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Cross-Interaction between Ni and Cu across Sn Layers with Different Thickness

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The Ni/solder/Cu material sequence is one of the most common material sequences in the solder joints of electronic packages. In this study, the Ni/Sn/Cu ternary diffusion couples were used to investigate the solder volume effect on the cross-interaction between Ni and Cu. Experimentally, a pure Sn layer with the thickness of 100–400 μm was electroplated over Cu foils. A pure Ni layer (20 μm) was then deposited over the as-deposited Sn surface. The diffusion couples were aged at 160°C for different periods of time. With this technique, the diffusion couples were assembled without experiencing any high temperature process, such as reflow, which would have accelerated the interaction and caused difficulties in analysis. This study revealed that the cross-interaction could occur in as short as 30 min. A detailed atomic flux analysis showed that the Cu flux through the Sn layer was about 25–40 times higher than the Ni flux. Moreover, it was found that $(Cu_{1-x}Ni_x)_6Sn_5$ on the Ni side reduced the consumption rate of the Ni layer, and the cross-interaction also reduced the Cu_3Sn thickness on the Cu side.

Key words: Ni-Sn-Cu, interfacial reaction, lead-free solder

INTRODUCTION

The Ni/solder/Cu material sequence is a very common material sequence in the solder joints of flip-chip and ball-grid array (BGA) packages. Figure 1 shows a schematic illustration showing the two types of solder joints, flip-chip and BGA, that have the Ni/solder/Cu sequence. In Fig. 1, the Au layer and organic surface preservative (OSP) layer will disappear from the interface during assembly, leaving the Cu and Ni layers directly exposed to the solder.

In the literature, the reaction between Ni and Sn-based solders (SnCu and SnAgCu) were reported to be very sensitive to the Cu concentration in the solder.[1–5] During soldering, if the Cu concentration in solder is lower than 0.4 wt.%, a continuous $(Ni_{1-y}Cu_y)_3Sn_4$ layer forms at the interface. In contrast, if the Cu concentration is higher than 0.6 wt.%, a continuous $(Cu_{1-x}Ni_x)_6Sn_5$ layer forms at the interface. During subsequent solid-state aging, the Cu atoms in the solder will be extracted out of the solder and incorporated into $(Cu_{1-x}Ni_x)_6Sn_5$, and consequently the Cu concentration in the solder will decrease with the aging time.[4–7] When the Cu concentration drops below 0.4 wt.%, $(Ni_{1-y}Cu_y)_3Sn_4$ forms between Ni and $(Cu_{1-x}Ni_x)_6Sn_5$. In addition, $(Cu_{1-x}Ni_x)_6Sn_5$ will be converted to $(Ni_{1-y}Cu_y)_3Sn_4$ gradually. In short, Cu has a very strong effect on the Ni/solder reaction during reflow and aging.

The Ni concentration also affects the solder/Cu reactions.[5,8,9] Addition of Ni to Sn3.5Ag solder in amounts as minute as 0.1 wt.% is able to change the Cu_6Sn_5 microstructure.[8] In addition, a small amount of Ni addition to solder joints is able to reduce the Cu_3Sn growth.[5] In short, Ni also has a very strong effect on the solder/Cu reaction during

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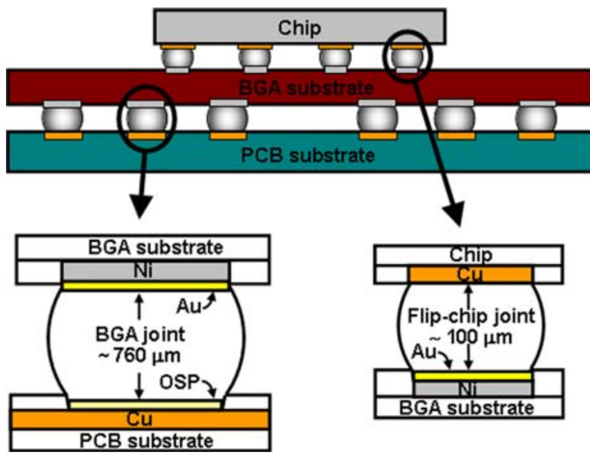

Fig. 1. Schematic illustration showing the two types of solder joints, flip-chip and BGA, that have the Ni/solder/Cu sequence. The Au layer and organic surface preservative (OSP) layer will disappear from the interface during assembly, leaving the Cu and Ni layers directly exposed to the solder.

