

## INTERMETALLIC EVOLUTION FOR ISOTHERMAL AGING UP TO 2000HOURS ON Sn-4Ag-0.5Cu AND Sn-37Pb SOLDERS WITH Ni/Au LAYERS

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### ABSTRACT

Reliability of a solder joint is closely related to the intermetallic compound formation during the joining process and its evolution after exposure to heat. Throughout this paper, interfacial reactions between Sn-4Ag-0.5Cu solders and Sn-37Pb solders with electroless nickel immersion gold (Ni/Au) surface finish were studied. Few of the parameters are solder type, thickness of nickel layer and aging time. The results focused on type of intermetallic compound formed and the intermetallic thickness. Aging changed the intermetallic morphology to become rounder, bigger and more compact with time. Aged Sn-4Ag-0.5Cu solders on Ni/Au exhibit the tendency for the intermetallic to change from  $(\text{Cu,Ni})_6\text{Sn}_5$  to  $(\text{Ni,Cu})_3\text{Sn}_4$  and finally  $\text{Ni}_3\text{Sn}_4$ . The results also showed that, with the parameters used in this experiment, nickel thickness 3micrometer is adequate to be a good diffusion barrier up to 2000hours aging time. In Sn-37Pb, redeposition of  $(\text{Au,Ni})\text{Sn}_4$  intermetallic start after 500hours.

**Keywords:** Ni/Au, lead free solders; Isothermal aging; Interfacial reaction; Sn-4Ag-0.5Cu; Sn-37Pb.

### INTRODUCTION

In the industry, the term flip chip refers to an electronic component or semiconductor device that can be mounted directly onto a substrate, board, or carrier in a face-down manner. The complexity of wiring closely spaced contact pads is eliminated in flip chip technology (Gilleo and Vardaman, 2002). Electroless nickel immersion gold (Ni/Au) is a well established surface finish that has been used for many years in flip chip technology. In this system, the nickel layer acts as a diffusion barrier to copper and is the surface to which the soldering or reflow occurs. The function of the immersion gold is to protect nickel from oxidation or passivation during storage (Coombs, 2001; Won Yoon et al., 2011).

The reaction products from reflow process between surface finish and the solders is called intermetallic compounds. This intermetallic layer or diffusion zone has a profound effect on the mechanical properties of the soldered joint and on its behaviour during service (Coombs, 2001; Strauss, 1994). In this research, the impact of isothermal aging were studied to further understand the growth behavior of intermetallics when exposed up to 2000hours isothermal aging with the parameters given.

## METHODOLOGY

High phosphorus electroless nickel with phosphorus content 9%wt phosphorus and more is used in this research. The electroless nickel solutions undergo optimization of the plating process to obtain the desired deposit thickness by varying the plating time. Table 1 showed the combination of chemicals used for high phosphorus electroless nickel bath.

