Effect of Nickel Doping on Interfacial Reaction between Lead-free Solder and Ni-P Substrate

O. Saliza Azlina[1, a], A. Ourdjini[2, b], I. Siti Rabiatull Aisha[2, c]

[1]Faculty of Mechanical & Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat, Johor, Malaysia

[2, 3] Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

[a]salizaz@uthm.edu.my, [b]ourdjini@fkm.utm.my, [c]aisha_hideaki@yahoo.com

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Abstract. Due to environmental concern, lead-free solder are taking the place of eutectic Sn-Pb solder in electronic packaging industry. Among various lead free alloys, Sn–Ag–Cu (SAC) alloys are leading lead-free candidate solders for various applications because it is offered better properties. This study investigates the interfacial reactions during reflow soldering and isothermal aging between Sn-3.0Ag-0.5Cu (SAC305) and Sn-3.0Ag-0.5Cu-0.05Ni (SACN30505) on electroless nickel/ immersion palladium/immersion gold (ENEPIG) surface finish. The substrates were subjected to isothermal aging at 125°C for up to 2000 hours with solder size diameter of 500µm. The results indicated that after reflow soldering, $(Cu, Ni)_6Sn_5$ IMC is formed between solder and substrate while after aging treatment a new IMC was formed between $(Cu, Ni)_6Sn_5$ and substrate known as $(Ni, Cu)_3Sn_4$. Moreover, after soldering and isothermal aging, Ni-doped (SACN) solder represents a thicker IMC compared to SAC solder. Aging time of solder joints results in an increase of IMC's thickness and changes their morphologies to become more spherical, dense and with larger grain size. In addition, the results also revealed that the thickness of intermetallics formed is proportional to the aging duration.

Introduction

Increasing environmental concerns on the use of lead are pushing electronics towards soldering with lead-free solder materials [1]. Among various lead free alloys, Sn–Ag–Cu (SAC) alloys family are leading lead-free candidate solders for various applications because of its relatively good soldering performance, excellent creep resistance, and thermal fatigue reliability, as well as their compatibility with current components [2,3,4]. There is a continuous interest to better understand and improve the properties of interfacial intermetallic compound (IMC) layers in order to increase the reliability of Sn-Ag-Cu solder joints [2]. Thus, in order to further enhance the properties and improve the performance of the interfacial IMC layers of SnAgCu solder alloys, alloying elements such as rare earth, Bi, Ni, Co etc. were selected by lots of researchers as alloys addition into these alloys [5].

Minor element doping also had a big influence on the solder joint quality, including solder microstructure and interface IMC formation [6]. Jiang *et al.* also mentioned from previous researcher which Ni doping could cause high solder joint strength but showed no effect on the failure mode [6]. In addition, a small amount of Ni addition has ability to enhance the wettability of Sn-Ag-Cu (SAC) alloys [5]. Gao *et al.* also indicated that rare earth (RE) element such as Ni would play an important role in providing better electronic interconnection [5].

Therefore, this study is performed to examine the effect of doping element (0.05wt% Ni) in the Sn-3.0Ag-0.5Cu (SAC305) lead-free solder on intermetallic growth and thickness, where ENEPIG (electroless nickel / electroless palladium/immersion gold) as a surface finish. Besides that, the effect of different aging temperature on interfacial reaction during reflow soldering and isothermal aging also has been investigated.