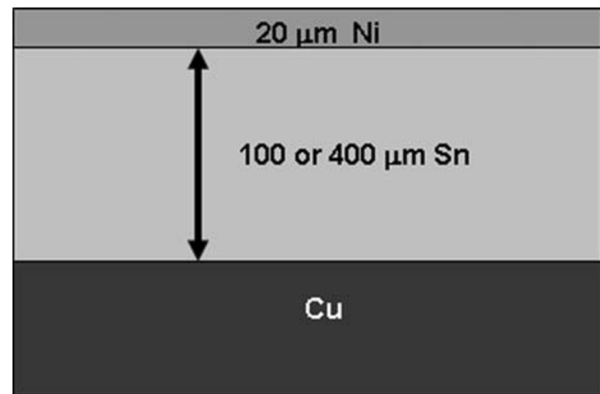

Fig. 2. Schematic drawing showing the structure of the Ni/Sn/Cu ternary diffusion couples.

reflow and aging. Moreover, the cross-interaction between Cu and Ni in a Cu/solder/Ni structure has been reported by Chen et al.[10] It was found that the cross-interaction did occur, and the uphill diffusion of Cu was observed.[10]

In all of these previous studies, the solder joints were assembled by reflow, which is a high temperature process involving molten solder. Substantial interactions occurred during the assembly process, and therefore it was difficult to tell whether the interactions occurred during the reflow stage or during the aging stage. The objective of this paper is to investigate the cross-interaction between Cu and Ni across the solder joints by means of diffusion couples that are prepared using the electroplating process. The electroplating process is a low temperature process so that one can be sure most of the observed phenomena really occur in the aging stage. This technique has the additional benefit of producing variable Sn layer thickness. Using different Sn layer thickness allows one to simulate solder joints of various sizes.

EXPERIMENTAL

The Ni/Sn/Cu diffusion couples were prepared by electroplating an Sn layer (100 μm or 400 μm) and then a Ni layer (20 μm) on Cu foil substrates. Similar preparation techniques have been described in detail elsewhere.[11,12] A schematic drawing of the sample structure is shown in Fig. 2. After electroplating the Sn and Ni layers, the foil was cut into 4 mm $\times$ 8 mm diffusion couples. We also prepared Sn/Cu and Ni/Sn diffusion couples as control experiments. The diffusion couples were directly subjected to aging at 160°C without going through the reflow step.

In addition, one of the Ni/Sn diffusion couple was aged at 160°C for 500 h to produce the structure $Ni/Ni_3Sn_4/Sn$ first, and then a layer of Cu was electroplated over the Sn to produce a multi-layer $Ni/Ni_3Sn_4/Sn/Cu$ diffusion couple. Then this diffusion couple was aged at 160°C for an additional 100 h.

After aging, the diffusion couples were mounted in epoxy and metallographically polished to reveal the microstructure. The reaction zone for each sample was examined by using scanning electron microscopy (SEM). Compositions of the intermetallic compounds were determined by electron probe micro-analysis (EPMA). In EPMA analysis, the concentration of each element was measured independently, and the total weight percentage of all elements was within 100 ± 1% in each case. The average value from at least three measurements was then reported. The thickness of the reaction product was defined as the total area occupied by that phase divided by the linear length of the interface. The total area occupied a particular phase was measured by using an image analyzing software.

RESULTS AND DISCUSSION

The as-deposited Ni/(100 μm Sn)/Cu diffusion couple is shown in Fig. 3. Even though the electroplating was performed at a relatively low temperature (60°C), a very thin layer of intermetallic had already formed at the Ni/Sn interface, as well as at the Sn/Cu interface. These two product layers were too thin to be positively identified by EPMA.

