
The influence of nano-particles on microstructural development at the interface of Sn3.5Ag-solder and Cu-substrate

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Abstract: Preliminary experimental results have shown that an unexpected large needle-like phase Ag₃Sn grows from the solder/substrate interface and large polygon-like Sn-Cu intermetallic compounds are present in the region, which is close to the interface when using lead-free binary Sn3.5Ag solder alloy. This paper summarises the efforts made to prevent the formation of these deleterious phases. An addition of 0.25 wt% of either copper nano-particles or nickel nano-particles was found to effectively avoid the formation of large Ag₃Sn phase and to modify the solder matrix through a random dispersion of the in-situ intermetallic compounds Cu₆Sn₅ or Sn₄Ni₃. The mechanism involved in influencing the interfacial structure is quite different for copper and nickel nano-particles. The addition of copper nano-particles stimulates the formation of the Sn-Cu compound Cu₆Sn₅ at the solder/substrate interface, while the nickel nano-particles promotes the formation of Sn-Cu-Ni-Ag compound to replace the regular scallop-like Cu₆Sn₅ having a round morphology.

Keywords: lead free solders; Sn3.5Ag solder; interfacial structure; nano-particles; microstructure; reinforcement; nickel; copper.

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1 Introduction

The electronics industry provides many products that have changed our lives. An important technology, which is helping to make these products available, is the electronics packaging and assembly technology (Lau, 1995). Recent developments in electronic technology involve the flip-chip-on-board assembly, which can be best described as joining a chip to a substrate through a soldering process. The trend towards miniaturisation of electronic products and the high input-output (I/O) density of semiconductors requires the use of smaller solder bumps having the desired mechanical properties.

As a joining material, solder is an interconnection of the chip to the Printed Circuit (PC) board. It provides electrical connection in the circuit and mechanical continuity in assemblies, and thus plays a crucial role in the creation of high quality products.

The quality of the solder bumps is important to the integrity of a solder joint, which in turn is vital to the overall functionality of the package (Lau, 1994). A solder joint actually involves a solder bump and two solder-substrate bounding interfaces containing Intermetallic compounds (IMC). Strengthening of the solder bump can be achieved using a high strength solder alloy, such as a Sn-Au alloy. However, for strengthening of the solder joint, the properties of the solder-substrate interface must be considered.

At the region of the solder/substrate interface, tin in the solder reacts with copper in the substrate to form Cu_xSn_y -type intermetallic compounds. These compounds are present as thin layers at the solder/substrate interface after the solidification of the solder. The formation of a thin layer of intermetallic compound is essential to promote bonding. However, an excessively thick layer of the IMC is detrimental to the solder joint because of its intrinsic brittleness that makes it susceptible to failure even at low operating loads. Furthermore, the IMC layer continues to grow during service (Kang et al., 2002; Lee et al., 2003; Lee and Chen, 2002).

An attractive and potentially viable method of enhancing a solder is by using composite solders formed by the addition of reinforcement in the form of particles to a conventional solder alloy. During the last few decades, a variety of particle reinforcements have been tried in an attempt to engineer composite solders. A large majority of the particulate reinforcements are either metallic or intermetallic compounds. The composite solders were found to have:

- 1 higher mechanical properties at ambient temperature
- 2 higher creep resistance at elevated temperatures
- 3 higher cycle fatigue resistance (Anon, 1986; Guo et al., 2003; Lee et al., 2000, 2002; Marshall et al., 1991; Reno et al., 1997; Sastry et al., 1993; Wu et al., 1993).

For example, the addition of microsized nickel particles to a Sn3.5Ag solder favoured the formation and presence of intermetallic compounds around the reinforcing nickel particles (Lee et al., 2002). The sunflower-shaped intermetallic compound, which forms around the Ni particles resulted in higher shear strength and better creep properties (Rhee et al., 2003). Lucas et al. (1999) compared the creep behaviour of small Sn3.5Ag single shear lap solder joints, with and without in-situ reinforcements and observed the global creep strain rate to be lower in the composite solder joints. Copper particles (average particle size of 8-microns) added to a Sn-Pb solder can enhance the creep-rupture lifetime of a soldered joint by an order of magnitude. It was attributed to the formation and presence of a thin layer of intermetallic compound between the particles and the solder matrix (Yan et al., 2004).