**Table 1.** Combination for high phosphorus electroless nickel plating bath solutions (Henry, 1984).

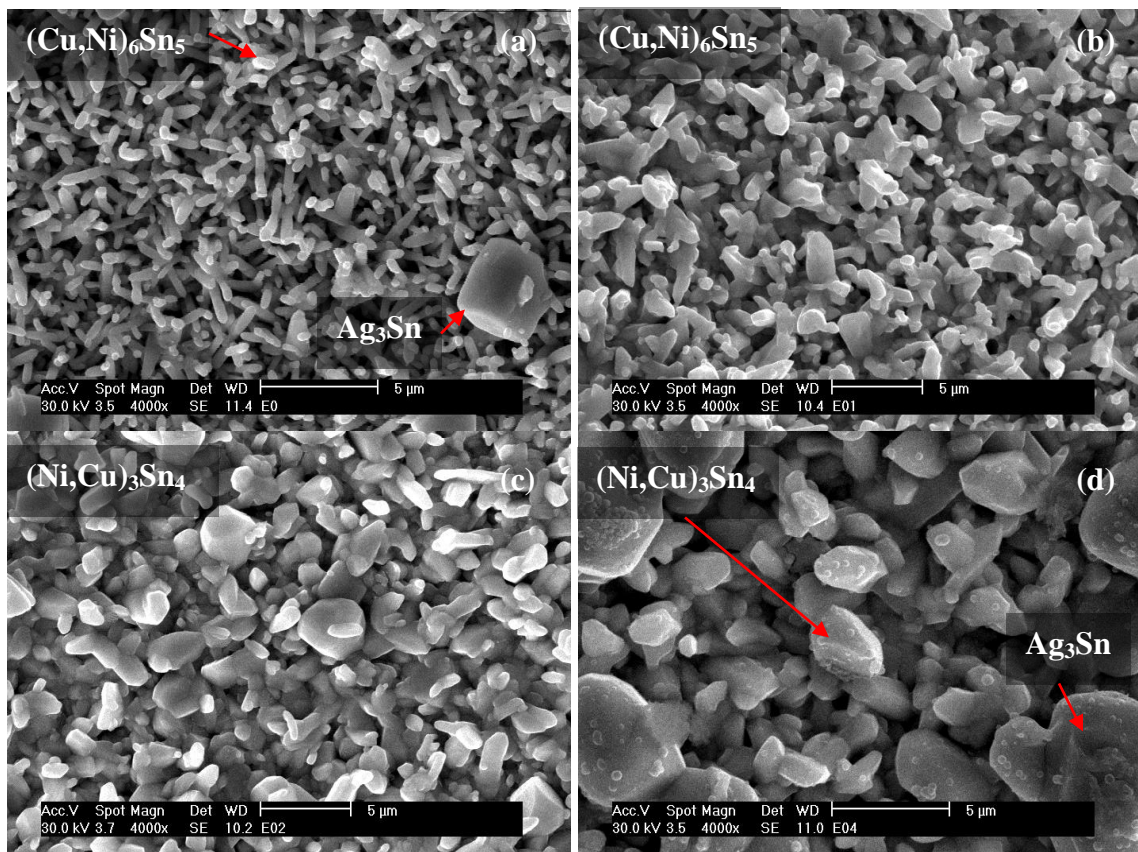
| Item                      | Quantity             |
|---------------------------|----------------------|
| Nickel sulfate            | 28g/L                |
| Sodium acetate            | 17g/L                |
| Sodium hypophosphite      | 24g/L                |
| Thiorea                   | 1.5mg/L              |
| PH                        | 4.4                  |
| Temperature               | 88°C                 |
| P %                       | >10%wt               |
| Plating time vs thickness | 10min ~3.1micrometer |
|                           | 20min ~6.5micrometer |

A thin layer of flux were applied to remove the oxides directly before the pads were populated with solder spheres. The reflow process was carried out in a furnace with peak temperature set at 250 °C for Sn-4Ag-0.5Cu solders and 216 °C for Sn-37Pb solders. After reflow, both cross section and top surface from the samples were then prepared and examined by means of optical and scanning electron microscopy. Energy dispersive x-ray (EDX) was used to identify the type and composition of intermetallics formed. Both image analyser and scanning electron microscopy (SEM) were used to measure the average thickness and examine the morphology of intermetallics formed.