When the aging time reached 30 min, the reaction products were thick enough for a more qualitative identification. As shown in Fig. 4a, a layer of a Ni-Sn-Cu ternary intermetallic, presumably $(Cu_{1-x}Ni_x)_6Sn_5$, existed at the original Ni/Sn interface, and a layer of Cu_6Sn_5 existed at the original Sn/Cu interface. We proposed that the Ni-Sn-Cu ternary intermetallic was $(Cu_{1-x}Ni_x)_6Sn_5$ based on our earlier study.[5] Results from the EPMA measurements also showed that the composition of this compound was $(Cu_{0.6}Ni_{0.4})_6Sn_5$. No Ni was detected

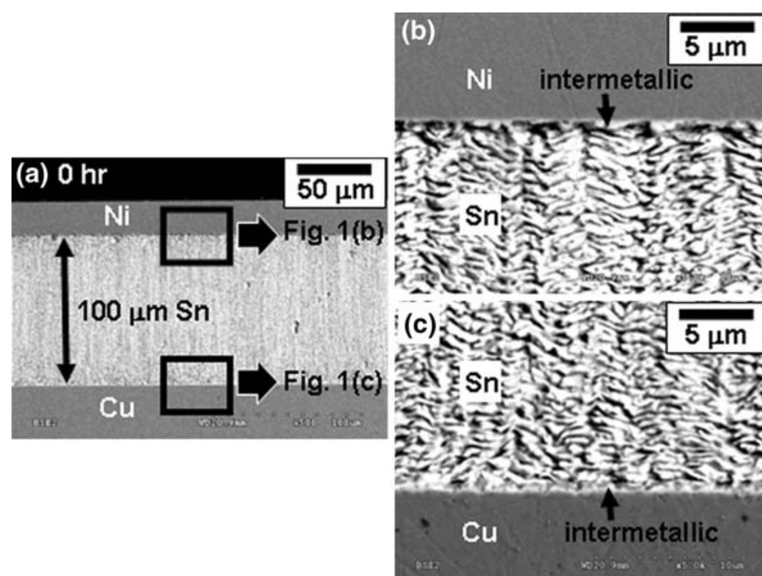

Fig. 3. Backscatter electron micrographs showing the as-deposited sample. (a) Entire diffusion couple. (b) Ni/Sn interface. (c) Solder/Cu interface.

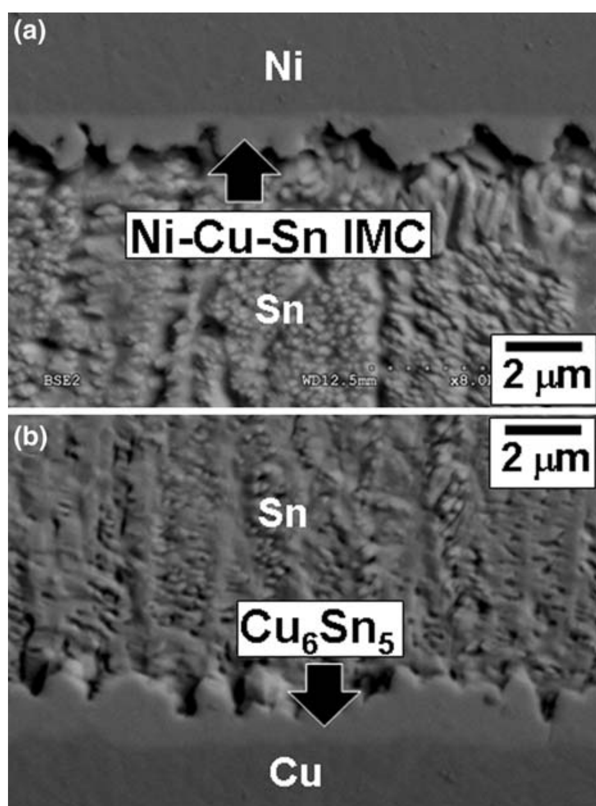

Fig. 4. Backscatter electron micrographs for the Ni/(100 μm Sn)/Cu that had been aged at 160°C for 30 min. (a) Ni side interface. (b) Cu side interface.

in the Cu_6Sn_5 layer formed between Sn and Cu. It is interesting to note that the Cu atoms from the Cu side were able to diffuse across the Sn layer and be incorporated into the Ni-Sn-Cu ternary compound on the Ni side. However, there was no evidence that Ni atoms from the Ni side had diffused through the Sn layer because no Ni signal was detected in Cu_6Sn_5 on the Cu side. This observation can be explained using the different diffusion coefficients of Cu and Ni in Sn. According to the literature, the diffusion coefficient of Cu in Sn is 2.5×10^{-7} cm^2/s at 160°C,[13] and that of Ni in Sn at the same temperature is two orders of magnitude smaller at 5.4×10^{-9} cm^2/s.[14] Using the diffusion distance $\approx \sqrt{Dt}$ estimation, where D is the diffusion coefficient and t is time, one can estimate that it requires Cu 7 min and Ni 5 h to diffuse across a 100 μm Sn layer at 160°C. This simple assessment supports our observation that in 30 min Cu was able to participate in the reaction on the other side, while Ni could not.