The effect of adding copper and silver particles (average powder size in several microns) to a eutectic Sn3.5Ag solder on microstructural development, isothermal aging evaluation and creep response, was studied by Guo et al. (2001a,b). It was found that creep resistance of the copper particle-reinforced composite solder, based on a Sn3.5Ag solder matrix, was noticeably improved for the soldered joints at temperatures of 25°C, 65°C and 105°C. Recent work in nano-technology has made available a spectrum of nano-sized particles. Several attempts have been made to form a composite solder by using nano-particles as the reinforcing agent for a 63Sn-37Pb solder (Lin et al., 2002, 2003b,d; Marshall and Calderon; 1997a,b) and even for lead-free solders (Fritz and David, 2005; Lin et al., 2003a).

The motivation of this paper is to understand the influence of tiny percentage of copper and nickel nano-particles added to a lead-free tin-silver solder (i.e. the Sn3.5Ag) in governing the kinetics of solidification and resultant microstructural development.

2 Experimental set-up and procedures

2.1 Selected materials and sample preparation

Three materials are used in this investigation, including:

- 1 Commercial no-clean Sn3.5Ag solder paste, with the alloy powder having an average size of 45 microns and the chemical flux occupying 10% in volume.
- 2 Pure copper and pure nickel nano-particles, which have an average particle size of less than 100 nm, respectively.

The technique to make a composite solder is to blend commercial Sn3.5Ag solder paste with either copper or nickel nano-particles at a specific percentage. To compare the effect of various additives in the solder, a 0.25% by weight was selected for either copper or nickel nano-particles. The mechanical stirring was performed for 30 min in order to ensure a near homogeneous distribution of nano-particles in the solder paste.

A schematic drawing of the experimental setup is shown in Figure 1, which reveals there are several key components:

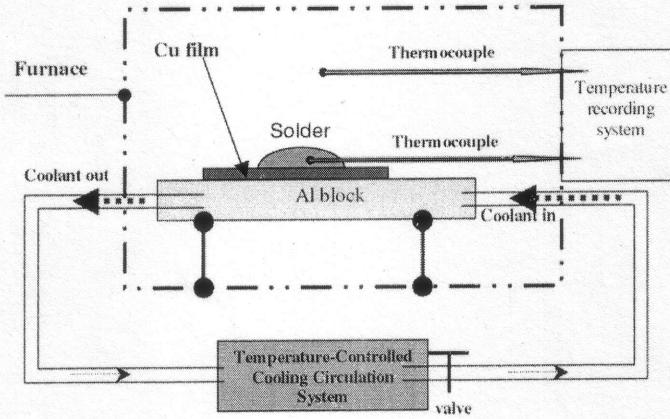
- 1 temperature-controlled furnace
- 2 Al block as a platform
- 3 temperature monitoring system to include thermocouples, data acquisition system, and visualisation.

Before turning on the power to the furnace, 0.2 g of the composite solder paste was printed on a clean copper sheet having thickness of 1.5 mm, which is then uploaded directly on the platform specifically built in the furnace. The peak temperature of the solder in the heating-cooling process is set to be 250°C. To precisely monitor the solder process for each solder, a fine J-type thermocouple having a diameter of 0.005 in. was placed inside of the solder paste mixture. The cooling and resultant solidification of the solder sample takes place within the furnace with the power off. In this study, the average cooling rate was found to be 12.3°C per min. The as-solidified samples were thoroughly cleaned using aqueous hydrochloric acid solution to remove the flux, surface oxides and other contaminants on the sample surface. This is followed by ultrasonic cleaning of the solder samples in isopropanol with subsequent cooling and drying in ambient air.

2.2 Microstructural characterisation

The as-solidified samples were prepared using standard metallographic procedures for examination in an optical microscope under bright field illumination. The composition was measured using Energy Dispersive X-ray (EDX) analysis to check:

- 1 the primary Sn-rich phase
- 2 the Sn-Ag compounds
- 3 Sn-Cu intermetallic compound
- 4 Sn-Cu-Ni intermetallic compound.

