Effect of Aging on the Interfacial Reactions of BGA Sn-Ag-Cu and Sn-Ag Solders with Ni(P)/Au Surface Finish on Cu Pad

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Abstract
The joint strength and the microstructure of Sn-3.5Ag and Sn-3.5Ag-0.5Cu (wt.%) solders on Cu/Ni(P)/Au ball grid array (BGA) pad metallization were investigated after solid state aging at 150°C (around 0.7% of solder alloys). Sn-Ag solder gave better results in terms of shear strength on high temperature aging than Sn-Ag-Cu. It was found that relatively high consumption of Ni(P) was observed in the case of Sn-Ag solder alloys during long time aging. It was also noticed that the mean thickness of the intermetallics (IMCs) at the interface and the dark P rich layer was higher for Sn-Ag solder alloy due to high interfacial reaction. For both cases Ni diffused through the interfacial IMCs and formed quaternary compounds for Sn-Ag-Cu system and ternary compounds for Sn-Ag system within the bulk solder.

Introduction
The most influential factor in the solder joint quality of a ball-grid-array (BGA) component is the metal surface finish on the Cu pads. Interaction and interdiffusion behavior between solder and Cu has been studied extensively elsewhere. It is found that at the Sn-containing solder/Cu interface, tin reacts rapidly with Cu to form Cu-Sn intermetallic compounds (IMCs), which make the solder joint weak due to the brittle nature of the IMCs. The strength of the solder joint decreases with the increasing thickness of IMCs that form at the interface and act as the initiation sites for micro-cracks [1-3]. Ni layer on Cu pad creates good solderable surface and acts as a good diffusion barrier layer.

Many works have been reported that the growth rate of intermetallic compounds is lower in the Ni/solder system than in the Cu/solder system [4-6]. The reaction rate of molten eutectic SnPb on Ni is about 100 times slower than that of the molten eutectic SnPb on Cu [7]. Electroless Nickel-Phosphorus (Ni-P) has attracted much interest and is widely used in the PCB fabrication and under bump metallization (UBM) for flip chip technology. This is because electroless Ni-P offers a low cost alternative to more expensive physical Ni deposition methods. Characteristics of the electroless nickel deposit, such as excellent solderability, corrosion resistance, uniform thickness, and selective deposition, make the electroless nickel plating more suitable as a material for a diffusion barrier than pure electroplated Ni UBM [2,8,9]. However, unlike in the Ni layer prepared by vacuum deposition or electrolytic Ni, in the electroless Ni, plated by hypophosphite, it is known that the phosphorus (P) in the electroless Ni greatly influences the interfacial reactions with solders. And, the reliability of the solder joints must also be closely related to the P in the electroless Ni [10]. Normally, electroless Ni(P) deposit is crystalline at lower-P contents (<9.5 at.%), while at higher-P levels (>9.5 at.%), the deposit is amorphous [10].

All alternatives to the standard eutectic tin-lead solder investigated so far are based on tin alloys with a tin content significantly over 90 weight percent in combination with copper, silver, antimony, bismuth or zinc. A key issue affecting the integrity and reliability of solder joints for such Sn-based alloys is the fast interfacial reactions between the molten solder and the UBM. Among the binary alloys, Sn/0.5-0.8% Cu and Sn/3-4% Ag play a dominant role. The Sn-Ag solders exhibit melting points in the range of 220-221°C, which is more than 30°C beyond the melting point of the conventional eutectic tin-lead solder. The melting point of Sn-3.5Ag-0.5Cu eutectic solder was established to be 216.8±1°C [11].

Because of increasing demands of the lead-free solder alloys in the advanced electronic packaging, it is indeed crucial to investigate the mechanical integrity of the solder joints of the Sn–Ag and Sn-Ag-Cu solder alloys with the electroless Ni(P) surface finish on Cu with solid state thermal treatment. In this article, we attempt to study the mechanical strength of the solder joints on electroless Ni(P) to investigate the effect of aging time on the interface formed between lead free solder alloys and Au/electroless Ni(P)/Cu.