When the aging time reached 1,000 h, $(Cu_{1-x}Ni_x)_6Sn_5$ formed on both sides as shown in Fig. 5. It should be noted that the Ni content in $(Cu_{1-x}Ni_x)_6Sn_5$ was higher on the Ni side. On the Cu side, there was also $(Cu_{1-x}Ni_x)_6Sn_5$ between Cu_3Sn and Sn. For the purpose of comparison, results from the Ni/Sn and Sn/Cu binary diffusion couples that had been aged at 160°C for 1,000 h are shown in Fig. 6a and b, respectively. The key difference between Figs. 5a and 6a is the type of compound formed at the interface. In the binary Ni/Sn couple shown in Fig. 6a, Ni_3Sn_4, instead of $(Cu_{1-x}Ni_x)_6Sn_5$, formed at the interface. This suggests that in Ni/Sn/Cu the Cu atoms diffused from the Cu side had effectively raised the local Cu concentration to a level so high (about >0.5 wt.%) that $(Cu_{1-x}Ni_x)_6Sn_5$ had replaced Ni_3Sn_4 as the stable phase.

A comparison between Figs. 5b and 6b shows that there is also a marked difference on the Cu side. The thickness of Cu_3Sn in Fig. 5b is clearly smaller than that in Fig. 6b. As will be presented later, this difference can be explained by the cross-interactions

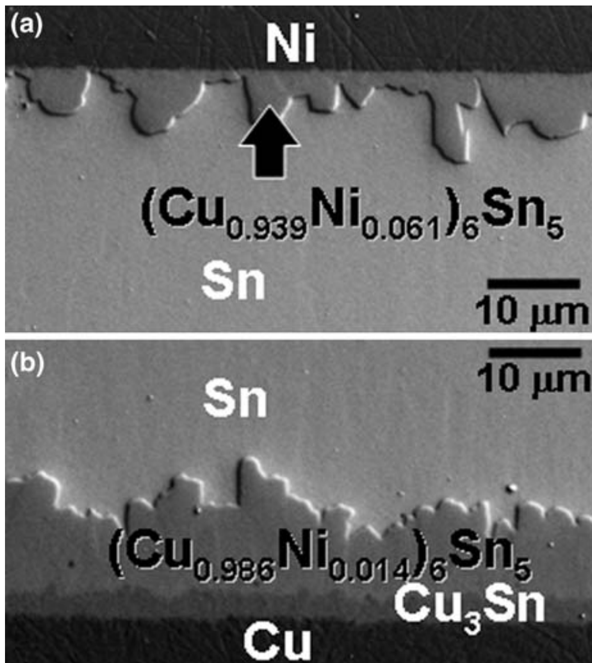

Fig. 5. Backscatter electron micrographs for the Ni/(100 μm Sn)/Cu that had been aged at 160°C for 1,000 h. (a) Ni side interface. (b) Cu side interface.