Figure 1 The Schematic drawing of the experiment set-up

Sample preparation involved diamond saw sectioning and cold mounting. This was followed by an initial coarse grind using progressively finer grades of silicon carbide impregnated emery paper using copious amounts of water as both coolant and lubricant. The samples were then fine polished using 3 and 1 μm alumina powder suspended in distilled water as the lubricant. Final polishing to a near mirror-like surface finish is achieved using 0.05 μm diamond paste suspended in distilled water. The as-polished samples were chemically etched using an etchant (a solution mixture of nitric acid (5 ml), hydrochloric acid (2 ml) and methanol (93 ml)) for a few seconds. The etched surfaces of the solder samples were observed in an optical microscope under bright field illumination with the objective of determining:

- 1 size and morphology of the primary grains
- 2 presence, distribution and morphology of intermetallic compounds.

3 Results and discussions

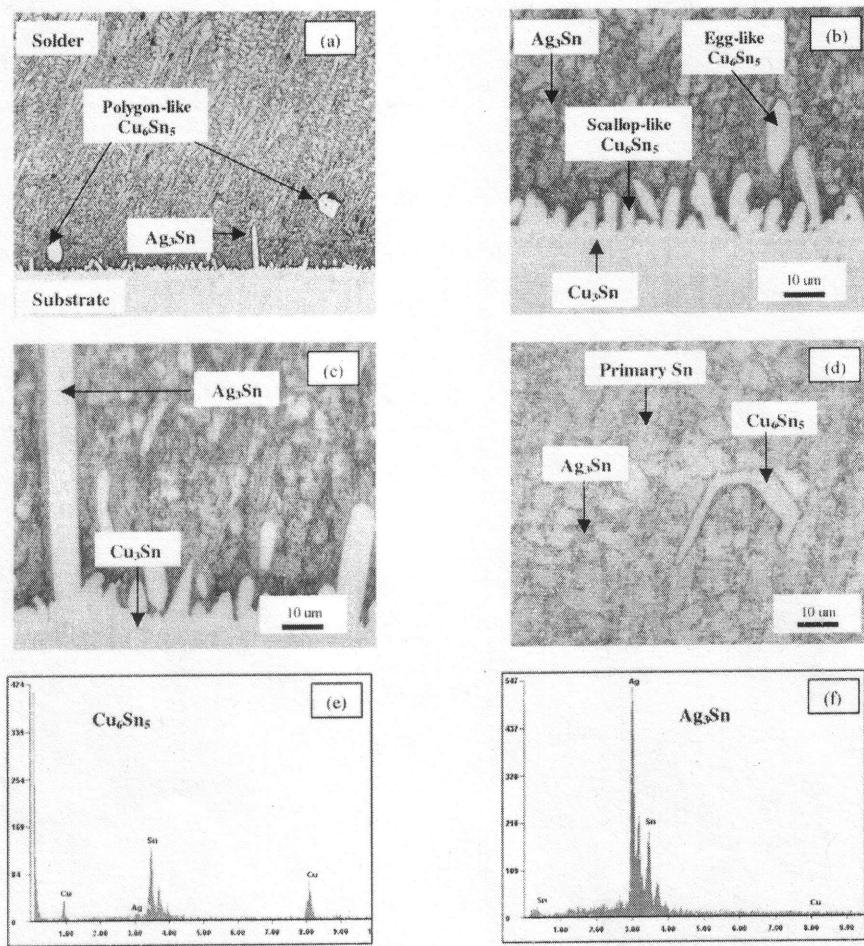
The primary objective of this study is to summarise the behaviour of nano-particles of either copper or nickel at the interface of solder and Cu-substrate from a microstructural point of view with in particular focus on the morphology changes of the Sn-Ag and Sn-Cu compounds.