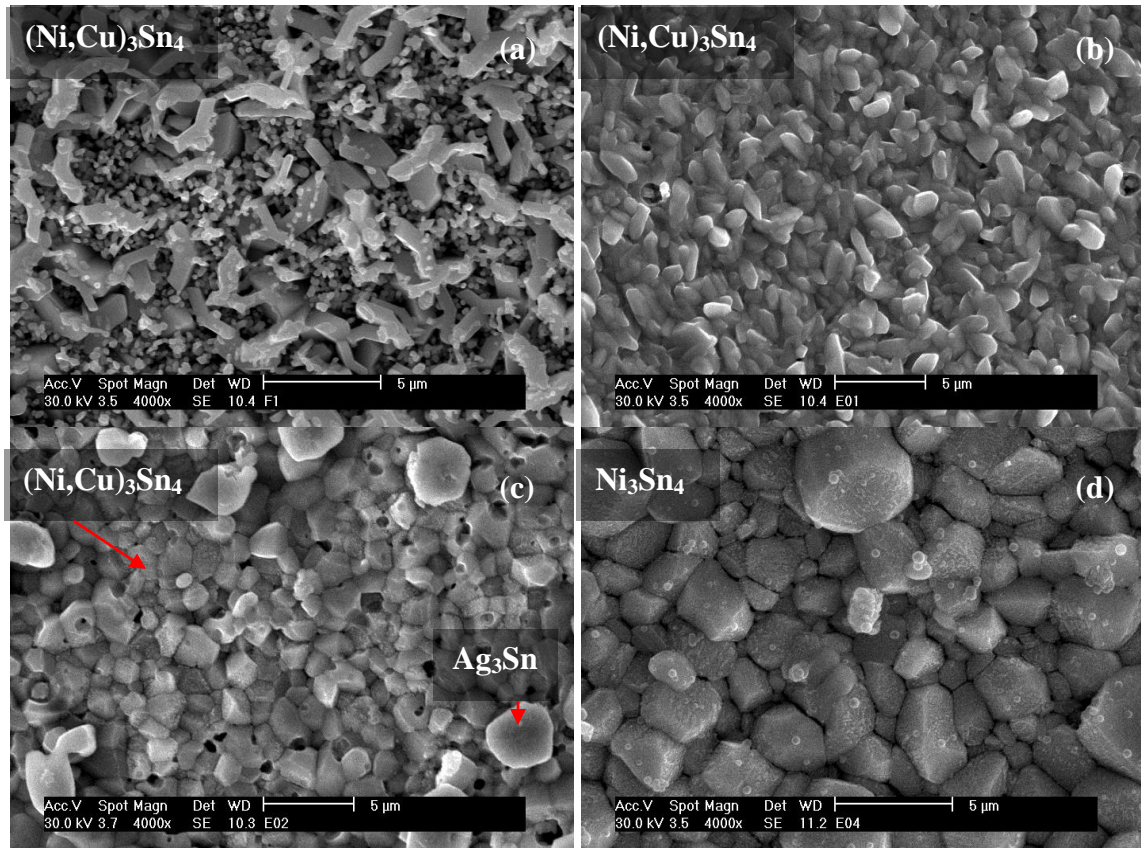
## RESULTS AND DISCUSSION

The nickel layer was deposited with two different thicknesses: around 6 micrometer and 3 micrometer. This is to compare the effect of different nickel thickness on intermetallic formation and to determine whether 3micrometer nickel thickness is thick enough to act as a diffusion barrier even after extended exposure to high temperature. Two type of solders were used; Sn-4Ag-0.5Cu and Sn-37Pb eutectic solder. First, the top surface intermetallic were compared using SEM.

Figures 1 and 2 shows the intermetallic evolution between Sn-4Ag-0.5Cu solder and Ni/Au surface finish with 3 micrometer nickel thickness. From these two figures, it can be seen that aging treatment transforms the intermetallic layer into rounder, bigger and more compact grains over the entire area of solder bump. The effect is more obvious as the aging time increased. Aside from these effects on the morphology of the intermetallic, the type of intermetallic formed also changed. Basically, the evolution of the intermetallic types are:  $(\text{Cu, Ni})_6\text{Sn}_5 \rightarrow (\text{Ni, Cu})_3\text{Sn}_4 \rightarrow \text{Ni}_3\text{Sn}_4$ . The change in intermetallic type depends on the availability of copper and nickel atoms. At first, during reflow,  $(\text{Cu, Ni})_6\text{Sn}_5$  formed because the copper content in the solder is 0.5% which is enough to form this type of intermetallic as in agreement with other research findings (Won Yoon and Boo Jung, 2005; Won Yoon et al., 2005; Azmah Hanim et al., 2013). After aging for 1000 hours the intermetallic changes to  $(\text{Ni, Cu})_3\text{Sn}_4$  because the copper content in the solder has decreased to a certain level. From the EDX analysis the ratio of nickel to copper is higher. However, since the copper percentage is still not too low, the copper element still plays a part in the intermetallic formation. After 2000hours, the intermetallic changes to  $\text{Ni}_3\text{Sn}_4$ . During this time, the copper percentage has decreased to a very low value that it is not enough to take part in the interfacial reaction.