Experimental procedure

The soldering reaction between SAC305 and SAC305 with 0.05% nickel doped (SACN30505) solders ball and Ni-P (ENEPIG) surface finish were examined in this study. The copper polymer sandwich substrate (FR-4) with dimensions 45 x 50 x 1 mm was prepared and then was subjected to a pretreatment process in order to remove oxides and activate the copper substrate surface before the electroless Ni/electroless Pd/immersion Au (ENEPIG) plating process is started. The nickel (Ni) plating solution used is made up from 28g/L of nickel sulfate, 17g/L of sodium acetate, 24 g/L of sodium hypophosphite, 1.5 mg/L of lead acetate and conducted at 85°C. After that, electroless palladium were applied on Ni layer and followed by deposited with gold layer through immersion plating without any pretreatment except rinsing in running tap water with bath temperature was set up at 45°C and 93°C respectively. Then, all samples were laminated with a layer of solder mask to restrict the molten solder from flat spreading during reflow. Next step is the solder mask together with the patterned film was cured by ultraviolet (UV) light in order to produce small openings of 0.15 mm in diameter. After curing samples, a thin layer of no clean flux is applied onto the substrate to remove the oxide layer and also to improve the wetting of molten solder during reflow. Then, the substrates were manually populated with solder balls with a diameter of 500μm arranged in several rows. Bonding to form the solder joints was made by reflow soldering in a furnace at temperature ~230˚C. Then, each sample was subjected to aging treatment at 125°C for 250 hours, 1000 hours and 2000 hours. Characterisation of samples involved both at top surface and cross section of solder joints. Several techniques including optical microscopy, NIKON optical microscope, scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX), image analyzer and field emission scanning electron microscope (FESEM) were used for the intermetallics characterization.

Results and Discussion

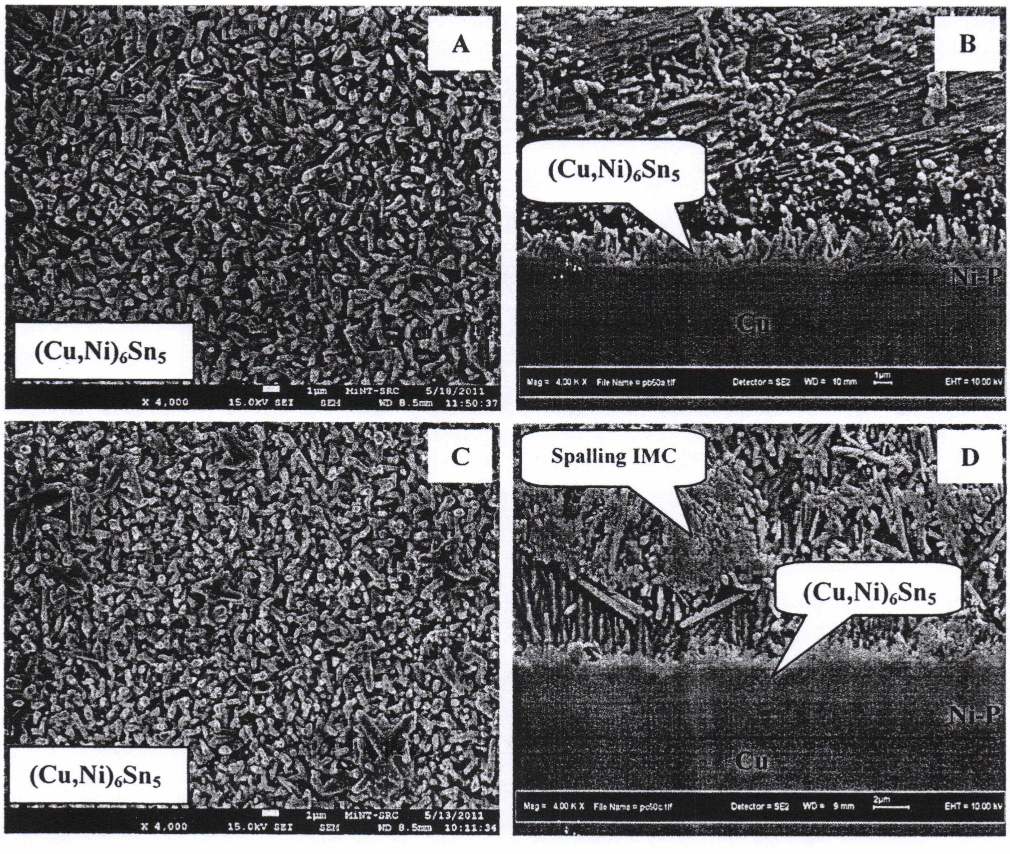

Fig. 1 Intermetallic compound of (Cu, Ni)$_6$Sn$_5$ between and SAC solder and ENEPIG (P) substrate after reflow soldering at Ø500μm (a,b) Sn-3Ag-0.5Cu (c,d) Sn-3Ag-0.5Cu-0.05Ni

