Suppression of (Cu,Ni)$_6$Sn$_5$ Intermetallic Compound in Sn-0.7Cu-0.05Ni+1wt. TiO$_2$ Solder Paste Composite Subjected to Isothermal Aging

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Abstract. This paper investigated the intermetallic compound (IMC) layer that formed in Sn-0.7Cu-0.05Ni+1wt.% TiO$_2$ (SCNT) composite solder paste added with reinforcement (TiO$_2$) particles. Besides, the growth of the IMC layer during subsequent aging at temperature of 75 °C, 125 °C and 150 °C also being studied. Scanning electron microscopy was used to observe the IMC growth and to measure the thickness of IMC layer. The interfacial IMC layer has been suppressed whereas the activation energy value of the composite solder paste was high (37.35 kJ/mol) which in turn improved the thermal stability of the IMC layer. Results also show the IMC formed at bulk solder microstructure of SCNT solder paste composite was refined. The presence of TiO$_2$ particles has become the obstacle for the Cu atom diffusion from the substrate to the solder and Sn atom from the solder, thus, successful for the suppression of the IMC layer.

1. Introduction

Restriction on the use of lead (Pb) containing solder paste in surface mount assemblies has promoted the development of lead-free solder paste. The Sn-based lead-free solder pastes such as tin silver (Sn-Ag), tin copper (Sn-Cu), and tin silver copper (Sn-Ag-Cu) have been identified to replace Pb containing solders in electronic assemblies [1]. In the electronic packaging industries, solder paste was used as primarily an interconnect material for surface mount assemblies. As the joining materials, solders paste to be used in electronic industries should provide necessary electrical, mechanical, and thermal continuity [2]. Therefore, the reliability and quality of solder paste are crucial to ensure proper functioning of the solder joint during surface mount assemblies.

Intermetallic compounds (IMCs) that formed and growth play an important role in electronic package. The formation of IMC occurred during soldering a solder on the substrate. When tin (Sn) in the molten solder reacts with the copper (Cu) from the substrate, the interfacial IMC formed on the interface between the solder and contacted substrate. Generally, the reaction between molten solder and substrate produces IMC layers, such as Cu$_6$Sn$_5$, Cu$_3$Sn, Ni$_3$Sn$_4$ and (Cu$_x$Ni)$_6$Sn$_5$ [3]. Excessive growth of IMC can jeopardize the solder joint performance which in turn influence the reliability of electronic devices. In order to improve the performance of Pb-free solders paste, variety reinforcements were incorporated into Pb-free solders paste to obtain composite solders paste.

Research conducted by Chellvarajoo et al. using diamond nanoparticles reinforcement found a significant improvement in Sn-3Ag-0.5Cu (SAC305) solder paste [4]. Microstructure and mechanical properties of as-reflowed Sn-0.7Ag-0.5Cu-2.5Bi-0.05Ni (SAC-BN) composite solder paste were
studied by Liu et al. The bulk microstructure of composite solder paste reveals that the grain size of the $\beta$-Sn phase has decreased which causes the increase of the hardness and elastic modulus [5]. Tang et al. have studied the effects of adding TiO$_2$ particles on the properties of Sn-3.0Ag-0.5Cu-xTiO$_2$ lead-free solder. The microstructure becomes more uniform with a decrease in Ag$_3$Sn grains size and the spacing between the Ag$_3$Sn grains has also decreased relatively. Other than that, an increase in microhardness and tensile strength was also reported. This is due to the strengthening effect attributed to the reduction of the spacing between Ag$_3$Sn grains [6].

In this study, the effect of TiO$_2$ particles added into Sn-0.7Cu-0.05Ni solder paste on microstructure evolution was investigated during isothermal aging. This study also aims at exploring the kinetic of IMC growth in Sn-0.7Cu-0.05Ni+1wt.% TiO$_2$ solder paste composite.

2. Experimental

Sn-0.7Cu-0.05Ni (SCN) solder paste supplied by Nihon Superior Co. Ltd, Japan was used in this studied. The solder joints were prepared by printing the solder paste onto Cu-OSP surface finish FR4 substrate using stainless steel with a thickness of 0.15 mm and reflowed in reflow oven followed the standard lead-free solder reflow profile. Then, solder joints were isothermally aged at various temperatures at 75, 125 and 150 °C for 24, 240 and 480 hours in a Memmert Oven to study the growth kinetic of the interfacial intermetallic compound.

