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## Communications

### Strong Effect of Cu Concentration on the Reaction between Lead-Free Microelectronic Solders and Ni

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The electronic industry has been using Pb-bearing solders for interconnection applications for over 50 years. These Pb-bearing solders include alloys such as 63Sn–37Pb (wt %, Sn37Pb), frequently used for soldering printed circuit boards (PCBs), and Sn95Pb, frequently used for chip-to-package connection. There are several pending national and international legislation proposals banning the use of Pb in these solders. The Sn3.9Ag0.6Cu solder is one of the most promising lead-free candidates to replace the Sn37Pb solder.<sup>1</sup> The allowance for concentration variation for each element in this solder is customarily taken to be  $\pm 0.2$  wt %.

Nickel is one of the most common metals to be in direct contact with solder during soldering and during the normal life cycle of electronic products. Therefore, the interactions between Ni and Sn3.9Ag0.6Cu solder have to be considered. In the literature, no study on the reaction between Ni and Sn3.9Ag0.6Cu can be found. There are a few studies on the reaction between SnAg solders and Ni,<sup>2–5</sup> and in these studies it was found

that Ni<sub>3</sub>Sn<sub>4</sub> would form at the interface. The objective of this study is to look into the reaction between Ni and Sn3.9Ag0.6Cu. Moreover, the reaction between Sn3.9Ag0.2Cu and Ni is also studied to investigate the effect of a small change in Cu concentration on the reaction.

The Sn3.9Ag0.6Cu and Sn3.9Ag0.2Cu solders were prepared from 99.99%-pure elements. Nickel disks (6.35-mm diameter  $\times$  0.50-mm thick, 99.995% pure) were utilized to react with the solders. Before the reaction, each Ni disk was metallurgically polished and fluxed with a mildly activated rosin flux. Each solder bath was formed by placing 6 g of solder into a 7-mm i.d. vial. Each fluxed disk was then vertically inserted into a fresh molten solder bath at 250 °C. The Ni disk was held in place vertically with tweezers. The surface oxide of the solder was displaced during the insertion and did not interfere with the reaction. Reaction times were 2 min, 10 min, and 25 h.

When Sn3.9Ag0.2Cu reacted with Ni at 250 °C for 2 or 10 min, a thin layer of (Ni<sub>1-x</sub>Cu<sub>x</sub>)<sub>3</sub>Sn<sub>4</sub> formed at the interface as shown in Figure 1 for the case of 10 min. The results for 2 min are very similar to those of 10 min except that the (Ni<sub>1-x</sub>Cu<sub>x</sub>)<sub>3</sub>Sn<sub>4</sub> layer was thinner. In this figure, two phases, Sn-rich solid solution phase and Ag<sub>3</sub>Sn intermetallic phase, can be identified in the solder. In addition, in the solder there was a very small amount of Cu–Ni–Sn ternary particles, which were not shown in this figure. The compound (Ni<sub>1-x</sub>Cu<sub>x</sub>)<sub>3</sub>Sn<sub>4</sub> is based on the Ni<sub>3</sub>Sn<sub>4</sub> structure as verified by X-ray diffraction analysis (Figure 2), but