Experimental procedures
Electroless Ni(P) layers were deposited on the solder mask defined copper pad of a substrate of the BGA package. The solder mask opening diameter was 0.6 mm at the ball pad. Immersion Au plating was immediately layered on top of the electroless Ni–P to avoid oxidation of the nickel surface. The thickness of the deposit layers was measured by using x-ray fluorescence. Lead-free eutectic Sn–Ag and Sn-Ag-Cu solder balls, having the composition 96.5% Sn–3.5% Ag and 96% Sn–3.5% Ag-0.5% Cu (wt.%) with a diameter of 0.76 mm, were placed on the flogged Au/Ni(P)/Cu bond pad of the substrates and reflowed at a temperature of 250 °C for 1 min in a convection reflow oven (BTU VIP-70N). The flux
used in this work was a commercial no-clean flux. After a reflow, samples are subjected to aging at 150°C for 0 to 400 hrs.

To investigate the microstructure, the samples were mounted in epoxy after each condition. The samples were ground and polished carefully and then gold coated. The chemical and microstructural analyses of the gold-coated cross-sectioned samples were obtained using the Philips XL 40 FEG scanning electron microscope (SEM) equipped with energy dispersive x-ray spectrometer (EDX).

The shear tests were performed on both the reflowed and aged samples using the Dage Series 4000 Bend Tester. The shear tool height and the test speed of the shear test in this work were about 100μm and 550μm/s, respectively. 20 randomly chosen solder balls were sheared to obtain the average and the extent of deviation.

Result and discussion

Fig. 1 depicts the solder ball shear testing results of solder/AuNi(P)/Cu bond pad joints. At the time of ball shear test mostly ductile fracture occurs within the solder and the IMC’s interface for both the reflow and the annealed samples. Initial average shear strength of the solder joint is around 1750 gmf and 1730 gmf for Sn-Ag-Cu and Sn-Ag solder samples respectively. Sn-Ag-Cu solder shows slightly higher shear strength in as bonded condition on electroless Ni(P) surface finish. Fig. 2 also shows that solder ball shear load during aging increases with the increase of aging time up to 100hrs for both the solder alloys. After 100 hrs a gradual decreasing tendency is observed with aging for both the solders. The maximum average shear strength is found after 100hrs of aging for both the solder alloys and the strengths are 1761 gmf and 1801 gmf for Sn-Ag-Cu solder and Sn-Ag solder alloys respectively. Solder joint shows minimum value of average shear strength after 400hrs of aging, for Sn-Ag solder it is around 1690 gmf, a 2% reduction from the initial strength, whereas for Sn-Ag-Cu solder, it is found 1620 gmf, a 7% reduction from the initial bonded strength. The Sn-Ag solders give relatively better ball shear strength with aging.

![Shear Load vs Aging Time](image)

Fig. 1. Solder ball attachment on flexible substrate.

These results demonstrate that electroless Ni(P)/Sn-Ag solder joints have greater solder joint integrity during solid state thermal aging as compared to the Sn-Ag-Cu solder joint. To investigate the shear strength and interfacial reaction at the solder joints, a detail cross-sectional studies are carried out by SEM. During reflow, molten solder absorbs the entire Au layer into the solution, allowing Sn and Cu from the solder to react with the Ni(P) layer and to form different type of IMCs at the interface. These IMCs together with untreated Ni(P) provides the adhesion between the solder and the substrate.

![Backscattered electron micrographs illustrating the interface after reflowed at 250°C of a) Sn-Ag-Cu and b) Sn-Ag solders.](image)

