Solid-State Reactions Between the Au/Ni Surface Finish and the SnAgCu Lead-Free Solders with Different Cu Concentrations

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Abstract
The reactions between the SnAgCu lead-free solders of various compositions and the Au/Ni surface finish in advanced electronic packages were studied. Three solder compositions, Sn-3.5Ag, Sn4Ag-0.5Cu, and Sn-3.5Ag-0.75Cu, were used, and their performances were compared. After reflow, the solder joints were subjected to aging at 180 °C for time up to 250 hrs. The shear strengths of the solder joints with different aging time were then tested. It was found that the Sn-4Ag-0.5Cu solder gave the worst results in shear strength. The microstructures of the solder joints were also examined using a scanning electron microscope. The poor performance of the Sn-4Ag-0.5Cu solder can be explained basing on the microstructure. The types of intermetallic compounds formed at the interface were different for different solder compositions. When there was no Cu (Sn-3.5Ag), the reaction product was Ni3Sn4. For the Sn-3.5Ag-0.75Cu solder, the reaction product was (Cu1-p-qAupNiq)6Sn5 right after reflow, and two intermetallic compounds (Cu1-p-qAupNiq)6Sn5 and (Ni1-yCuy)3Sn4 formed after aging at 180 °C for 250 hrs. For the Sn-4Ag-0.5Cu solder, both Ni3Sn4 and (Cu1-p-qAupNiq)6Sn5 were present near the interface right after reflow, and there was a layer of solder between these two intermetallic compounds. After aging, a layer of (Cu1-p-qAupNiq)6Sn5 over a layer of (Ni1-yCuy)3Sn4 formed at the interface. Moreover, there was a series of voids at the (Cu1-x-yNixAuy)6Sn5 /solder interface. These voids were responsible for the weak Sn-4Ag-0.5Cu solder joints. It is proposed that Sn in the solder between Ni3Sn4 and (Cu1-xNix)6Sn5 had been consumed and converted into (Cu1-p-qAupNiq)6Sn5 and (Ni1-yCuy)3Sn4, leaving a series of voids behind.

1. Introduction
The eutectic Sn-Ag solder and its Sn-Ag-Cu ternary derivatives are very promising lead-free replacements for the eutectic Pb-Sn solder. The eutectic Sn-Ag alloy has the composition of 96.5%Sn-3.5%Ag (wt.%, Sn-3.5Ag), and a eutectic temperature of 221 °C. The alloying element Cu can be added to produce a wide variety of solders intended for different environments and soldering applications. Minor adjustment in Ag content is also common to fine-tune the solder properties. The solders Sn-4Ag-0.5Cu and Sn-3.5Ag-0.75Cu are common examples. The objective of this study is to look into the chemical properties of this series of alloys. More specifically, we intend to investigate the reactions between these solders, Sn-3.5Ag, Sn-4Ag-0.5Cu, and Sn-3.5Ag-0.75Cu, and the Au/Ni surface finish. The Au/Ni is a very common surface finish both for component leads and for soldering pads of area-array packages. The surface layer Au, with a thickness of 0.1-1.0 µm, is for oxidation protection, and is usually deposited by immersion or electroplating. The inner Ni layer can be deposited either by electroless plating or electroplating, and is about 5-10 µm thick. The function of the Ni layer is to prevent rapid reaction between solder and the Cu layer, which is under the Ni layer and is part of the internal conducting trace.

Reflow soldering is one of the key soldering approaches to produce solder joints. During reflow, reaction between the solder and the surface finish occurs. After reflow, the reaction continues during the subsequent packaging steps that may include another reflow and other high temperature processes. Even during the normal life cycle of a package, the reaction between the solder and the surface finish continues.

Many surprisingly interesting phenomena occurred during and after the reflow for the Sn-37Pb solder over the Au/Ni surface finish [1-8]. First of all, the Au layer would disappear from the interface extremely fast, leaving the Ni layer exposed to the solder [3]. According to our earlier study [3], the entire Au layer (one µm thick initially) would be converted to AuSn4 in less than 10 s reflow time. This newly formed AuSn4 would then break off from the interface and fall into the solder in less than 30 s reflow time. This reaction rate seemed unreasonably high at first even for liquid-solid reaction. However, this high reaction rate was quite reasonable in view of the fact that pure Au reacted extremely fast with PbSn solders [9-10]. Immediately after reflow, the AuSn4 particles were more or less evenly distributed throughout the whole solder joint [1, 2, 4-8]. Quite surprisingly, after the package was subjected to a few hundred hours of solid-state aging at 100-150 °C, most of these AuSn4 particles would disappear from inside the solder joints and reappear at the interface as a continuously layer of (Au0.55Ni0.45)Sn4 [4-8]. A second reflow would again make the (Au0.55Ni0.45)Sn4 disappear from the interface and reappear inside the solder as isolated (Au0.55Ni0.45)Sn4 particles. The x value in (Au0.45Ni0.55)Sn4 now was greater than 0.45 [4]. This phenomenon repeated itself upon additional reflow-aging cycles. The continuous (Au0.45Ni0.55)Sn4 layer at the interface will inevitably
make the interface brittle, thus reduce the overall strength of the solder joints. One major objective of this work is to see whether the above phenomenon will occur for the SnAgCu solders.