3.1 Interfacial microstructure of Sn3.5Ag solder wetting on a Cu-substrate

The as-solidified microstructure of lead-free Sn3.5Ag solder, wetted on a copper substrate and experienced heating-cooling reflow process, is shown in Figure 2. The key findings from this figure are:

- 1 an unexpected large needle-like grain, shown in Figure 2(a) and (c), identified by EDS as Ag_3Sn phase, was found to grow from the solder/substrate interface
- 2 large polygon-like Cu_6Sn_5 intermetallic compound was found located close to the solder-substrate interface (Figure 2(a)).

Figure 2 The micrograph of the interface of solder/copper substrate for Sn3.5%Ag solder.
 (a) Over view at the interface of solder/substrate, (b) Magnified interface to show the Sn-Cu compounds, (c) Magnified interface to show the large needle-like Ag_3Sn phase, (d) Cu_6Sn_5 compounds in the solder matrix, (e) EDX analysis for Cu_6Sn_5 and (f) EDX analysis for Ag_3Sn phase



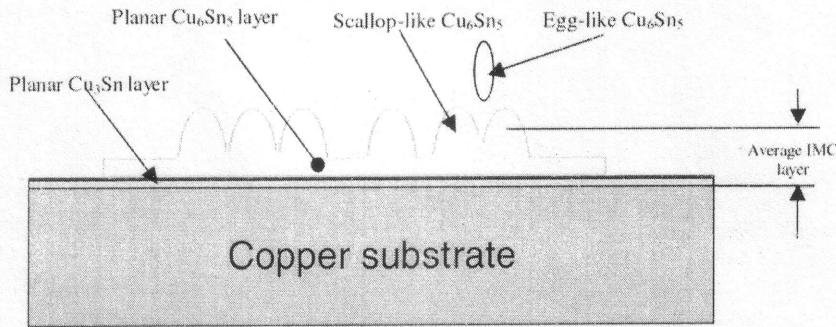
The solder alloy used in this study is Sn3.5Ag having no copper content. Consequently, the Sn-Cu intermetallic compounds identified in the solder matrix are believed to originate from the copper substrate. The interface between the solder and the copper substrate is composed of two well-defined layers of the intermetallic. These are:

- 1 a very thin planar layer of Cu_3Sn (less than 1 μm thick), with a larger concentration of copper located immediately adjacent to the copper substrate as shown in Figure 2(b) and (c).
- 2 scallop-like Cu_6Sn_5 compounds nucleating from the Cu_3Sn layer and growing into the solder side.

An exhaustive examination at higher magnifications (Figure 2(b) and (c)) reveals other phases to be present in the solder-copper substrate system. These are:

- 1 A planar layer of the Cu_6Sn_5 compounds located between the Cu_3Sn layer and scallop-like Cu_6Sn_5 compounds, shown schematically in Figure 3. The average thickness of this layer was 5 μm .
- 2 Scallop-like Cu_6Sn_5 compounds growing over the Cu_6Sn_5 compounds and extending into the solder matrix, shown schematically in Figure 3.
- 3 Egg-like Cu_6Sn_5 compounds in the solder side but very close to the scallop-like Cu_6Sn_5 compounds, which is believed to come from the scallop-like Cu_6Sn_5 compounds layer because of segregation and escaping (shown in Figure 2(b) and (c) and schematically in Figure 3).
- 4 The Cu_6Sn_5 intermetallic compounds with varying size and shapes located far away from the interface, which are believed to come from the dissolved copper, shown in Figure 2(d), and could reinforce the primary Sn phase.
- 5 Regular eutectic structure with the Ag_3Sn phase embedded in the primary Sn phase, shown in Figure 2(d).

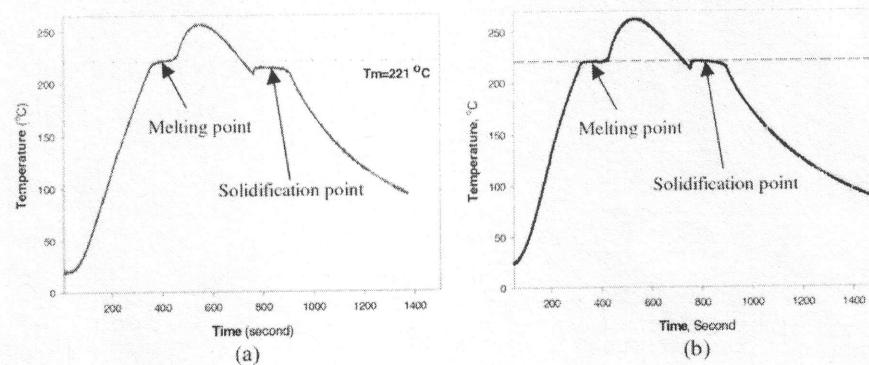
Figure 3 The schematically drawing at the interface of solder/substrate