The reflowed samples were cross sectioned and undergo metallographic processes samples preparation for microstructure observation. The IMC layer formed at solder/substrate was observed using the optical microscope (Eclipse L300N) and Scanning Electron Microscope (SEM). For each specimen, at least five SEM images were taken at different positions. The thickness of interfacial IMC growth was measured using the J-Image software. The average IMC thickness was determined by dividing IMC area (A) by its total length (L) as shown in Figure 1.

![J-Image software](image1.png)

**Figure 1.** (a) J-Image software and (b) Illustration of the area of IMC layer and length of the measured area.
3. Results and Discussion

3.1. Bulk Microstructure

Figure 2 (a and c) shows the SEM image for the bulk solder microstructure after reflowed for Sn-0.7Cu-0.05Ni (SCN) and Sn-0.7Cu-0.05Ni-1wt.%TiO$_2$ (SCNT) solder paste composite. Figure 2 (b and d) shows the SEM morphology of all solders after deep etched. The microstructure of SCN solder consists of β-Sn and small (Cu,Ni)$_6$Sn$_5$ IMC particles and SCNT solder possess finer (Cu,Ni)$_6$Sn$_5$ IMC particles. In the case of SCNT solder paste composite, refinement of (Cu,Ni)$_6$Sn$_5$ IMC is due to the heterogeneous nucleation site that formed when TiO$_2$ particles added into SCNT solder paste [7]. During soldering, the areas in which the area containing reinforcement particles has become the heterogeneous nucleation sites for (Cu,Ni)$_6$Sn$_5$ IMC. With the addition of TiO$_2$ reinforcement particles, the surface energy of (Cu,Ni)$_6$Sn$_5$ grains has decreased resulting in a decrease of the growth energy of (Cu,Ni)$_6$Sn$_5$ grains. According to heterogeneous nucleation theory, the (Cu,Ni)$_6$Sn$_5$ will nucleate on the reinforcement surface in order to reduce the thermodynamic barrier for the nucleation process. When the reinforcement particles were added into the solder, it will lead the particles to precipitate on the top of the substrate thus produce nucleation site. The increase in the nucleation of Cu$_6$Sn$_5$ grains consequently leads to the refinement of the grains [8].

Figure 3 presenting the SEM image for bulk solder microstructure evolution of SCN solder paste after aging for varying aging temperatures (75, 125 and 150 °C) at 24 h, 240 h and 480 h. The bulk solder microstructure of SCNT solder pastes composite subjected to isothermal aging for 75 °C, 125 °C, and 150 °C at 24 h, 240 h and 480 h were presented in Figure 4. After increasing the aging time, the IMC particles have become larger and coarsened. The results reveal that the aging temperature and time significantly influenced the microstructure evolution by increasing the β-Sn area. The plausible reason is that the growth of (Cu,Ni)$_6$Sn$_5$ IMC is governed by coarsening process. During isothermal aging, coarsening and the growth of (Cu,Ni)$_6$Sn$_5$ IMC was promoted due to the diffusion of Cu atoms from the substrate and Sn atoms from the solder. High temperature aging such as 150 °C provided enough energy for the reaction of Cu and Sn elements to reach each another.

![Figure 2. SEM morphology of (a-b) SCN and (c-d) SCNT solder after reflowed and deep etching.](image)

Furthermore, the number of Cu-Sn IMC particles in the aged solders joints has reduced as shown in Figure 3 and 4 (i). This is due to the reduction in smaller IMC particles and the larger IMC particles increased in size. It is likely the IMCs undergo phase coarsening with exposure to prolong aging time and aging temperature. During coarsening, smaller IMC particles are combined with larger IMC particles. The coarsening process occurs in accordance with Thompson-Freundlich solubility relationship, according to which concentration gradient exists between adjacent particles in a matrix [9].
According to Thompson-Freundlich solubility relationship, due to the concentration gradient that exists in the matrix, it will cause the particles to diffuse in the direction of the largest particles and away...
from the smallest particles. As a result, phase coarsening causes small particles to combine with large particles. The small particles dissolve to compensate for the decrease in the concentration at their interface as the flow of particles continue. This dissolution and growth process continue until the system is finally phase separated [9]. After aged to 480 hours for high temperatures such as 125 °C and 150 °C, the total amount of (Cu, Ni)₆Sn₅ IMC has reduced and the size of IMC was getting larger. In addition, it can be seen that the β-Sn area has increased.