Typical top surface and cross-sectional FESEM micrographs for the SAC305 and SACN30505 after reflow are shown in Fig. 1(a, c) and Fig. 1(b, d) respectively. EDX spectrum analysis shows the IMC layer compositions at the interface are consistent with the stoichiometry of the compound $(Cu,Ni)_6Sn_5$. Deep etching indicated that the morphology of $(Cu,Ni)_6Sn_5$ were rough needled shaped compound for both solders (Fig. 1a and 1c). Similiar findings was reported by Yao *et al.* [7]. From the cross-sectional examination, scallop-like of $(Cu,Ni)_6Sn_5$ layer IMC (Fig. 1b and 1d) was detected along interface as the typical phase for the reaction between Cu and a Sn-based solder during liquid-solid reaction. These observation are in good agreement with the previous reseacher [8,9]. Liu and his reseachers [10] reported the Ni-barrier at the interface between solder and Cu pads prevents diffusion of Cu atoms from the pads into the interface, and the Cu content in $(Cu,Ni)_6Sn_5$ layer is mainly originated from the SAC solder alloy.

Besides that, there are no intermetallic compound (IMC) spalling were observed on SAC305 solder while for SACN30505 solder shows a contrast result as represent in Fig. 1 (d). Moreover, the spalling of the IMC was detected at along the interface. Previous reseacher Ho *et al.* [11] explained the spalling word refers to the detachment of a compound from the interface into one of the reacting phases. The shifting of the interfacial equilibrium causes the product phase to separate itself from the interface. Thus, this separation of the IMCs from interface is not good and may also affect the solder joint reliability [11,12]. However, the mechanism of spalling IMC is still not fully understood.