2. Experimental

The solder balls used in this study were made of Sn-3.5Ag, Sn-4Ag-0.5Cu, or Sn-3.5Ag-0.75Cu solders, and had a diameter of 750 µm. The soldering pads had an Au/Ni surface finish over Cu trace. The Au and Ni layers were grown by electroplating, and were 1 µm and 7 µm thick, respectively. Each pad had a diameter of 720 µm, but the outer rim of each pad was covered with the solder mask, so that only the inner 600 µm diameter of the surface finish was directly exposed to the solder. The pads were made on 5cmx5cm substrates, and each substrate had 352 pads. A water-soluble flux was used for the soldering. The solder balls were dipped into flux and then planted on the pads manually. The flux was viscous enough to hold the solder balls in place during subsequently handling. Twenty solder balls were planted on each substrate, and five substrates were used for each reflow condition.

For the reflow, a hot-air reflow oven was used. The peak reflow temperature was fixed at 240 °C, and the heating rate and cooling rate were fixed at 1 and 3 °C/s, respectively. Reflow time of 120 s was used. After the reflow, the samples were subjected to aging at 180 °C for time up to 250 hrs. After aging, the solder joints were either cross-sectioned and examined or subjected to shear strength test.

For the cross-sectional analysis, the substrates were sectioned using a low-speed diamond saw and metallographically polished to reveal the interface and the internal microstructure of the solder joints (cross-section view). The samples were then examined using an optical microscope and a scanning electron microscope. The composition of each phase was determined using a JEOL JXA-8800M electron microprobe, operated at 20 keV. During the microprobe measurement, the measured X-rays were Kα, Kα, Lα, Lα, and Lα for Ni, Cu, Au, Ag, and Sn, respectively, and the standards used were pure Ni, Cu, Au, Ag, and Sn, respectively. In the microprobe analysis, the concentration of each element was measured independently, and the total weight percentage was within 100±1% in each case. For every data point, at least four measurements were made and the average value was reported.

For the shear test, the shear rate was set at 300µm/s. At least 20 measurements were performed for each solder joint condition. The average strengths were then reported.

3. Results and Discussion

The shear strengths of the solder joints versus the aging time were shown in Fig. 1. The solder joints with zero aging time were the solder joints right after reflow. The strength was measured in gram-force, which is customarily used by the electronic packaging industry. One gram-force is equal to 0.0098 N. For a 750 µm solder joint, 1000 gram-force is generally considered the minimum strength required by the industry. For each data point in Fig. 1, the error bar represents two standard deviations. The common trend in Fig. 1 is that the joint strength decreased with aging time. Right after reflow, the joint strengths were similar for all solders, but their behaviors started to differ with aging. The Sn-3.5Ag-0.75Cu solder performed the best against aging, and Sn-4Ag-0.5Cu suffered the greatest loss in strength. In fact, the strength of Sn-4Ag-0.5Cu joint fell below 1000 gram-force only after 100 hrs of aging. In the following the interfacial microstructures will be used to rationalize the behaviors observed here.

Shown in Fig. 2 are the microstructures of the interfaces for different alloys right after reflow. Very different results were obtained for different alloys. For the Sn-3.5Ag alloy [Fig. 2 (a)], a thin layer of Ni3Sn4 formed at the interface. For the Sn-3.5Ag-0.75Cu alloy [Fig. 2 (b)], a layer of (Cu1-p-qAupNiq)6Sn5 formed at the interface. For the Sn-4Ag-0.5Cu alloy [Fig. 2 (c)], both Ni3Sn4 and (Cu1-p-qAupNiq)6Sn5 were present near the interface. The (Cu1-p-qAupNiq)6Sn5 layer, however, was detached from the Ni3Sn4 layer, and a layer of solder was between (Cu1-p-qAupNiq)6Sn5 and Ni3Sn4. In summary, the initial reaction products right after reflow were very sensitive to the solder composition. With increasing Cu concentration, the reaction product switched from Ni3Sn4 to (Cu1-p-qAupNiq)6Sn5+Ni3Sn4, then to (Cu1-p-qAupNiq)6Sn5Ni3Sn4. The compound (Cu1-p-qAupNiq)6Sn5 has the Cu6Sn5 structure as verified by x-ray diffraction analysis reported in our previous study [11]. The data in Fig. 1 indicate that the strengths for different alloys right after reflow were essentially the same. This suggests that these three types of interfacial microstructures did not have much impact on the shear strength.