3.2. **Intermetallic compound growth**

Figure 5 show the interfacial intermetallic compound (IMC) evolutions of SCN and SCNT solder joint subjected to reflow and subsequent isothermal aging at different temperature for 240 h. After isothermal aging, morphology of the IMC layer changed from scallop type to the combination of layer and scallop type of (Cu,Ni)₆Sn₅ intermetallic was clearly observed in the solder joint. Moreover, it can be seen that the IMC of aged solder grew thicker. However, IMC thickness for SCNT composite seems to be reduced as compared to SCN solder paste.

Generally, Cu atoms from the Cu substrate can diffuse into the (Cu,Ni)₆Sn₅ solder interface to react with Sn atoms, causing (Cu,Ni)₆Sn₅ IMC to grow towards the solder and attributed to an increase in the IMC thickness during isothermal aging. It is possible that TiO₂ particles in intimate contact with IMC interfacial layer stabilize the Cu dissolution path which in turn prevent the IMC from growing further during isothermal aging. The main mechanism on the growth of IMC layer in solder joints when TiO₂ was added is the grain boundary pinning [10]. During isothermal aging, the diffusion of the constituent atomic species through the IMC layer to reaction sites located at the solder/Cu₆Sn₅ and Cu₆Sn/Cu interface led to the growth of IMC layer of solder joints.

Normally, the diffusion of elements through grain boundaries is more rapid through the grain in order to maintain the continuous interfacial reaction. The existence of TiO₂ particles on the Cu₆Sn₅ grain boundary might be significantly helpful in suppressing the IMC growth during aging. The TiO₂ particles will obstruct the grain boundaries diffusion of Sn and Cu atom via the IMC layer and hence inhibit the growth of the IMC [11]. A study by Chen et al. (2016) shows that addition TiC particles notably suppressed the growth of interfacial layer of Sn-3.0Ag-0.5Cu under isothermal aging condition [12].

![Figure 5. SEM micrograph of intermetallic compound formation of Sn-Cu based solder paste of (a - d) SCN and (e-h) SCNT aged for 240 h.](image)

3.3. **Interfacial Intermetallic Compound Layer Growth Kinetic**

The activation energy for Sn-0.7Cu-0.05Ni (SCN) and Sn-0.7Cu-0.05Ni-1wt.%TiO₂ (SCNT) solder paste composite depicted in Figure 6. Results reveal that the activation energies of IMC growth are 34.12 kJ/mol and 37.35 kJ/mol for SCN and SCNT solder paste respectively. It was found that the activation energy of SCNT composite solder is higher compared to SCN solder paste. Generally, the activation energy of a reaction is known as the minimum energy required for the reaction to occur. The higher the activation energy of the solder, the higher the thermodynamic stability of the reaction. The presence of
Ni had stabilized the (Cu,Ni)₆Sn₅ IMC after reflowed and during subsequent aging. Apart from Ni, TiO₂ particles additions revealed that it can suppress the growth of IMC in SCNT solder paste composite. During aging, the presence of TiO₂ particles can prevent excessive IMC growth by restricting the diffusion activity of Cu atom from the substrate and Sn atom from the solder to react to each another. This finding indicates that the IMC growth of TiO₂ containing solder can be suppressed and could improve the solder joint reliability.

![Figure 6. Arrhenius plot of ln k versus 1000/T for the solid-state IMC growth kinetics in SCN and SCNT.](image)

4. Conclusion
The effect of TiO₂ particles addition on the microstructure evolution and interfacial intermetallic layer growth kinetic of Sn-0.7Cu-0.05Ni+1wt.%TiO₂ (SCNT) solder paste composite was examined through this work. The conclusion that can be drawn from this research are:

a) The (Cu,Ni)₆Sn₅ IMC in bulk solder area of SCNT solder paste composite are finer after introducing the TiO₂ particles.

b) The interfacial (Cu,Ni)₆Sn₅ IMC of SCNT solder paste was thinner during soldering and after isothermal aging.

c) The thermodynamically stable SCNT solder joint composite with high activation energy of 37.35 kJ/mol was obtained.

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