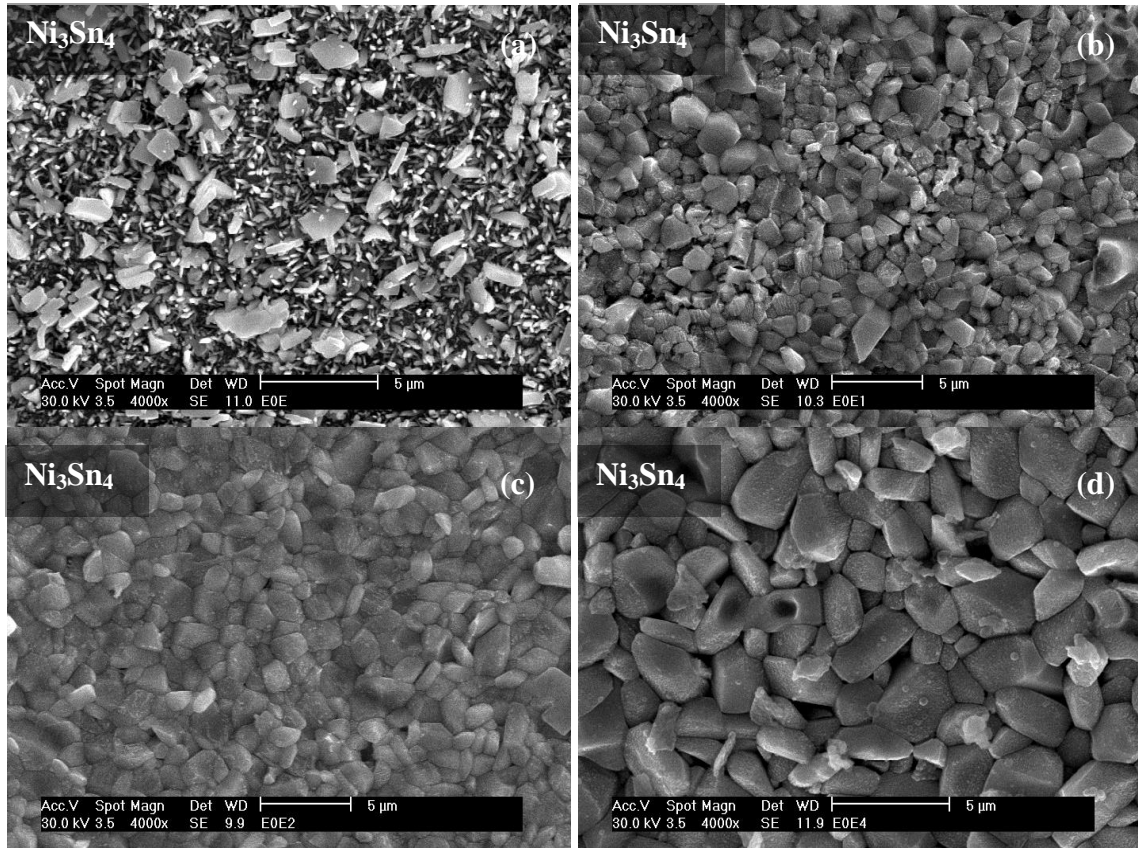
**Figure 1:** SEM top surface morphology of intermetallic between Ni/Au (3 micrometer nickel) /Sn-4Ag-0.5Cu solder. Intermetallic is taken in a region near the centre of solder joint: a) after reflow, b) 500hours aging, c) 1000hours aging, and d) 2000hours aging.