Figure 2. Backscattered electron micrographs illustrating the interface after reflowed at 250°C of a) Sn-Ag-Cu and b) Sn-Ag solders. In electrolytic Ni(P)/Sn-Ag-Cu solder joint (Fig.2a), the thickness of electroless Ni(P) is about 1.86-2.46μm. According to EDX analysis, the IMCs form on the electroless Ni(P) layer is composed of Sn-Ni-Cu i.e. (Cu0.1Ni0.9)Sn. Similar results also reported by other investigators [12, 13]. The composition of the IMCs layer is determined to be Cu0.1Ni0.9Sn. Cu-Sn IMCs are found within the bulk solder. A dark layer of about 200 nm is observed between the Sn-Ni-Cu IMC and Ni(P) layer from the SEM images. EDX analysis shows that the phosphorous percentage of this dark layer is about 25 at.%. This observation implies that the dark layer is composed of Ni3P compound. Jang et al. [14] confirmed a crystalline Ni3P compound at the interfaces through TEM studies, and proposed that amorphous electroless Ni(P) underwent crystallization during soldering with the Sn-Pb solder alloys. This kind of crystallization process is referred to as solder-reaction-assisted crystallization. The P content in the original Ni(P) is around 9.8 at% before soldering, decreases to 7.1 at% (average) from the top of original electroless Ni(P) layer after soldering due to diffusion of P atoms into the dark
P rich Ni layer, similar results are also reported by other investigators \[10\]. For Sn-Ag solder, the thickness of intermetallics was about 2.44-3.2μm and the IMCs are composed of Ni-Sn that has formed on the top of Ni layer (Fig.2b). As per EDX analysis, it seems that these IMCs are the mixture of stable Ni$_5$Sn$_4$ and Ni$_3$Sn and/or Ni$_3$Sn$_2$ compounds and the thin dark layer would be Ni$_3$P. The P content in the dark layer is also around 25%. The P content decreases to 7.1 at% (average) from the top of original Ni(P) layer after soldering. In this case, the thickness of the dark P rich Ni layer is about 382nm. Dissolve Au form Au-Sn compound within the bulk for both the solder alloys. Ni-Sn compounds are also found in the bulk of Sn-Ag solder. In both cases, the interfacial intermetallic compounds are of irregular shape, and chunky type. The intermetallic growth rate in the Sn-Ag solder is relatively higher than in the Sn-Ag-Cu solder joints. It implies that the nucleation and the growth of binary Ni-Sn IMCs is faster than that of ternary Cu-Ni-Sn IMCs on electroless Ni(P) in the initial molten state. Due to the consumption of Ni to form interfacial IMCs, P is expelled to the remaining Ni-P layer and form a P-rich layer. The higher the interfacial reaction, the greater the tendency to form continuous P-rich layer. P-rich layer is thicker for Sn-Ag solder. The shear strength of solder joints for the Sn-Ag solder is lower than the Sn-Ag-Cu solder in as bonded condition. It seems that the higher thickness of IMCs is the main reason for such lower shear strength. The above analysis shows that the electroless Ni(P) dissolution is higher in the case Sn-Ag solder with the rapid growth of IMCs and dark P rich Ni layer at the solder joint interface.

The IMCs thickness gradually increases with the increase of aging time, as in Fig. 3a. For both the solder alloys the P rich layer thickness also increases with aging (Fig.3b), but for Sn-Ag solder the rate is little bit higher. By measuring the remaining Ni(P) thickness from the SEM micrograph and by subtracting it from the initial thickness, the consumed Ni(P) thickness is deduced. For both cases the consumed Ni(P) thickness increases with time. Fig.4 shows the comparison of the Ni consumption thickness from the substrate between the solder alloys for 150°C. Initial consumption rate are higher for both the solder alloys upto 100hrs of aging. After that the consumption rate is decreased for both the cases. For Sn-Ag solder, the consumption occurs at a faster rate after 300hrs. It is seen that Ni consumption is faster in the Sn-Ag solder than in the Sn-Ag-Cu solder during long time aging.

![Figure 4. The consumed thickness of Ni vs. aging time at 150°C of Sn-Ag-Cu and Sn-Ag solders](image)