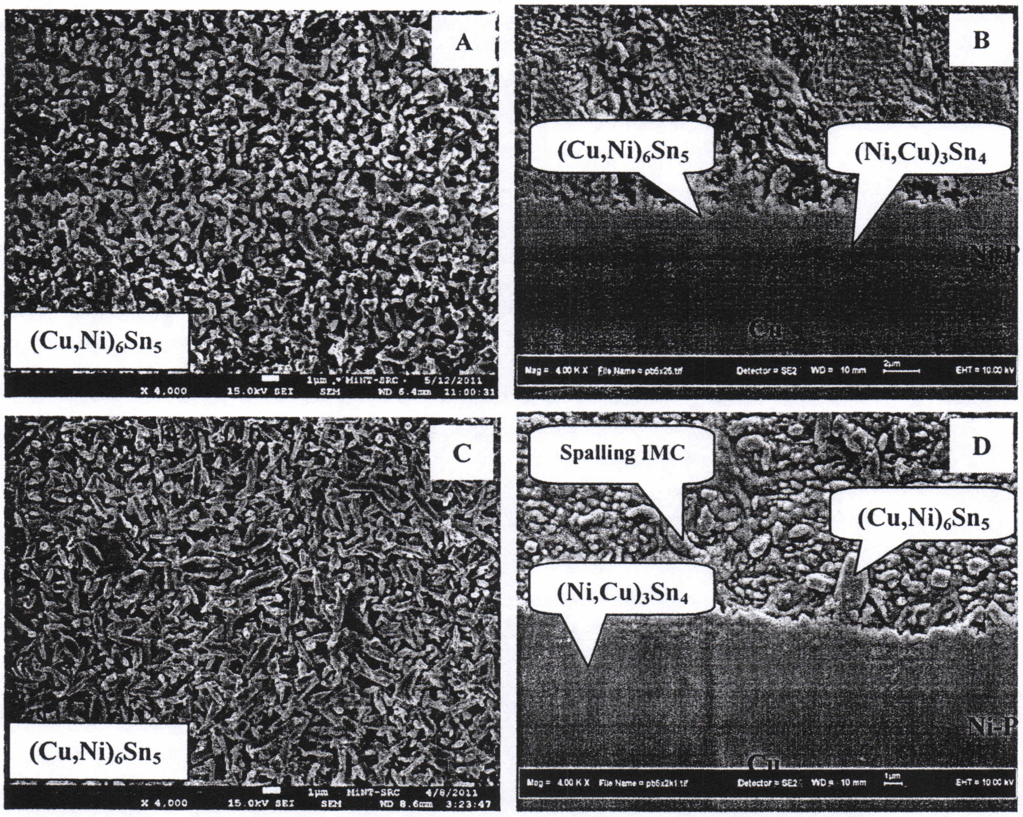

Fig. 2 Top surface and cross-sectional view of FESEM between ENEPIG (Phosphorus) and Sn-3Ag-0.5Cu solder with solder size Ø500 (a, b) aging 250 hours, (c,d) aging 2000 hours

After reflow soldering, the solder bumps were subjected to 250 hours up to 2000 hours of isothermal aging at 125°C. During a liquid-solid reaction, rapid volume growth of $(Cu,Ni)_6Sn_5$ IMC may offset the high surface energy or in other word is fast IMC growth rate which requested for forming the scallop-type morphology. However, the growth of $(Cu,Ni)_6Sn_5$ IMC is apparently slowed and a flat front morphology is favored for a lower interfacial energy during solid state reaction [8, 13]. After isothermal aging exposure, duplex IMC were detected at the interface for both SAC305 and

SACN30505 solder where a new IMC layer formed beneath a $(Cu,Ni)_6Sn_5$ layer known as $(Ni, Cu)_3Sn_4$. The FESEM cross sectional micrographs will be an evident for this finding as seen in Fig. 2 and Fig. 3. In addition, uniform IMC thickness layer was observed for both solder after aging compared to scallop-type during soldering. Besides that, small effect on spalling IMC at interface has been detected on SAC305 after aging compared to reflow soldering (Fig. 2d). In Sun *et al.* [14] research work, they reported that electroless Ni-P still existed after 1000 hours aging, so it is reasonable to suggest that some IMC spalling may occur when the interfacial IMC layer becomes thick during aging. In contrast, spalling IMC is still happened at interface even after aging for SACN30505 as represent in Fig 3b and Fig. 3d. Furthermore, the morphology of $(Cu, Ni)_6Sn_5$ for both solder significantly increased when a aging time is increased. Besides that, it clearly showed that there was no change in the type and morphology of intermetallics formed after the joints were subjected to aging for both solder type.