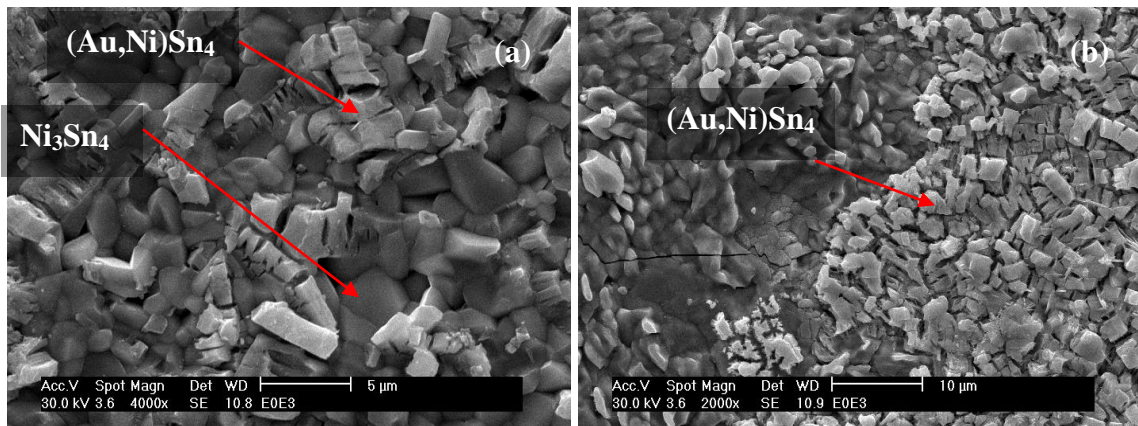
**Figure 2:** SEM top surface morphology of intermetallic between Ni/Au (3 micrometer nickel) /Sn-4Ag-0.5Cu solder. Intermetallic is observed in regions near the edge of solder joint. a) after reflow, b) 500hours aging, c) 1000hours aging and d) 2000hours aging.

Analysis on the samples with 6 micrometer of electroless nickel yield the same results as the 3 micrometer thickness nickel in terms of type and morphology of intermetallic observed. It can then be concluded that 3micrometer of electroless nickel is adequate to act as diffusion barrier between copper substrate and solder alloy.