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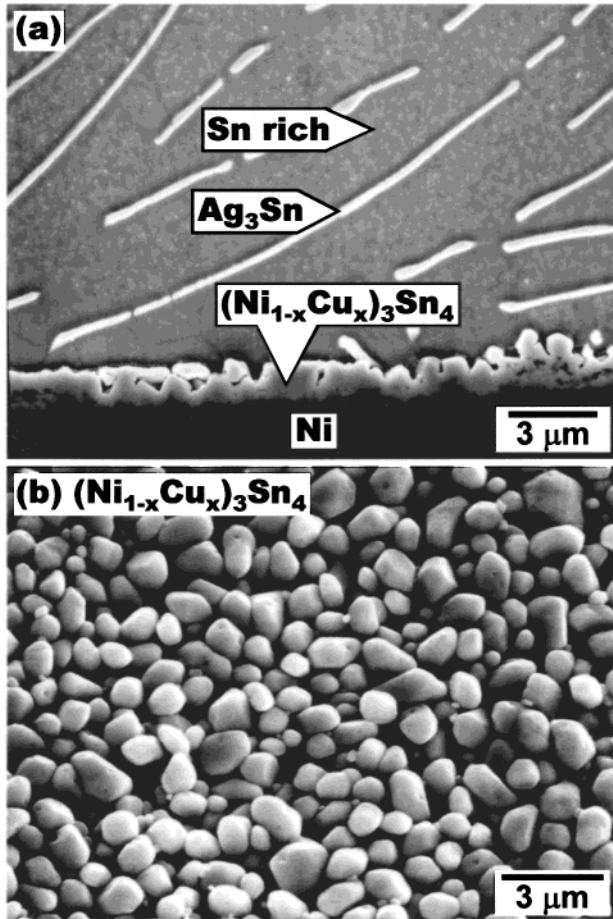
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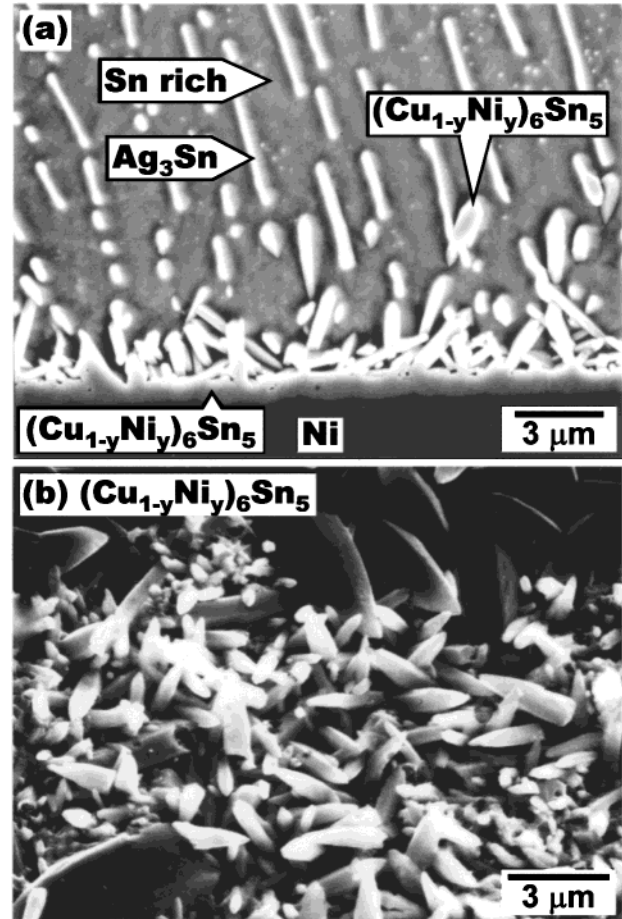
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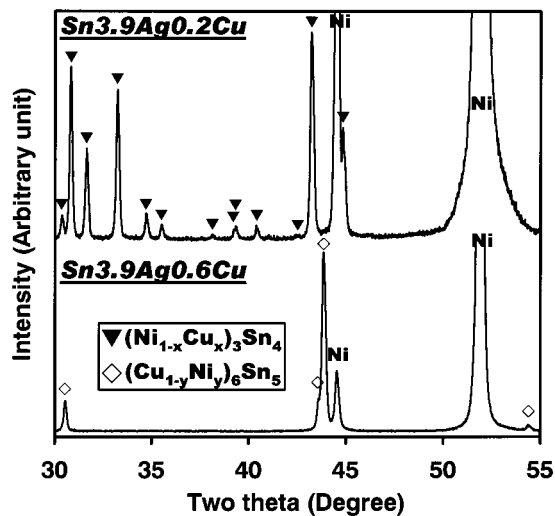
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**Figure 1.** (a) Interface for the reaction between Sn3.9Ag0.2Cu and Ni at 250 °C for 10 min. This picture is a cross-section view with the sectioning plane perpendicular to the Ni surface. A thin layer of  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$  formed at the interface. (b) A top-view picture showing the grain structure of  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ . The solder had been etched away with acids.



**Figure 3.** (a) Interface for the reaction between Sn3.9Ag0.6Cu and Ni at 250 °C for 10 min. This picture is a cross-section view with the sectioning plain perpendicular to the Ni surface. A thin layer of  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  formed at the interface. (b) A top-view picture showing the grain structure of  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$ . The solder had been etched away with acids.



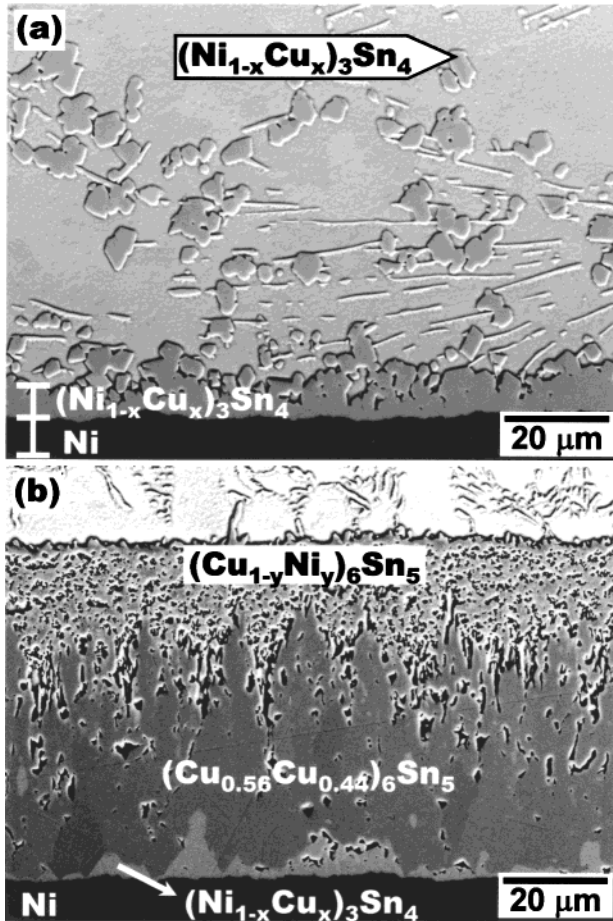
**Figure 2.** X-ray powder diffraction patterns for the reaction products for reactions at 250 °C for 10 min. The reaction between Sn3.9Ag0.2Cu and Ni produced  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ , while the reaction between Sn3.9Ag0.6Cu and Ni produced  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$ . The Ni signals originated from the Ni layer beneath the intermetallic compounds.