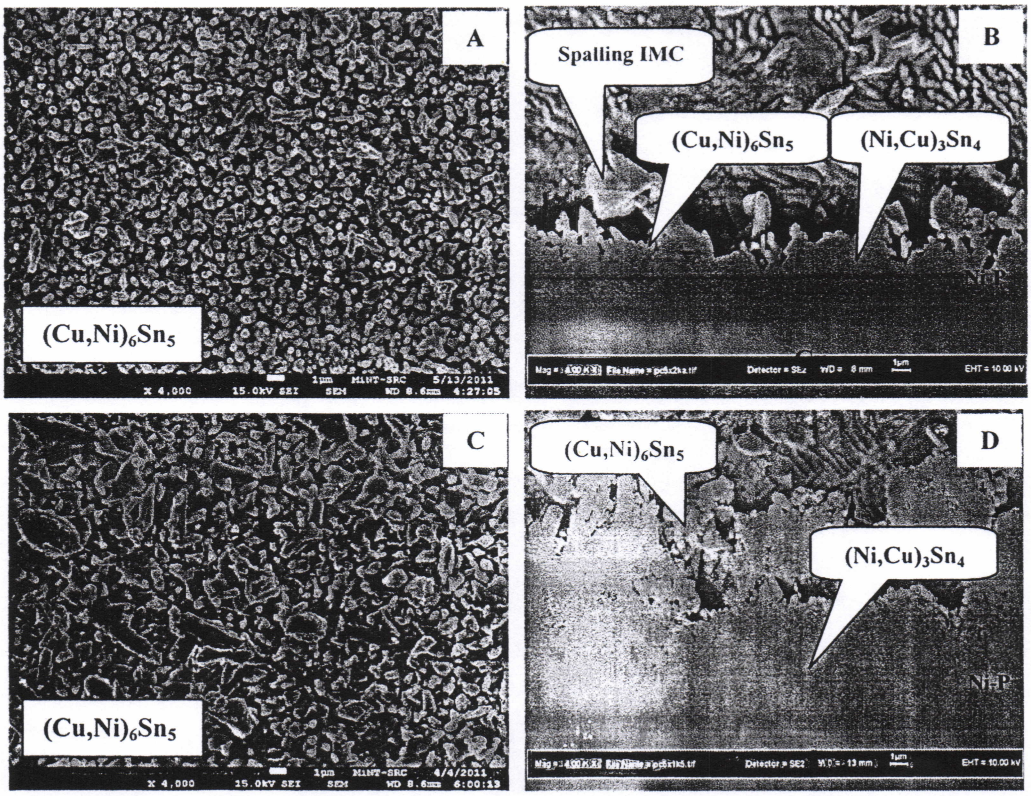

Fig. 3 Top surface and cross-sectional view of FESEM between ENEPIG (Phosphorus) and Sn-3Ag-0.5Cu-0.05Ni solder with solder size Ø500 (a, b) aging 250 hours, (c,d) aging 2000 hours

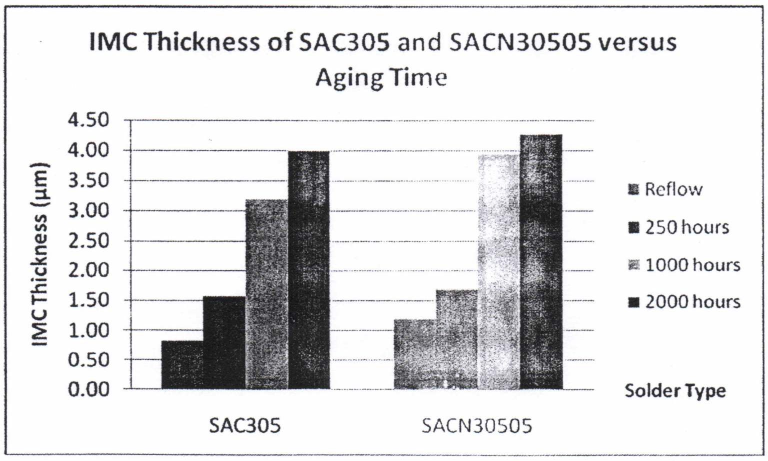

Fig. 4 IMC thickness of SAC305 and SACN30505 solder at 125°C with solder size Ø500µm

The average thickness of IMC layer that formed at the interface between solder and substrate after reflow and aging is given in Fig. 4. From qualitative data, the interfacial IMC layer formed of SAC305 solder is thinner than SACN30505 after reflow as well as aging treatment. Besides that, it can clearly seen that with increased addition of Ni percentage, the IMC thickness also significantly increased when aging time was increased. This findings was also agreed by Song *et al.* [15]. They reported that this should be caused by higher reflow peak temperature of SACN30505/Ni substrate done at 250°C (SAC family) and 268°C (SACN).

Summary

During reflow soldering and isothermal aging, Ni-doped solder (SACN30505) represents a thicker IMC compared to SAC305 solder. Only $(Cu, Ni)_6Sn_5$ IMC was found at the interface after reflow soldering while both $(Cu, Ni)_6Sn_5$ and $(Ni, Cu)_3Sn_4$ IMC has been observed after isothermal aging. Aging time of solder joints results in an increase of IMC's thickness and changes their morphologies to become more spherical, dense and with larger grain size. In addition, the results also revealed that the thickness of intermetallics formed is proportional to the aging duration.

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