particle helps to refine the Cu₆Sn₅ IMC microstructure for bulk solder composite Sn-Cu-Ni solder paste. Besides, the addition of TiO₂ particles into Sn-Cu-Ni solder paste has caused decreases in thickness and diameter of the IMC at the interface. Apart from that, the presence of TiO₂ particles is believed to retard the IMC growth of solder paste composite resulting in a thinner IMC.

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