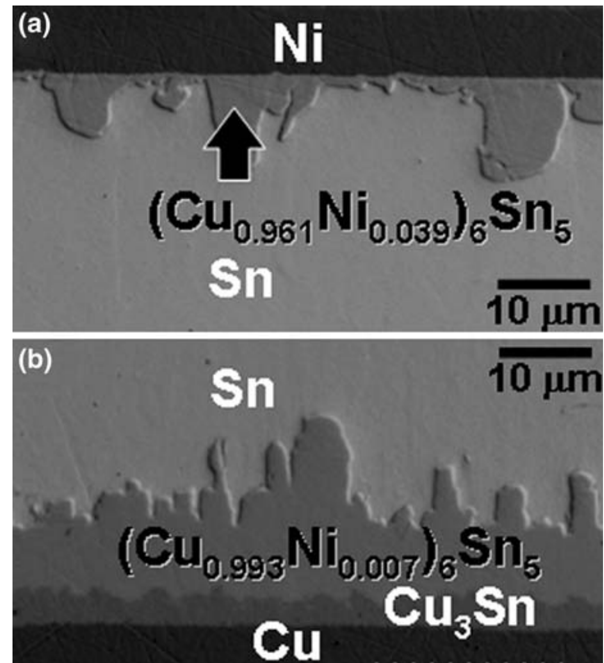

Fig. 7. Backscatter electron micrographs showing the interfaces of Ni/(400 μm Sn)/Cu that had been aged at 160°C for 1,000 h. (a) Ni side interface.(b) Cu side interface.

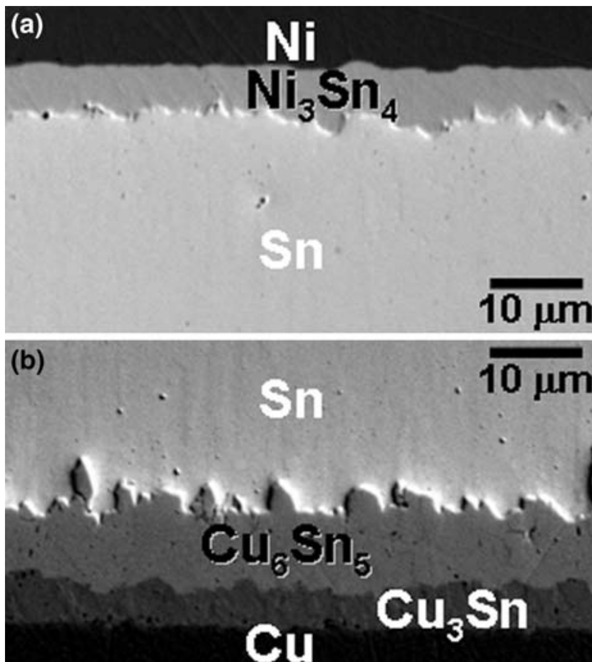

Fig. 6. Backscatter electron micrographs showing the interfaces from binary Ni/Sn and Sn/Cu diffusion couples that had been aged at 160°C for 1,000 h. (a) Ni/Sn binary diffusion couple. (b) Sn/Cu binary diffusion couple.

between Cu and Ni in Ni/Sn/Cu. Before going into the details of this cross-interaction, the effect of increasing the distance between Ni and Cu, thus the thickness of Sn in Ni/Sn/Cu, will be shown first.

Figure 7 shows the Ni/(400 μm Sn)/Cu diffusion couple after aging at 160°C for 1,000 h. Although the Sn layer thickness had been increased by four times, evidences for the cross-interaction are still clearly visible. First of all, on the Ni side $(Cu_{1-x}Ni_x)_6Sn_5$, instead of Ni_3Sn_4, was still the only compound formed, as shown in Fig. 7a. On the Cu side, shown in Fig. 7b, both $(Cu_{1-x}Ni_x)_6Sn_5$ and Cu_3Sn were present as in the Ni/(100 μm Sn)/Cu case, but now Cu_3Sn was thinner than that in the binary Cu/Sn couple (Fig. 6b), and thicker than that in the Ni/(100 μm Sn)/Cu couple (Fig. 5b). The EPMA measurements revealed that the compositions of $(Cu_{1-x}Ni_x)_6Sn_5$ were also different for Ni/(100 μm Sn)/Cu and Ni/(400 μm Sn)/Cu, as summarized in Table I. On the Cu side, the Ni concentrations in $(Cu_{1-x}Ni_x)_6Sn_5$ were very low in both cases, but thicker Sn did have the effect of lowering the Ni concentration by one half, from 0.8 at.% to 0.4 at.%. On the Ni side, where Cu atoms had to diffuse from the Cu side, the Cu concentrations of $(Cu_{1-x}Ni_x)_6Sn_5$ almost remained the same when the Sn thickness increased from 100 μm to 400 μm. It seems that when the Sn thickness increased, the faster diffusion of Cu was affected to a smaller extent compared to Ni, which diffused slower.