This observation suggests that copper atoms at the substrate immediately adjacent to the solder dissolve into the Sn-dominated solder once the molten solder encounters the substrate. The Cu-Sn phase diagram is used to rationalise the presence of intermetallic compounds under conditions of furnace slow cooling (Okamoto, 2002). The existence of the large needle-like Ag_3Sn phase is not expected. It grows from and adheres to the Cu_6Sn_5 compound layer, while extending into the solder matrix. It poses a risk to the overall reliability of the solder joint since the interface between the large Ag_3Sn phase and the surroundings provides a preferential path for crack propagation. A similar phenomena has been reported using Sn-Ag-Cu alloy system (Henderson et al., 2002a) and the solution has been found to control the formation of the Ag_3Sn plate achieved by increasing the cooling rate or by reducing the Ag content or by trace additions of zinc to the Sn-Ag-Cu alloy system (Henderson et al., 2002b; Kang et al., 2003, 2004a-c). It has also been reported that an increase in the cooling rate of the Sn3.5Ag alloy suppresses the formation of a large needle-like Ag_3Sn phase (Lin et al., 2003c). The evidence of coexistence of the Sn-Ag-Cu and Sn-Ag alloys close to the solder/substrate interface is observed from a monitoring of the temperature during solder processing, as shown in

Figure 4. From this figure, the solidification point for the Sn3.5Ag solder is found to be around 218°C (Figure 4(a)). This is marginally below the melting point of the bulk eutectic Sn3.5Ag alloy (221°C, shown in Figure 4(b)). This suggests that an area close to the copper substrate is no longer the binary Sn-Ag alloy but has now become a mixture of the Sn3.5Ag and the Sn-Ag-Cu system since the near eutectic Sn-Ag-Cu system has a solidification point of around 217°C (Loomans and Fine, 2000).

Figure 4 Temperature variations during reflow process. (a) Sn3.5Ag solder wetting on copper substrate and (b) Bulk Sn3.5Ag solder (eutectic alloy)



3.2 Influence of copper nano-particles on interfacial microstructure of the Sn3.5Ag solder wetting the copper substrate

The addition of 0.25 wt% copper nano-particles to a commercial no-clean Sn3.5Ag solder paste produces in-situ Sn-Cu intermetallic compound and reveals changes in the overall microstructure at the interface of the solder and the copper substrate, shown in Figure 5(a). The presence of copper nano-particles in the solder exerts two independent yet mutually interactive functions:

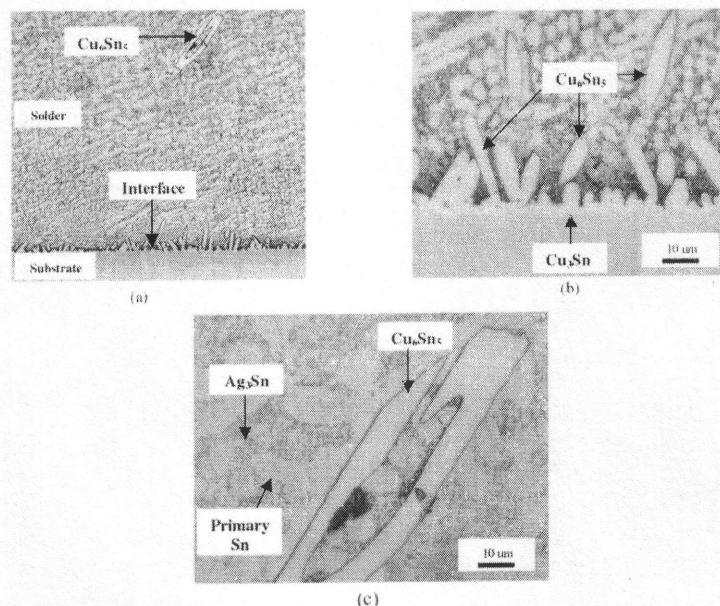
- 1 Stimulates the formation and presence of the scallop-like and egg-like Cu₆Sn₅ intermetallic compounds either at and close to the interface of the solder-copper substrate (Figure 5(a) and (b)). The average IMC thickness (5.8 µm) is much larger than in the eutectic counterpart of the Sn3.5Ag solder (4.5 µm). The thickness of the IMC layer is determined by dividing the total area, occupied by Sn-Cu intermetallic compounds, by the length.
- 2 Produces large polygon-like Cu₆Sn₅ compound with partial porosity in the solder matrix (Figure 5(a) and (c)).