After 4 days aging Sn-Ni-Cu intermetallics shows more planner morphology in the case of Sn-Ag-Cu solder alloy than the Sn-Ni IMCs in the Sn-Ag solder (Fig. 5a(i) and 5b(i)). The composition in the middle of the IMCs layer in Sn-Ag-Cu is determined to be (Cu$_{0.62}$Ni$_{0.38}$)$_2$Sn$_3$ with small amount gold in it. The atomic percentage of Au is around 2% in the upper portion of the IMCs near the solder side. The size of the P rich Ni layer is about 207nm. Au-Sn and Ag-Sn compounds are found within the both solder alloys. Small sized Cu-Sn-Au compounds are observed in the bulk Sn-Ag-Cu solder. In thorough investigation, it is noticed that the amount of Au-Sn compounds are decreased significantly in the Sn-Ag-Cu solder. It is believed that during aging Cu-Sn compound absorb Au and form Cu-Sn-Au compounds. Few quaternary Cu-Ni-Sn-Au IMCs are found very close to the interface. There is no such quaternary compound observed in the bulk of the solder away from the interface. For Sn-Ag-Cu solders, it is believed that Ni atoms diffuse through the interfacial IMCs and react with the Cu-Sn-Au compound near the interface. For Sn-Ag solder, the P rich Ni layer is about 408nm thick. Small sized Au-Ni-Sn compounds are observed throughout the bulk solder. Ni may come from two possible sources, firstly from the interfacial IMCs and secondly from the Ni-Sn IMCs that are formed in the bulk solder during reflow. Observing the distribution of the
ternary Au-Ni-Sn compounds in the bulk Sn-Ag solder, it is assumed that Ni from existing Ni-Sn IMCs reacts with the near by Au-Sn compound. Still some unreacted Au-Sn compounds are observed in the solder. In this stage, no Ni-Sn IMCs are observed in the bulk Sn-Ag solder. No such Sn-Au-Ni compound is observed on Sn-Ag-Cu solders system. So it may be stated that the affinity of chemical reactivity of Ni is higher for Cu-Sn compound than Au-Sn compound. In this stage highest shear strength is found for both the solder alloys. It may be due to the removal of residual stress and strength hardening effects of the alloys, because aging is done beyond the recrystallization temperature (0.6T_m~130°C) of the solder alloys.

The average shear strength of Sn-Ag-Cu solder alloy after 300hrs of aging is around 1650g/mm, which is around 6% lower from the initial as bonded condition. In this stage, IMCs thickness of Sn-Ag-Cu solder is about 3.01μm and the P rich Ni layer is about 251nm (Fig. 5a(ii)). For Sn-Ag system, the IMCs thickness is about 4.73μm. The P rich Ni layer is about 507nm (Fig. 5b(ii)). The phosphorous percentage of the dark layer for both the solder alloys is about 25 at.% The atomic ratio of 3Ni:1P indicates that there remains the same Ni₃P phase through out the aging. The compositions of the Au-Ni-Sn IMCs in the solder relatively remain the same. The Au percentage in the solder side interfacial IMCs for both the solders is increased. Relatively less no of Au-Sn IMCs are observed in the bulk. Most of the Au-Sn compounds in the solder are transformed to ternary Au-Ni-Sn compounds in the Sn-Ag solder alloys. As all the Ni-Sn compounds in the bulk are already consumed, now it seems that diffusion of Ni atoms through the interfacial IMCs have occurred to react with the Au-Sn compounds in the bulk of the Sn-Ag solders. Although the solubility of Ni in Sn is nearly zero at 150°C (from the Ni-Sn binary phase diagram), it is interesting to see the diffusion of Ni in the bulk solder. Song et al. [15] observes a high Ni solubility in the AuSn₇ phase which is approximately 1.24 at.% at 150°C. Since the Ni from the interface has the shortest diffusion path to the AuSn₇ intermetallics nearest the interface, it will be consumed first. Ni from AuSn₇ near interface will diffuse toward the intermetallics located further out in the bulk due to the concentration gradient of Ni in the bulk. Both Cu-Sn compound and AuSn₇ may act as the carrier of Ni from the interface, but ultimately Cu-Sn with small amount Au produce the more stable Cu-Ni-Sn-Au compounds in the bulk Sn-Ag-Cu solder.