The growth kinetics of $(Cu_{1-x}Ni_x)_6Sn_5$ on the Cu and Ni side in both Ni/(100 μm Sn)/Cu and Ni/(400 μm Sn)/Cu couples are shown in Fig. 8. The four sets of data all seemed to follow the parabolic kinetics. The $(Cu_{1-x}Ni_x)_6Sn_5$ on the Cu side was always thicker than that on the Ni side, but there

Table I. Compositions of $(Cu_{1-x}Ni_x)_6Sn_5$ Formed in Ni/(100 μm Sn)/Cu and Ni/(400 μm Sn)/Cu After 1,000 h of Aging

		Cu (at.%)	Ni (at.%)	Sn (at.%)
Ni/(100 μm Sn)/Cu	Ni side	50.6	3.3	46.1
	Cu side	53.4	0.8	45.8
Ni/(400 μm Sn)/Cu	Ni side	51.4	2.1	46.5
	Cu side	53.5	0.4	46.1

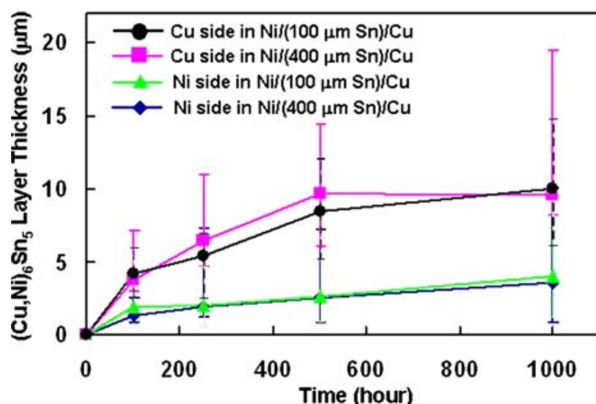

Fig. 8. Thicknesses of $(Cu_{1-x}Ni_x)_6Sn_5$ on the two interfaces of both Ni/(100 μm Sn)/Cu and Ni/(400 μm Sn)/Cu plotted versus the aging time versus time at 160°C.

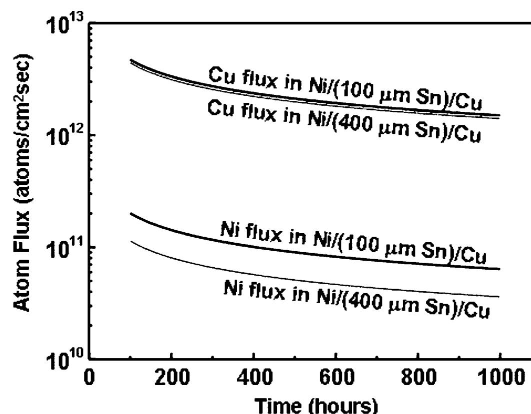

Fig. 9. Cu flux and Ni flux across the Sn layer versus the aging time.

was practically no difference between Ni/(100 μm Sn)/Cu and Ni/(400 μm Sn)/Cu in this matter. The data in Fig. 8 enables us to calculate the Ni flux and Cu flux through the Sn layer. Since the maximum solubility of Ni or Cu in solid Sn is very limited, about 0.005 at.% for Ni[15] and 0.01 at.% for Cu,[16] we assume the amount of Ni and Cu present in the Sn layer can be ignored. With this assumption, the integration of the Cu flux over time corresponds to the amount of Cu that had been incorporated into $(Cu_{1-x}Ni_x)_6Sn_5$ on the Ni side on a per unit area basis, and the integration of the Ni flux over time corresponded to the amount of Ni in $(Cu_{1-x}Ni_x)_6Sn_5$ on the Cu side on a per unit area basis. Therefore, knowing the composition of the intermetallics, one can obtain the atomic flux at any instant by making a derivative of the thickness versus time data,[12] such as that shown in Fig. 8. The resulting Ni flux and Cu flux calculated in this manner are shown in Fig. 9. In calculating the flux, the densities of all the $(Cu_{1-x}Ni_x)_6Sn_5$ are taken to be the same as that of pure Cu_6Sn_5, which was reported to be 8.28 g/cm^3.[17] It can be seen that the Cu flux through the Sn layer was about 25–40 times higher than the Ni flux at any moment. As had been pointed out earlier, the diffusion coefficient of Cu in Sn is about two orders of magnitude higher than that of Ni at 160°C. Apparently, the difference in the ratio of the diffusivity is larger than the ratio of the atomic flux. The difference between the ratio of the flux and the diffusivity is probably due to the difference in the driving force for the diffusion of Ni and Cu across the Sn layer, because according to the Fick's first law the flux is proportional to the product of the driving force gradient and the diffusivity.