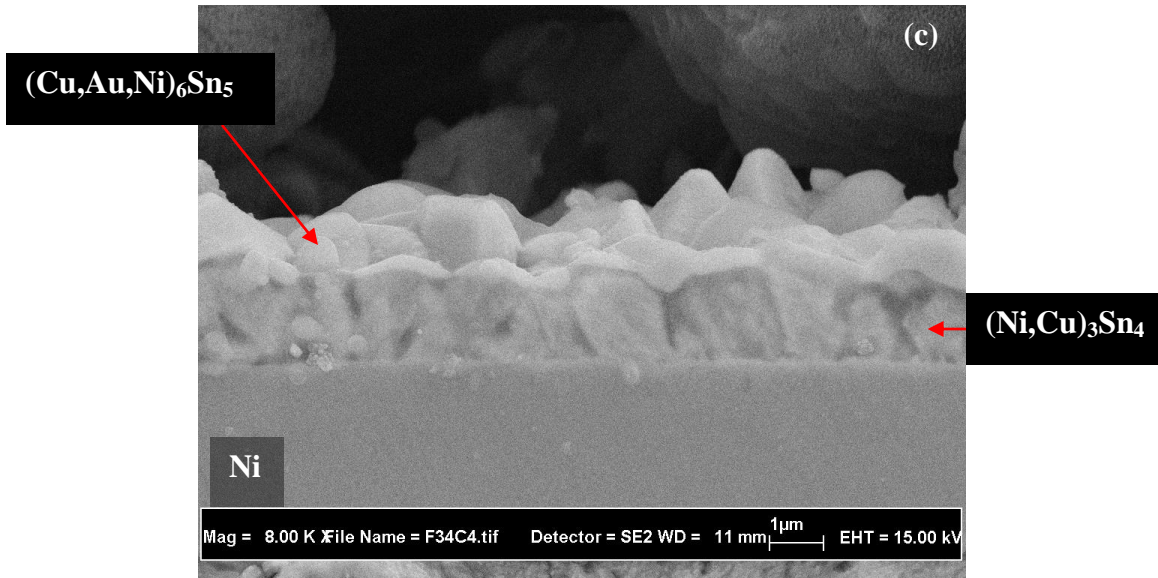
During reflow between Sn-37Pb solder and Ni/Au surface finish  $Ni_3Sn_4$  intermetallic is formed at the interface. Figure 3 shows the SEM top surface morphology of intermetallic formed in Sn-37Pb solder. Aging also induced changes in the intermetallic morphology to become more rounded and compact with bigger grains. As shown from Figure 4, aging of the solder joints using both Sn-4Ag-0.5Cu lead-free and Sn-37Pb solder results in the re-deposition of Au-Sn intermetallic at the interface. These results are in agreement with previous studies (Laurila et al., 2005; Riet et al., 2006).



**Figure 3:** SEM top surface of Ni/Au with 3 micrometer nickel thickness, reflowed with Sn-37Pb eutectic solder, mag 4000x; (a) as reflow, (b) 500 hours aging, (c) 1000hours aging, and (d) 2000hours aging.

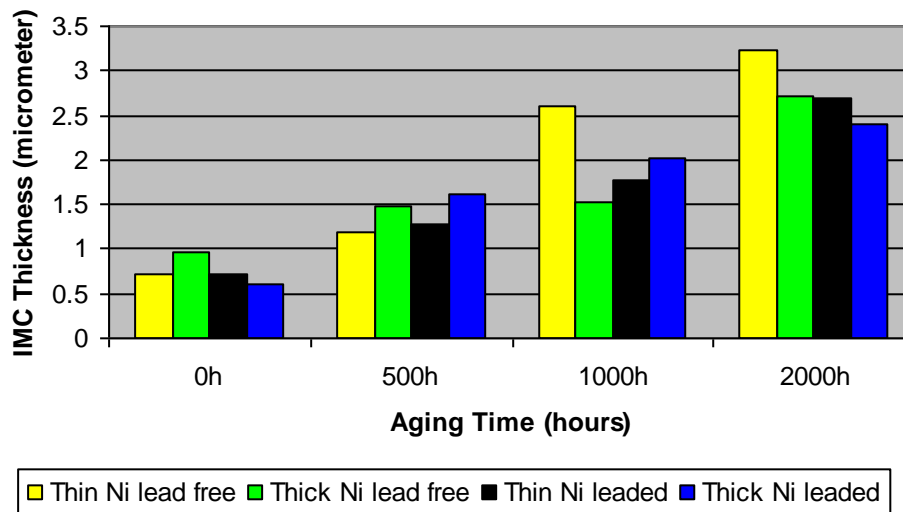


**Figure 4:** Formation of Au-Sn intermetallic at interface after aging for Ni/Au with Sn-37Pb eutectic solder and Sn-4Ag-0.5Cu solder; (a) Sn-37Pb eutectic solder after aging 1500hours at 150°C, (b) Sn-37Pb eutectic solder after aging 1500hours at 150°C, and (c) Sn-4Ag-0.5Cu solder after aging 2000hours at 150°C.