The IMCs thickness of Sn-Ag-Cu is around 3.6μm after 400hrs of aging (Fig.5a(iii)). The composition in the middle of the IMCs layer is determined to be the same Cu-Ni-Sn IMCs with relatively high amount gold in it. In this stage, the shear strength does not change to any significant amount for Sn-Ag-Cu. The quaternary phase (Fig.6a) in the bulk solder contains slightly more Ni than the short period aging quaternary IMCs and the composition is found to be 48.5Sn, 37.5Cu, 8.6Ni and 5.4Au (in at.%). Through aging the size of the quaternary IMCs in the bulk solder get bigger. For Sn-Ag solder, minimum shear strength is observed and still it is higher than that of the Sn-Ag-Cu solder. The average IMCs thickness of Sn-Ag solder is around 5.4μm at the interface (Fig. 5b(iii)). The average thickness of the P rich Ni layer is about 585nm. The ternary phase (Fig.6b) within the bulk solder has the same composition. From the SEM micrographs, it seems that Au resettlement is relatively higher for Sn-Ag solder. The solubility of Au in Ni-Sn IMCs is very low at 150°C [15]. Here Au-Ni-Sn compound appeared on the top of interfacial IMCs as a discrete island. In the case of Sn-Ag-Cu solder, the EDX results show that the Au solubility in the Cu-Ni-Sn compound is around 10 at.% at 150°C. It is also noticed that the amount of Au-Sn compound in the Sn-Ag-Cu bulk solder is decreased further. No Au resettlement as Au-Ni-Sn compounds is observed on the interface, on the other hand higher amount of Au is absorbed to form quaternary IMCs in the interface for Sn-Ag-Cu solder.

Though both the interfacial IMCs thickness and the P rich Ni layer are higher for Sn-Ag solder, the results of ball shear tests showed that aging cause little improvement in shear strength in Sn-Ag solders than the Sn-Ag-Cu solders. As all the tested samples failed inside the solder in a more or less ductile manner, the constituent in the bulk solder may play a major role on the mechanical reliability of the solder joints. Several factors may affect the solder strength i.e. depletion of Cu from the solder to the interface, presence of Cu-Ni-Sn-Au or the absence of Au-Ni-Sn in the bulk solder etc. Considering the appearance, Cu-Ni-Sn-Au may be the suspected link to failure for Sn-Ag-Cu solders for long time aging.

**Conclusion**

The Sn-Ag solders show relatively better ball shear strength than Sn-Ag-Cu solders during aging. During the early soldering reaction between the eutectic Sn-Ag and Sn-Ag-Cu solder and the electroless amorphous Ni(P) deposit, thin Ni₃P formed on the original electroless Ni(P) layer. As the aging time increases, the Ni in electroless Ni(P) layer is successively consumed. As the time increases, the consumption of Ni increases. Relatively high consumption of Ni is observed in the case of Sn-Ag solder alloys. The IMCs growth rate in the interface for Sn-Ag solder is higher than that of the Sn-Ag-Cu solder. It implies that the reaction rate is much faster for Sn-Ag solder in the high temperature solid state aging. IMCs at the solder interface are well adhered to substrate pads for both type of solder alloy. Diffusion of Ni through the interface in to bulk solder is noticed for both the solder. Redistribution of Au as Au-Ni-Sn is detected at the interface of the Sn-Ag solders. Higher amount of Au is engrossed in the interfacial IMCs of Sn-Ag-Cu solder at solid state aging. It is also observed that the reaction affinity of Ni is higher for Cu-Sn-Au compounds than Au-Sn compounds in annealing. Overall, both the solder alloys do not illustrate any significant deterioration of the joint strength within the reported aging period.
Figure 5. SEM micrographs showing the interface after aging for i) 100hrs ii) 300hrs and iii) 400hrs at 150°C of a) Sn-Ag-Cu and b) Sn-Ag solder.

Figure 6. SEM micrographs showing the bulk solder after aging for 400hrs at 150°C of a) Sn-Ag-Cu and b) Sn-Ag solder.
Acknowledgements

The authors would like to acknowledge the financial support provided by Research Grant Council of Hong Kong for the project “Wetting Kinetics and Interfacial Interaction Behavior between Lead-free Solders and Electroless Nickel Metallizations,” CERG project no. CityU 1187/01E (CityU Project No. 9040621) and the research studenthip of City University of Hong Kong. They are grateful to M. N. Islam of the E.E. Dept., City University of Hong Kong, for his assistance in the experimental works.

References