In Fig. 9, both the Cu flux and the Ni flux decreased steadily with time. The reason can be attributed to the diminishing driving force with time. In a study by Ho et al.,[18] it was pointed out that Cu_6Sn_5 was an effective diffusion barrier for Ni. As the $(Cu_{1-x}Ni_x)_6Sn_5$ layer on the Ni side grew thicker, this $(Cu_{1-x}Ni_x)_6Sn_5$ layer effectively screened the Ni substrate so that the driving forces for the diffusion of both Cu and Ni became smaller and smaller, and the flux became smaller accordingly.

The total consumed thicknesses of Cu and Ni for diffusion couples aged at 160°C for 1,000 h are plotted in Fig. 10. Taking the Cu consumption in Ni/(100 μm Sn)/Cu as an example (the first vertical bar in Fig. 10), the consumed Cu was distributed into three intermetallics: Cu_3Sn, Ni side $(Cu_{1-x}Ni_x)_6Sn_5$, and Cu side $(Cu_{1-x}Ni_x)_6Sn_5$. Figure 10 reveals that the cross-interaction between Cu and Ni in Ni/Sn/Cu effectively reduces the Ni consumption compared to the binary Ni/Sn reaction. On the other hand, the cross-interaction slightly increased the Cu consumption because Cu now had to be distributed over two interfaces. This observation shows that the presence of Cu in solder has the benefit of reducing the Ni consumption effectively.

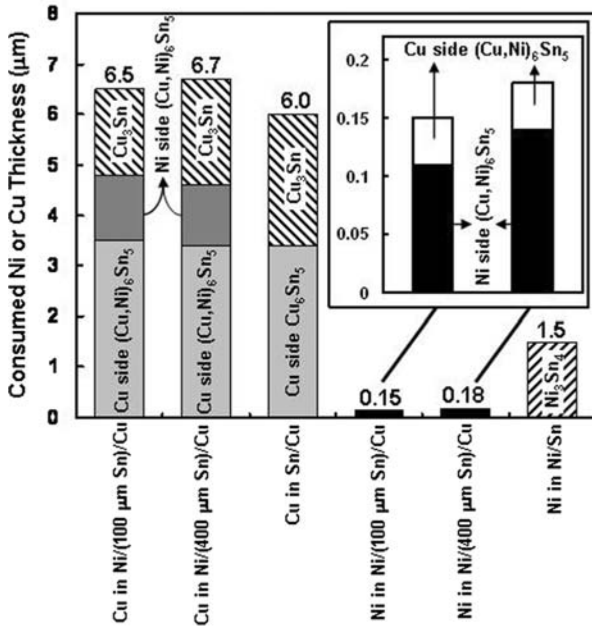

Fig. 10. Total consumed thickness of Ni and Cu in Ni/(100 μm Sn)/Cu, Ni/(400 μm Sn)/Cu, Ni/Sn, and Sn/Cu diffusion couples aged at 160°C for 1,000 h.

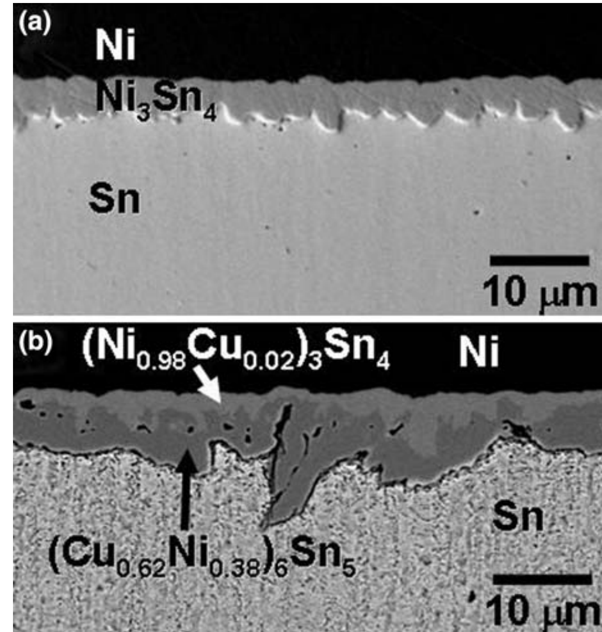

Fig. 12. Backscatter electron micrographs showing (a) interface of Ni/Sn diffusion couple that had been aged 500 h at 160°C, and (b) Ni side interface of the Ni/Ni_3Sn_4/Sn/Cu diffusion couple that had been aged at 160°C an additional 100 h.