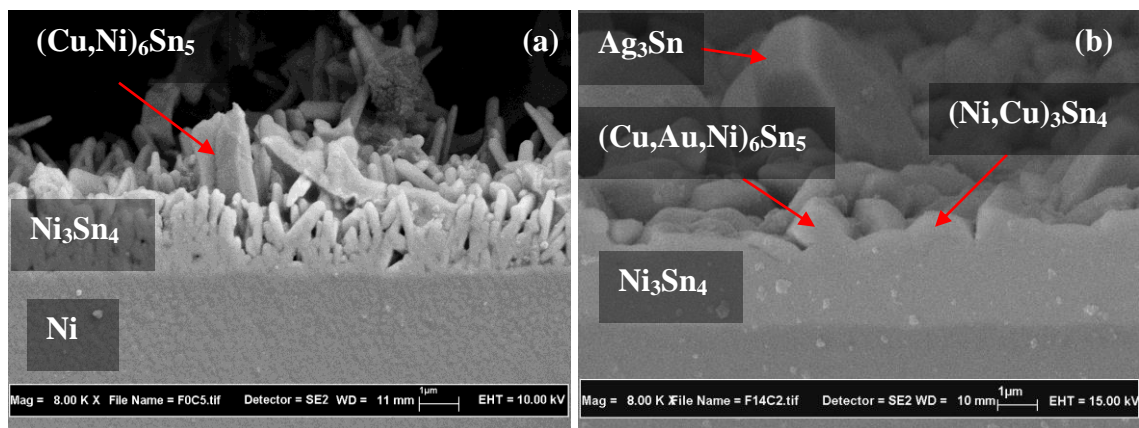
**Figure 4 (Cont.):** Formation of Au-Sn intermetallic at interface after aging for Ni/Au with Sn-37Pb eutectic solder and Sn-4Ag-0.5Cu solder; (a) Sn-37Pb eutectic solder after aging 1500hours at 150°C, (b) Sn-37Pb eutectic solder after aging 1500hours at 150°C, and (c) Sn-4Ag-0.5Cu solder after aging 2000hours at 150°C.

Figure 5 showed that for all samples, the intermetallic thickness increases as the aging time increase. As we go into detail for each type of solder, it can also be seen that for the lead free solder, the 6 micrometer electroless nickel gives thicker intermetallic compared to the 3 micrometer electroless nickel up until 500 hours. After 1000 hours, the growth rate of the 3 micrometer electroless nickel increases rapidly until 2000hours of aging.

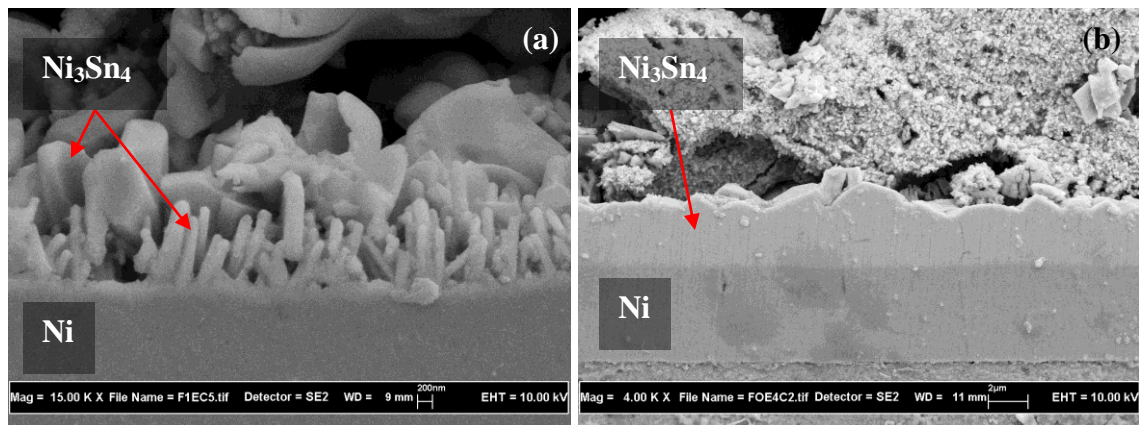


**Figure 5:** Graph of intermetallic thickness for Ni/Au with and without aging at 150°C, reflowed with Sn-4Ag-0.5Cu and Sn-37Pb eutectic solder.