Comparing Figure 5 to 2, it is seen that the thickness of the planar Cu₆Sn₅ compounds at the interface of the solder and the substrate, with and without copper nano-particles, was found to be similar. No evidence was found for the presence of the Ag₃Sn phase. Formation of this phase is suppressed by the overwhelming growth of the Cu₆Sn₅ intermetallic compound.

The role of Cu particles in lead-bearing solder was studied by Wu et al (1993) through adding Cu particles to Sn-Pb solder. The result demonstrated excellent improvement in the mechanical properties of the solder joints. It has been reported that for copper particles containing composite solders, the solder/substrate interface consisted

of thinner Cu_6Sn_5 layer and a thicker Cu_3Sn layer, than the eutectic Sn-Pb solder counterpart, since the addition of copper resulted in an increased activation energy for the formation of Cu_6Sn_5 and decreased activation energy for the formation of Cu_3Sn , as compared to the eutectic Sn-Pb solder. The data shown in this experiment is that the thickness of the Cu_6Sn_5 layer in the copper-containing Sn3.5Ag solder is larger than the eutectic lead-free Sn3.5Ag solder. This is a conflicting result with regard to the thickness of the Cu_6Sn_5 layer between the two solder alloys.

Figure 5 The micrographs of interface for Sn3.5Ag solder with 0.25 % copper nano-particles.
(a) Overall view, lower magnification, (b) Interface between the solder and Cu-substrate and (c) Polygonal-like Cu_6Sn_5 compound in the solder matrix



3.3 Influence of nickel nano-particles on interfacial microstructure of the Sn3.5Ag solder wetting the copper substrate

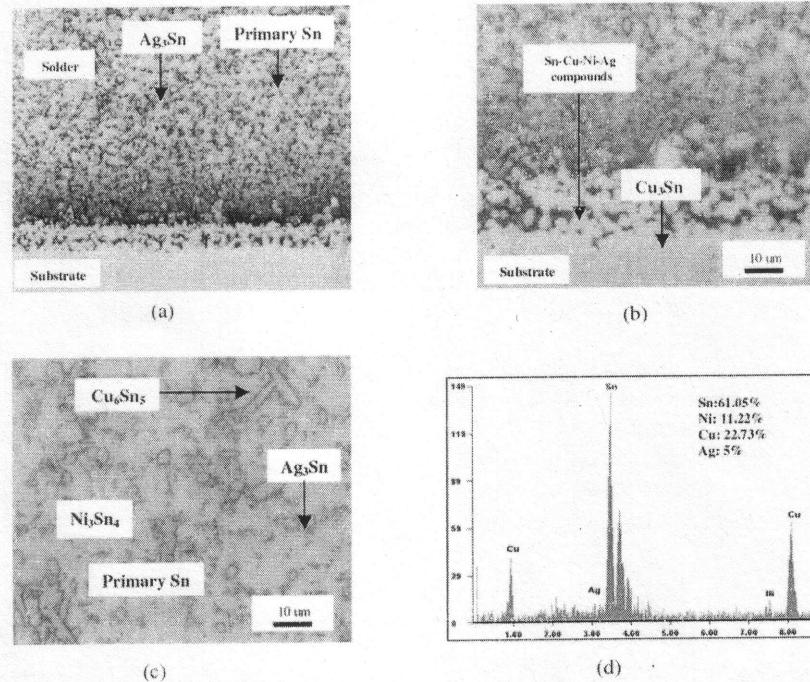
The addition of 0.25 wt % nickel nano-particles to a commercial no-clean Sn3.5Ag solder paste reveals changes in the overall microstructure shown in Figure 6(a). Comparing Figures 6(a) with 2(a), noticeable changes can be found in the regions of:

- 1 the scallop-like Cu_6Sn_5 layer
- 2 the matrix of the solder. Several phases are suppressed by the addition of nickel nano-particles:
 - a no scallop-like Cu_6Sn_5 phase at the solder/substrate interface
 - b no large-sized polygon-like and egg-like Cu_6Sn_5 compounds close to the interface or in the solder matrix, and more importantly
 - c no large needle-like Ag_3Sn phase growing at the solder-substrate interface.

High magnification micrographs reveal the following features in the solder-substrate system for the solder containing nickel nano-particles:

- 1 There is a curved thin layer of the Cu_3Sn adjacent to the Copper-substrate.
- 2 The typical scallop-like Cu_6Sn_5 layer is replaced by the Sn-Cu-Ni-Ag layer having a round grain morphology at diameter around 2 μm . A random dispersion of the nickel nano-particles at the solder/substrate interface results in the formation, presence and distribution of the Sn-Cu-Ni-Ag intermetallic compound while concurrently refining the grain size of the IMC.
- 3 The primary Sn phase in solder matrix (Figure 6(c)) is refined to an average grain size of 1 μm in diameter, which is significantly smaller than the Sn3.5Ag counterpart (about 4 μm in diameter).
- 4 The formation of the needle-shaped Ag_3Sn phase is suppressed (see Figure 6(a) and (b)).
- 5 The Ni_3Sn_4 compounds are dispersed randomly through the solder matrix (see Figure 6(c)).

Figure 6 The micrograph of interface for Sn3.5Ag solder with 0.25% nickel nano-particles, (a) Overall view, lower magnification, (b) Solder/substrate interface, high magnification, (c) Solder side, higher magnification and (d) EDX analysis for Sn-Cu-Ni



It is found that the net thickness of the IMC layer along the interface of the solder/substrate for the Sn3.5Ag solder containing 0.25% nickel nano-particles is twice the value of the unreinforced counterpart. In the matrix of the solder, the particles of Sn-

Ni compound have a polygonal morphology without the presence of particles of nickel in the centre. This suggests the occurrence of complete dissolution of the nickel nano-particles into the tin-rich phase. This type of intermetallic compound has been reported in the open literature to be the binary Sn-Ni phase and not the Sn-Ag-Ni ternary phase (Hsu and Chen, 2004). It has been reported that the nickel particles of a few microns in diameter had a morphology of a sunflower in the solder matrix (Lee et al., 2002).

In summary, nickel nano-particles modify the structure of both the solder matrix and the solder/substrate interface, and suppress the formation of the large needle-like Ag_3Sn phase. These changes result in an improvement in mechanical properties of the solder joint, which was has been reported in an earlier study (Lin et al., 2004).

4 Conclusions

Based on an investigation of the influence of nano-particles reinforcement on the microstructural development of a tin-silver solder, the following are the key findings:

- 1 Experiments were successfully performed to understand the kinetics governing solidification and resultant microstructural development for a tin-silver solder containing nanometer-sized particles of copper and nickel.
- 2 The addition of copper nano-particles modifies the solder matrix, but stimulates the formation and presence of the Cu_6Sn_3 compound at the solder/substrate interface, which is conducive for promoting brittle fracture.
- 3 The nano-particles of nickel are a good agent for reinforcing a conventional Sn3.5Ag solder both in the solder matrix and both at and along the interface of the solder and the copper substrate.
- 4 Reinforcing of the Sn3.5Ag solder with 0.25% of nickel nano-particles leads to the suppression of the Sn_3Ag phase, which has a needle-like morphology, in the Sn3.5Ag solder.

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