Figures 3-5 show the microstructures of the interfaces for the three different alloys after aging at 180 °C for 250 hrs. Figures 3 (a) and (b) are a scanning electron micrograph and an optical micrograph, respectively, for the Sn-3.5Ag solder. The optical micrograph is shown because it has better contrast between neighboring phases. As shown in Figs. 3 (a) and 3 (b), a continuous Ni3Sn4 layer formed at the interface. Very little did the (Au1-xNi1)xSn4 intermetallic compound relocate back to the interface. These results are consistent with our earlier study reported in the literature [12]. For this solder, the intermetallic compound before and after aging was the same type, but its thickness increased.
The interface for the Sn-3.5Ag-0.75Cu case is shown in Fig. 4 (a) and (b). Two intermetallic layers were presented at the interface, \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) and \((\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4\). These two compounds are based on the \(\text{Cu}_6\text{Sn}_5\) and \(\text{Ni}_3\text{Sn}_4\) crystal structure, respectively. Aging for this solder made the compound \((\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4\) grew beneath the \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) layer. This \((\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4\) layer grew because most of the Cu had been consumed and incorporated into the \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) layer, and the only metal left to react with Sn is Ni.

Figures 5 (a) and (b) show the interface for the Sn-4Ag-0.5Cu. Two intermetallic layers were again presented at the interface, \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) and \((\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4\). Moreover, there were a series of voids at the \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) /solder interface. The presence of these voids was the main reason why this interface was weak. Shown in Fig. 6 was a Sn-4Ag-0.5Cu solder joint that had been partially fractured. It is very clear that the fracture occurred along the solder/(\(\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) interface, where the voids were located. Comparing Figs. 2 (c) and 5 (b), we believe these voids have their origin closely linked to the solder layers between \(\text{Ni}_3\text{Sn}_4\) and \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\). It is proposed that Sn in this region had been consumed and converted into \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) and \((\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4\), leaving voids behinds. However, more detailed study is needed to verify this suggestion.

4. Conclusion

The Cu concentration in the SnAgCu ternary solder has a very strong effect on the compound formation and the shear strength in solder joints with the Au/Ni surface finish. When there was no Cu (Sn-3.5Ag), the reaction product was \(\text{Ni}_3\text{Sn}_4\). When the Cu concentration was high (Sn-3.5Ag-0.75Cu), the reaction product was \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) right after reflow, and two intermetallic compounds \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) and \((\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4\) formed after aging at 180 °C for 250 hrs. When the Cu concentration was 0.5 Wt.% (Sn-4Ag-0.5Cu), both \(\text{Ni}_3\text{Sn}_4\) and \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) were present near the interface right after reflow, and there was a layer of solder between these two intermetallic compounds. After aging, a layer of \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) over a layer of \((\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4\) formed at the interface. Moreover, there were a series of voids at the \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) /solder interface. These voids were responsible for the weak Sn-4Ag-0.5Cu solder joints. It is proposed that Sn in the solder between \(\text{Ni}_3\text{Sn}_4\) and \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) had been consumed and converted into \((\text{Cu}_{1-p-q}\text{Au}_{p}\text{Ni}_{q})_6\text{Sn}_5\) and \((\text{Ni}_{1-y}\text{Cu}_y)_3\text{Sn}_4\), leaving a series of voids behinds.

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References

Aging time (hr) vs Shear strength (gram-force)

- Sn3.5Ag
- Sn4Ag0.5Cu
- Sn3.5Ag0.75Cu
Figure 2: Cross-sectional microstructures at the interface for different solder compositions.
Figure 3: (a) Secondary electron micrograph and (b) optical micrograph for Sn-3.5 Ag solder joint that was aged at 180°C for 250 hrs.
Figure 4: (a) Secondary electron micrograph and (b) optical micrograph for Sn-3.5Ag-0.75Cu solder joint that was aged at 180°C for 250 hrs.
Figure 5: (a) Secondary electron micrograph and (b) optical micrograph for Sn-4Ag-0.5Cu solder joint that was aged at 180°C for 250 hrs.
**Figure 6:** Partially fracture Sn-4Ag-0.5Cu solder joint showing the major fracture interface is along the solder/(Cu_{1-p-q}Au_pNi_q)_{6}Sn_{5} interface.
Figure 7: (a) Secondary electron micrograph and (b) optical micrograph for Sn-3.5Ag solder joint that was aged at 180°C for 500 hrs.

Figure 1: Shear strength of solder joints plotted against the aging time at 180°C.
aged at 180°C for 500 hrs.
Figure 9: (a) Secondary electron micrograph and (b) optical micrograph for Sn-3.5Ag-0.75Cu solder joint that was aged at 180°C for 500 hrs.
Figure 10: (a) Secondary electron micrograph and (b) optical micrograph for Sn-4Ag-0.5Cu solder joint that was aged at 180°C for 500 hrs.