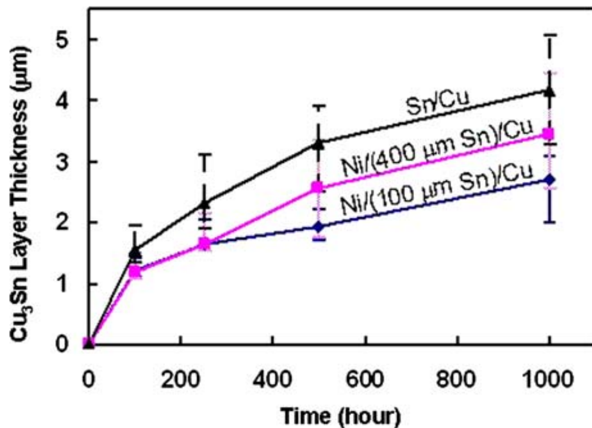

Fig. 11. Thickness of Cu_3Sn versus time at 160°C for different diffusion couples.

The thicknesses of Cu_3Sn in different diffusion couples that had been aged at 160°C for 1,000 h are shown in Fig. 11. It can be seen that in general, Cu_3Sn in Ni/(100 μm Sn)/Cu was thinner than that in Ni/(400 μm Sn)/Cu, which in turn was thinner than that in Sn/Cu. This effect was caused by the Ni effect on the Sn/Cu reaction.[8] It has been reported that Ni-doped Sn-bared solders can reduce the Cu_3Sn growth rate in the Sn/Cu reaction.[8] When the Sn layer was thinner, more Ni atoms could reach the Cu side, and this is the reason why Cu_3Sn in Ni/(100 μm Sn)/Cu was thinner than that in Ni/(400 μm Sn)/Cu. This proposition was confirmed by the fact that $(Cu_{1-x}Ni_x)_6Sn_5$ in Fig. 5b has more Ni than $(Cu_{1-x}Ni_x)_6Sn_5$ in Fig. 7b.

Figure 12a shows the Ni/Sn diffusion couples after aging at 160°C for 500 h. A layer of Ni_3Sn_4 had formed at the interface, resulting in Ni/Ni_3Sn_4/Sn. A layer of Cu was then electroplated on the Su surface of Ni/Ni_3Sn_4/Sn, forming a Ni/Ni_3Sn_4/Sn/Cu diffusion couple. This diffusion couple was then aged at 160°C for an additional 100 h. Figure 12b shows the resulting microstructure. It can be seen that part of the original Ni_3Sn_4 layer had been converted into $(Cu_{1-x}Ni_x)_6Sn_5$ because of the Cu atoms coming from the Cu side. This result vividly shows the rapid diffusion of Cu across the Sn layer. In fact, given enough aging time, the entire Ni_3Sn_4 phase will be replaced by $(Cu_{1-x}Ni_x)_6Sn_5$.

SUMMARY

In this study on the Ni/Sn/Cu diffusion couples at 160°C, the Cu atoms could diffuse through the 100 μm or even 400 μm Sn layer and change the reaction product on the Ni side in a few hundreds hours. Under the same conditions, the Ni atoms could also diffuse through the Sn layer and became incorporated into Cu_6Sn_5 on the Cu side, and the incorporated Ni atoms would then reduce the growth rate of Cu_3Sn. This study is the first positive proof that, even in the solid state, Ni and Cu can cross-interact across hundreds of μm Sn in a few hundred hours. During reflow soldering, the solder becomes molten and the cross-interaction becomes even more substantial. Therefore, the results of this

study show that the cross-interaction of Ni and Cu in solders is extremely rapid, and cannot be ignored in those solder joints that have both elements present.

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