Comparison of the intermetallic thickness of reflowed and aged solder joints made with the Sn-37Pb and Sn-4Ag-0.5Cu lead-free solders shows that after reflow the intermetallic growth is faster in the lead-free solder than in the leaded solder. But, with extended aging at 150°C for up to 2000 hours the intermetallic growth on the lead-free solder is slowed down to be surpassed by the leaded solder. According to Huang, during aging, in order for the  $(\text{Cu, Ni})_6\text{Sn}_5$  intermetallic layer to grow, the copper atoms must diffuse over a long distance from the bulk solder to the interface, which slows down the growth rate of this  $(\text{Cu, Ni})_6\text{Sn}_5$  layer (Huang et al., 2006). As shown in the top surface views, more  $(\text{Cu, Ni})_6\text{Sn}_5$  were detected at the interface of solder joints aged for 2000 hours at 150°C. Figure 6 and 7 show the cross section pictures on the aging effect from side view.



**Figure 6:** Cross section micrographs of intermetallic at interface between Ni/Au/ Sn-4Ag-0.5Cu solder. a) after reflow, and b) aged for 2000 hours.



**Figure 7:** Cross section pictures for Ni/Au/ Sn-37Pb eutectic solder: a) after reflow, and b) aged for 2000 hours.

Intermetallic layer has a planarization tendency during isothermal aging (Azmah Hanim et al., 2013; Xia et al., 2006; Chen et al., 2006). Morphology transition is due to

the reduction in surface-free energy. Scallop like morphology (lots of peaks and valleys) intermetallics had larger surface area than a planar layer of similar thickness, resulting in a large driving force for surface energy change. Because of the shorter diffusion distance between valleys and copper substrate, when compared to the distance between peak and copper substrate, copper diffuses faster to the valley than to the peak, leading to faster growth rate at the valley and subsequent planarization of the whole intermetallics layer. This theory is proven when we compared the cross sectional views of joints after reflow with those after aging for both leaded and lead free solders.

## CONCLUSION

In this research, the effect from aging time at 150°C from 500hours to 2000hours on high phosphorus nickel layer with 3 micrometer and 6 micrometer nickel thickness for Ni/Au surface finish on the formation of intermetallics compound when reflowed with Sn-4Ag-0.5Cu and Sn-37Pb solders were investigated. It was found that aging changes the intermetallic to become more rounded, bigger and compact. This effect is more pronounced as we increase the aging time. In the cross sections, aging changes the morphology of IMC from scallop like to a planar layer of intermetallic. For lead free solder, the intermetallic type changes from  $(\text{Cu,Ni})_6\text{Sn}_5 \rightarrow (\text{Ni,Cu})_3\text{Sn}_4 \rightarrow \text{Ni}_3\text{Sn}_4$  as the aging time increases. This is because the formation of intermetallic for lead free solder depends on the availability of copper and nickel. As the aging time increases, the amount of copper from solder reduces because most of it was consumed during the formation of intermetallic. Different nickel thickness in electroless nickel immersion gold does not influence the intermetallic top surface formation. Nickel thickness 3 micrometer is adequate to be a good diffusion barrier up until 2000hours aging at 150°C. Redeposition of Au-Sn intermetallic occurs in leaded samples. The Au-Sn intermetallic were known as  $(\text{Au,Ni})\text{Sn}_4$ . The redeposition started after aging 500hours and increases as we increase the aging time.

## ACKNOWLEDGEMENTS

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