has a small amount of Cu dissolved in the Ni sublattice. The exact amount of Cu in  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$  could

not be determined accurately because this layer is too thin for accurate electron microprobe measurement. This was because strayed signals from the neighboring solder and the Ni layer were also collected. Figure 1b is a top-view picture showing the grain structure of  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ . In this picture, the solder had been etched away with a 30 vol %  $\text{HNO}_3$  solution. The reaction between Sn3.9Ag0.2Cu and Ni is similar to that between SnAg and Ni reported in the literature<sup>2-5</sup> in the respect that only  $\text{Ni}_3\text{Sn}_4$ -based compound formed at the interface.

The reaction between Sn3.9Ag0.6Cu and Ni, however, was strikingly different. The reaction produced a thin layer of  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$ , instead of  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ , at the interface. Figure 3 shows the cross-section and top-view pictures of the interface. The reaction product  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  has the  $\text{Cu}_6\text{Sn}_5$  structure as verified by X-ray diffraction analysis (Figure 2). The  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  layer was thick enough to allow us to determine its composition accurately at the center of the  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  layer to be  $(\text{Cu}_{0.60}\text{Ni}_{0.40})_6\text{Sn}_5$ . The  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  grains have a microstructure distinctively different from that of  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$ .

The fact that a 0.4 wt % difference in Cu concentration could produce different reaction products is very surprising. To verify that this is not a transient phe-



**Figure 4.** (a) Interface for the reaction between Sn3.9Ag0.2Cu and Ni at 250 °C for 25 h. A thick layer of  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$  formed at the interface. (b) The interface for the reaction between Sn3.9Ag0.6Cu and Ni at 250 °C for 25 h. Two layers of  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  and one layer of  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$  are present.

nomenon for a short reaction time, the reactions were carried out for a reaction time of 25 h. Figure 4a shows the interface for the reaction between Sn3.9Ag0.2Cu and Ni, and Figure 4b shows that for Sn3.9Ag0.6Cu. The same types of intermetallic compounds formed next to the solders as their counterparts for a shorter reaction time. This observation confirms that this phenomenon is not a transient phenomenon and is stable for time

longer than 25 h. However, there is some difference between the short and long reaction time. As shown in Figure 4b, the compound  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  exhibits two types of microstructure: an upper layer with many voids in it and a lower layer which is much denser. The mechanism for the formation of two distinct  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  layers need more detailed study. Moreover, a thin layer of  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$  showed up under the  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  layer as shown in Figure 4b. Electron microprobe measurements showed that  $(\text{Ni}_{1-x}\text{Cu}_x)_3\text{Sn}_4$  in Figure 4a,b had the compositions of  $(\text{Ni}_{0.88}\text{Cu}_{0.12})_3\text{Sn}_4$  and  $(\text{Ni}_{0.83}\text{Cu}_{0.17})_3\text{Sn}_4$ , respectively. The lower layer of  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  in Figure 4b had a composition of  $(\text{Cu}_{0.56}\text{Ni}_{0.44})_6\text{Sn}_5$ . The upper layer of  $(\text{Cu}_{1-y}\text{Ni}_y)_6\text{Sn}_5$  in Figure 4b had too many voids, making its composition difficult to measure.

For industrial applications, the allowance for concentration variation for this solder under fresh conditions is taken to be  $\pm 0.2$  wt %. This practice is a customary extension from the standard developed for the Sn37Pb solder, where a  $\pm 0.2$  wt % limit is rather safe considering both Pb and Sn exist in large quantity. This study points out that different compounds formed at the interface when the Cu concentration merely changed from 0.6 to 0.2 wt %. This change in Cu concentration is already very close to the  $\pm 0.2$  wt % allowance set by the industry for fresh solders, and the Cu concentration might shift out of specification easily in industrial production. In other words, the electronic industry must adopt a tighter standard for Cu concentration and monitor the Cu concentration very closely in their production facilities. Moreover, the composition Sn3.9Ag0.6Cu was selected based more on its physical and mechanical properties of the solder itself and not on its properties related to interfacial reactions. Not many chemical properties about this alloy were known when this alloy was selected. The industry might have to re-assess their choice of the optimal solder composition in view of more available information on interfacial reactions.

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